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QUANTUM MECHANICAL CALCULATIONS
ON WEAKLY INTERACTING COMPLEXES

EEN WETENSCHAPPELIJKE PROEVE OP HET GEBIED
VAN DE NATUURWETENSCHAPPEN

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE KATHOLIEKE UNIVERSITEIT NIJMEGEN,
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Introduction

The present thesis is devoted to the study of intermolecular forces in weakly interacting atom–molecule complexes. Weak interactions between closed-shell atoms and molecules play a crucial role in a wide range of physical, chemical, and biological phenomena. They are important in the studies of, among others, molecular scattering dynamics, the spectroscopy of molecular complexes, and the bulk properties of gases, liquids, and solids. In the current thesis potential energy surfaces have been computed \textit{ab initio} (i.e., from first principles) for a number of complexes. These potentials have subsequently been applied in the calculation of properties that can be compared with experiment. These include energy levels and infrared spectra of bound complexes; collision-induced Raman spectra; integral and differential scattering cross sections; rotational de-excitation rate constants and pressure broadening coefficients; and second pressure and dielectric virial coefficients.

A. General concepts

Before going into the details of the studies presented in the current thesis, we will first discuss the theoretical concepts on which this work is based. We will concentrate on a special class of weakly interacting complexes, namely those containing an atom and a molecule. Such complexes will be referred to as dimers while the atom and molecule that constitute the complex will be called monomers.

Molecules and clusters of molecules are composed of electrons and nuclei. The latter are three to five orders of magnitude heavier than the former. Because of the large difference in mass, electrons move much faster and with regard to the electrons it is as if the nuclei are fixed in space. On the other hand, the nuclei do move, namely in an effective field due to the electrons. This separation of electronic and nuclear motions is known as the Born–Oppenheimer approximation and will be applied in the present thesis.

Studies of intermolecular interactions can then be divided into two parts. First, the electronic energy of the system of interest is determined with the nuclei fixed in space. Such calculations are performed for different sets of nuclear configurations. The interaction energy is then obtained as a function of the coordinates of the complex, i.e., the intermolecular distance, the mutual orientations of the monomers, and the internal monomer bond lengths, bond angles, and torsion angles. Often a fitting procedure is performed to obtain
the interaction energy as a continuous function of these coordinates, which is a requirement for many further applications.

In the second step of the Born–Oppenheimer approximation the electronic energy is treated as the effective potential energy that governs the motions of the nuclei inside the complex. Accordingly, the function describing the dependence of the interaction energy on the coordinates of the system is called a potential energy surface (PES) or shortly potential.

Typically for weakly bound complexes is the distinction between relatively weak intermolecular forces and chemical bonds, i.e., interactions between atoms inside the monomers, which are much stronger. Just as the Born–Oppenheimer approximation separates the slow nuclear from the fast electronic motions, intra- and intermolecular vibrations can be separated as well. The first are modes that govern the mutual motions of the nuclei inside one monomer. Their frequencies are usually a few orders of magnitude larger than those of the intermolecular modes, which correspond to the relative displacements of the whole monomers inside the dimer. As a consequence, in general intra- and intermolecular vibrations are largely decoupled.

To a good approximation, the intermolecular interactions can be regarded as forces between molecules in vibrationally averaged states, implying that in practice the internal bond lengths and angles are fixed at values corresponding to the vibrational averages. This decoupling approximation has been applied in the work described in the current thesis, except for the study of the He–CO complex, in which its validity is tested by comparison with full three-dimensional dynamical calculations.

If a potential is available the solutions of the Schrödinger equation for the nuclear motions can be obtained in good approximation. The resulting eigenstates can be divided into bound and continuum states; in the continuum there are resonances (quasi-bound states) that correspond to predissociation. If the complex is in a bound state, it is held together by intermolecular forces. Such complexes are known as van der Waals molecules. Dimers that are in predissociation states possess sufficient energy to dissociate but this energy is contained in other than intermolecular modes, e.g. in the vibration or rotation of one of the monomers. In dimers in continuum states, called scattering or collisional complexes, the monomers interact mutually without being bound.

B. Intermolecular interactions

In the present thesis we regard two-body intermolecular interactions. Basically, these can be categorized into four different types: electrostatic, induction, dispersion, and exchange interactions. Electrostatic forces are caused by the
Intermolecular interactions

interactions between multipole moments on different monomers, i.e., net charges, dipole moments, quadrupole moments, etc. Because of charge penetration effects, the interaction energy has in any case an electrostatic component, also if one of the monomers is a noble gas atom in its electronic ground state, which has no multipole moments when isolated. Induction, or polarization, forces are due to the induction of dipole moments, quadrupole moments, etc., on one monomer by permanent multipoles on the other. The induced moments then interact with the permanent multipole moments of the other monomer. Dispersion, or London–van der Waals, forces have a purely quantum mechanical origin. They are caused by the correlation between the motions of electrons on different monomers. Although they have short-range contributions because of charge penetration, the electrostatic, induction, and dispersion interactions are long-range forces in the sense that they fall off as inverse powers of the intermolecular distance $R$. The fourth component of the interaction energy, the exchange, or Born repulsion, force is a purely short-range term, decaying exponentially with increasing $R$. This component originates from the tunneling of electrons from one monomer to the other. Just as dispersion, this is a quantum mechanical effect. For closed-shell molecules, which are considered in the present thesis, exchange interactions increase the potential energy of the dimer as a consequence of the Pauli postulate. Induction and dispersion interactions, on the other hand, are always attractive, while electrostatic forces can be both attractive and repulsive. The latter often show a strong dependence on the mutual orientations of the monomers.

\textit{Ab initio} methods to calculate interaction energies can be divided into supermolecular and perturbation theory approaches. Supermolecular methods compute the energies of the dimer and the monomers and then obtain the interaction energy by subtraction. A major problem of this method is that the interaction energy is orders of magnitude smaller than the molecular energies, which thus have to be determined very accurately. However, high quality potentials can be obtained if accurate computational methods are used.\textsuperscript{2} The supermolecular approach is therefore widely applied in theoretical chemistry.

Alternatively, interaction energies can be computed by applying perturbation theory. Because of the relative weakness of intermolecular forces, this is a natural and elegant approach. If standard Rayleigh–Schrödinger perturbation theory is applied, the electrostatic, induction, and dispersion contributions to the interaction energy are obtained. To compute the exchange component, however, intermolecular tunneling of electrons must be taken into account. For this purpose, the many-body formulation of symmetry-adapted perturbation theory (SAPT) for intermolecular interactions has been developed,\textsuperscript{3,4} where the adjective “symmetry-adapted” refers to the permutation symmetrization
of the electronic wave functions.

The SAPT method starts from unperturbed monomer wave functions at the Hartree-Fock level of theory, in which each electron is assumed to be moving in an effective field due to the others. If only intermolecular interactions were regarded, contributions to the interaction energy corresponding to the correlation of electronic motions in the unperturbed monomers would be neglected. In order to include these correlation contributions, the SAPT approach uses a double perturbation formalism. Each of the basic interaction components (electrostatics, exchange, induction, and dispersion) is expressed as a perturbation series in the intramolecular correlation of the monomers. The terms in these series are then summed as far as necessary for the component of interest.

A major advantage of the SAPT approach is that the various contributions to the interaction energy, which have different dependences on the intermolecular distance \( R \), are computed separately. Hence, each contribution can be fitted individually, with adjustable and physically interpretable parameters. During the last few years, the SAPT method has been applied to obtain highly accurate potentials for a wide range of complexes.

When the intermolecular separation is large enough to neglect the overlap of the electron clouds of the monomers, the long-range contributions to the interaction energy (electrostatics, induction, and dispersion) can be calculated by expanding the charge distributions of the monomers in series of multipole moments.\(^5\) Once the multipole moments and polarizabilities of the monomers are computed, the interaction energy in the multipole expansion approximation can be immediately obtained for any geometrical configuration. Note that the SAPT approach does not use the multipole expansion. Therefore all charge penetration effects are automatically taken into account.

C. Concise review of the thesis

In the first chapter of the current thesis the SAPT method is applied to calculate interaction-induced electronic properties of collisional complexes. When two molecules collide, the dipole moment and polarizability of the complex differ from the sums of these properties for the non-interacting monomers. The excess dipole moment and polarizability of the dimer are obtained by computing the interaction energy in the presence of an external electric field. Also asymptotic (large \( R \)) expressions are derived by extending the multipole expansion formalism to interaction-induced properties. Numerical results are presented for the dipole moment of He–H\(_2\) and the polarizability of the helium dimer.

In Chapter 2 the interaction-induced polarizability of He\(_2\) is computed as a function of the intermolecular distance \( R \) applying the SAPT method as
Concise review of the thesis

described in Chapter 1. This polarizability is then used to calculate binary collision-induced Raman spectra for this complex. The accuracy of the trace of the computed polarizability is further tested by calculating second dielectric virial coefficients with inclusion of first- and second-order quantum corrections. A full quantum-statistical expression for these virial coefficients is derived in Chapter 3. Using this expression, virial coefficients for the helium gas at various temperatures are computed and compared with results from both experiment and the semiclassical expansion applied in Chapter 2.

In Chapters 4–6 we present SAPT calculations of ab initio potentials for the He–CO, Ne–C₂H₂, and Ar–CH₄ complexes, respectively. In Chapter 4 the PES for He–CO, with inclusion of the CO bond length dependence, is applied in the calculation of bound state levels and the infrared absorption spectrum for transitions accompanying the fundamental band of CO. The accuracy of the SAPT potential is tested by comparing the theoretical infrared spectrum with experiment. Infrared transition frequencies probe particularly the anisotropy of the potential well.

The SAPT approach is applied in Chapter 5 to compute an ab initio PES for Ne–C₂H₂. The potential is used to generate bound state levels for Ne–C₂H₂ and its isotopomer Ne–C₂HD and in the calculation of infrared transition frequencies and intensities corresponding to the simultaneous excitation of the ν₃ mode and the hindered rotation of the (deuterated) acetylene monomer inside the complex. The calculation of an ab initio potential for Ar–CH₄ is discussed in Chapter 6. Work on infrared transitions of Ar–CH₄ accompanying the fundamental ν₁ mode of methane is in progress. As an example, the total infrared spectrum as computed from the SAPT potential is depicted in Fig. 1. Also shown in this figure is the experimental spectrum reported by Miller and co-workers. The experimental and theoretical spectra agree quite well but further analysis is necessary to assign quantum numbers to the individual transitions.

In Chapter 6 integral (i.e., integrated over the scattering angle) cross sections for the scattering of CH₄ molecules on argon atoms are calculated. The highly accurate close-coupling (CC) method is applied with integration parameters, monomer basis, number of included partial waves, and length of the potential expansion chosen such that the resulting cross sections have converged within 1% at worst. The results are compared with experimental integral state-to-state cross sections obtained from measurements involving crossed molecular jets.

The dependence of state-to-state and total cross sections on the scattering angle is investigated in Chapter 7. Differential cross sections are obtained from converged CC calculations. In order to compare with results from molecular beam experiments, the cross sections are transformed from the center-of-mass
FIG. 1. (a) *Ab initio* calculated infrared spectrum of Ar–CH₄ accompanying the ν₃ fundamental mode of methane at T = 1 K obtained from a SAPT potential. (b) Experimental spectrum at T = 1 K. Lines corresponding to free CH₄ are indicated.
Concise review of the thesis

To the laboratory frame and averaged over the velocity and angular distributions of the Ar and CH$_4$ beams. Contrary to calculations on bound state levels and infrared spectra, computational studies of molecular scattering properties also test the onset and the anisotropy of the repulsive part of the potential, because of the relatively high energies involved.

Not only infrared spectra and scattering cross sections, but also bulk properties of gases, liquids, and solids can be obtained from intermolecular potentials. In Chapter 8 of the present thesis, second (pressure) virial coefficients are generated from SAPT potentials with inclusion of first-order quantum corrections for a number of atom–molecule complexes. Second virial coefficients correspond to the deviations from the ideal gas law that are proportional to the square of the number density and are determined by two-body intermolecular interactions. They are mainly sensitive to the potential well depth.

In the two final chapters of the present thesis we study the He–C$_2$H$_2$ complex. A SAPT potential calculated in an earlier work is applied in the computation of scattering properties in Chapter 9. Total differential cross sections and differential energy loss spectra are generated by means of converged CC calculations. Averaging procedures are performed and the resulting differential cross sections and energy loss spectra are compared with results from experiments involving crossed molecular beams.

Finally, in Chapter 10 we present the calculation of rate constants for the (de-)excitation of rotational states and pressure broadening coefficients, corresponding to the broadening of spectral lines due to molecular collisions.
Chapter 1

Symmetry-adapted perturbation theory applied to interaction-induced properties of collisional complexes*

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Abstract

A symmetry-adapted perturbation theory (SAPT) is formulated for the interaction-induced electrical properties of weakly bound complexes. Asymptotic (large \( R \)) expressions are reported for the contributions to the collision-induced dipole moments and polarizabilities up to and including second order in the intermolecular potential. These long-range expressions only require knowledge of the multipole moments and (hyper)polarizabilities of the isolated monomers. Numerical results are given for the dipole moment of He\(_2\) and the polarizability of He\(_2\) and the accuracy of the SAPT approach is examined by comparison with full configuration interaction results. The role of various physical contributions to the dipole moment of He–H\(_2\) and the polarizability of He\(_2\) is investigated. The validity of the long-range approximation and the importance of charge penetration (damping) effects are discussed.

I. INTRODUCTION

During a collision between two molecules the intermolecular interaction leads to distortions of their charge distributions, so that a collisional complex may possess a dipole moment and polarizability in excess of the sum of these properties of the isolated molecules. These excess properties, referred to as the interaction-induced or collision-induced dipole moment and polarizability, are defined as the incremental parts of the properties of the complex A–B due to intermolecular interactions.

The interaction-induced dipole moments and polarizabilities are responsible for a wide range of dielectric, refractive, and optical properties of gases and fluids. In pioneering studies Crawford et al. and Chisholm and Welsh have shown that during a collision of a helium atom with a hydrogen molecule the complex becomes temporarily infrared-active because of its relative translational motions, so that absorption and emission bands can be observed. Much work has been done on the measurements of these collision-induced spectra; see, for instance, a recent monograph by Frommhold for an interview review.

Levine and Birnbaum predicted that all Raman spectra of gases should have a component caused by the collision-induced changes in the polarizabilities. Indeed, it was first demonstrated by McTague and Birnbaum that colliding argon atoms undergo transitions between translational states when interacting with photons. These transitions are exclusively due to the collision-induced light scattering, i.e., to the interaction-induced fluctuations of the polarizabilities of the atoms and molecules. Since the early work on argon, collision-induced light scattering has been experimentally studied in several optically isotropic systems (see Ref. 15 for a review).

Despite the growing body of experimental work on collision-induced absorption and light scattering, not many numerical studies have been devoted to the mechanisms that yield the collision-induced properties themselves. Most ab initio calculations were limited to the Hartree–Fock level (see e.g. Refs. 16 and 17). In a series of papers Meyer and Frommhold showed that the dipole moment contributions from intramonomer and intermonomer electronic correlation are both substantial. At present, supermolecular results from correlated ab initio calculations are available for a limited number of systems: the dipole moments of He–H (Ref. 18), He–Ar (Ref. 19), He–F$^-$ and He–Cl$^-$ (Ref. 25), He–H$_2$ (Refs. 20, 21 and 26), Ar–H$_2$ (Ref. 22), H$_2$–H$_2$ (Refs. 23 and 24), and the polarizabilities of He$_2$ (Refs. 27 and 28, cf. Chapter 2), Ne$_2$ (Ref. 29), He–F$^-$ and He–Cl$^-$ (Ref. 25), and He–CH$_4$ (Ref. 30). See also Refs. 31 and 32 for recent reviews. Only a few of these dipole and polarizability surfaces have been applied to generate collision-induced infrared and Raman spectra (Ref. 34 and Chapter 2 of the present thesis).
On the other hand, perturbation theory studies of the interaction-induced properties have been mainly based on the Rayleigh–Schrödinger polarization treatment (with neglect of the electron exchange) coupled with the multipole expansion of the intermolecular interaction operator (with neglect, in turn, of charge overlap (damping) effects).\textsuperscript{35–47} See also Refs. 48–52 for papers describing computations of the long-range coefficients for the interaction-induced dipole moments and polarizabilities of various dimers. Moreover, the asymptotic expressions derived in the framework of the multipole approximation pertain to specific systems and are usually restricted to the leading power of the reciprocal intermolecular distance. Applications of various exchange perturbation theory schemes to interaction-induced properties are scarce and limited to the simplest approximations.\textsuperscript{53–60} Consequently, very little is known about the importance of the charge overlap and exchange effects.

Recently, the many-body formulation\textsuperscript{61–68} of the symmetry-adapted perturbation theory (SAPT) of intermolecular interactions\textsuperscript{3,69–71} was developed. In this approach all physically important contributions to the potential, such as electrostatics, exchange, induction, and dispersion, are identified and computed separately. By making a perturbation expansion in the intermolecular interaction as well as in the intramolecular electronic correlation, it is possible to sum the correlation contributions to the different physical effects only as far as necessary. The SAPT approach does not use the multipole expansion\textsuperscript{5,72} so all charge penetration (damping) effects are automatically included. Since various contributions to the interaction energy show a different dependence on the intermolecular distance $R$, they can be fitted separately, with adjustable and physically interpretable parameters.\textsuperscript{73,74} This method has been applied to determine interaction potentials for the He–K$^+$ (Ref. 75), He–Na$^+$ (Ref. 76), Ar–H$_2$ (Ref. 77), He–HF (Ref. 78), He–C$_2$H$_2$ (Ref. 79), He–CO (Ref. 80), and Ar–HF (Ref. 81) systems (see Ref. 4 for a recent review of SAPT theory and applications). In most cases, excellent agreement is achieved when compared with the accurately determined (semi)empirical potentials available for these systems. The SAPT potentials have been used to generate the far- and near-infrared spectra of Ar–H$_2$ (Ref. 82), and the near-infrared spectra of He–HF (Ref. 83), He–C$_2$H$_2$ (Ref. 79), and He–CO (Ref. 80). In general, the resulting line positions are in very good agreement with the experimental data (see Ref. 1 for a review of dynamical calculations).

Since the SAPT theory of intermolecular interactions is well developed, it is natural to study its applicability to interaction-induced properties. It is the aim of the current chapter to report such a study. In Sec. II we formulate the symmetry-adapted perturbation theory approach to interaction-induced properties. In Sec. III we present open-ended multipole-expanded formulas...
Chapter 1: SAPT applied to interaction-induced properties

for the polarization contributions to the interaction-induced dipole moments and dipole polarizabilities through the second order of perturbation theory. In Sec. IV we shortly describe the computational details. In Sec. V we apply the theory of Secs. II and III to the interaction-induced dipole moment of He–H₂ and the polarizability of He₂. By comparison with full configuration interaction (FCI) results we study the applicability of the many-body SAPT expansion to the interaction-induced dipole moments and polarizabilities of model systems. We discuss the role of various physical contributions to the interaction-induced dipole moment and polarizability, investigate the validity of the multipole expansion, and study the importance of the charge overlap (damping) effects. Finally, in Sec. VI we present conclusions.

II. SYMMETRY-ADAPTED PERTURBATION THEORY OF INTERACTION-INDUCED PROPERTIES

The interaction-induced dipole moment of a pair of molecules A and B is given by the difference between the dipole moment of the complex A–B and the sum of the dipole moments of the noninteracting molecules A and B,

\[ \Delta \mu_i = \mu_i^{AB} - \mu_i^A - \mu_i^B, \]

where \( \mu_i^{AB} \) is a Cartesian component of the dipole moment of the dimer A–B, and \( \mu_i^A \) and \( \mu_i^B \) denote the components of the dipole moments of the isolated molecules A and B, respectively. Similarly, the interaction-induced polarizability of a pair of molecules A and B is defined as the excess polarizability of the collisional pair A–B due to intermolecular interactions, i.e.,

\[ \Delta \alpha_{ij} = \alpha_{ij}^{AB} - \alpha_{ij}^A - \alpha_{ij}^B, \]

where \( \alpha_{ij}^{AB} \) is a Cartesian component of the dimer polarizability tensor, and \( \alpha_{ij}^A \) and \( \alpha_{ij}^B \) denote the components of the polarizability tensors of the isolated monomers A and B, respectively. Equations (1) and (2) can be rewritten conveniently as

\[ \Delta \mu_i = - \left( \frac{\partial E_{\text{int}}}{\partial F_i} \right)_{F=0}, \]

\[ \Delta \alpha_{ij} = - \left( \frac{\partial^2 E_{\text{int}}}{\partial F_i \partial F_j} \right)_{F=0}, \]

where \( E_{\text{int}} \) is the interaction energy for the dimer A–B in the presence of a static, uniform electric field \( F \). Equations (3) and (4) show that the interaction-induced dipole moment and polarizability can be obtained from standard finite
field calculations, if the field-dependent interaction energy can be computed. In the present work we utilized this possibility, i.e., we first performed calculations on the interaction energy in the static electric field using the symmetry-adapted perturbation theory, and subsequently obtained the interaction-induced dipole moments and polarizabilities from finite difference formulas.

The SAPT approach calculates the interaction energy $E_{\text{int}}$ directly, as a sum of physically distinct polarization and exchange contributions,

$$E_{\text{int}} = E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{pol}}^{(2)} + E_{\text{exch}}^{(2)} + \cdots ,$$

where $E_{\text{pol}}^{(1)}$ is the classical electrostatic energy calculated with full account of the charge-overlap (penetration) effects, and $E_{\text{pol}}^{(2)}$ is the sum of the induction and dispersion energies, $E_{\text{pol}}^{(2)} = E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)}$, rigorously damped by the charge-overlap effects. $E_{\text{exch}}^{(1)}$ and $E_{\text{exch}}^{(2)}$ are the exchange contributions in first and second order in the intermolecular potential, respectively. They can be physically interpreted as an effect of the resonance tunneling of electrons between the interacting systems. In second order it is possible to split the exchange term into an induction and a dispersion part, $E_{\text{exch}}^{(2)} = E_{\text{exch,ind}}^{(2)} + E_{\text{exch,disp}}^{(2)}$.

The exchange-induction energy $E_{\text{exch,ind}}^{(2)}$ and the exchange-dispersion energy $E_{\text{exch,disp}}^{(2)}$ represent the effect of the antisymmetrization of the first-order induction and dispersion wave functions and can be viewed as a result of the coupling of the electron exchange with the induction and dispersion interaction. In view of Eqs. (3) and (4), the components of the interaction-induced dipole moment and polarizability can written as

$$\Delta \mu_i = \Delta \mu_i^{(1)} + \Delta \mu_i^{(1)}_{\text{exch}} + \Delta \mu_i^{(2)} + \Delta \mu_i^{(2)}_{\text{exch}} + \cdots ,$$

$$\Delta \alpha_{ij} = \Delta \alpha_{ij}^{(1)} + \Delta \alpha_{ij}^{(1)}_{\text{exch}} + \Delta \alpha_{ij}^{(2)} + \Delta \alpha_{ij}^{(2)}_{\text{exch}} + \cdots ,$$

where the superscripts again indicate the order in the intermolecular potential. Obviously an $n$th-order contribution to $\Delta \mu_i$ or $\Delta \alpha_{ij}$ is obtained by differentiating once or twice the corresponding contribution of the $n$th-order interaction energy, cf. Eqs. (3)–(5).

Equation (6) relates the interaction-induced part of the dipole moment of the complex $A-B$ to the distortion of the electron density associated with the electrostatic, exchange, induction, and dispersion interaction energies of the monomers in the external electrostatic field. The polarization contributions to the dipole moment through second order of perturbation theory ($\Delta \mu_i^{(1)}$, $\Delta \mu_i^{(2)}_{\text{ind}}$, and $\Delta \mu_i^{(2)}_{\text{disp}}$) have an appealing, partly classical, partly quantum, physical interpretation, and can also be obtained from the multipole approximation. Basically there are two points of view: the finite field approach considers the terms of the interaction energies which are linear in an external field,
Chapter 1: SAPT applied to interaction-induced properties

whereas the perturbation approach considers expectation values of the dimer dipole operator. In the finite field point of view the first-order multipole-expanded polarization contribution $E^{(1)}_{\text{pol}}$ is due to the interactions of permanent multipole moments on A with moments induced on B by the external field $F$, and vice versa. The terms linear in $F$ give $\Delta \mu^{(1)}_{i,\text{pol}}$. The mechanism that yields the second-order induction dipole $\Delta \mu^{(2)}_{i,\text{ind}}$ is somewhat more complicated, and one can distinguish two principal categories. The first mechanism is the interaction of a permanent multipole on monomer A with a multipole on B induced by the nonlinear (second-order) effect of both a permanent multipole on A and the external field $F$ (plus a contribution obtained by interchanging the roles of the monomers A and B). The second mechanism is the interaction of a multipole moment on A, induced by a permanent multipole on B, with a moment on B induced by the external field $F$, and vice versa. Again, the energy terms that are linear in $F$ give the corresponding interaction induced dipoles. In Sec. III A we will return to the perturbation interpretation of these quantities. Finally, the dispersion term $\Delta \mu^{(2)}_{i,\text{disp}}$ represents the intermonomer correlation contribution to the dipole moment of the dimer A–B. The various physical contributions to the interaction-induced polarizability can be classified analogously.

For interactions of many-electron systems one has to use the many-body version of SAPT, which includes order by order the intramonomer correlation effects. The many-body SAPT is based on the partitioning of the total Hamiltonian as $H = F + V + W$, where the zero-order operator $F = F_A + F_B$ is the sum of the Fock operators for the monomers A and B. The intermolecular interaction operator $V = H - H_A - H_B$ is the difference between the Hamiltonians of the interacting and noninteracting systems, and the intramonomer correlation operator $W = W_A + W_B$ is the sum of the Möller–Plesset fluctuation potentials of the monomers: $W_X = H_X - F_X$, $X = A$ or B. The interaction operator $V$ is taken in the nonexpanded form, i.e., it is not approximated by the multipole expansion. The interaction energy components of Eq. (5) are now given in the form of a double perturbation series

$$E^{(n)}_{\text{pol}} = \sum_{l=0}^{\infty} E^{(nl)}_{\text{pol}} \quad \text{and} \quad E^{(n)}_{\text{exch}} = \sum_{l=0}^{\infty} E^{(nl)}_{\text{exch}},$$

where the superscripts $n$ and $l$ at $E^{(nl)}_{\text{pol}}$ and $E^{(nl)}_{\text{exch}}$ denote the orders of perturbation in $V$ and in $W$, respectively. Note that also the induction and dispersion parts of $E^{(2)}_{\text{pol}}$ and $E^{(2)}_{\text{exch}}$ can be written as $E^{(2l)}_{\text{pol}} = E^{(2l)}_{\text{ind}} + E^{(2l)}_{\text{disp}}$ and $E^{(2l)}_{\text{exch}} = E^{(2l)}_{\text{exch-ind}} + E^{(2l)}_{\text{exch-disp}}$. For further discussion it is useful to introduce the quantities
which represent the cumulative effect of all intramonomer correlation contributions to \( \epsilon^{(n)}_{\text{pol}} \) and \( \epsilon^{(n)}_{\text{exch}} \), respectively.

It can be shown\(^{84-87} \) that the Hartree-Fock interaction energy \( E_{\text{HF}} \), defined as the difference of the Hartree-Fock energies for the complex and for the free monomers, is a sum of certain SAPT contributions under neglect of the intermonomer and intramonomer correlation effects. Specifically, the terms \( E^{(10)}_{\text{pol}} \), \( E^{(10)}_{\text{exch}} \), \( E^{(20)}_{\text{ind}} \), \( E^{(20)}_{\text{exch-ind}} \), and some higher-order induction and exchange contributions are included in \( E_{\text{HF}} \). Thus, \( E_{\text{HF}} \) can be represented as

\[
E_{\text{HF}} = E^{(10)}_{\text{pol}} + E^{(10)}_{\text{exch}} + E^{(20)}_{\text{ind}} + E^{(20)}_{\text{exch-ind}} + \delta E_{\text{HF}},
\]

where \( E^{(20)}_{\text{ind}} \) and \( E^{(20)}_{\text{exch-ind}} \) are the second-order induction\(^{67,86} \) and exchange-induction energies\(^{87} \) calculated with the inclusion of the coupled Hartree-Fock type response of a perturbed system, and \( \delta E_{\text{HF}} \) collects all higher-order induction and exchange terms.

Equation (10) allows one to incorporate the Hartree-Fock interaction energy \( E_{\text{HF}} \) into the expression for \( E_{\text{int}} \) by replacing in Eq. (5) the low-order energy contributions, given explicitly in Eq. (10), by the Hartree-Fock interaction energy \( E_{\text{HF}} \). We used this possibility and the field-dependent interaction energy computed in this work is defined as

\[
E_{\text{int}} = E_{\text{int}} + \epsilon^{(1)}_{\text{pol}} + \epsilon^{(1)}_{\text{exch}} + \epsilon^{(2)}_{\text{ind}} + E^{(2)}_{\text{disp}} + E^{(2)}_{\text{exch-disp}}.
\]

In practice, one has to truncate the expansions (8) and (9). Recent studies of the convergence of the many-body perturbation expansions of the electrostatic,\(^{64} \) exchange,\(^{65,67} \) induction,\(^{67} \) and dispersion\(^{68} \) energies for weakly bound complexes have shown that the following approximations are sufficient to reproduce the interaction energy with an error of a few percent or less:

\[
\begin{align*}
\epsilon^{(1)}_{\text{pol}} &= E^{(12)}_{\text{pol,resp}} + E^{(13)}_{\text{pol,resp}}, \\
\epsilon^{(1)}_{\text{exch}} &= E^{(11)}_{\text{exch}} + E^{(12)}_{\text{exch}} + \Delta^{(1)}_{\text{exch}}(\text{CCSD}), \\
\epsilon^{(2)}_{\text{ind}} &= E^{(22)}_{\text{ind}}, \\
E^{(2)}_{\text{disp}} &= E^{(20)}_{\text{disp}} + E^{(21)}_{\text{disp}} + E^{(22)}_{\text{disp}}, \\
E^{(2)}_{\text{exch-disp}} &= E^{(20)}_{\text{exch-disp}}.
\end{align*}
\]
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$\Delta_{\text{exch}}^{(1)}$ (CCSD) is the sum of higher-order terms (in the intramonomer correlation) obtained by replacing the first- and second-order cluster operators entering the expression for $E_{\text{exch}}^{(12)}$ by the converged coupled-cluster singles and doubles (CCSD) operators. The induction term $\epsilon_{\text{ind}}^{(22)}$ represents the true correlation contribution to the nonrelaxed correction, as defined in Ref. 67. The dispersion components $E_{\text{disp}}^{(2n)}$ are derived in Ref. 63. Finally, $E_{\text{exch-disp}}^{(0)}$ is the so-called Hartree-Fock exchange-dispersion energy.

III. THE MULTIPOLe EXPANSION OF INTERACTION-INDUCED ELECTRIC PROPERTIES

In this section we will give the asymptotic (large $R$) expressions for the electrostatic, induction, and dispersion contributions to the interaction-induced dipole moment and polarizability by introducing the multipole expansion of the intermolecular interaction operator through second order of perturbation theory. The great advantage of the multipole expansion is that it yields expressions for the interaction-induced properties in which only properties of the free monomers appear. An additional advantage is that the geometry dependence is given explicitly in terms of simple functions. We shall use the spherical form of the multipole expansion since, in contrast to the Cartesian formalism, it gives the orientational dependence of the interaction energy components in closed form. Because the spherical expressions found in the literature pertain to specific systems and are usually restricted to the leading powers of the $1/R$ expansion, we report below open-ended asymptotic formulas for the first- and second-order contributions to the interaction-induced dipole moment and polarizability. In particular, we show how the electrostatic, induction, and dispersion contributions to these properties can be written solely in terms of the following monomer properties: multipole moments, polarizabilities and hyperpolarizabilities.

In the derivations of the expressions in this section the monomer properties are initially expressed with respect to an arbitrary space-fixed frame. Since the electric properties are usually calculated or measured with respect to axes fixed to the molecule, we then transform from the space-fixed to the body-fixed frame of either monomer. The angular momentum coupling used in all our formulas has the purpose to make this transformation as simple as possible. All properties on each monomer are coupled to spherical tensors of rank $L_X$, $X = A, B$, which transform under the frame rotation by the use of irreducible Wigner rotation matrices $D^{L_X}(\omega_X)$. Here $\omega_X$ is a set of three Euler angles of monomer $X$. These angles describe the rotation of a frame parallel to the space-fixed frame (with its origin in the mass center of $X$), so that it coincides
with the body-fixed frame of X. The geometry dependence of various physical contributions to the interaction-induced dipole moment and polarizability is thus described by a product of two $D$ matrices, one for each monomer, times a function depending on the spherical polar coordinates of the vector $\mathbf{R}$ pointing from the nuclear center of mass of monomer A to that of monomer B, cf. Eq. (23) below. We designate the polar angles of $\mathbf{R}$ with respect to a space-fixed frame by $\hat{\mathbf{R}}$ (which is a unit vector along $\mathbf{R}$), and its length by $R$.

The quantity $Q_m^l$ denotes the monomer expectation value of a component of the multipole operator with rank $l$,

$$Q_m^l \equiv \langle 0 | \hat{Q}_m^l | 0 \rangle,$$

where

$$\hat{Q}_m^l \equiv \sum_{i=1}^{N} Z_i r_i^l C_m^l (\theta_i, \phi_i)$$

is a sum over the particles of the monomer with charge $Z_i$ and polar coordinates $(r_i, \theta_i, \phi_i)$. The function $C_m^l$ is a spherical harmonic function normalized to $4\pi/(2l+1)$. Below we consider multipoles belonging to monomer A or B, which will be indicated by a corresponding subscript on the indices. We will designate a reducible frequency-dependent polarizability by

$$\alpha_{m,m'}^{ll'}(\omega) \equiv 2 \sum_{n \neq 0} \frac{E_n - E_0}{(E_n - E_0)^2 - \omega^2} \langle 0 | \hat{Q}_m^l | n \rangle \langle n | \hat{Q}_{m'}^{l'} | 0 \rangle,$$  \hspace{1cm} (19)

where $|n\rangle$, $n = 0, 1, \ldots$ are the molecular eigenstates with eigenvalues $E_n$. The corresponding irreducible polarizability $\alpha_{\mu}^{ll'}(\omega)$ is obtained by Clebsch–Gordan coupling,

$$\alpha_{\mu}^{ll'}(\omega) \equiv \sum_{m,m'} \langle l, m; l', m' | \lambda, \mu \rangle \alpha_{m,m'}^{ll'}(\omega).$$  \hspace{1cm} (20)

Often the Clebsch–Gordan coupled product of spherical tensors will also be denoted as $[T^l \otimes S^{l'}]^L_M$, i.e., as a binary product between square brackets,

$$[T^l \otimes S^{l'}]^L_M \equiv \sum_{m,m'} \langle l, m; l', m' | L, M \rangle T^l_m S^{l'}_{m'},$$  \hspace{1cm} (21)

The multipole-expanded expressions for the electrostatic, induction, and dispersion contributions to the interaction-induced dipole moments and dipole-dipole polarizabilities can be obtained by applying double perturbation theory to the Schrödinger equation with the Hamiltonian
where $H_0$ is the sum of Hamiltonians of the isolated monomers, $\tilde{V}$ is the intermolecular interaction operator, with the tilde indicating that it is in the multipole approximation, $\hat{Q}_m^l$ is the spherical component of the sum of the dipole operators on A and B, and $F_{-m}$ denotes a component of an external homogeneous static electric field. Alternatively, the multipole-expanded formulas can be found by applying Eqs. (3) and (4) to the multipole-expanded expressions for $E_{\text{pol}}^{(1)}$, $E_{\text{ind}}^{(2)}$, and $E_{\text{disp}}^{(2)}$. Since the final expressions for the interaction-induced properties in the multipole approximation are quite involved, we have followed both routes of derivation to check the correctness of our formulas. The required multipole-expanded expressions for the second-order interaction energies are given in Ref. 5.

Introducing $\{\Lambda\} = \{L_A, K_A, L_B, K_B, L\}$ we define an irreducible tensorial set of angular expansion functions

\[
A^{(\lambda)l}_{\{\Lambda\}m}(\omega_A, \omega_B, \hat{R}) = \sum_{M_A=-L_A}^{L_A} \sum_{M_B=-L_B}^{L_B} \sum_{\lambda} \sum_{L} \langle L_A, M_A; L_B, M_B | \lambda, \mu \rangle \\
x \langle \lambda, \mu; L, M | l, m \rangle D^{L_A}_{M_A, K_A}(\omega_A)^* D^{L_B}_{M_B, K_B}(\omega_B)^* C^l_M(\hat{R}).
\]  

(23)

When we expand a scalar property with $l = m = 0$, such as the energy, this expression can be simplified by noting that the product of two Clebsch-Gordan coefficients in the angular function $A^{(L)0}_{\{\lambda\}0}(\omega_A, \omega_B, \hat{R})$ reduces to a $3jm$ symbol: \(^{89}\)

\[
\sum_{\mu=-L}^{L} \langle L_A, M_A; L_B, M_B | l, \mu \rangle \langle L, \mu; L, M | 0, 0 \rangle = (-1)^{L_A+L_B+L} \binom{L_A}{L_B} \binom{L_B}{L_M} \binom{L_M}{M}. \tag{24}
\]

We will, however, work with Clebsch–Gordan coupled angular functions throughout the current chapter, also when expanding interaction energies. The energy coefficients of the angular functions in Eq. (23) for $E_{\text{pol}}^{(1)}$, $E_{\text{ind}}^{(2)}$, and $E_{\text{disp}}^{(2)}$ are

\[
\Delta E_{\text{mult}, \{\Lambda\}}^{(1)} = (-1)^{L_A} \delta_{L_A+L_B, L} \left[\frac{(2L_A + 2L_B + 1)^{1/2}}{(2L_A)! (2L_B)!} (2L_A)^L_A Q_{K_A}^L_A Q_{K_B}^L_B \right], \tag{25}
\]
\[
\Delta E_{\text{ind,mult.}}^{(2)}(\lambda) = -\frac{1}{2} \sum_{l_A, l_B, l_A', l_B'} R^{-(l_A + l_B + t_B + t_A + 2)} \zeta_{l_A, l_B, l_A', l_B'}^{L_A, L_B, L} \times \left\{ \begin{array}{ccc}
l_A & l_A' & L_A \\
l_B & l_B' & L_B \\
l_A + l_B & l_A' + l_B' & L & \end{array} \right\} \\
\times \left( 1 + \hat{P}_{AB} \right) \hat{a}_{K_A}^{(l_A')(L_A)}(0) \left[ Q_B^{l_B'} \otimes Q_{B'}^{l_B'} \right]_{K_B},
\]
\[
\Delta E_{\text{disp,mult.}}^{(2)}(\lambda) = -\sum_{l_A, l_B, l_A', l_B'} R^{-(l_A + l_B + t_B + t_A + 2)} \zeta_{l_A, l_B, l_A', l_B'}^{L_A, L_B, L} \times \left\{ \begin{array}{ccc}
l_A & l_A' & L_A \\
l_B & l_B' & L_B \\
l_A + l_B & l_A' + l_B' & L & \end{array} \right\} \\
\times \frac{1}{2\pi} \int_0^{\infty} \alpha_{K_A}^{(l_A')(L_A)}(i\omega) \alpha_{K_B}^{(l_B')(L_B)}(i\omega) \, d\omega,
\]
respectively, where \(\hat{P}_{AB}\) interchanges all symbols pertaining to molecules A and B, while the quantity between large curly braces is a \(9j\) symbol. The algebraic coefficient given by
\[
\zeta_{l_A, l_B, l_A', l_B'}^{L_A, L_B, L} = (-1)^{l_A + l_A'} \left[ \frac{(2l_A + 2l_B + 1)! (2l_A' + 2l_B' + 1)!}{(2l_A)! (2l_B)! (2l_A')! (2l_B')!} \right]^{1/2} \\
\times [L_A, L_B, L]^{1/2} \langle l_A + l_B, 0; l_A' + l_B' | L, 0 \rangle,
\]
where \([l_1, l_2, \ldots, l_n] = (2l_1 + 1)(2l_2 + 1) \cdots (2l_n + 1).

We will frequently use the following equations,
\[
\left( \frac{\partial Q_m^l}{\partial F^{m'}} \right)_{F=0} = \sum_{\lambda, \mu} \langle l, m; 1, m' | \lambda, \mu \rangle a_{\mu \lambda}^{(l)}(0),
\]
\[
\left( \frac{\partial \alpha_{\mu \lambda}^{(l_1l_2)}(\omega)}{\partial F^{m'}} \right)_{F=0} = \sum_{\lambda', \mu'} \langle \lambda, \mu; 1, m' | \lambda', \mu' \rangle \beta_{\mu \lambda}^{(l_1l_2)}(\lambda') (\omega, 0),
\]
\[
\left( \frac{\partial^2 \alpha_{\mu \lambda}^{(l_1l_2)}(\omega)}{\partial F^{m'} \partial F^{m''}} \right)_{F=0} = \sum_{\lambda', \mu'} \sum_{\lambda''} \langle \lambda, \mu; 1, m' | \lambda', \mu' \rangle \langle \lambda', \mu'; 1, m'' | \lambda'' \rangle \\
\times \gamma_{\mu' \mu''}^{(l_1l_2)}(\lambda') (\omega, 0, 0),
\]
where \(\beta_{\mu \lambda}^{(l_1l_2)}(\lambda')(\omega, \omega')\) and \(\gamma_{\mu' \mu''}^{(l_1l_2)}(\lambda')(\omega, \omega', \omega'')\) are the irreducible components of the first and second frequency-dependent hyperpolarizability tensors obtained by successive Clebsch–Gordan coupling in the order indicated by the parentheses in the superscripts. Their reducible counterparts are, for instance, given in Ref. 90. The derivatives \(\partial / \partial F_m\) are cogredient to \(F_m\), i.e.,
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\[
\frac{\partial}{\partial F_1} = -\frac{1}{\sqrt{2}} \left( \frac{\partial}{\partial F_x} + i \frac{\partial}{\partial F_y} \right),
\]
\[
\frac{\partial}{\partial F^0} = \frac{\partial}{\partial F_z},
\]
\[
\frac{\partial}{\partial F^{-1}} = \frac{1}{\sqrt{2}} \left( \frac{\partial}{\partial F_x} - i \frac{\partial}{\partial F_y} \right).
\] (32)

A. The multipole expansion of the interaction-induced dipole moment

By applying Eqs. (29) and (30) to the asymptotic expressions for \( E_{\text{pol}}^{(k)} \), Eqs. (25)-(27), one can show that the contribution from the \( k \)th-order polarization term \( E_{\text{pol}}^{(k)} \) to \( \Delta \mu_m \), denoted as \( \Delta \mu_{m,\text{pol}}^{(k)} \), can be written in terms of the complete orthogonal set of angular functions given in Eq. (23) and labeled by \( \{\Lambda\} = \{L_A, K_A, L_B, K_B, L\} \), \( \lambda \) and \( m \),

\[
\Delta \mu_{m,\text{pol}}^{(k)} = \frac{1}{\sqrt{8}} \sum_{\{\Lambda\}} \sum_{\lambda} d_{\text{pol},\{\Lambda\}M}(R) \Lambda^{(\lambda)}_{\{\Lambda\}M}(\omega_A, \omega_B, \hat{R}).
\] (33)

The radial expansion coefficients \( d_{\text{pol},\{\Lambda\}M}(R) \) in Eq. (33) can exclusively be written in terms of multipole moments and (hyper)polarizabilities. In particular, the radial part of the electrostatic contribution to \( \Delta \mu_m \) in the multipole approximation can be written as

\[
d_{\text{pol},\{\Lambda\}M}(R) = R^{-(L+1)} \left( 1 + (-1)^{L_A+L_B+L+\lambda} \hat{P}_{AB} \right) (-1)^{L_A} [L_A, L, \lambda]^{1/2} \\
\times \left( \frac{2L}{2L_B} \right)^{1/2} \left\{ \begin{array}{ccc} L_A & L_B & \lambda \\ L & 1 & L-B \end{array} \right\} \alpha_{K_A}^{(L-L_B+1)L_A} (0) Q_{K_B}^{L_B},
\] (34)

where the quantity between curly braces is a \( 6j \) symbol. We see that the first-order polarization contribution \( \Delta \mu_{m,\text{pol}}^{(1)} \) is due to the polarization of \( A \) by the electric field created by the permanent multipole moments on \( B \) and vice versa.

If we denote the set of indices \( \{l_A, l'_A, l_B, l'_B\} \) by \( \{I\} \), the radial components of the induction contributions to the interaction-induced dipole in the multipole approximation can be written as

\[
d_{\text{ind},\{\Lambda\}M}(R) = (-1)^{L_A+L_B+L} \sum_{\{I\}} R^{-(l_A+l'_A+l_B+l'_B+2)} \alpha_{K_A}^{(L_A+L_B+1)L_A} L_A L_B L \\
\times \left( 1 + (-1)^{L_A+L_B+\lambda} \hat{P}_{AB} \right) \\
\times \left( \sum_{\lambda_A} (-1)^{l_A+\lambda_A} [\lambda, \lambda_A]^{1/2} \times 
\]
The multipole expansion of the interaction-induced dipole moment

\[
\times \left\{ \frac{l_A}{L}, \frac{l_A + l_B}{L}, \frac{l_B}{L}, \frac{l_B}{L}, \frac{L_B}{L}, \frac{L_A}{L}, \frac{\lambda}{L}, \frac{1}{L} \right\}
\times \left[ \alpha^{(l_A l_B)}_{\lambda A}(0) \otimes Q^L_{K_A} \alpha^{(l_B l_A')}_{K_B}(0) \right]
\times \left[ -\frac{1}{2} \sum_{\lambda_A} [\lambda, \lambda_A]^{1/2} \left\{ \begin{array}{ccc}
L_A & L_B & \lambda \\
L & 1 & \lambda_A
\end{array} \right\} \left\{ \begin{array}{ccc}
l_A & l_B & \lambda_A \\
l_B & l_B & L
\end{array} \right\} \left\{ \begin{array}{ccc}
l_A + l_B & l_A' + l_B' & L \\
l_B & l_B & L
\end{array} \right\} \right]
\times \beta^{(l_A l_B)}_{K_A} \left[ Q^L_{K_B} \otimes Q^L_{K_B}(0,0) \right],
\]

where the first quantity between curly braces denotes a 12j symbol of the first kind. This can be written as a single sum of products of four 6j symbols, see Appendix A. Note that the second-order induction dipole \( \Delta \mu_{\text{m,ind}} \) is caused by two different mechanisms. In the first mechanism a permanent moment on \( A \) induces a moment on \( B \), which in turn induces a dipole on \( A \) (and vice versa). In the second mechanism, system \( A \) is polarized by two electric fields created by two permanent moments on \( B \), and vice versa. This nonlinear effect requires a nonvanishing first hyperpolarizability on \( A \) (and \( B \)).

The dispersion contribution to the interaction induced dipole is

\[
disp_{\text{disp},A}(R) = (-1)^{L_A + L_B + L + 1} \sum_{\{l\}} R^{-(l_A + l_B + l_A' + l_B' + 1)} \zeta^{L_A L_B L}_{l_A l_B l_A' l_B'}
\times \left( 1 + (-1)^{L_A + L_B + \lambda} \hat{P}_{AB} \right) \sum_{\lambda_A} [\lambda, \lambda_A]^{1/2}
\times \left\{ \begin{array}{ccc}
L_A & L_B & \lambda \\
L & 1 & \lambda_A
\end{array} \right\} \left\{ \begin{array}{ccc}
l_A & l_B & \lambda_A \\
l_B & l_B & L
\end{array} \right\} \left\{ \begin{array}{ccc}
l_A + l_B & l_A' + l_B' & L \\
l_B & l_B & L
\end{array} \right\}
\times \frac{1}{2\pi} \int_0^\infty \beta^{(l_A l_B)}_{K_A} \left[ Q^L_{K_B} \otimes Q^L_{K_B}(i\omega,0) \alpha^{(l_B l_A')}_{K_B}(i\omega) \right] d\omega,
\]

where the algebraic coefficients \( \zeta^{L_A L_B L}_{l_A l_B l_A' l_B'} \) are given by Eq. (28).

Equations (34), (35), and (36) can be further simplified by considering the molecular symmetry groups of the monomers \( A \) and \( B \). For instance, if \( A \) is a diatom in a \( \Sigma \) state, only irreducible tensors with total magnetic quantum number \( K_A = 0 \) are nonvanishing. If \( B \) is an atom in an \( S \) state, only irreducible tensors with \( L_B = 0 \) survive. In systems with inversion symmetry in a gerade state the sum of the orders of the multipole operators must be even; this gives, for example, the requirement that \( l_1 + l_2 + 1 \) must be even in order that the hyperpolarizability \( \beta^{(l_1 l_2 l_3)}_{\mu} \) is nonzero. Thus we have for \( \text{H}_2 - \text{He} \):

\[
K_A = L_B = K_B = 0, \quad \lambda = L_A, \quad L_A - \text{even}, \quad L - \text{odd}.
\]
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By substituting conditions (37) into Eq. (23) one finds that the angular function $A_{LM}^{\text{Ang}}(\hat{r}, \mathbf{R})$ reduces to

$$A_{LM}^{\text{Ang}}(\hat{r}, \mathbf{R}) = [C_{LM}^{\text{Ang}}(\hat{r}) \otimes C_{LM}^{\text{R}}(\mathbf{R})]_{m}^{1},$$

(38)

where $\hat{r}$ is a unit vector along the axis of the diatom. Further simplification of Eq. (38) is obtained by assuming that $\mathbf{R}$ lies along the $z$ axis. Using $C_{M}^{L}(0, 0) = \delta_{M,0}$, we obtain

$$A_{LM}^{\text{Ang}}(\hat{r}) = \langle L_{A}, m; L, 0 | 1, m \rangle C_{m}^{L}_{m}^{\text{Ang}}(\hat{r}).$$

(39)

The radial electrostatic function is given by

$$d_{\text{pol},LM}^{(1)}(R) = \delta_{L,L_{A}+1} R^{-(L_{A}+2)} \times [(2L_{A} + 1)(L_{A} + 1)(2L_{A} + 3)]^{1/2} Q_{0}^{L_{A}} \alpha_{0},$$

(40)

where $\alpha_{0} = -\sqrt{1/3} \alpha_{0}^{(11)}(0)$ denotes the static polarizability of the atom. The induction term can be written as†

$$d_{\text{ind},LM}^{(2)}(R) = \sum_{\{l\}} R^{-(l_{A}+l_{A}'+I_{B}+l_{B}'+2)} c_{L_{A}0L}^{L_{A}0L} \times \left( \sum_{\lambda} \delta_{\lambda_{B}'}^{\lambda_{B}} \left[ \lambda_{L}^{1/2} \right] ight)^{-1/2} \left\{ \begin{array}{ccc} l_{A} & l_{A}' & L \\ l_{A} + I_{B} & l_{A} + I_{B} & l_{B} \\ \end{array} \right\} \times \left\{ \begin{array}{ccc} L & l_{A}' & l_{A} \\ 1 & 1 & \end{array} \right\} \left[ \alpha_{0}^{\langle l_{A}1 \rangle \lambda_{L}} Q_{0}^{L_{A}} \alpha_{0}^{(l_{B}l_{B})} (0) \right] \times \left[ Q_{0}^{L_{A}} \otimes Q_{0}^{L_{A}'} \right] \left( L_{A}^{(l_{B})} \right) \left( \beta_{0}^{(l_{B}l_{B})} (0,0) \right),$$

(41)

where in the first term $l_{A}$ is odd and both $\lambda_{A}$ and $l_{A}'$ are even, while in the second term both $l_{A}$ and $l_{A}'$ are even, and $l_{B} + l_{B}'$ is odd. Finally, the dispersion term reads†

$$d_{\text{disp},LM}^{(2)}(R) = \sum_{\{l\}} R^{-(l_{A}+l_{A}'+l_{B}+l_{B}'+2)} c_{L_{A}0L}^{L_{A}0L} \times \left( \delta_{\lambda_{B}'}^{\lambda_{B}} \left[ l_{B}^{1/2} \right] \right)^{-1/2} \left\{ \begin{array}{ccc} l_{A} & l_{A}' & L \\ l_{A} + I_{B} & l_{A} + I_{B} & l_{B} \\ \end{array} \right\} \times$$

†The minus sign in the first term of Eq. (41) of the original article is incorrect.
†The minus sign in Eq. (42) of the original article is incorrect.
The multipole expansion of the interaction-induced dipole moment

\[ \times \frac{1}{2\pi} \int_0^\infty \beta_0^{(l_A l'_A L_1 l_B)}(i\omega, 0) \alpha_0^{(l_B l'_B 0)}(i\omega) d\omega \]

\[ + \left\{ \begin{array}{c} l_A & l'_A & L_A \\ l_B & l'_B & 1 \\ l_A + l_B & l'_A + l'_B & L \end{array} \right\} 

\[ \times \frac{1}{2\pi} \int_0^\infty \alpha_0^{(l_A l'_A L_A)}(i\omega) \beta_0^{(l_B l'_B 11)}(i\omega, 0) d\omega \right), \]

(42)

where in the first term \( l_A + l'_A \) is odd, and in the second term \( l_A + l'_A \) is even and \( l_B + l'_B \) is odd.

### B. The multipole expansion of the interaction-induced polarizability

The contribution from the \( k \)th-order polarization term \( L_{pol}^{(k)} \) to \( \Delta \alpha_m^{(11)} \), denoted as \( (\Delta \alpha_m^{(11)})_{pol}^{(k)} \), can be written in terms of the orthogonal set of angular functions labeled by \( \{\Lambda\} = \{L_A, K_A, L_B, K_B, L\} \), \( \lambda, l, \) and \( m \), cf. Eq. (23),

\[ \begin{aligned} 
(\Delta \alpha_m^{(11)})_{pol}^{(k)} &= \sum_{\{\Lambda\}} \sum_\lambda \mathcal{P}_{pol,\{\Lambda\}}^{(k)}(R) \mathcal{A}_{\{\Lambda\}m}(\omega_A, \omega_B, \hat{R}), 
\end{aligned} \]

(43)

where \( l = 0 \) or \( 2 \).

Similarly as in the case of the dipole moments, the final formulas for the interaction-induced polarizabilities can be solely expressed in terms of multipole moments and (hyper)polarizabilities. For instance, the electrostatic contribution to \( \Delta \alpha_m^{(11)} \) in the multipole approximation can be written as

\[ \begin{aligned} 
p_{pol,\{\Lambda\}m}^{(1)}(R) &= R^{-(L+1)} \left( 1 + (-1)^{L_A + L_B + L} \mathcal{P}_{AB} \right) 
\times \left( \sum_{\lambda_A \lambda_B} (-1)^{\lambda_A + 1} \delta_{L_A \lambda_A + \lambda_B} \alpha_{K_A}^{(\lambda_A 1 L_A)}(0) \alpha_{K_B}^{(\lambda_B 1 L_B)}(0) 
\right) \times \left( \frac{2L}{2 \lambda_A} \right)^{1/2} [L_A, L_B, L, \lambda]^{1/2} \left\{ \begin{array}{c} L_A & L_B & \lambda \\ \lambda_A & \lambda_B & L \end{array} \right\} 1 1 l 
\times \left( \frac{2L}{2 \lambda_B} \right)^{1/2} [L_A, L, \lambda_A, \lambda]^{1/2} \left\{ \begin{array}{c} L - L_B & l \\ \lambda_A & 1 \end{array} \right\} \left\{ \begin{array}{c} L_A & \lambda \\ L & L - L_B \end{array} \right\} 
\times \left( \frac{2L}{2 \lambda_B} \right)^{1/2} [L_A, L, \lambda_A, \lambda]^{1/2} \left\{ \begin{array}{c} L - L_B & l \\ \lambda_A & 1 \end{array} \right\} \left\{ \begin{array}{c} L_A & \lambda \\ L - L_B & L \end{array} \right\}. \end{aligned} \]

(44)
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The multipole-expanded formula for the induction contribution to the interaction-induced polarizabilities is more involved, and can be conveniently expressed as

\[
p_{\text{ind}}^{(2)}(\Lambda)_{\lambda}^{(2)}(R) = \sum_{\{l_i\}} \frac{1}{\alpha_{\lambda}^{(2)}} \langle (l_A l'_A + l_B l'_B + l) \rangle (l_A l'_A l_B l'_B) \left(1 + (l_A + l_B + \lambda) \alpha_{AB} \right)
\]

\[
\times \left( \sum_{\lambda_A \lambda_B} \xi_{\lambda} \gamma_{(l_A l'_A) \lambda} \alpha_{(l_B l'_B) \lambda} (l_A l'_A l_B l'_B) \left[Q_{l A} \otimes Q_{l B}^{(2)} \right]_{K_B}^{L_B}
\]

\[
+ \sum_{\lambda_A \lambda_B} \xi_{\lambda} \alpha_{(l_A l'_A) \lambda} (l_A l'_A l_B l'_B) \left[Q_{l A}^{(2)} \otimes Q_{l B} \right]_{K_B}^{L_B}
\]

\[
+ \sum_{\lambda_A \lambda_B} \xi_{\lambda} \alpha_{(l_B l'_B) \lambda} (l_B l'_B l_A l'_A) \left[Q_{l B} \otimes Q_{l A}^{(2)} \right]_{K_B}^{L_B}
\]

\[
+ \sum_{\lambda_A \lambda_B} \xi_{\lambda} \alpha_{(l_A l'_A) \lambda} (l_A l'_A l_B l'_B) \left[Q_{l A} \otimes Q_{l B}^{(2)} \right]_{K_B}^{L_B}
\)

\]

(45)

with the algebraic coefficients \( \xi \) given by

\[
\xi_I = \frac{1}{2} (-1)^{L_B + L + \lambda} \left[ \lambda, \lambda', \lambda \right]^{1/2} \left\{ \begin{array}{c}
\lambda_A \\
l_A \\
L_A \\
\lambda_B \\
l_B \\
L_B \\
\lambda \\
l_B + L
\end{array} \right\}
\]

\[
\times \left\{ \begin{array}{c}
1 \\
\lambda_A \\
L_A \\
\lambda_B \\
L_B \\
\lambda \\
l_A + l_B + l_B
\end{array} \right\}
\]

(46)

\[
\xi_{\Pi} = 2 \left[ \lambda, \lambda_B, \lambda \right]^{1/2} \left\{ \begin{array}{c}
\lambda_A \\
l_A \\
L_A \\
\lambda_B \\
l_B \\
L_B \\
\lambda \\
l_B + l_B + l_B
\end{array} \right\}
\]

(47)

\[
\xi_{\lambda} = (-1)^{L + \lambda} \left[ \lambda_B, \lambda', \lambda \right]^{1/2}
\]

\[
\times \left\{ \begin{array}{c}
\lambda_A \\
l_A \\
L_A \\
\lambda_B \\
l_B \\
L_B \\
\lambda \\
l_B + l_B + l_B
\end{array} \right\}
\]

(48)

\[
\xi_{\lambda} = (-1)^{L_A + L_B + L} \left[ \lambda, \lambda_B, \lambda \right]^{1/2}
\]

\[
\times \left\{ \begin{array}{c}
l_A' \\
l_B' \\
L_A \\
\lambda_B \\
L_B \\
\lambda \\
l_B + l_B + l_B
\end{array} \right\}
\]

(49)

where the symbol between curly braces occurring in Eqs. (47) and (49) denotes a \( 15j \) symbol of the third kind (see Appendix A for its definition). Finally, the
The multipole expansion of the interaction-induced polarizability

The multipole-expanded formula for the dispersion contribution to the interaction-induced polarizabilities can be expressed as

\[ p_{\text{disp}, \{\lambda\}}^{(2)}(R) = \sum_{\{l\}} R^{-\{(l_A + l_A') + (l_B + l_B') + 2\}} \xi_{l_Al_A'l_Bl_B'}^{l_Al_Bl_A'l_B'} \left( 1 + (-1)^{l_A + l_B + l_A' + l_B'} \hat{p}_{AB} \right) \]

\[ \times \left( \sum_{\lambda_A \lambda_B} \xi_1 \frac{1}{\pi} \int_0^\infty \gamma_{K_A}^{l_A l_A' \lambda_A \lambda_A' \lambda_A \lambda_A'} L_A(i \omega, 0, 0) \alpha_{K_B}^{l_B l_B' \lambda_B \lambda_B' \lambda_B \lambda_B'} L_B(i \omega, 0) \, d\omega \right) \]

\[ + \sum_{\lambda_A \lambda_B} \xi_V \frac{1}{\pi} \int_0^\infty \beta_{K_A}^{l_A l_A' \lambda_A \lambda_A' \lambda_A \lambda_A'} L_A(i \omega, 0) \beta_{K_B}^{l_B l_B' \lambda_B \lambda_B' \lambda_B \lambda_B'} L_B(i \omega, 0) \, d\omega \right) \), (50)\]

where \( \xi_1 \) is given by Eq. (46) and \( \xi_V \) is defined as

\[ \xi_V = \frac{1}{2} [\lambda_A, \lambda_B, \lambda]^{1/2} \left\{ \begin{array}{c} l_A \\ l_B \\ l_A' \\ l_B' \end{array} \right\} \left\{ \begin{array}{c} L_A \\ L_B \\ \lambda_A \\ \lambda_B \end{array} \right\} \left\{ \begin{array}{c} L \\ \lambda \\ 1 \\ l \end{array} \right\} . \] (51)\]

If \( A \) and \( B \) are identical atoms in the same \( S \) state, the multipole expressions reported above are drastically simplified, since in this particular case we have

\[ L_A = K_A = L_B = K_B = \lambda = m = 0, \quad L = l. \] (52)\]

Taking further the \( z \) axis along \( R \), so that the angular function \( A_{0000}^{0000} = \delta_{m0} \), we find that the electrostatic functions are given by the following expressions, cf. also Eqs. (43) and (44),

\[ (\Delta \alpha_0^{(11)0})_{\text{pol}}^{(1)} = 0, \] (53)\]

\[ (\Delta \alpha_0^{(11)2})_{\text{pol}}^{(1)} = 2\sqrt{6} R^{-3} (\alpha_0)^2. \] (54)\]

In some applications it is more convenient to use the trace polarizability \( \alpha \equiv (\Delta \alpha_{zz} + 2 \Delta \alpha_{xx})/3 \) and the anisotropy \( \Delta \alpha_{zz} - \Delta \alpha_{xx} \). These are related to the components \( \Delta \alpha_0^{(11)0} \) and \( \Delta \alpha_0^{(11)2} \) by the equations

\[ \alpha = -\frac{1}{\sqrt{3}} \Delta \alpha_0^{(11)0}, \quad \Delta \alpha_{zz} - \Delta \alpha_{xx} = \frac{1}{2} \sqrt{6} \Delta \alpha_0^{(11)2}. \] (55)\]

Equation (53) shows that the electrostatic contribution to the interaction-induced polarizability of two identical atoms is traceless in the multipole approximation. This relation generally holds for any complex consisting of two atoms in \( S \) states.

The induction term can be written as

\[ (\Delta \alpha_0^{(11)2})_{\text{ind}}^{(2)}(R) = 2 \sum_{l'} (-1)^{l'} R^{-2(l'+1)(2l'+1)(l'+1)(2l'+3)} \]

\[ \times (\alpha_0)^2 \alpha_{l'}(0;l' + 1, 0; l' + 1, 0) \left\{ \begin{array}{l} l' + 1 \\ 1 \\ 1 \\ l' \end{array} \right\}, \] (56)\]
where \( \alpha_I(0) = (-1)^I (I')^{-1/2} \alpha_0^{(I'I)} \) is the static \( 2I' \)-pole polarizability of the atom. The dispersion term reads

\[
(\Delta \alpha_0^{(11)}(1))^{(2)}_{\text{disp}}(R) = \sum_{\{l\}} R^{-((l_A' + l_B' + l_A + l_B')/2)} \langle l_A + l_B; 0; l_A' + l_B' 0 | l, 0 \rangle \\
\times \left[ \frac{(2l_A + 2l_B + 1)!(2l_A' + 2l_B' + 1)!}{(2l_A)!(2l_B)!(2l_A')!(2l_B')!} \right]^{1/2} \\
\times \delta_{l_B', l_B} \delta_{l_A', l_A} \left\{ \begin{array}{c} l_A + l_B' \ l_A' + l_B \ l \\ l_A \\ l_B \end{array} \right\} \\
\times \frac{1}{\pi} \int_0^\infty \gamma_{(l_A' l_B)}^{(l(l'_A l'_B)00)}(i \omega, 0, 0) \alpha_0^{(l l'_B 0)}(i \omega) d \omega \\
- \left\{ \begin{array}{c} l_A \\ l_B \\ l_A' + l_B' \ l_A' \end{array} \right\} \\
\times \frac{1}{\pi} \int_0^\infty \beta_0^{(l(l'_A l'_B)00)}(i \omega, 0) \beta_0^{(l l'_B 0)}(i \omega, 0) d \omega \right).
\]

IV. COMPUTATIONAL DETAILS

The collision-induced dipole of He–H\(_2\) and the collision-induced dipole polarizability of He\(_2\) are computed from SAPT interaction energies. Calculations on He–H\(_2\) were performed for several intermolecular distances \( R \) and angles \( \theta \), where \( R \) is the vector pointing from the center of mass of H\(_2\) to the He nucleus, and \( \theta \) is the angle between the vectors \( \mathbf{r} \), pointing from one hydrogen atom to the other, and \( \mathbf{R} \). The H–H distance was fixed at 1.449 bohr. Computations on He\(_2\) were performed for several interatomic distances \( R \).

For the He atom in He–H\(_2\) we used a \([5s4p3d2f]\) basis. The \( s \) orbitals were represented by the (61111) contraction of Van Duijneveldt’s 10s set,\(^{92}\) and the exponents of the polarization functions were taken from Gutowski et al.\(^{93}\) For H\(_2\) we used a \([4s3p2d1f]\) basis, where we took the \( s \) and \( p \) functions from Hobza et al.,\(^{94}\) and the \( d \) and \( f \) functions from basis \( D \) of Williams et al.\(^{77}\) For the helium atom in He\(_2\) we used a larger \([7s5p4d3f2g]\) basis. The \( s \) orbitals were again represented by the 10s set of Ref. 92, now contracted to (411111) and the exponents of the polarization functions were taken from Ref. 93. To check the convergence of the SAPT expansion by comparison with full CI (FCI) results, we performed additional calculations in smaller basis sets. For the He atom in He–H\(_2\) we used a \([5s3p1d]\) basis, where the \( s \) functions are the same as in the larger basis and the polarization functions were again taken from Ref. 93. (The \( 3p \) set was represented by the optimal even-tempered basis.)
For H$_2$ we used a [3s1p;3s2p1d] basis, including bond functions at the center of the molecule. The s and p functions were taken from Meyer et al.,$^{20}$ while we assigned the value 0.3 to the exponent of the d functions, as suggested by Ref. 94. For the FCI computations on He$_2$ we used a [5s3p2d] basis, where the s and p functions are the same as in He–H$_2$ and the d functions were taken from Ref. 93. The spherical form of the polarization functions has been used (5 d functions and 7 f functions). In order to fully account for the charge-overlap effects all calculations have been performed using the full dimer basis set.

All calculations of interaction energies have been performed with the SAPT system of codes.$^{95}$ In addition, FCI results have been obtained from the program by Zarrabian et al.$^{96,97}$ We used the Boys–Bernardi counterpoise correction to eliminate the basis set superposition error from the supermolecular Hartree–Fock and FCI calculations.$^{98}$ The components of the interaction-induced dipole moment $\Delta \mu_{ii}$ of He–H$_2$ and of the interaction-induced polarizability tensor $\Delta \alpha_{ii}$ of He$_2$ have been obtained from the equations

$$\Delta \mu_{ii} = -\frac{E_{\text{int}}(F_i) - E_{\text{int}}(-F_i)}{2F_i} + O(F_i^3), \quad (58)$$

$$\Delta \alpha_{ii} = -\frac{E_{\text{int}}(F_i) + E_{\text{int}}(-F_i) - 2E_{\text{int}}(0)}{F_i^2} + O(F_i^4), \quad (59)$$

where the index $i = z$ or $x$ denotes the direction along the intermolecular axis $R$, or perpendicular to this axis, respectively. Note that for He$_2$ only the diagonal components of the collision-induced polarizability tensor are nonzero. We used field strengths equal to ±0.001 a.u. in the calculations of the interaction-induced polarizability of He$_2$ and field strengths of ±0.0001 a.u. in the calculations of the interaction-induced dipole moment of He–H$_2$.

In addition, long-range van der Waals coefficients corresponding to the multipole-expanded electrostatic, induction, and dispersion contributions to the interaction-induced dipole moment of He–H$_2$ and polarizability of He$_2$ have been computed through $R^{-11}$ and $R^{-10}$, respectively. We used the same level of theory and the same basis sets as in the SAPT calculations. The long-range electrostatic coefficients of Eqs. (40) and (54) were calculated including intramolecular correlation up to and including third order. Zero-order multipole moments and polarizabilities were computed at the Hartree–Fock and coupled Hartree–Fock (CHF) level of theory, respectively. The true correlation contributions to the moments and polarizabilities were calculated with the inclusion of coupled Hartree–Fock type response of the orbitals.

The long-range induction coefficients of Eqs. (41) and (56) were calculated up to and including second order of true correlation. The zero-order multipole moments and (hyper)polarizabilities were computed at the Hartree–Fock and CHF level, respectively. The second-order true correlation contributions to
TABLE 1. Comparison of the parallel component of the interaction-induced dipole moment of He-\(H_2\) computed by SAPT with the FCI results (in \(10^{-3}\) a.u.). All results were computed in the \([5s3p1d/3s1p; 3s2p1d]\) basis.

<table>
<thead>
<tr>
<th>(R)</th>
<th>(\vartheta = 0^\circ)</th>
<th>(\vartheta = 90^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R = 5\ a_0)</td>
<td>12.377</td>
<td>13.056</td>
</tr>
<tr>
<td>(R = 6.5\ a_0)</td>
<td>1.835</td>
<td>1.869</td>
</tr>
<tr>
<td>(R = 7\ a_0)</td>
<td>0.217</td>
<td>0.215</td>
</tr>
<tr>
<td>(R = 10\ a_0)</td>
<td>3.629</td>
<td>3.875</td>
</tr>
<tr>
<td>(R = 5\ a_0)</td>
<td>-0.318</td>
<td>-0.306</td>
</tr>
<tr>
<td>(R = 7\ a_0)</td>
<td>-0.114</td>
<td>-0.113</td>
</tr>
</tbody>
</table>

\(\Delta^a\) = \(-5.2\%\) \(-1.8\%\) \(0.9\%\) \(-6.3\%\) \(3.9\%\) \(0.88\%\)

\(^a\)Relative error of the SAPT result with respect to the FCI result.

the moments and polarizabilities were obtained from the POLCOR package\(^{73, 74}\) and the hyperpolarizabilities were obtained by differentiating the corresponding polarizabilities. Finally, the long-range dispersion coefficients of Eqs. (42) and (57) were computed from dynamic (hyper)polarizabilities with both true and apparent correlation included up to and including second order.\(^{78}\) The correlation contributions to the polarizabilities were obtained from POLCOR and the hyperpolarizabilities by differentiation. The long-range induction and dispersion coefficients were calculated without the inclusion of coupled Hartree–Fock type response of the orbitals.

In the calculation of the hyperpolarizabilities by a finite field approach we used the following equations, which hold for \(S\) state atoms,

\[
\beta_0^{(l_{l_A} l_{l_A}^{(1)} l_{l_A}^{(1)})0} (\omega, 0) = -\sqrt{3} \left( \frac{\partial \alpha_0^{(l_{l_A} l_{l_A}^{(1)} l_{l_A}^{(1)})} (\omega)}{\partial F_0} \right)_{F=0},
\]

\[
\gamma_0^{(l_{l_A} l_{l_A}^{(1)} l_{l_A}^{(1)})0} (\omega, 0, 0) = \left[ \begin{array}{ccc} 1 & 1 & 1 \\ 0 & 0 & 0 \end{array} \right]^{-1} \left( \frac{\partial^2 \alpha_0^{(l_{l_A} l_{l_A}^{(1)} l_{l_A}^{(1)})} (\omega)}{\partial F_0^2} \right)_{F=0}.
\]

See Eqs. (56) and (57) and Appendix B for the expressions used in the case of \(H_2\) and Eqs. (40)–(42) for the required \(He-H_2\) expressions. We choose as the \(xz\) plane the mirror plane spanned by the \(H_2\) axis and the external field. The \(H_2\) irreducible components then satisfy

\[
\alpha_M^{(l_{l_A} l_{l_A}^{(1)})} = (-1)^{l+l'+l+M} \alpha_M^{(l_{l_A} l_{l_A}^{(1)})}.
\]

The Casimir–Polder integrals occurring in Eqs. (42) and (57) were computed on a 10 point grid as described in Ref. 99.
TABLE 2. SAPT contributions (in $10^{-3}$ a.u.) to the parallel component of the interaction-induced dipole moment of He–H$_2$ as functions of the angle $\theta$ at $R = 5$ and 7 bohr. The numbers in parentheses represent the intramonomer correlation contributions. All results were computed in the [5s4p3d2f/4s3p2d1f] basis.

<table>
<thead>
<tr>
<th>$\theta = 0^\circ$</th>
<th>$\theta = 30^\circ$</th>
<th>$\theta = 60^\circ$</th>
<th>$\theta = 90^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = 5$ bohr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \mu_{[1]}^{(1)}_{\text{pol}}$</td>
<td>0.308 (-0.053)</td>
<td>-0.660 (+0.003)</td>
<td>-2.485 (+0.094)</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{exch}}$</td>
<td>15.840 (+0.018)</td>
<td>14.120 (-0.046)</td>
<td>11.202 (-0.137)</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{ind}}$</td>
<td>-1.017 (+0.020)</td>
<td>-1.074 (+0.024)</td>
<td>-1.137 (+0.030)</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{exch-ind}}$</td>
<td>2.003</td>
<td>1.873</td>
<td>1.500</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{disp}}$</td>
<td>-2.805</td>
<td>-2.524</td>
<td>-2.027</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{exch-disp}}$</td>
<td>0.433</td>
<td>0.387</td>
<td>0.307</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}$</td>
<td>12.107</td>
<td>9.627</td>
<td>5.300</td>
</tr>
<tr>
<td>$R = 7$ bohr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \mu_{[1]}^{(1)}_{\text{pol}}$</td>
<td>0.7727 (-0.0160)</td>
<td>0.4480 (-0.0079)</td>
<td>-0.1749 (+0.0072)</td>
</tr>
<tr>
<td>$\Delta \mu_{[1]}^{(1)}_{\text{exch}}$</td>
<td>0.5244 (-0.0092)</td>
<td>0.4712 (-0.0099)</td>
<td>0.3811 (-0.0108)</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{ind}}$</td>
<td>0.0057 (+0.0011)</td>
<td>-0.0078 (+0.0012)</td>
<td>-0.0290 (+0.0013)</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{exch-ind}}$</td>
<td>0.0451</td>
<td>0.0407</td>
<td>0.0331</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{disp}}$</td>
<td>-0.2727</td>
<td>-0.2478</td>
<td>-0.2030</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}^{(1)}_{\text{exch-disp}}$</td>
<td>0.0198</td>
<td>0.0179</td>
<td>0.0145</td>
</tr>
<tr>
<td>$\Delta \mu_{[2]}$</td>
<td>1.0207</td>
<td>0.6627</td>
<td>-0.0271</td>
</tr>
</tbody>
</table>

V. NUMERICAL ILLUSTRATION

A. The interaction-induced dipole moment of He–H$_2$

As discussed in Sec. II, the symmetry-adapted perturbation theory in low orders provides the basis for understanding the mechanisms that yield the interaction-induced properties. However, the convergence of the SAPT expansion with respect to both the intermolecular interaction and the intramolecular electronic correlation must be fast enough to enable practical applications of the ansatz (11) in the calculation of collision-induced properties. Table 1 compares the components of the interaction-induced dipole moment of He–H$_2$ computed at the FCI level with the SAPT results in the same basis set. For each geometry of the complex considered in this table, SAPT recovers at least 94% of the FCI results. The convergence rate of the SAPT expansion slightly depends on the intermolecular separation $R$. In the region of the van der Waals minimum our SAPT results recover more than 96% of the FCI values. At smaller $R$ the accuracy of SAPT deteriorates somewhat due to the increase of the strength of the perturbation. Although these calculations were performed in the small basis set of $spd$ quality, we expect the error to be largely independent of the basis. It is reasonable then to assume that the effect of the truncation of the perturbation series on the components of the interaction-induced dipole moment of He–H$_2$ should be smaller than 6%.
### TABLE 3. SAPT contributions (in $10^{-3}$ a.u.) to the perpendicular component of the interaction-induced dipole moment of He–H$_2$ as functions of the angle $\theta$ at $R = 5$ and 7 bohr. The numbers in parentheses represent the intramonomer correlation contributions. All results were computed in the $[5s4p3d2f/4s3p2df]$ basis.

<table>
<thead>
<tr>
<th>$R = 5$ bohr</th>
<th>$\theta = 30^\circ$</th>
<th>$\theta = 45^\circ$</th>
<th>$\theta = 60^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \mu_{z,exch}^{(1)}$</td>
<td>-1.644 (+0.029)</td>
<td>-1.818 (+0.033)</td>
<td>-1.510 (+0.029)</td>
</tr>
<tr>
<td>$\Delta \mu_{z,exch}^{(2)}$</td>
<td>0.770 (+0.025)</td>
<td>0.811 (+0.024)</td>
<td>0.642 (+0.016)</td>
</tr>
<tr>
<td>$\Delta \mu_{z,ind}^{(1)}$</td>
<td>0.095 (-0.001)</td>
<td>0.096 (-0.000)</td>
<td>0.071 (-0.000)</td>
</tr>
<tr>
<td>$\Delta \mu_{z,exch-ind}^{(3)}$</td>
<td>0.026</td>
<td>0.027</td>
<td>0.021</td>
</tr>
<tr>
<td>$\Delta \mu_{z,disp}^{(2)}$</td>
<td>-0.257</td>
<td>-0.282</td>
<td>-0.231</td>
</tr>
<tr>
<td>$\Delta \mu_{z,exch-disp}^{(2)}$</td>
<td>0.032</td>
<td>0.034</td>
<td>0.027</td>
</tr>
<tr>
<td>$\Delta \mu_{z}$</td>
<td>-1.038</td>
<td>-1.196</td>
<td>-1.029</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$R = 7$ bohr</th>
<th>$\theta = 30^\circ$</th>
<th>$\theta = 45^\circ$</th>
<th>$\theta = 60^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \mu_{z,exch}^{(1)}$</td>
<td>-0.3775 (+0.0083)</td>
<td>-0.4280 (+0.0094)</td>
<td>-0.3640 (+0.0079)</td>
</tr>
<tr>
<td>$\Delta \mu_{z,exch}^{(2)}$</td>
<td>0.0178 (+0.0003)</td>
<td>0.0185 (+0.0003)</td>
<td>0.0144 (+0.0002)</td>
</tr>
<tr>
<td>$\Delta \mu_{z,ind}^{(1)}$</td>
<td>0.0094 (-0.0001)</td>
<td>0.0094 (-0.0001)</td>
<td>0.0069 (-0.0000)</td>
</tr>
<tr>
<td>$\Delta \mu_{z,exch-ind}^{(2)}$</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0004</td>
</tr>
<tr>
<td>$\Delta \mu_{z,disp}^{(2)}$</td>
<td>-0.0244</td>
<td>-0.0271</td>
<td>-0.0225</td>
</tr>
<tr>
<td>$\Delta \mu_{z,exch-disp}^{(2)}$</td>
<td>0.0010</td>
<td>0.0010</td>
<td>0.0008</td>
</tr>
<tr>
<td>$\Delta \mu_{z}$</td>
<td>-0.3745</td>
<td>-0.4268</td>
<td>-0.3649</td>
</tr>
</tbody>
</table>

### FIG. 1. Comparison of the different SAPT contributions to the parallel component of the interaction-induced dipole moment of He–H$_2$ as functions of the angle $\theta$ at $R = 5$ bohr. Open circles correspond to $\Delta \mu_{z,exch}^{(1)}$, open squares to $\Delta \mu_{z,exch}^{(2)}$, open triangles to $\Delta \mu_{z,ind}^{(2)}$, lozenges to $\Delta \mu_{z,exch-ind}^{(2)}$, crosses to $\Delta \mu_{z,disp}^{(2)}$, filled triangles to $\Delta \mu_{z,exch-disp}^{(2)}$ and filled circles to the sum value (dashed line).
The interaction-induced dipole moment of He–H$_2$ is reported as functions of the angle $\vartheta$ in Tables 2 and 3 for two distances: 5 and 7 bohr, bracketing the minimum in the isotropic van der Waals potential which is at 6.42 bohr. See also Figs. 1–4 for graphical illustrations. An inspection of Table 2 and Fig. 1 shows that at 5 bohr the first-order exchange term is by far the largest contribution to the parallel component of the interaction-induced dipole. However, other terms are non-negligible, and the final anisotropy of the dipole surface results from the cancellation of large positive and negative contributions. By contrast, the $\vartheta$ dependence of the dipole surface for the perpendicular component is to a large extent determined by the sum $\Delta \mu_{z,\text{pol}} + \Delta \mu_{z,\text{exch}}^{(1)}$. Other contributions are relatively less important and amount to 15% of $\Delta \mu_z$. It is interesting to note that among various post-Hartree-Fock contributions to $\Delta \mu_z$ and $\Delta \mu_x$, the intermonomer correlation, i.e., the sum of the dispersion and exchange-dispersion contributions, is dominant. The exchange quenching of the dispersion contribution is unexpectedly important, since it represents as much as 15% of $\Delta \mu_{x,\text{disp}}^{(2)}$ and 12% of $\Delta \mu_{x,\text{disp}}^{(2)}$. The intramonomer correlation contributions to $\Delta \mu_{\text{pol}}^{(1)}$, $\Delta \mu_{\text{exch}}^{(1)}$, and $\Delta \mu_{\text{ind}}^{(2)}$ are negligibly small and amount to a fraction of a percent of $\Delta \mu_z$ at all angles. This suggests that the “Hartree–Fock plus dispersion”
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FIG. 3. Comparison of the different SAPT contributions to the parallel component of the interaction-induced dipole moment of He–H₂ as functions of the angle \( \theta \) at \( R = 7 \) bohr. Labels as for Fig. 1.

model could possibly be applied in practice, provided that the dispersion contribution is not approximated by its multipole expansion (cf. the discussion below). These findings are in agreement with the supermolecule results of Meyer and Frommhold²² from localized coupled electron pair approximation calculations.

At 7 bohr, just outside the isotropic van der Waals minimum, the first-order electrostatic and exchange contributions are equally important for the parallel component, while the perpendicular component is dominated by the electrostatic contribution. At this distance \( \Delta \mu_{z,\text{pol}}^{(1)} \) is mainly due to the polarization of the He atom by the H₂ quadrupole, as is witnessed by the factor of about 2 between the values at \( \theta = 0^\circ \) and 90°. Recall that the SAPT approach does not use the multipole expansion,⁵,⁷² so that in the present calculations all charge overlap (damping) effects are fully included. We see that charge overlap gives a negative contribution to the parallel component of the dipole, which explains that at \( \theta = 90^\circ \) the ratio between the \( R = 5 \) to \( R = 7 \) bohr values of \( \Delta \mu_{z,\text{pol}}^{(1)} \) is much larger than the value \((7/5)^4 \) (≈3.84), which one would expect from expression Eq. (40). We also observe that at 5 bohr and \( \theta = 0^\circ \) the negative contribution from charge penetration quenches to a large extent the positive long-range contribution to \( \Delta \mu_{z,\text{pol}}^{(1)} \).

Since the multipole-expanded expressions for the interaction-induced dipole
moments are sometimes used in the calculations of the collision-induced spectra (see e.g. Ref. 101), it is interesting to check in somewhat more detail whether this approximation correctly reproduces the polarization contributions to $\Delta \mu_i$. In Figs. 5 and 6 we compare the anisotropy of $\Delta \mu_{i,\text{pol}}^{(1)}$, $\Delta \mu_{i,\text{ind}}^{(2)}$, and $\Delta \mu_{i,\text{disp}}^{(2)}$, $i = z$ or $x$, as computed by SAPT and from the multipole expansion at the intermolecular distance of 5 bohr. The region around 5 bohr dominates the infrared absorption, see e.g. Ref. 16. In Figs. 7 and 8 we compare $\Delta \mu_{i,\text{pol}}^{(1)}$, $\Delta \mu_{i,\text{ind}}^{(2)}$, and $\Delta \mu_{i,\text{disp}}^{(2)}$, $i = z$ or $x$, computed by SAPT and in the multipole approximation at $R=7$ bohr. Since the multipole-expanded calculations were performed at the same level of theory and in the same basis sets, all differences can be attributed to the neglect of the charge overlap (damping) effects. An inspection of Fig. 5 shows that the multipole approximations to the electrostatic, induction, and dispersion contributions reproduce the shape of the anisotropy of these components. The actual values are rather different, however. For instance, the electrostatic and dispersion contributions are strongly overestimated, while the induction term is underestimated. It is interesting to note that the multipole approximations to $\Delta \mu_{i,\text{pol}}^{(1)}$ and $\Delta \mu_{i,\text{ind}}^{(2)}$ do not even reproduce correctly the signs of these components. This suggests that the electrostatic and induction terms are dominated by the exponential charge-overlap contributions. Consequently, these contributions cannot be represented by introducing damping functions into the multipole-expanded expressions. The situation is somewhat different for the perpendicular component $\Delta \mu_{i}$ (cf. Fig. 6). The $\vartheta$ dependence of $\Delta \mu_{x,\text{pol}}^{(1)}$, $\Delta \mu_{x,\text{ind}}^{(2)}$, and $\Delta \mu_{x,\text{disp}}^{(2)}$ is again correctly predicted by the multipole approximation. But also the actual values of the electrostatic and induction contributions are rather well reproduced (within about 10% or better), while the dispersion term is again overestimated.

### B. The interaction-induced polarizability of $\text{He}_2$

In Table 4 we compare the components of the interaction-induced polarizability computed at the FCI level with the SAPT results in the same basis set. For all distances considered in this table, the SAPT results underestimate the values from the FCI calculations by 2% at worst. Similarly as in the case of $\text{He}--\text{H}_2$ the convergence rate of the SAPT expansion shows a weak dependence on the interatomic distance.

In Tables 5 and 6 we analyse the computed values of $\Delta \alpha_{zz}$ and $\Delta \alpha_{xx}$ in terms of SAPT contributions at various interatomic distances. The largest contributions to the components of the interaction-induced polarizability are given by the first-order terms. Except for the smallest interatomic distance ($R = 3$ bohr), the sum $\Delta \alpha_{i,\text{pol}}^{(1)} + \Delta \alpha_{i,\text{exch}}^{(1)}$, $i = z$ or $x$, reproduces more than...
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FIG. 4. Comparison of the different SAPT contributions to the perpendicular component of the interaction-induced dipole moment of \( \text{He-H}_2 \) as functions of the angle \( \vartheta \) at \( R = 7 \) bohr. Labels as for Fig. 1.

TABLE 4. Comparison of the components of the interaction-induced polarizability of \( \text{He}_2 \) computed by SAPT with the FCI results (in \( 10^{-3} \) a.u.). All results were computed in the \([5s3p2d]\) basis.

<table>
<thead>
<tr>
<th>( R ) (bohr)</th>
<th>( R = 4 ) bohr</th>
<th>( R = 5.6 ) bohr</th>
<th>( R = 8 ) bohr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta \alpha_{zz} )</td>
<td>( \Delta \alpha_{xx} )</td>
<td>( \Delta \alpha_{zz} )</td>
</tr>
<tr>
<td>SAPT</td>
<td>39.64</td>
<td>-70.88</td>
<td>39.38</td>
</tr>
<tr>
<td>FCI</td>
<td>40.35</td>
<td>-71.57</td>
<td>40.25</td>
</tr>
<tr>
<td>( \Delta^\alpha )</td>
<td>-1.74%</td>
<td>-0.96%</td>
<td>-2.14%</td>
</tr>
</tbody>
</table>

*Relative error of the SAPT result with respect to the FCI result.
FIG. 5. Comparison of the multipole-expanded (dashed lines) and nonexpanded (solid lines) polarization contributions to the parallel component of the interaction-induced dipole moment of He–H₂ as functions of the angle $\vartheta$ at $R = 5$ bohr. The first-order contributions are labeled with open circles, the second-order induction contributions with open triangles and the second-order dispersion contributions with crosses.
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FIG. 6. Comparison of the multipole-expanded (dashed lines) and nonexpanded (solid lines) polarization contributions to the perpendicular component of the interaction-induced dipole moment of He–H₂ as functions of the angle \( \vartheta \) at \( R = 5 \) bohr. Labels as for Fig. 5.

FIG. 7. Comparison of the multipole-expanded (dashed lines) and nonexpanded (solid lines) polarization contributions to the parallel component of the interaction-induced dipole moment of He–H₂ as functions of the angle \( \vartheta \) at \( R = 7 \) bohr. Labels as for Fig. 5.
FIG. 8. Comparison of the multipole-expanded (dashed lines) and nonexpanded (solid lines) polarization contributions to the perpendicular component of the interaction-induced dipole moment of He–H₂ as functions of the angle θ at \( R = 7 \) bohr. Labels as for Fig. 5.

88% of the total interaction-induced polarizability. Observe further that the intra-atomic correlation contributions to \( \Delta \alpha_{\text{rt,po}l}^{(1)} \) and \( \Delta \alpha_{\text{rt,exch}}^{(1)} \) are important. For the electrostatic term this contribution represents 7%–8% of the uncorrelated result, while for the exchange component it amounts to as much as 10% to 20%. The interatomic correlation contributions are of relatively modest importance, being of the same order of magnitude as the intra-atomic correlation contributions. For example, in the region of the potential minimum (\( R = 5.6 \) bohr) the sum of the dispersion and exchange-dispersion terms contributes to \( \Delta \alpha_{zz} \) and \( \Delta \alpha_{xx} \) only 7% and 4%, respectively.

Finally, in Tables 7 and 8 we compare the multipole-expanded and nonexpanded polarization contributions to the parallel and perpendicular components of the interaction-induced polarizability of He₂. For both components the multipole expansion yields results which differ considerably from the nonexpanded data. Except for large interatomic distances, the multipole expansion is clearly seen to diverge. It is interesting to note that the rate of divergence is different for the perpendicular and parallel components, as well as for various contributions. For instance, at intermediate distances near the van der Waals minimum the electrostatic contribution is rather well represented by the multipole approximation, while the induction and dispersion terms are
### TABLE 5. SAPT contributions (in $10^{-3}$ a.u.) to the parallel component of the interaction-induced polarizability of $\text{He}_2$ as functions of the interatomic distance $R$ (in bohr). The numbers in parentheses represent the intramonomer correlation contributions. All results were computed in the $[7s5p4d3f2g]$ basis.

<table>
<thead>
<tr>
<th>$R$</th>
<th>3.0</th>
<th>5.6</th>
<th>7.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \alpha_{zz}^{(1)}$, pol</td>
<td>342.217</td>
<td>44.626</td>
<td>22.184</td>
<td>7.572</td>
</tr>
<tr>
<td></td>
<td>(+28.037)</td>
<td>(+3.542)</td>
<td>(+1.732)</td>
<td>(+0.587)</td>
</tr>
<tr>
<td>$\Delta \alpha_{zz}^{(1)}$, exch</td>
<td>−616.256</td>
<td>−9.498</td>
<td>−0.627</td>
<td>−0.001</td>
</tr>
<tr>
<td></td>
<td>(−66.056)</td>
<td>(−1.315)</td>
<td>(−0.097)</td>
<td>(−0.000)</td>
</tr>
<tr>
<td>$\Delta \alpha_{zz}^{(2)}$, ind</td>
<td>143.300</td>
<td>1.507</td>
<td>0.217</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>(+8.840)</td>
<td>(+0.093)</td>
<td>(+0.013)</td>
<td>(+0.001)</td>
</tr>
<tr>
<td>$\Delta \alpha_{zz}^{(2)}$, exch−ind</td>
<td>−129.820</td>
<td>−0.799</td>
<td>−0.034</td>
<td>−0.000</td>
</tr>
<tr>
<td>$\Delta \alpha_{zz}^{(2)}$, disp</td>
<td>57.033</td>
<td>2.976</td>
<td>0.603</td>
<td>0.045</td>
</tr>
<tr>
<td>$\Delta \alpha_{zz}^{(2)}$, exch−disp</td>
<td>−7.158</td>
<td>−0.250</td>
<td>−0.021</td>
<td>0.000</td>
</tr>
<tr>
<td>$\Delta \alpha_{zz}$</td>
<td>−5.744</td>
<td>39.645</td>
<td>22.370</td>
<td>7.653</td>
</tr>
</tbody>
</table>

### TABLE 6. SAPT contributions (in $10^{-3}$ a.u.) to the perpendicular component of the interaction-induced polarizability of $\text{He}_2$ as functions of the interatomic distance $R$ (in bohr). The numbers in parentheses represent the intramonomer correlation contributions. All results were computed in the $[7s5p4d3f2g]$ basis.

<table>
<thead>
<tr>
<th>$R$</th>
<th>3.0</th>
<th>5.6</th>
<th>7.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \alpha_{xy}^{(1)}$, pol</td>
<td>−114.194</td>
<td>−21.407</td>
<td>−11.037</td>
<td>−3.785</td>
</tr>
<tr>
<td></td>
<td>(−7.854)</td>
<td>(−1.651)</td>
<td>(−0.857)</td>
<td>(−0.293)</td>
</tr>
<tr>
<td>$\Delta \alpha_{xy}^{(1)}$, exch</td>
<td>−112.193</td>
<td>−1.140</td>
<td>−0.057</td>
<td>−0.000</td>
</tr>
<tr>
<td></td>
<td>(−13.393)</td>
<td>(−0.198)</td>
<td>(−0.011)</td>
<td>(−0.000)</td>
</tr>
<tr>
<td>$\Delta \alpha_{xy}^{(2)}$, ind</td>
<td>10.974</td>
<td>0.203</td>
<td>0.047</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>(+0.854)</td>
<td>(+0.012)</td>
<td>(+0.003)</td>
<td>(+0.000)</td>
</tr>
<tr>
<td>$\Delta \alpha_{xy}^{(2)}$, exch−ind</td>
<td>1.300</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$\Delta \alpha_{xy}^{(2)}$, disp</td>
<td>18.550</td>
<td>0.923</td>
<td>0.217</td>
<td>0.021</td>
</tr>
<tr>
<td>$\Delta \alpha_{xy}^{(2)}$, exch−disp</td>
<td>−2.888</td>
<td>−0.047</td>
<td>−0.003</td>
<td>0.000</td>
</tr>
<tr>
<td>$\Delta \alpha_{xx}$</td>
<td>−185.932</td>
<td>−21.442</td>
<td>−10.851</td>
<td>−3.752</td>
</tr>
</tbody>
</table>
TABLE 7. Multipole contributions (in $10^{-3}$ a.u.) to the parallel component of the interaction-induced polarizability of He$_2$ as functions of the interatomic distance $R$ (in bohr). All results were computed in the [7s5p4d3f2y] basis. The numbers in parentheses represent the relative error of the multipole result with respect to the SAPT result (cf. Table 5).

<table>
<thead>
<tr>
<th>$R$</th>
<th>3.0</th>
<th>5.6</th>
<th>7.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \alpha_{1}^{(1)}$</td>
<td>280.315 (-18.1%)</td>
<td>43.097 (-3.4%)</td>
<td>22.066 (-0.5%)</td>
<td>7.569 (-0.0%)</td>
</tr>
<tr>
<td>$\Delta \alpha_{2}^{(2)}$</td>
<td>47.498 (-66.9%)</td>
<td>0.717 (-52.0%)</td>
<td>0.178 (-18.0%)</td>
<td>0.020 (-0.0%)</td>
</tr>
<tr>
<td>$\Delta \alpha_{2r,ind}$</td>
<td>217.150 (-280.4%)</td>
<td>1.984 (-33.3%)</td>
<td>0.426 (-29.0%)</td>
<td>0.041 (-9.0%)</td>
</tr>
</tbody>
</table>

TABLE 8. Multipole contributions (in $10^{-3}$ a.u.) to the perpendicular component of the interaction-induced polarizability of He$_2$ as functions of the interatomic distance $R$ (in bohr). All results were computed in the [7s5p4d3f2y] basis. The numbers in parentheses represent the relative error of the multipole result with respect to the SAPT result (cf. Table 6).

<table>
<thead>
<tr>
<th>$R$</th>
<th>3.0</th>
<th>5.6</th>
<th>7.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \alpha_{1}^{(1)}$</td>
<td>-140.157 (22.7%)</td>
<td>-21.548 (0.7%)</td>
<td>-11.033 (-0.0%)</td>
<td>-3.784 (-0.0%)</td>
</tr>
<tr>
<td>$\Delta \alpha_{2}^{(2)}$</td>
<td>14.051 (28.0%)</td>
<td>0.188 (-7.4%)</td>
<td>0.046 (-2.0%)</td>
<td>0.005 (-0.0%)</td>
</tr>
<tr>
<td>$\Delta \alpha_{2r,disp}$</td>
<td>99.999 (439.1%)</td>
<td>0.860 (-6.8%)</td>
<td>0.196 (-10.0%)</td>
<td>0.021 (-0.0%)</td>
</tr>
</tbody>
</table>

underestimated, especially for the parallel component. Hence, we conclude that the full inclusion of the charge-overlap effects is very important. The difference between the expanded and nonexpanded dispersion contribution to the parallel component at $R = 10$ bohr may be caused partly by numerical errors in the finite field method.

VI. CONCLUSION

A symmetry-adapted perturbation theory has been formulated for the calculation of the interaction-induced electrical properties of weakly bound complexes, and general asymptotic expressions have been derived for the first- and second-order contributions to the collision-induced dipole moments and polarizabilities in terms of the multipole moments and (hyper)polarizabilities of the isolated monomers. Numerical results for model four-electron systems (He–H$_2$ and He$_2$) reported in the present work suggest that the SAPT method could be routinely used in the calculations of the collision-induced properties. Below we summarize the major features of the SAPT approach:

1. The interaction-induced properties are computed directly as a sum of well-defined physical contributions, which have a clear, partly classical, partly quantum, physical interpretation.
2. Since the interaction-induced properties are obtained directly (not as a difference of large numbers) they are free from basis set superposition errors.

3. The multipole expansion is not employed, so all charge penetration (damping) effects are automatically included.

4. The multipole expansion has its use, however, in offering asymptotic constraints to the fits of the SAPT contributions to the interaction-induced dipole moments and polarizabilities. This is because the long-range contribution can be computed separately in terms of monomer properties [multipole moments and (hyper)polarizabilities], which in turn can be calculated in the same basis and at the same level of approximation as used in the SAPT approach.

5. The convergence of the SAPT expansion for the interaction-induced dipole moment and polarizability appears to be satisfactory, at least for model four-electron systems like He–H$_2$ and He$_2$.

Of course, the final judgement of the accuracy of the computed collision-induced dipole moments and polarizabilities is by comparison with experiment. In Chapters 2 and 3 we report the collision-induced Raman spectra and second dielectric virial coefficients for the He diatom computed using the interaction-induced polarizability tensor from SAPT calculations.

**ACKNOWLEDGMENTS**

We thank Dr. Piotr Piecuch for his help with Zarrabian’s FCI program. This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and Polish Scientific Research Council (KBN), Grant No. 3T09A 072 09.
APPENDIX A: 12- AND 15J-SYMBOLS

For the convenience of the reader, we give the $12j$ symbol of the first kind occurring in Eq. (35), expressed as a single sum of products of four $6j$ symbols:

$$
\sum_x [x] \left[ (-1)^{l_A + l_B + l + \lambda_A + 1 + x} \right. \\
\left. \times \left\{ \begin{array}{c}
\begin{array}{ccc}
l_A & l_B & L \\
L_A & 1 & 1
\end{array} \\
\begin{array}{ccc}
l_A' & l_B' & \lambda_A \\
L_A & l & 1
\end{array}
\right\} \right\} \\
\times \left\{ \begin{array}{c}
\begin{array}{ccc}
l_B & l' & x \\
L & l_A + l_B & 1
\end{array} \\
\begin{array}{ccc}
l_B' & l' & \lambda \\
L & \lambda_A & 1
\end{array}
\right\} \right\}.
$$

A similar expression holds for the $12j$ symbol of the first kind in Eq. (48). Note that in this work only integer quantum numbers appear. We simplified the phases accordingly.

Analogously, the $15j$ symbol of the third kind appearing in Eq. (47) can be written as a single sum of products of one $6j$ and two $9j$ symbols:

$$
\sum_x [x] \left[ (-1)^{\lambda_B + l_A + 1 + x} \right. \\
\left. \times \left\{ \begin{array}{c}
\begin{array}{ccc}
L_A & l' & \lambda \\
1 & l_A & 1
\end{array} \\
\begin{array}{ccc}
L_B & l' & l \\
l_B & l_A + l_B & 1
\end{array}
\right\} \right\} \\
\times \left\{ \begin{array}{c}
\begin{array}{ccc}
L_B & l' & x \\
1 & l & 1
\end{array} \\
\begin{array}{ccc}
L & l_A & \lambda \\
L_A & \lambda & 1
\end{array}
\right\} \right\} \left\{ \begin{array}{c}
\begin{array}{ccc}
l_B & l' & \lambda \\
L & l_A + l_B & 1
\end{array} \\
\begin{array}{ccc}
l_B' & l' & \lambda \\
L & \lambda_A & 1
\end{array}
\right\} \right\}.
$$

The other $15j$ symbol of the third kind appearing in the present chapter [Eq. (49)], can be expressed similarly.

APPENDIX B: SPECIAL FORMULAS FOR HE$_2$

Below we list the multipolar dispersion contributions to the collision induced polarizabilities of two identical $S$ state atoms. We write

$$
(\Delta \delta_0^{(11)0})_{disp}^{(2)}(R) \approx -\sqrt{3} \left( \frac{A_6}{R_6} + \frac{A_8}{R_8} + \frac{A_{10}}{R_{10}} \right)
$$

and

$$
(\Delta \delta_0^{(11)2})_{disp}^{(2)}(R) \approx \frac{2}{\sqrt{6}} \left( \frac{B_6}{R_6} + \frac{B_8}{R_8} + \frac{B_{10}}{R_{10}} \right),
$$

cf. Eq. (57). The coefficients $A_n$ and $B_n$ are
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\[ A_6 = -\frac{2}{3\pi} \sqrt{3} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((11)0)(11)0}(i\omega, 0, 0) d\omega \]

\[ A_8 = \frac{1}{\pi} \sqrt{5} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((22)0)(11)0}(i\omega, 0, 0) d\omega \]

\[ + \frac{1}{\pi} \sqrt{5} \int_0^\infty \alpha_0^{(22)0}(i\omega) \gamma_0^{((11)0)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{1}{\pi} \int_0^\infty \beta_0^{(21)110}(i\omega, 0) \beta_0^{(21)110}(i\omega, 0) d\omega \]

\[ A_{10} = -\frac{4}{3\pi} \sqrt{7} \int_0^\infty \alpha_0^{(23)0}(i\omega) \gamma_0^{((11)0)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{14}{3\pi} \sqrt{7} \int_0^\infty \alpha_0^{(22)0}(i\omega) \gamma_0^{((22)0)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{4}{3\pi} \sqrt{7} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((33)0)(11)0}(i\omega, 0, 0) d\omega \]

\[ + \frac{8}{3\pi} \sqrt{14} \int_0^\infty \beta_0^{(33)110}(i\omega, 0) \beta_0^{(21)110}(i\omega, 0) d\omega \]

\[ B_6 = -\frac{1}{10\pi} \sqrt{15} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((11)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ B_8 = \frac{6}{5\pi} \int_0^\infty \alpha_0^{(22)0}(i\omega) \gamma_0^{((11)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ + \frac{12}{35\pi} \sqrt{35} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((22)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ + \frac{12}{35\pi} \sqrt{210} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((31)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{48}{5\pi} \int_0^\infty \beta_0^{(21)110}(i\omega, 0) \beta_0^{(21)110}(i\omega, 0) d\omega \]

\[ B_{10} = -\frac{2}{7\pi} \sqrt{35} \int_0^\infty \alpha_0^{(33)0}(i\omega) \gamma_0^{((11)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{10}{7\pi} \sqrt{21} \int_0^\infty \alpha_0^{(22)0}(i\omega) \gamma_0^{((22)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{30}{7\pi} \sqrt{14} \int_0^\infty \alpha_0^{(22)0}(i\omega) \gamma_0^{((31)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{5}{21\pi} \sqrt{210} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((33)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ - \frac{10}{7\pi} \sqrt{35} \int_0^\infty \alpha_0^{(11)0}(i\omega) \gamma_0^{((42)21)(11)0}(i\omega, 0, 0) d\omega \]

\[ + \frac{80}{7\pi} \sqrt{14} \int_0^\infty \beta_0^{(33)110}(i\omega, 0) \beta_0^{(21)110}(i\omega, 0) d\omega \]
Chapter 2

Ab initio collision-induced polarizability, polarized and depolarized Raman spectra, and second dielectric virial coefficient of the helium diatom*

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Abstract
Symmetry-adapted perturbation theory has been applied to compute the interaction-induced polarizability for the helium diatom. The computed polarizability invariants have been analytically fitted and used in quantum-dynamical calculations of the binary collision-induced Raman spectra. The predicted intensities of the depolarized spectrum are in good agreement with the experimental data [M. H. Proffitt et al., Can. J. Phys. 59, 1459 (1981)]. The computed polarized spectrum shows agreement with the experiment within the large experimental uncertainties. The calculated trace polarizability has also been tested by comparison of computed second dielectric virial coefficients with the experimental data. The ab initio dielectric virial coefficients, including first- and second-order quantum corrections, agree well with the experimental data from indirect measurements.

I. INTRODUCTION

Interactions between colliding atoms in gases or fluids lead to distortions of their charge distributions, so that a collisional pair of atoms possesses a polarizability in excess of the sum of polarizabilities of the isolated atoms. This excess polarizability, referred to as the interaction-induced or collision-induced polarizability, is defined as the incremental part of the diatom polarizability tensor due to interatomic interactions, i.e., as the difference between the diatom polarizability tensor and the sum of polarizabilities of the noninteracting atoms.

The interaction-induced pair polarizabilities are responsible for a wide range of dielectric, refractive, and optical properties of gases and fluids. Levine and Birnbaum predicted that all Raman spectra of gases should have a component due to the collision-induced changes in the polarizabilities and it was first demonstrated by McTague and Birnbaum that free argon atoms in a collisional encounter undergo transitions between translational states when interacting with photons. At very low densities the light scattering leads to the well known Rayleigh–Brillouin process. At higher densities nearly exponential Stokes and anti-Stokes wings appear, with intensities proportional to the square of the gas density. These components of the Raman spectra of gases (referred to as the translational Raman effect) are due to the collision-induced light scattering, i.e., to the interaction-induced fluctuations of the polarizabilities of atoms and molecules. In particular, in atomic fluids the anisotropy of the polarizability tensor will give rise to the depolarized Raman spectrum, while the small trace polarizability will lead to the polarized Raman spectrum. Since the early work on argon, the collision-induced light scattering has been experimentally studied in several optically isotropic systems (see Refs. 15 and 102 for reviews).

Besides giving rise to the collision-induced light scattering, the interaction-induced polarizability invariants also affect the dielectric and refractive properties of gases. The trace polarizability determines the second virial coefficient of the dielectric Clausius–Mosotti function, while the square of the anisotropy of the interaction-induced polarizability tensor is related to the Kerr constant of gases and to the pressure-dependent depolarization ratio. At present, the second dielectric virial coefficients and Kerr constants are available for various atomic and molecular systems (see Refs. 103 and 104 for reviews of the experimental data).

The collision-induced polarizability of the He diatom has been investigated using various experimental techniques. Several studies of the collision-induced light scattering in helium have been reported in the literature. Most of these measurements were performed at high densities, so the reported
Raman intensities were affected by three-body contributions and pure pair spectra had to be separated by the application of some simplified models. Only the polarized and depolarized Raman spectra for the $^3$He and $^4$He gases reported by Proffitt, Keto, and Frommhold were shown to be free from three-body contributions, i.e., the recorded Raman intensities showed the correct quadratic dependence on the gas density. Also the refractivity and second dielectric virial coefficients at various temperatures as well as the depolarization ratio of the He gas have been reported.

Because of the small number of electrons involved, the interaction-induced polarizability of He$_2$ has been object of many *ab initio* studies. Most of these studies were performed at the Hartree–Fock level of theory, neglecting important inter- and intra-atomic correlation effects. To our knowledge, the only correlated results for the collision-induced polarizability of He$_2$ were reported by Dacre. These calculations were performed using the configuration interaction method restricted to single and double excitations (CISD) and medium-size spd basis sets. In addition, also the long-range coefficients have been computed for this system at various levels of approximation.

The quantum-mechanical theory of the collision-induced Raman spectra is now well established and *a priori* calculations of the Raman intensities are feasible once the pair interaction potential and the interaction-induced polarizability are available. Various *ab initio* polarizability data for He$_2$ have been used to compute the collision-induced Raman spectra of the He diatom for comparison with experiment (see also Ref. 15 for a review of these results). In an extensive theoretical study Dacre and Frommhold have investigated the accuracy of the *ab initio* CISD trace and anisotropy polarizabilities of He$_2$ (Ref. 28) by exposing them to the test of computing the observed Raman intensities. While the depolarized spectra computed from Dacre’s polarizability showed good agreement with the experiment for both isotopes of helium, the theoretical polarized spectrum was much less intense than the spectrum derived from the experiment.

The reasons for the less satisfactory agreement between the theoretical and experimental polarized Raman spectra may be both on the theoretical and on the experimental side. The experimental polarized spectrum is obtained as the difference of two nearly equal signals excited with different beam polarizations and the accuracy of the polarized intensities deduced from the experiment may be poor. On the other hand, the theoretical values of the interaction-induced trace may suffer from the approximate corrections for the size-inconsistency of the CISD method, the basis set superposition error, or basis set incompleteness. Finally, the computed polarized spectra showed a
rather strong dependence on the interatomic potential. The potentials used in the calculations of Ref. 34 differ from the best empirical potentials available at present.\textsuperscript{137,138} Thus, an attempt to refine the accuracy of the \textit{ab initio} polarizability invariants of He\textsubscript{2} and to check these by computing the Raman spectra is now in order.

We have shown in Chapter 1 that the interaction-induced properties of collisional complexes can be accurately computed using the many-body formulation\textsuperscript{61-67} of the symmetry-adapted perturbation theory (SAPT)\textsuperscript{3,69-71} (see Ref. 4 for a recent review of SAPT). In the present work we report SAPT calculations of the interaction-induced polarizability for the He diatom and dynamical calculations of the polarized and depolarized Raman intensities. We also test the \textit{ab initio} collision-induced polarizability by the computation of the second dielectric virial coefficient and comparison with the available experimental data.

\section*{II. OUTLINE OF SAPT CALCULATIONS}

\subsection*{A. Method and definitions}

The interaction-induced polarizability \( \Delta \alpha_{ij} \) of a pair of atoms A and B is defined as the excess polarizability of the collisional pair AB due to intermolecular interactions, i.e.,

\begin{equation}
\Delta \alpha_{ij} = \alpha_{ij}^{AB} - (\alpha_0^A + \alpha_0^B) \delta_{ij},
\end{equation}

where \( \alpha_{ij}^{AB} \) is a component of the dimer polarizability tensor and \( \alpha_0^A \) and \( \alpha_0^B \) denote polarizabilities of the isolated atoms A and B, respectively. Equation (1) can be conveniently rewritten as

\begin{equation}
\Delta \alpha_{ij} = - \left( \frac{\partial^2 E_{\text{int}}}{\partial F^i \partial F^j} \right)_{F_i=F_j=0},
\end{equation}

where \( E_{\text{int}} \) is the interaction energy for the dimer AB in the presence of a static, uniform electric field \( F \). Equation (2) shows that the interaction-induced polarizability can be obtained from standard finite field calculations, if the field-dependent interaction energy can be computed. In the present work we utilize this possibility, i.e., we first perform calculations of the interaction energy in the static electric field using the symmetry-adapted perturbation theory and subsequently obtain the interaction-induced polarizability components from finite difference formulas. Below we shortly summarize the SAPT \textit{ansatz} for the field-dependent interaction energy \( E_{\text{int}} \). The components of the interaction-induced polarizability tensor \( \Delta \alpha_{ij} \) are obtained from the equation
\[
\Delta \alpha_{ii} = -\frac{E_{\text{int}}(F_i) + E_{\text{int}}(-F_i) - 2E_{\text{int}}(0)}{F_i^2} + O(F_i^4),
\]

where the index \( i = z \) or \( x \) denotes the direction along the dimer axis or perpendicular to this axis, respectively.

In the calculations of the interaction energy in the static electric field we follow the approach proposed and tested in Chapter 1 (see also Refs. 75–80 for applications to the interaction energy calculations). The SAPT interaction energy is represented as a sum of components corresponding to the Hartree–Fock (\( E_{\text{int}}^{\text{HF}} \)) and correlated (\( E_{\text{int}}^{\text{corr}} \)) levels of the theory,

\[
E_{\text{int}} = E_{\text{int}}^{\text{HF}} + E_{\text{int}}^{\text{corr}}.
\]

The Hartree–Fock interaction energy can be decomposed as

\[
E_{\text{int}}^{\text{HF}} = E_{\text{pol}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch–ind,resp}}^{(20)} + \delta E_{\text{int}}^{\text{HF}},
\]

where \( E_{\text{pol}}^{(10)} \) and \( E_{\text{exch}}^{(10)} \) are the electrostatic and exchange contributions, respectively, with complete neglect of the intra-atomic correlation effects. \( E_{\text{ind,resp}}^{(20)} \) and \( E_{\text{exch–ind,resp}}^{(20)} \) are the Hartree–Fock induction and exchange-induction energies, respectively, accounting for the coupled-Hartree–Fock type response, i.e., for the perturbation-induced modification of the Hartree–Fock potential, \( \delta E_{\text{int}}^{\text{HF}} \) collects higher-order induction and exchange contributions.

At the correlated level, the SAPT interaction energy is represented by

\[
E_{\text{int}}^{\text{corr}} = \epsilon_{\text{pol}}^{(1)} + \epsilon_{\text{exch}}^{(1)} + \epsilon_{\text{ind}}^{(1)} + E_{\text{disp}}^{(2)} + E_{\text{exch–disp}}^{(2)},
\]

where \( E_{\text{disp}}^{(2)} \) is the dispersion energy and \( \epsilon_{\text{pol}}^{(1)}, \epsilon_{\text{exch}}^{(1)}, \) and \( \epsilon_{\text{ind}}^{(1)} \) are the electron correlation contributions to the exact electrostatic (\( E_{\text{pol}}^{(1)} \)), exchange (\( E_{\text{exch}}^{(1)} \)), and induction (\( E_{\text{ind}}^{(1)} \)) energies, respectively, i.e., \( \epsilon_{\text{pol}}^{(1)} \equiv E_{\text{pol}}^{(1)} - E_{\text{pol}}^{(10)} \), \( \epsilon_{\text{exch}}^{(1)} \equiv E_{\text{exch}}^{(1)} - E_{\text{exch}}^{(10)} \), and \( \epsilon_{\text{ind}}^{(1)} \equiv E_{\text{ind}}^{(1)} - E_{\text{ind,resp}}^{(1)} \). Each term on the r.h.s. of Eq. (6) can be evaluated using many-body perturbation expansions with respect to the intra-atomic electronic correlation,

\[
E_{\text{pol}}^{(k)} = \sum_{n=0}^{\infty} E_{\text{pol}}^{(kn)} \quad \text{and} \quad E_{\text{exch}}^{(k)} = \sum_{n=0}^{\infty} E_{\text{exch}}^{(kn)},
\]

where \( E_{\text{pol}}^{(kn)} \) and \( E_{\text{exch}}^{(kn)} \) are the polarization and exchange corrections of \( k \)th-order in the intermolecular interaction and \( n \)th-order in the intra-atomic correlation. In the present study the contributions to \( E_{\text{int}}^{\text{corr}} \) were approximated as follows:
The electrostatic corrections $E_{\text{pol,resp}}^{(1n)}$ are defined as in Ref. 64. The first-order exchange components $E_{\text{exch}}^{(1n)}$ are defined as in Refs. 65 and 66, while $\Delta_{\text{exch}}^{(1)}$ (CCSD) is the sum of higher-order terms (in the intra-atomic correlation) obtained by replacing the first- and second-order cluster operators entering the expression for $E_{\text{exch}}^{(12)}$ by the converged coupled-cluster singles and doubles (CCSD) operators. The dispersion components $E_{\text{disp}}^{(2n)}$ are derived in Ref. 63. The induction-correlation term $E_{\text{ind-cor}}^{(22)}$ represents the true correlation contribution to the nonrelaxed $E_{\text{ind}}^{(22)}$ correction, as defined in Ref. 67. Finally, $E_{\text{exch-disp}}^{(20)}$ is the so-called Hartree-Fock exchange-dispersion energy.

The SAPT approach applied in the present paper is expected to give more accurate results for the interaction-induced polarizability tensor of He$_2$ than the CISD model used by Dacre. Unlike the CISD method, the perturbation theory approach is size-consistent and all contributions to the collision-induced trace and anisotropy vanish in the limit $R \to \infty$. Although Dacre’s calculations included approximate corrections for the size-consistency error, it is not a priori obvious that the resulting polarizability components are correct. In SAPT calculations the components of the interaction-induced polarizability tensor are obtained directly (not as a difference of large numbers), so they are free from basis set superposition errors plaguing correlated supermolecule calculations. Let us also mention that our approach accounts for the major part of the triple-excitation contribution to the dispersion term, while the CI method restricted to single and double excitations does not.

### B. Computational details

Calculations of the interaction-induced polarizability for the He dimer have been performed for ten interatomic distances $R$ ranging from $R = 3$ to 10 bohr. For the helium atom we used a [5s4p3d2f] basis. The $s$ orbitals were represented by the (61111) contraction of Van Duijneveldt’s 10s set and the exponents of the polarization functions were taken from Ref. 93. To test the basis set convergence, we performed additional calculations for $R = 3, 4, \text{and } 5$ bohr in two spdfg basis sets: [5s4p3d2f1g] and [7s5p4d3f1g], and in a smaller [5s3p2d] basis.
The exponents of the polarization functions were again taken from Ref. 93. The spherical form of the polarization functions has been used (5 \( d \) functions and 7 \( f \) functions). In order to fully account for the charge-overlap effects all calculations have been performed using the full dimer basis set.

The calculations have been performed with the SAPT system of codes.\(^9\) In addition, full configuration interaction (FCI) results have been obtained from the program by Zarrabian et al.\(^{96,97}\) The components of the interaction-induced polarizability tensor have been obtained by numerical differentiation of the field-dependent interaction energies, cf. Eq. (3). For both directions of the external electric field its strength was equal to \pm 0.001 \text{ a.u.} In addition, long-range van der Waals coefficients corresponding to the multipole-expanded electrostatic, induction, and dispersion polarizabilities have been computed at the same level of theory and the same basis sets using the \textsc{polcor} package\(^{73,74}\) (cf. Chapter 1). These coefficients have been subsequently used in the analytical fits of the interaction-induced polarizabilities. We used the Boys–Bernardi counterpoise correction to eliminate the basis set superposition error from the supermolecular Hartree–Fock calculations.\(^98\)

As discussed in Ref. 34, the intensities of the collision-induced Raman spectra depend on the invariants of the interaction-induced polarizability tensor at the laser wavelength \( \lambda \). Our SAPT calculations were performed for \( \lambda = \infty \), i.e., for the static case, and an extension of the SAPT theory to include the \( \lambda \) dependence would be very difficult. To investigate the importance of the wavelength dependence we have performed additional calculations using the supermolecule random phase approximation (RPA) and the second-order Møller–Plesset (MP2) approaches.\(^{73,74}\)

C. Analytical fits

The intensities of the collision-induced Raman transitions and the second dielectric virial coefficients depend on the invariants of the interaction-induced polarizability tensor. Therefore, in what follows we will consider the anisotropy \( \beta \) and the trace \( \alpha \), defined through the components of the tensor by the equations

\[
\beta = \Delta \alpha_{zz} - \Delta \alpha_{xx},
\]

\[
\alpha = \frac{1}{3} (\Delta \alpha_{zz} + 2 \Delta \alpha_{xx}).
\]

In SAPT calculations different physical contributions to the polarizability invariants exhibit different distance dependence and each contribution to the trace and anisotropy of the interaction-induced polarizability can be fitted separately. Therefore, it is convenient to represent \( \alpha \) and \( \beta \) as
\[ \alpha = \alpha^{(1)}_{\text{pol}} + \alpha^{(2)}_{\text{ind}} + \alpha^{(2)}_{\text{disp}} + \alpha_{\text{exch}}, \]
\[ \beta = \beta^{(1)}_{\text{pol}} + \beta^{(2)}_{\text{ind}} + \beta^{(2)}_{\text{disp}} + \beta_{\text{exch}}. \] (15)

Here \( \alpha^{(1)}_{\text{pol}} \) is the contribution to the trace due to electrostatic interactions (i.e., is obtained by differentiation of the field-dependent electrostatic energy \( E^{(1)}_{\text{pol}} = E^{(10)}_{\text{pol}} + E^{(11)}_{\text{pol}} \)), \( \alpha^{(2)}_{\text{ind}} \) and \( \alpha^{(2)}_{\text{disp}} \) are contributions due to second-order induction and dispersion interactions, respectively, and \( \alpha_{\text{exch}} \) is obtained by differentiation of the total exchange energy, \( E_{\text{exch}} = E^{(10)}_{\text{exch}} + E^{(20)}_{\text{exch}} + E^{(11)}_{\text{exch}} + E^{(12)}_{\text{exch}} + \delta E_{\text{HF}} \). Similar definitions hold for the contributions to \( \beta \). One may note that each term on the r.h.s. of Eq. (15) has a well-defined \( R \) dependence which is to a large extent determined by its multipole expansion (cf. Sec. III of Chapter 1).

Therefore, we performed separate fits of the exchange, electrostatic, induction, and dispersion contributions to \( \alpha \) and \( \beta \).

It is well known that the exchange terms \( \alpha_{\text{exch}} \) and \( \beta_{\text{exch}} \) depend exponentially on \( R \), so we represented the exchange components by the functions

\[ \alpha_{\text{exch}}(R) = \left( A^{(a)}_{\text{exch}} + B^{(a)}_{\text{exch}} R \right) \exp(-c^{(a)}_{\text{exch}} R) \]
\[ + \left( C^{(a)}_{\text{exch}} + D^{(a)}_{\text{exch}} R \right) \exp(-e^{(a)}_{\text{exch}} R), \] (16)

\[ \beta_{\text{exch}}(R) = \left( A^{(b)}_{\text{exch}} + B^{(b)}_{\text{exch}} R \right) \exp(-f^{(b)}_{\text{exch}} R) \]
\[ + \left( C^{(b)}_{\text{exch}} + D^{(b)}_{\text{exch}} R \right) \exp(-g^{(b)}_{\text{exch}} R), \] (17)

where the parameters \( A^{(a)}_{\text{exch}}, B^{(a)}_{\text{exch}}, C^{(a)}_{\text{exch}}, D^{(a)}_{\text{exch}}, \) and \( e^{(a)}_{\text{exch}} \), and similar parameters for \( \beta_{\text{exch}} \) were determined using the weighted least-square method with weights exponential in \( R \).

The electrostatic contribution to \( \beta \) was represented by the damped multipole term and an exponential function representing the short-range penetration terms due to the charge overlap,

\[ \beta^{(1)}_{\text{pol}}(R) = \left( A^{(\beta)}_{\text{pol}} + B^{(\beta)}_{\text{pol}} R \right) \exp(-a^{(\beta)}_{\text{pol}} R) + \frac{C^{(\beta)}_{\text{pol}}}{R^{3}} f_{3}(R; b^{(\beta)}_{\text{pol}}), \] (18)

where \( f_{n}(R; b) \) is the damping function in the Tang–Toennies form,\(^{140}\)

\[ f_{n}(R; b) = 1 - \exp(-b R) \sum_{k=0}^{n} \frac{(b R)^{k}}{k!}, \] (19)

and the parameters \( A^{(\beta)}_{\text{pol}}, B^{(\beta)}_{\text{pol}}, a^{(\beta)}_{\text{pol}}, \) and \( b^{(\beta)}_{\text{pol}} \) were determined using the weighted least-square method with \( R^{3} \) weights. One may note that the long-range coefficient \( C^{(\beta)}_{3,\text{pol}} \) was not fitted but computed \textit{ab initio} in the same basis set and at the same level of theory as \( \beta^{(1)}_{\text{pol}} \).
In the multipole approximation the electrostatic contribution to the inter­
action-induced polarizability tensor of two \( S \) state atoms is traceless (cf. Chap­
ter 1). Thus, \( \alpha_{\text{pol}}^{(1)} \) is exclusively due to short-range charge-overlap effects. Therefore, we represented \( \alpha_{\text{pol}}^{(1)} \) by the function

\[
\alpha_{\text{pol}}^{(1)}(R) = \left( A_{\text{pol}}^{(\alpha)} + B_{\text{pol}}^{(\alpha)} R \right) \exp(-\alpha_{\text{pol}}^{(\alpha)} R),
\]

where the parameters \( A_{\text{pol}}^{(\alpha)}, B_{\text{pol}}^{(\alpha)} \), and \( \alpha_{\text{pol}}^{(\alpha)} \) were determined using the weighted least-square method with weights exponential in \( R \).

The induction components \( \beta_{\text{ind}}^{(2)} \) and \( \alpha_{\text{ind}}^{(2)} \) were represented as sums of damped multipole expansions and exponential functions representing the short-range charge-overlap contributions,

\[
\alpha_{\text{ind}}^{(2)}(R) = \left( A_{\text{ind}}^{(\alpha)} + B_{\text{ind}}^{(\alpha)} R \right) \exp(-\alpha_{\text{ind}}^{(\alpha)} R) + \sum_{n=6}^{10} f_n(R; b_{\text{ind}}^{(\alpha)}) C_{n,\text{ind}}^{(\alpha)} R^{-n},
\]

\[
\beta_{\text{ind}}^{(2)}(R) = \left( A_{\text{ind}}^{(\beta)} + B_{\text{ind}}^{(\beta)} R \right) \exp(-\alpha_{\text{ind}}^{(\beta)} R) + \sum_{n=6}^{10} f_n(R; b_{\text{ind}}^{(\beta)}) C_{n,\text{ind}}^{(\beta)} R^{-n},
\]

where the prime on the summation symbol reminds us that the summation is restricted to even terms. The induction long-range coefficients \( C_{n,\text{ind}}^{(\alpha)} \) and \( C_{n,\text{ind}}^{(\beta)} \) are defined as in Sec. III of Chapter 1. These coefficients were not fitted but computed \textit{ab initio} in the same basis set and at the level of theory corresponding to the fitted functions \( \alpha_{\text{ind}}^{(2)}(R) \) and \( \beta_{\text{ind}}^{(2)}(R) \). We assumed the damping function \( f_n(R; b) \) in the Tang–Toennies form, cf. Eq. (19). The parameters \( A_{\text{ind}}^{(\alpha)}, B_{\text{ind}}^{(\alpha)}, a_{\text{ind}}^{(\alpha)}, \) and \( b_{\text{ind}}^{(\alpha)} \), and similar parameters for \( \beta_{\text{ind}}^{(2)} \), were determined using the weighted least-square method with \( R^6 \) weights.

The analytical representations of the dispersion contributions were the same as those of the induction terms, Eqs. (21) and (22), with the induction long-range coefficients \( C_{n,\text{ind}}^{(\alpha)} \) and \( C_{n,\text{ind}}^{(\beta)} \) replaced by the dispersion long-range coefficients \( C_{n,\text{disp}}^{(\alpha)} \) and \( C_{n,\text{disp}}^{(\beta)} \), defined as in Sec. III of Chapter 1. Again, these coefficients were not fitted but computed \textit{ab initio} in the same basis set and at the level of theory corresponding to the fitted functions \( \alpha_{\text{disp}}^{(2)}(R) \) and \( \beta_{\text{disp}}^{(2)}(R) \). Here too, the damping function was assumed in the Tang–Toennies form.

The comparison of the final fitted functions with the \textit{ab initio} points on which the fits were based shows that the typical approximation error is of the order of 0.4%. The only exception is, for obvious reasons, the region where the trace goes through zero. The values of the parameters are reported in in Tables 1 and 2. FORTRAN subroutines for generating the trace and anisotropy are available from the authors at the electronic mail address avda@theochem.kun.nl.
### TABLE 1. Parameters defining the analytical fits to the computed electrostatic and exchange components of the collision-induced trace and anisotropy of He$_2$. All parameters are in Hartree and proper powers of bohr.

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<th>$\alpha(R)$</th>
<th>$\beta(R)$</th>
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### TABLE 2. Parameters defining the analytical fits to the computed induction and dispersion components of the collision-induced trace and anisotropy of He$_2$. All parameters are in Hartree and proper powers of bohr.

<table>
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<th>$\beta(R)$</th>
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<tr>
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<td>9.653</td>
<td>14.345</td>
</tr>
<tr>
<td></td>
<td>$C_{8,\text{ind}}^{\alpha}$</td>
<td>$C_{8,\text{ind}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>42.118</td>
<td>50.541</td>
</tr>
<tr>
<td></td>
<td>$C_{10,\text{ind}}^{\alpha}$</td>
<td>$C_{10,\text{ind}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>334.021</td>
<td>357.880</td>
</tr>
<tr>
<td><strong>Dispersion</strong></td>
<td>$A_{\text{disp}}^{\alpha}$</td>
<td>$A_{\text{disp}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>-2.360</td>
<td>-6.145</td>
</tr>
<tr>
<td></td>
<td>$B_{\text{disp}}^{\alpha}$</td>
<td>$B_{\text{disp}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>1.836</td>
<td>3.329</td>
</tr>
<tr>
<td></td>
<td>$a_{\text{disp}}^{\alpha}$</td>
<td>$a_{\text{disp}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>1.604</td>
<td>1.649</td>
</tr>
<tr>
<td></td>
<td>$b_{\text{disp}}^{\alpha}$</td>
<td>$b_{\text{disp}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>1.246</td>
<td>1.709</td>
</tr>
<tr>
<td></td>
<td>$C_{6,\text{disp}}^{\alpha}$</td>
<td>$C_{6,\text{disp}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>23.205</td>
<td>13.504</td>
</tr>
<tr>
<td></td>
<td>$C_{8,\text{disp}}^{\alpha}$</td>
<td>$C_{8,\text{disp}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>356.165</td>
<td>646.947</td>
</tr>
<tr>
<td></td>
<td>$C_{10,\text{disp}}^{\alpha}$</td>
<td>$C_{10,\text{disp}}^{\beta}$</td>
</tr>
<tr>
<td></td>
<td>966.497</td>
<td>-6213.695</td>
</tr>
</tbody>
</table>
III. OUTLINE OF DYNAMICAL CALCULATIONS

The theory of collision-induced Raman spectra is well understood.\textsuperscript{134,135} Below we only give a short summary. The laser light of wave number $\omega_0$ is scattered inelastically by the interacting atoms. The intensities of the depolarized and polarized scattered light are given by

\begin{equation}
D(\nu) = \frac{2}{15} \omega^3 \omega_0 G(\nu),
\end{equation}

\begin{equation}
P(\nu) = \omega^3 \omega_0 A(\nu),
\end{equation}

where $\nu$ is the frequency shift, $\omega = \omega_0 - 2\pi \nu/c$, and $c$ is the speed of light. The frequency shift $\nu$ is negative for the Stokes and positive for the anti-Stokes lines. The spectral functions of the anisotropy and trace, $G(\nu)$ and $A(\nu)$, can be written as

\begin{equation}
G(\nu) = \frac{2\hbar c \lambda_B^3}{(2I+1)^2} \sum_{J,J'} g_J(2J+1) b^J_{J'} \int_0^\infty |\langle E', J' | \beta(R) | E, J \rangle|^2 e^{-E/k_B T} dE,
\end{equation}

\begin{equation}
A(\nu) = \frac{2\hbar c \lambda_B^3}{(2I+1)^2} \sum_{J} g_J(2J+1) \int_0^\infty |\langle E', J | \alpha(R) | E, J \rangle|^2 e^{-E/k_B T} dE,
\end{equation}

where $E' - E = h\nu$, $J' = J, J \pm 2$, $h$ is the Planck constant, $k_B$ is the Boltzmann constant, $T$ denotes the temperature, $\lambda_B = (\hbar^2/2\pi \mu k_B T)^{1/2}$ is the De Broglie wavelength, $\mu$ is the reduced mass of the collisional complex, and $I$ and $g_J$ designate the nuclear spin and nuclear spin statistical weight, respectively. The constants $b^J_{J'}$ are given by\textsuperscript{141,142}

\begin{equation}
b^J_{J'} = (2J' + 1) \left( \begin{array}{ccc} J' & J & 2J \\ 0 & 0 & 0 \end{array} \right)^2,
\end{equation}

where the expression in round brackets is a $3j$ symbol.\textsuperscript{89} Finally, the matrix elements of the trace and anisotropy appearing in Eqs. (25) and (26) are defined as

\begin{equation}
\langle E', J' | X(R) | E, J \rangle = \int_0^\infty \psi^*(R; E', J') X(R) \psi(R; E, J) dR,
\end{equation}

where $X = \alpha$ or $\beta$ and the radial wave functions $\psi(R; E, J)$ are solutions of the radial Schrödinger equation describing the relative motion of the atoms in the potential $V(R)$,

\begin{equation}
-\frac{\hbar^2}{2\mu} \frac{d^2 \psi}{dR^2} + \left[ V(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} - E \right] \psi = 0,
\end{equation}

subject to the energy normalization condition.
\[ \int_0^\infty \psi^*(R; E, J) \psi(R; E', J) dR = \delta(E - E'). \] (30)

Note that in Eqs. (25) and (26) we neglected transitions from a bound state to a continuum state and vice versa. Numerical results reported in Refs. 15 and 135 show that even for heavier rare gas pairs these transitions contribute usually less than 2% of the total intensity at any frequency shift. Since the He dimer is bound by 1.684 mK only, the contribution from bound-to-free and free-to-bound transitions at \( T = 296 \text{ K} \) should be even smaller. One may also note that the invariants of the interaction-induced polarizability tensor appearing in Eqs. (25) and (26) should be taken at the laser wave number \( \omega_0 \). We have checked (cf. Sec. IV A for the discussion of this point) that the dependence of \( \alpha(R) \) and \( \beta(R) \) on \( \omega_0 \) is very weak. Consequently, in the computations of the Raman spectra we used the static polarizability invariants from SAPT calculations.

The polarized and depolarized Raman intensities on the Stokes side were generated for the frequency shifts ranging from \( \nu_{\text{min}} = -400 \text{ cm}^{-1} \) to \( \nu_{\text{max}} = -10 \text{ cm}^{-1} \) with a step of 10 \( \text{cm}^{-1} \). The Schrödinger equation (29) was solved using the Numerov method. The calculations were performed with the bcont program of Le Roy\(^{143,144} \) adapted for the present purposes. The integration parameters and the number of partial wave components were chosen to yield spectral functions of the anisotropy and trace converged to 3\% at worst. In all calculations we have used the empirical He–He potential of Aziz \textit{et al.}\(^{137} \) The mass of \(^4\text{He} \) was fixed at 4.00260 amu\(^{145} \).

IV. NUMERICAL RESULTS

A. Interaction-induced polarizability of the He dimer

The residual error in the computed collision-induced polarizabilities is due to two sources: the neglect of higher-order terms in the SAPT expansion and deficiencies of the basis set used in the calculations. Table 3 compares the interaction-induced trace and anisotropy computed at the full CI level with the SAPT results in the same basis set. For each of the distances considered in this table, SAPT reproduces the full CI results to within 3\%. The only exception is the trace for \( R \geq 6 \text{ bohr} \) but in this region of \( R \) the trace is very small and does not contribute to the polarized Raman intensities.\(^{113} \) Although these calculations were performed in the small \textit{spd} basis, we expect the error to be largely independent of the basis set. It is reasonable then to assume that the effect of the truncation of the perturbation series on the computed interaction-induced polarizability invariants is smaller than 3\%. It is worth
TABLE 3. Comparison of the interaction-induced trace and anisotropy of He₂ computed by SAPT with the FCI results (in 10⁻³ a.u.). All results were computed in the \([5s3p2d]\) basis.

<table>
<thead>
<tr>
<th></th>
<th>(R = 3) bohr</th>
<th>(R = 4) bohr</th>
<th>(R = 5) bohr</th>
<th>(R = 8) bohr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\alpha(R))</td>
<td>(\beta(R))</td>
<td>(\alpha(R))</td>
<td>(\beta(R))</td>
</tr>
<tr>
<td>SAPT</td>
<td>-130.034</td>
<td>175.693</td>
<td>-34.037</td>
<td>110.519</td>
</tr>
<tr>
<td>FCI</td>
<td>-133.327</td>
<td>171.826</td>
<td>-34.262</td>
<td>111.912</td>
</tr>
<tr>
<td>(\Delta^a)</td>
<td>-2.47%</td>
<td>2.25%</td>
<td>-0.66%</td>
<td>-1.24%</td>
</tr>
</tbody>
</table>

*Relative error of the SAPT result with respect to the FCI result.

TABLE 4. Basis set dependence of the interaction-induced trace and anisotropy of He₂. All results are in 10⁻³ a.u.

<table>
<thead>
<tr>
<th></th>
<th>(R = 3) bohr</th>
<th>(R = 4) bohr</th>
<th>(R = 5) bohr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\alpha(R))</td>
<td>(\beta(R))</td>
<td>(\alpha(R))</td>
</tr>
<tr>
<td>([5s3p2d])</td>
<td>-130.034</td>
<td>175.696</td>
<td>-34.037</td>
</tr>
<tr>
<td>([5s4p3d2/g])</td>
<td>-128.438</td>
<td>178.530</td>
<td>-32.984</td>
</tr>
<tr>
<td>([5s4p3d2f1g])</td>
<td>-128.564</td>
<td>178.321</td>
<td>-32.971</td>
</tr>
<tr>
<td>([7s5p4d3f1g])</td>
<td>-125.975</td>
<td>180.934</td>
<td>-32.393</td>
</tr>
</tbody>
</table>

noting that a similar estimate of the convergence rate of the SAPT expansion for the interaction potential of He₂ has been recently reported.\(^{146}\)

The remaining errors are due to the basis set unsaturation. An examination of the basis set convergence presented in Table 4 shows that the results in the \(spdf\) basis are probably converged to within 2% or better. The extension of the basis set from \(spd\) to \(spdf\) quality improved the results by 1% on the average (the only exception is the trace for \(R = 5\) bohr, which changed by 7%). The next increase of the basis, i.e., the addition of a basis function of \(g\) symmetry, led only to changes smaller than 0.1% (again an exception is the trace for \(R = 5\) bohr, here the change amounts to 0.7%). Finally, an extension of the \(spdfg\) basis with additional basis functions of \(s, p, d,\) and \(f\) symmetry changes the results by less than 2%. Certainly, some of the errors discussed above will mutually cancel, so it is safe to assume that our results for the interaction-induced trace and anisotropy have an error of at most 5%.

In Table 5 we summarize the results of SAPT calculations, while in Figs. 1 and 2 we illustrate the behaviour of the trace and anisotropy with the interatomic separation. For all distances the interaction-induced anisotropy is positive and it decays slowly with \(R\). The trace is much smaller because of the large cancellations involved. At short and intermediate distances the trace is negative. The sign change occurs at larger distances, where the trace itself is negligibly small. It is interesting to note that both the anisotropy and the trace result from a balance of the positive and negative contributions. For example,
TABLE 5. Interaction-induced trace and anisotropy of He₂ (in 10⁻³ a.u.) as functions of the interatomic distance R (in bohr).

<table>
<thead>
<tr>
<th>R</th>
<th>α(R)</th>
<th>β(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>-128.438</td>
<td>178.350</td>
</tr>
<tr>
<td>3.5</td>
<td>-69.903</td>
<td>132.262</td>
</tr>
<tr>
<td>4.0</td>
<td>-32.984</td>
<td>111.930</td>
</tr>
<tr>
<td>4.5</td>
<td>-13.801</td>
<td>95.118</td>
</tr>
<tr>
<td>5.0</td>
<td>-5.096</td>
<td>78.791</td>
</tr>
<tr>
<td>5.6</td>
<td>-1.131</td>
<td>61.138</td>
</tr>
<tr>
<td>6.0</td>
<td>-0.220</td>
<td>51.287</td>
</tr>
<tr>
<td>7.0</td>
<td>0.189</td>
<td>33.996</td>
</tr>
<tr>
<td>8.0</td>
<td>0.166</td>
<td>22.366</td>
</tr>
<tr>
<td>10.0</td>
<td>0.022</td>
<td>11.416</td>
</tr>
</tbody>
</table>

for $R \leq 5$ bohr $\alpha(R)$ represents about 50% of the negative exchange contribution $\alpha_{\text{exch}}(R)$ and is approximately equal to the sum of the positive components, $\alpha_{\text{pol}}^{(1)}(R) + \alpha_{\text{ind}}^{(2)}(R) + \alpha_{\text{disp}}^{(2)}(R)$. See also Chapter 1 for a more detailed discussion of this point. Also presented in Figs. 1 and 2 are the interaction-induced trace and anisotropy, as computed by Dacre⁷ at the CISD level (including the size-consistency correction). In general the agreement between the two calculations is good. The largest difference in the anisotropy amounts to 2% at $R = 3$ bohr, while the same number for the trace is 7% at $R = 5$ bohr. The only exception is the trace at distances larger than $R = 5$ bohr. Since in this region of $R$ the trace is very small this disagreement is probably due to some numerical inaccuracies of the CISD calculations.

As discussed in Sec. III, the invariants of the interaction-induced polarizability tensor that enter the expression for the Raman intensities should be taken at the laser wavelength $\lambda$ (corresponding to the wave number $\omega_0$). Our SAPT calculations were performed at $\lambda = \infty$ and it is not a priori obvious whether $\alpha(R)$ and $\beta(R)$ at the laser wavelength $\lambda = 5145$ Å would not change considerably. To investigate this point we have tested the importance of the $\lambda$ dependence of $\alpha(R)$ and $\beta(R)$ using the supermolecule RPA and MP2 approaches. Although the RPA and MP2 levels of the theory are not expected to give very accurate results, the comparison of the polarizability invariants at $\lambda = \infty$ and $\lambda = 5145$ Å will give an estimate of the $\lambda$ dependence. The results of these additional calculations are reported in Table 6. As expected, the differences between the static and dynamic trace and anisotropy polarizabilities are small and do not strongly depend on the interatomic distance. Hence, approximating $\beta(R)$ and $\alpha(R)$ in Eqs. (25) and (26) by their static values appears to be justified.
FIG. 1. Trace polarizability $\alpha(R)$ of He$_2$ (in $10^{-3}$ a.u.) as a function of the interatomic separation $R$ (in bohr). Full line represents the SAPT trace polarizability, while the dashed line shows the \textit{ab initio} CISD results of Dacre (Ref. 28) corrected for the size-consistency error.

FIG. 2. Anisotropy $\beta(R)$ of He$_2$ (in $10^{-3}$ a.u.) as a function of the interatomic separation $R$ (in bohr). Full line represents the SAPT anisotropy, while the dashed line shows the \textit{ab initio} CISD results of Dacre (Ref. 28) corrected for the size-consistency error.
TABLE 6. Wavelength dependence of the interaction-induced trace and anisotropy of He\(_2\) (in \(10^{-3}\) a.u.) computed using the supermolecule RPA and MP2 methods for selected interatomic distances \(R\) (in bohr).

<table>
<thead>
<tr>
<th>(R) (in bohr)</th>
<th>(\lambda)</th>
<th>(\alpha^{\text{RPA}}(\lambda; R))</th>
<th>(\beta^{\text{RPA}}(\lambda; R))</th>
<th>(\alpha^{\text{MP2}}(\lambda; R))</th>
<th>(\beta^{\text{MP2}}(\lambda; R))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>(\infty)</td>
<td>-129.3</td>
<td>154.1</td>
<td>-128.0</td>
<td>156.8</td>
</tr>
<tr>
<td>5145 (\text{Å})</td>
<td>-131.7</td>
<td>155.8</td>
<td>-130.3</td>
<td>158.5</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>(\infty)</td>
<td>-34.6</td>
<td>98.3</td>
<td>-33.4</td>
<td>99.8</td>
</tr>
<tr>
<td>5145 (\text{Å})</td>
<td>-35.4</td>
<td>99.2</td>
<td>-34.2</td>
<td>100.7</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>(\infty)</td>
<td>-6.5</td>
<td>70.4</td>
<td>-5.8</td>
<td>71.2</td>
</tr>
<tr>
<td>5145 (\text{Å})</td>
<td>-6.7</td>
<td>71.3</td>
<td>-6.0</td>
<td>72.1</td>
<td></td>
</tr>
</tbody>
</table>

B. Collision-induced Raman spectrum of the helium diatom

In Table 7 we summarize the results of quantum-dynamical calculations of the binary Raman spectra for the He diatom (see also Figs. 3 and 4 for graphical illustrations). An inspection of Table 7 and Fig. 3 shows that the agreement of the theoretical depolarized Raman intensities with the results of measurements\(^{113}\) is satisfactory. Most of the intensities agree within 3\% or better. Only at very low and high frequency shifts this good agreement deteriorates somewhat. Still, the predicted intensities at high frequencies are within the experimental error bars [the estimated experimental uncertainty is 6\% for the frequency shifts below \(-150\) cm\(^{-1}\), 10\% at \(-220\) cm\(^{-1}\), up to 35\% at \(-300\) cm\(^{-1}\) (Refs. 34 and 113)]. At very low frequencies the theoretical results are outside the experimental error bars. However, since the depolarized intensities depend on the square of the anisotropy, these discrepancies (of the order of 14\%) are consistent with the estimated 5\% error in our SAPT calculations, combined with the 3\% error in the quantum-dynamical calculations and the 2\% error due to the neglect of the \(\lambda\) dependence of \(\beta(R)\).

Theoretical polarized Raman intensities agree with the experiment within the large (±50\% - 60\%) experimental error bars over a wide range of the frequency shifts. Except for the low frequency region, the predicted polarized spectrum is less intense (from 30\% at \(\nu = -150\) cm\(^{-1}\) to 58\% at \(\nu = -300\) cm\(^{-1}\)). This level of agreement between theory and experiment is not in contradiction with our estimated 5\% accuracy of the interaction-induced trace polarizability, but further checks both on the theoretical and the experimental sides are visibly needed.

As discussed in the previous section, our estimate of the convergence rate of the SAPT expansion for the interaction-induced trace polarizability of He\(_2\) is similar to the convergence rate of the perturbation series for the interaction potential\(^{114}\). The results of Ref. 146 suggest that the 5\% inaccuracy in the present SAPT calculations may be partly due to the neglect of higher-order
**TABLE 7.** Comparison of the computed and measured depolarized and polarized Raman intensities (in \(10^{-58}\) cm\(^6\)) of \(^3\)He\(_2\) as functions of the frequency shift (in cm\(^{-1}\)) at 296 K.

<table>
<thead>
<tr>
<th>(\nu)</th>
<th>(D(\nu))</th>
<th>(P(\nu))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-30)</td>
<td>37.0</td>
<td>42.6</td>
</tr>
<tr>
<td>(-50)</td>
<td>25.7</td>
<td>29.3</td>
</tr>
<tr>
<td>(-70)</td>
<td>17.5</td>
<td>18.7</td>
</tr>
<tr>
<td>(-90)</td>
<td>11.8</td>
<td>12.2</td>
</tr>
<tr>
<td>(-100)</td>
<td>9.62</td>
<td>9.90</td>
</tr>
<tr>
<td>(-110)</td>
<td>7.84</td>
<td>8.05</td>
</tr>
<tr>
<td>(-120)</td>
<td>6.40</td>
<td>6.56</td>
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<tr>
<td>(-130)</td>
<td>5.25</td>
<td>5.36</td>
</tr>
<tr>
<td>(-140)</td>
<td>4.31</td>
<td>4.39</td>
</tr>
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<td>(-150)</td>
<td>3.56</td>
<td>3.60</td>
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<td>(-160)</td>
<td>2.93</td>
<td>2.96</td>
</tr>
<tr>
<td>(-170)</td>
<td>2.42</td>
<td>2.44</td>
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<td>(-180)</td>
<td>1.99</td>
<td>2.01</td>
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<tr>
<td>(-190)</td>
<td>1.68</td>
<td>1.66</td>
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<td>(-200)</td>
<td>1.42</td>
<td>1.38</td>
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<tr>
<td>(-210)</td>
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<td>1.14</td>
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<tr>
<td>(-220)</td>
<td>1.05</td>
<td>0.948</td>
</tr>
<tr>
<td>(-230)</td>
<td>0.899</td>
<td>0.789</td>
</tr>
<tr>
<td>(-240)</td>
<td>0.762</td>
<td>0.657</td>
</tr>
<tr>
<td>(-250)</td>
<td>0.649</td>
<td>0.549</td>
</tr>
<tr>
<td>(-260)</td>
<td>0.548</td>
<td>0.459</td>
</tr>
<tr>
<td>(-270)</td>
<td>0.464</td>
<td>0.384</td>
</tr>
<tr>
<td>(-280)</td>
<td>0.385</td>
<td>0.322</td>
</tr>
<tr>
<td>(-290)</td>
<td>0.318</td>
<td>0.270</td>
</tr>
<tr>
<td>(-300)</td>
<td>0.259</td>
<td>0.227</td>
</tr>
</tbody>
</table>

*a*In parentheses, polarized Raman intensities computed from the scaled polarizability trace.
FIG. 3. Comparison of the theoretical and experimental depolarized spectra for the $^4$He diatom. The experimental data are represented by circles.

FIG. 4. Comparison of the theoretical and experimental polarized spectra for the $^4$He diatom. The solid and dashed lines represent polarized intensities generated from the ab initio and scaled trace polarizabilities, respectively. The experimental data are represented by circles.
intra-atomic correlation contributions to the exchange energy. Indeed, the total exchange contribution to the He$_2$ interaction potential as computed from the present SAPT ansatz is underestimated by 2.5%. We repeated the dynamical calculations using a trace polarizability in which the exchange contribution, Eq. (16), was increased by 2.5%. The resulting polarized intensities are reported in Table 7 in parentheses (see also Fig. 4). In general the agreement with the experimental results is somewhat better: this scaling increases the polarized intensities by $\sim 7\% - 10\%$ and reduces the discrepancy with the experiment from 30\% to 24\% at $\nu = -150$ cm$^{-1}$ and from 59\% to 54\% at $-250$ cm$^{-1}$.

The scaling of the exchange contribution to the interaction-induced trace polarizability of He$_2$ does not substantially improve the agreement between the theoretical and experimental polarized spectra. It is also worth noting that our results for the depolarized and polarized Raman intensities are in good agreement with those generated from Dacre’s polarizability invariants. Both these observations suggest that the theoretical results are rather well converged. We estimate that the error in our polarized intensities is considerably smaller than the experimental error of 50 to 60\%, so that the improvement of the agreement between theory and experiment for these intensities should mainly come from the experimental side.

V. SECOND DIELECTRIC VIRIAL COEFFICIENT OF HE$_2$

Using our ab initio interaction-induced trace data and the accurate empirical potential we have computed the second dielectric virial coefficient over the range of temperatures in which it has been measured (4 K $\leq T \leq 323$ K). At high temperatures the second dielectric virial coefficient is given by the standard classical expression,

$$ B^{(0)}_v(T) = \frac{8\pi^2 N^2_0}{3} \int_0^\infty \alpha(R) \exp(-V(R)/k_BT) R^2 dR, \quad (31) $$

where $N_0$ is the Avogadro constant. At lower temperatures quantum corrections may become important. The semiclassical expansion of the second dielectric virial coefficient as a power series in $\hbar^2$ has been considered in Refs. 148 and 149. Ely and McQuarrie derived an expression for the leading quantum correction $B^{(1)}_v(T)$ and applied it in calculations for a Lennard–Jones gas with the interaction-induced trace from the simple dipole-induced-dipole model. They concluded that at low temperatures the first-order quantum correction was very important and represented as much as 53\%, 25\%, and 13\% of the classical term at $T = 15.33$, 25.55, and 40.88 K, respectively. To our knowledge, approximate quantum calculations have been only reported by Fortune
Unfortunately, these authors restricted their work to a single temperature and did not compare the quantum results with the (semi)classical results. In the present work we report a more systematic study of the importance of the quantum corrections by considering also the second-order terms and using a realistic representation of the interaction-induced trace and the interaction potential for He$_2$. We approximated $B_e(T)$ as

$$B_e(T) = B_e^{(0)}(T) + B_e^{(1)}(T) + B_e^{(2)}(T),$$

i.e., we computed the classical term $B_e^{(0)}(T)$ and included quantum corrections of the order $\hbar^2$ and $\hbar^4$ (denoted by $B_e^{(1)}(T)$ and $B_e^{(2)}(T)$, respectively). The classical term $B_e^{(0)}(T)$ is given by Eq. (31), while the first-order quantum correction to $B_e^{(0)}(T)$ can be written as

$$B_e^{(1)}(T) = -\frac{\pi^2\hbar^2N_2^2}{9\mu k_B^2 T^2} \int \left[ \frac{\alpha(R)}{k_B T} \left( \frac{dV}{dR} \right)^2 - 2 \frac{dV}{dR} \frac{d\alpha}{dR} \right] \exp(-V(R)/k_B T) \, R^2 \, dR.$$  \tag{33}$$

To our knowledge the explicit formula for the second-order quantum correction to the dielectric virial coefficient has not been reported in the literature thus far. The derivation is based on the relation between the pressure virial coefficient of the gas in a uniform static electric field and the dielectric virial coefficient (See Ref. 150 and Chapter 3). The resulting expression for $B_e^{(2)}(T)$ is somewhat more involved and can be written as

$$B_e^{(2)}(T) = \frac{\pi^2\hbar^4N_2^2}{180\mu^2 k_B^3 T^3} \int \left[ \frac{\alpha(R)}{k_B T} f(R) + g(R) \right] \exp(-V(R)/k_B T) \, R^2 \, dR,$$

where the functions $f(R)$ and $g(R)$ are given by

$$f(R) = \left( \frac{d^2V}{dR^2} \right)^2 + \frac{2}{R^2} \left( \frac{dV}{dR} \right)^2 + \frac{10}{9k_B T} \frac{1}{R} \left( \frac{dV}{dR} \right)^3 - \frac{5}{36k_B T^2} \left( \frac{dV}{dR} \right)^4,$$

$$g(R) = -2 \frac{d^2V}{dR^2} \frac{d^2\alpha}{dR^2} - 4 \frac{dV}{dR} \frac{d\alpha}{dR} - \frac{10}{3k_B T} \frac{1}{R} \left( \frac{dV}{dR} \right) \frac{d\alpha}{dR} + \frac{5}{9k_B^2 T^2} \left( \frac{dV}{dR} \right)^3 \frac{d\alpha}{dR}.$$  \tag{36}$$

The integration over $R$ has been performed in the range from $R = 3\sigma$ to 100 bohr using a composite Simpson rule. In the inner region ($R < 3$ bohr) the function $\exp(-V/k_B T)$ is effectively zero, while in the outer region, $R > 100$ bohr, all contributions are negligibly small. The number of radial
TABLE 8. Comparison of the computed and measured second dielectric virial coefficients of $^4$He (in cm$^6$ mol$^{-2}$) at various temperatures (in K).

<table>
<thead>
<tr>
<th>$T$</th>
<th>$B_0(T)$</th>
<th>$B_1(T)$</th>
<th>$B_2(T)$</th>
<th>$B_3(T)$</th>
<th>Experiment</th>
<th>$\Delta_0$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.799</td>
<td>-0.0961</td>
<td>0.89(±0)</td>
<td>-0.88(±1)</td>
<td>-7.9723</td>
<td>-0.023</td>
<td>-b</td>
<td>115</td>
</tr>
<tr>
<td>4.220</td>
<td>-0.0739</td>
<td>0.58(±0)</td>
<td>-0.49(±1)</td>
<td>-4.3714</td>
<td>0.084</td>
<td>±0.026</td>
<td>120</td>
</tr>
<tr>
<td>7.199</td>
<td>-0.0288</td>
<td>0.95(±1)</td>
<td>-0.39(±0)</td>
<td>-0.3212</td>
<td>-0.037</td>
<td>±0.035</td>
<td>120</td>
</tr>
<tr>
<td>13.804</td>
<td>-0.0178</td>
<td>0.20(±1)</td>
<td>-0.37(±1)</td>
<td>-0.0345</td>
<td>-0.010</td>
<td>±0.022</td>
<td>120</td>
</tr>
<tr>
<td>20.271</td>
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<td>0.98(±2)</td>
<td>-0.12(±1)</td>
<td>-0.0189</td>
<td>-0.063</td>
<td>±0.010</td>
<td>120</td>
</tr>
<tr>
<td>27.098</td>
<td>-0.0178</td>
<td>0.62(±2)</td>
<td>-0.54(±2)</td>
<td>-0.0170</td>
<td>-0.089</td>
<td>±0.026</td>
<td>120</td>
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<tr>
<td>77.4</td>
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<td>0.17(±2)</td>
<td>-0.49(±3)</td>
<td>-0.0285</td>
<td>-0.02</td>
<td>±0.02</td>
<td>123</td>
</tr>
<tr>
<td>242.95</td>
<td>-0.0527</td>
<td>0.63(±3)</td>
<td>-0.55(±4)</td>
<td>-0.0522</td>
<td>-0.07</td>
<td>±0.01</td>
<td>123</td>
</tr>
<tr>
<td>298.15</td>
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<td>0.54(±3)</td>
<td>-0.38(±4)</td>
<td>-0.0587</td>
<td>-0.11</td>
<td>±0.02</td>
<td>117</td>
</tr>
<tr>
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<td>-0.0597</td>
<td>0.54(±3)</td>
<td>-0.37(±4)</td>
<td>-0.0592</td>
<td>-0.059</td>
<td>±0.009</td>
<td>116</td>
</tr>
<tr>
<td>322.15</td>
<td>-0.0617</td>
<td>0.51(±3)</td>
<td>-0.33(±4)</td>
<td>-0.0613</td>
<td>-0.06</td>
<td>±0.01</td>
<td>124</td>
</tr>
<tr>
<td>323</td>
<td>-0.0618</td>
<td>0.51(±3)</td>
<td>-0.33(±4)</td>
<td>-0.0614</td>
<td>-0.068</td>
<td>±0.01</td>
<td>122</td>
</tr>
<tr>
<td>323.15</td>
<td>-0.0618</td>
<td>0.51(±3)</td>
<td>-0.33(±4)</td>
<td>-0.0614</td>
<td>-0.07</td>
<td>±0.01</td>
<td>123</td>
</tr>
</tbody>
</table>

*aExperimental error bars.
*bExperimental error was not reported.
*cExperimental data from direct measurements.
*dExperimental data from indirect measurements.

points was $N = 2^n - 1$. We increased $n$ by 1 in each iteration and stopped when the relative error was smaller than $10^{-6}$. We checked that our results are stable against changes in the boundaries and/or integration parameters.

The results of our calculations, presented in Table 8 and Fig. 5, are compared with the available experimental data. Also presented in this table is the classical dielectric virial coefficient computed with the aid of Eq. (31) and the first- and second-order quantum corrections. An inspection of Table 8 shows that the quantum effects are very small for temperatures larger than 70 K and $B_3(T)$ can be efficiently computed from the classical expression. At lower temperatures the dielectric virial coefficient of the $^4$He gas starts to deviate from the classical value and at very low temperatures the semiclassical expansion of the second dielectric virial coefficient in powers of $\hbar^2$ clearly diverges.

At high temperatures our results agree well with the data from indirect measurements. The only exception is the value at $T = 242.95$ K. Here the theoretical result is slightly outside the experimental error bars. The agreement with the results of direct measurements is less satisfactory. The present $ab initio$ results agree very well with the old experimental data of Orcutt and Cole and disagree with the data of Vidal and Lallemand. Since our results agree with the majority of the high-temperature experimental data and since the second dielectric virial coefficient changes very slowly with temperature, it is very likely that the results of direct measurements reported by Vidal and Lallemand are contaminated by nonadditive three-body effects.
FIG. 5. Comparison of the ab initio and experimental second dielectric virial coefficients of $^4$He at various temperatures. The solid line represents the second dielectric virial coefficients generated from the ab initio SAPT polarizability trace and the empirical potential of Ref. 137. Crosses label the indirect measurements from Refs. 116, 122–124, open circles the measurements from Ref. 114, and filled squares represent experimental data from Refs. 117, 118.

At low temperatures the situation is more complex. Our result at 77.4 K agrees very well with the value from indirect measurements reported by Huot and Bose. Other low temperature experimental data cannot be compared with our theoretical values due to the divergence of the semiclassical expansion and full quantum calculations are needed. Work in this direction is presented in Chapter 3.

VI. SUMMARY AND CONCLUSIONS

Symmetry-adapted perturbation theory has been applied to compute the invariants of the interaction-induced polarizability for the He diatom. The accuracy of the computed response properties has been tested by comparison with benchmark full CI results and by extensive studies of the basis set convergence. We have estimated that the present SAPT results for the interaction-induced trace and anisotropy of He$_2$ should be accurate to about 5%.

Using the computed trace and anisotropy we have performed converged quantum-dynamical calculations of the depolarized and polarized binary
Summary and conclusions

Raman spectra. The predicted depolarized intensities are in good agreement with the experimental data\textsuperscript{113} over a wide range of the frequency shifts. The agreement between theory and experiment for the polarized spectrum is within the experimental error bars, although the theoretical spectrum is less intense than the experimental one. The analysis of the accuracy of the present calculations suggests that the error in the predicted polarized intensities is much smaller than the experimental error bars, so the improvement of agreement between theory and experiment must mainly come from the experimental side.

Further tests of the accuracy of the computed trace polarizability have been performed by computing the second dielectric virial coefficients (including first- and second-order quantum corrections) at various temperatures and by comparing with the available experimental data\textsuperscript{114-118,120,122-124}. Our results agree well with the majority of the high-temperature experimental data. The low temperature experimental results of Kerr and Sherman\textsuperscript{115} and Gugan and Michel\textsuperscript{120} could not be used to assess the accuracy of the computed trace polarizability due to the divergence of the semiclassical expansion.

ACKNOWLEDGMENTS

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Chapter 3

Second dielectric virial coefficient of helium gas: quantum-statistical calculations from an ab initio interaction-induced polarizability*

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Abstract

A quantum-statistical expression for the second virial coefficient of the dielectric Clausius-Mossotti function is derived. Calculations of the second dielectric virial coefficient of He gas at various temperatures are reported. The role of quantum mechanical effects and the convergence properties of the semiclassical expansion are discussed. The calculated second dielectric virial coefficients at various temperatures are compared with experimental data.

I. INTRODUCTION

It is well known that for atomic gases at low densities the Clausius-Mossotti function can be related to the atomic polarizability via the relation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi \alpha_0}{3} \rho,$$

where \(\epsilon\) is the dielectric constant, \(\alpha_0\) is the atomic polarizability, and \(\rho\) denotes the gas number density. At higher pressures deviations from this relation are observed and they can be attributed to intermolecular interactions. Buckingham and Pople\(^{147}\) have shown that the leading correction to Eq. (1), quadratic in the gas density, is given by \(B_r(T)\rho^2\), where at high temperatures the second dielectric virial coefficient \(B_r(T)\) is related to the interatomic potential and interaction-induced polarizability by

$$B_r(T) = \frac{2\pi}{3} \int \Delta \alpha(R) \exp\left[-V(R)/k_B T\right] dR.$$

Here \(T\) is the temperature, \(k_B\) is the Boltzmann constant, \(V(R)\) is the pair interaction potential, and \(\Delta \alpha(R)\) is the trace of the interaction-induced polarizability tensor.

Much progress has been made in the development of various experimental techniques to measure the second dielectric virial coefficients and at present data are available for various atomic and molecular systems (see Refs. 103 and 104 for recent reviews of the experimental data). The dielectric properties of helium gas are of particular interest, since for this system accurate theoretical data can be obtained. Consequently, since the early 1960s more and more accurate measurements\(^{114-118,120,122-124,151}\) have been reported in the literature. Recent low-temperature results\(^{120,122}\) are especially interesting since they enable theoretical investigations of the quantum effects on the second dielectric virial coefficient.

While the classical calculations of the second dielectric virial coefficient for helium have been reported by several authors (see Ref. 103 for a review), the importance of the quantum corrections has been the object of only a few studies.\(^{148,149,152-154}\) The semiclassical expansion of the second dielectric virial coefficient as a power series in \(\hbar^2\) has been considered in Refs. 148 and 149. Ely and McQuarrie\(^{148}\) derived an expression for the leading quantum correction to the classical term of Eq. (1), and applied it in calculations for a Lennard-Jones gas with the interaction-induced polarizability trace from the simple dipole-induced-dipole model. They concluded that at low temperatures the first-order quantum correction was important and represents as much as 53%
and 25% of the classical term at $T = 15.33$ and 25.55 K, respectively. To our knowledge, approximate quantum calculations have only been reported by Bruch et al.\textsuperscript{149} Unfortunately, these authors restricted their work to a single temperature and did not compare the quantum results with the (semi)classical results.

In Chapter 2 we reported symmetry-adapted perturbation theory (SAPT) calculations (see Ref. 4 for a recent review of SAPT and its applications) of the interaction-induced polarizability for the He diatom and dynamical calculations of the polarized and depolarized Raman intensities. We also tested the \textit{ab initio} collision-induced polarizability by the computation of the semiclassical approximations to the second dielectric virial coefficient and by comparison with experiment. Our results suggested that at low temperatures the semiclassical expressions for $B_v(T)$ are no longer valid. Hence, it seems that a more systematic study of the quantum effects on the second dielectric virial coefficients is needed.

A general expression relating the second dielectric virial coefficient to the pressure virial coefficient in an electric field has been reported by Hill\textsuperscript{150} (see also Ref. 155). Unfortunately, Hill introduced some simplifying assumptions in his derivation and at high temperatures his formula for $B_v(T)$ does not reduce to the classical result of Buckingham and Pople,\textsuperscript{147} cf. Eq. (2). Thus, the expression of Ref. 150 must be modified before it could be used to derive the quantum equivalent of Eq. (2).

In the present chapter we report the derivation of the quantum expression for the second dielectric virial coefficient and \textit{ab initio} calculations of $B_v(T)$ for He at various temperatures. The results of the exact quantum-statistical calculations are compared with the semiclassical approximations including first- and second-order quantum corrections, as well as with the experimental data.

\section*{II. THEORY}

We follow Hill\textsuperscript{150} and consider an atomic gas in a parallel plate capacitor with surface charges which yield in the vacuum a uniform electric field $\mathbf{F}$. For simplicity we assume the z direction to be parallel to the field, so $\mathbf{F} = (0, 0, F)$. As shown in Ref. 150, the polarization $P$ along the electric field vector $\mathbf{F}$ can be written as a power series expansion in the gas density $\rho$,

$$P = P_1 V \rho - k_B T \sum_{n=2}^{\infty} \frac{1}{n-1} \left( \frac{\partial B_n(T; F)}{\partial F} \right) \rho^n,$$  \hspace{1cm} (3)

where $P_1$ is the polarization of a single atom, cf. Eq. (6), $V$ is the volume, and $B_n(T; F)$ denotes ordinary (pressure) virial coefficients for the gas in the
electric field $F$. Since we are interested in the low field limit, Eq. (3) can conveniently be rewritten as

$$P = P_i V \rho - k_B T \sum_{n=2} \frac{1}{n-1} \left( \frac{\partial^2 B_n(T; F)}{\partial F^2} \right)_{F=0} F \rho^n + O(F^3).$$

(4)

When deriving Eq. (4) we have used the fact that $B_n(T; F)$ is an even function of $F$, so

$$\frac{\partial B_n(T; F)}{\partial F} = \left( \frac{\partial^2 B_n(T; F)}{\partial F^2} \right)_{F=0} F + O(F^3).$$

(5)

Furthermore, from the Lorentz equation we have

$$P_i V = \alpha_0 F_{\text{loc}} = \alpha_0 \frac{\epsilon + 2}{3} F,$$

(6)

where $F_{\text{loc}}$ is the local electric field which actually polarizes an atom or the assembly of atoms in the gas. Note that at this point our derivation differs from that of Hill. In the latter it was assumed that $P_i V$ is proportional to the field $F$ with the proportionality constant $\alpha_1(T)$ approximated by $\alpha_0$, or equivalently, the local field $F_{\text{loc}}$ was approximated by the field $F$. Substituting

$$P = \frac{\epsilon - 1}{4\pi} F,$$

(7)

we obtain

$$\epsilon - 1 = (\epsilon + 2) \frac{4\pi \alpha_0}{3} \rho - 4\pi k_B T \sum_{n=2} \frac{1}{n-1} \left( \frac{\partial^2 B_n(T; F)}{\partial F^2} \right)_{F=0} \rho^n.$$

(8)

Equation (8) can be transformed to a power series expansion of the Clausius–Mossotti function,

$$\frac{\epsilon - 1}{\epsilon + 2} = A \rho + B(T) \rho^2 + C(T) \rho^3 + \cdots,$$

(9)

where

$$A = \frac{4\pi \alpha_0}{3},$$

(10)

$$B(T) = \frac{4\pi k_B T}{3} \left( \frac{\partial^2 B_2(T; F)}{\partial F^2} \right)_{F=0},$$

(11)

$$C(T) = -2A B(T) - \frac{2\pi k_B T}{3} \left( \frac{\partial^2 B_3(T; F)}{\partial F^2} \right)_{F=0}.$$

(12)

Our expression for $B(T)$ differs from the formula derived by Hill and it is not difficult to show that at high temperatures Eq. (11) reduces to the classical
expression, Eq. (2). Our Eq. (11) can be obtained from his Eq. (33) by assuming that \( \alpha_1(T) \) is not approximated by the polarizability of the atom, but that it is instead given by a power series expansion in \( \rho \).

The field-dependent second virial coefficient for an atomic gas can conveniently be written as:

\[
B_2(T; F) = \frac{1}{2} \int [W(R; F) - 1] \, dR, \tag{13}
\]

where \( W(R; F) \) denotes the Slater sum,

\[
W(R; F) = \frac{\lambda_B^3}{2I + 1} \langle R | e^{-\beta H(F)} | R \rangle - \frac{\lambda_B^3}{2I + 1} \langle -R | e^{-\beta H(F)} | -R \rangle.
\]

Here, \( \lambda_B = (4\pi \hbar^2 \beta/m)^{1/2} \) is the thermal wavelength, \( m \) is the atomic mass, \( \beta \equiv 1/k_B T \), \( I \) is the nuclear spin quantum number, and \( \langle R' | X | R \rangle \) denotes the matrix element of the operator \( X \) in the coordinate representation. Finally, the Hamiltonian for the relative motion of two atoms in the electric field is given by

\[
H(F) = H_0 + \Delta \alpha_{zz}(R) F^2,
\]

where \( V(R) \) is the pair interaction potential and \( \Delta \alpha_{zz}(R) \) denotes the \( zz \) component of the interaction-induced polarizability. For further discussion it is useful to write \( \Delta \alpha_{zz}(R) \) as

\[
\Delta \alpha_{zz}(R) = \Delta \alpha(R) + \frac{2}{3} \gamma(R) P_2(\cos \vartheta),
\]

where \( \Delta \alpha(R) \) and \( \gamma(R) \) denote the interaction-induced trace and anisotropy of the polarizability tensor, \( P_2 \) is the second Legendre polynomial, and \( \vartheta \) is the angle between the \( z \) axis and the dimer axis.

To derive a quantum expression for \( B_2(T) \) we need the second derivative of the Slater sum in the electric field. Using simple algebraic arguments one can show that

\[
\left( \frac{\partial^2}{\partial F^2} \langle R' | e^{-\beta H(F)} | R \rangle \right)_{F=0} = \beta \langle R' | \exp(-\beta H_0) \Delta \alpha_{zz}(R) | R \rangle.
\]

Note that \( \Delta \alpha_{zz}(R) \) is diagonal in \( R \), so Eq. (17) can be further simplified to

\[
\langle R' | \exp(-\beta H_0) \Delta \alpha_{zz}(R) | R \rangle = \Delta \alpha_{zz}(R) \langle R' | \exp(-\beta H_0) | R \rangle.
\]
In view of Eqs. (11), (13), (17), and (18), the expression for $B_2(T)$ takes the form

$$B_2(T) = \frac{2\pi}{3} \int W(R; 0) \Delta\alpha_{zz}(R) dR. \quad (19)$$

A similar formula has been reported by Bruch et al.\textsuperscript{149} One may note that in practical applications the evaluation of this expression requires knowledge of the Slater sum at zero field.

Equation (19) can be further simplified by introducing a complete set of (bound and continuum) eigenfunctions of the Hamiltonian $H_0$,

$$H_0\Psi_{nJM} = E_{nJ}\Psi_{nJM}, \quad H_0\Psi_{kJM} = \frac{\hbar^2 k^2}{m}\Psi_{kJM}, \quad (20)$$

where $E_{nJ}$ and $E_k \equiv \hbar^2 k^2/m$ are the eigenvalues of bound and continuum states, respectively, and the corresponding wave functions are given by

$$\Psi_{nJM}(R) = R^{-1} \chi_{nJ}(R) Y_{JM}(\theta, \varphi), \quad (21)$$

$$\Psi_{kJM}(R) = \sqrt{\frac{2}{\pi}} R^{-1} \chi_{kJ}(R) Y_{JM}(\theta, \varphi), \quad (22)$$

where $Y_{JM}(\theta, \varphi)$ are normalized spherical harmonics. We assume that the radial wave functions are solutions of the radial Schrödinger equation describing the relative motion of the atoms in the potential $V(R)$,

$$-\frac{\hbar^2}{m} \frac{d^2\chi}{dR^2} + \left[ V(R) + \frac{\hbar^2 J(J + 1)}{mR^2} - E \right] \chi = 0, \quad (23)$$

subject to the following normalization conditions,

$$\int_0^\infty \chi_{nJM}(R) \chi_{n'JM}(R) dR = \delta_{nn'},$$

$$\int_0^\infty \chi_{kJM}(R) \chi_{k'JM}(R) dR = \delta(E_k - E_{k'}). \quad (24)$$

The expression for $W(R; 0)$ can conveniently be written as a sum-over-states formula,\textsuperscript{159}

$$W(R; 0) = \frac{\lambda B}{4\pi} \sum_{J=0}^\infty (2J + 1) \left[ 1 + \frac{(-1)^{J+2I}}{2I + 1} \right] \times \sum_n \exp(-\beta E_{nJ}) \chi_{nJ}^*(R) \chi_{nJ}(R) +$$
FIG. 1. Trace polarizability of He\textsubscript{2} (in 10\textsuperscript{-3} a.u.) as a function of the interatomic separation $R$ (in bohr).

By substituting into Eq. (19) the expression for $W(R;0)$ in terms of the complete set of eigenfunctions of $H_0$ one finds that $B_f(T)$ is given by

$$B_f(T) = \frac{2\pi \lambda_B^3}{3} \sum_{j=0}^{\infty} (2J + 1) \left[ 1 + \frac{(-1)^{j+2J}}{2J + 1} \right]$$

$$\times \left[ \sum_j \langle \chi_{nJ}(R) | \Delta \alpha(R) | \chi_{nJ}(R) \rangle \text{exp}(-\beta E_{nJ}) \right.$$

$$\left. + \frac{2}{\pi} \int_0^{\infty} \langle \chi_{nJ}(R) | \Delta \alpha(R) | \chi_{nJ}(R) \rangle \text{exp}(-\beta \hbar^2 k^2/m) \, dk \right],$$

(26)

where the matrix elements of the trace appearing in Eq. (26) are defined as

$$\langle \chi | \Delta \alpha(R) | \chi \rangle = \int_0^{\infty} \chi^*(R) \Delta \alpha(R) \chi(R) \, dR.$$  

(27)

Using our \textit{ab initio} interaction-induced trace data from Chapter 2 (see Fig. 1 for a graphical illustration of the dependence of $\Delta \alpha(R)$ on the interatomic distance $R$) and the empirical interaction potential,\textsuperscript{137} we have computed the
TABLE 1. Second dielectric virial coefficient of \(^4\)He (in cm\(^6\) mol\(^{-2}\)) as a function of the temperature (in K).

<table>
<thead>
<tr>
<th>(T)</th>
<th>(B^{(0)}_c(T))</th>
<th>(B^{(1)}_c(T))</th>
<th>(B^{(2)}_c(T))</th>
<th>(B_c(T)^a)</th>
<th>(1/1)^b</th>
<th>(B_c(T)^c)</th>
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<tbody>
<tr>
<td>4</td>
<td>-0.0842</td>
<td>0.7178</td>
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<td>-0.0001</td>
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<td>0.0006</td>
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<td>-0.0000</td>
<td>-0.0588</td>
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<td>-0.0588</td>
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</tbody>
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\(^a\)Semiclassical approximation through the second order.
\(^b\)Padé approximant applied to the series \(B^{(0)}_c(T) + B^{(1)}_c(T) + B^{(2)}_c(T)\).
\(^c\)Exact quantum-statistical calculation.

The results of quantum statistical calculations of \(B_c(T)\) as a function of the temperature are presented in Table 1. The main contribution to the second dielectric virial coefficient of \(^4\)He gas comes from the summation over the continuum in Eq. (26). The bound state contribution is always small and even at the lowest temperatures it does not exceed 2%. Also presented in this table is the classical dielectric virial coefficient computed with Eq. (2) [denoted

III. NUMERICAL RESULTS AND DISCUSSION

The results of quantum statistical calculations of \(B_c(T)\) as a function of the temperature are presented in Table 1. The main contribution to the second dielectric virial coefficient of \(^4\)He gas comes from the summation over the continuum in Eq. (26). The bound state contribution is always small and even at the lowest temperatures it does not exceed 2%. Also presented in this table is the classical dielectric virial coefficient computed with Eq. (2) [denoted
Numerical results and discussion

FIG. 2. Temperature dependence of the second dielectric virial coefficient (in cm$^6$ mol$^{-2}$) of $^4$He gas.

by $B_t^{(0)}(T)$ and the first- and second-order quantum corrections [denoted by $B_t^{(1)}(T)$ and $B_t^{(2)}(T)$, respectively]. The quantum corrections have been computed from the expressions reported in Chapter 2. These formulas were derived by applying Eq. (11) to the semiclassical expansion of the ordinary (pressure) virial coefficient in an electric field. An inspection of Table 1 shows that the quantum effects are small for temperatures larger than 100 K and $B_t(T)$ can be approximated by the classical expression with an error smaller than 2.5%. At lower temperatures the dielectric virial coefficient of $^4$He starts to deviate from the classical value. Still, for $T > 50$ K the quantum effects can be efficiently accounted for by the sum of the first- and second-order quantum corrections. Indeed, for $T = 50, 75, 100$ K the series $B_t^{(0)}(T) + B_t^{(1)}(T) + B_t^{(2)}(T)$ reproduces the exact results with errors smaller than 2%. One may note that at these temperatures the second-order quantum correction is small and can be neglected for all practical purposes. In fact, the sum $B_t^{(0)}(T) + B_t^{(1)}(T)$ slightly overestimates the exact result, while $B_t^{(0)}(T) + B_t^{(1)}(T) + B_t^{(2)}(T)$ slightly underestimates it. At temperatures below 50 K the semiclassical expansion of the second dielectric virial coefficient in powers of $\hbar^2$ starts to diverge. This divergence is clearly illustrated in Fig. 2, where various approximations to $B_t(T)$ are plotted as functions of the temperature. This behaviour of the power series...
TABLE 2. Comparison of the computed and measured second dielectric virial coefficients of $^4$He (in cm$^6$ mol$^{-2}$) at various temperatures (in K).

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$B_2(T)$</th>
<th>Experiment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.799</td>
<td>-0.0081 ± 0.0004</td>
<td>-0.023 $^b$</td>
<td>115</td>
</tr>
<tr>
<td>4.220</td>
<td>-0.0081 ± 0.0004</td>
<td>0.083 ± 0.026</td>
<td>120</td>
</tr>
<tr>
<td>7.199</td>
<td>-0.0092 ± 0.0004</td>
<td>-0.036 ± 0.026</td>
<td>120</td>
</tr>
<tr>
<td>13.804</td>
<td>-0.0104 ± 0.0005</td>
<td>-0.010 ± 0.026</td>
<td>120</td>
</tr>
<tr>
<td>20.271</td>
<td>-0.0123 ± 0.0006</td>
<td>-0.062 ± 0.010</td>
<td>120</td>
</tr>
<tr>
<td>27.098</td>
<td>-0.0144 ± 0.0007</td>
<td>-0.088 ± 0.026</td>
<td>120</td>
</tr>
<tr>
<td>77.4</td>
<td>-0.0265 ± 0.0013</td>
<td>-0.02 ± 0.02</td>
<td>123</td>
</tr>
<tr>
<td>242.95</td>
<td>-0.0522 ± 0.0026</td>
<td>-0.07 ± 0.01</td>
<td>123</td>
</tr>
<tr>
<td>298.15</td>
<td>-0.0587 ± 0.0029</td>
<td>-0.11 ± 0.02</td>
<td>117</td>
</tr>
<tr>
<td>303</td>
<td>-0.0592 ± 0.0031</td>
<td>-0.039 ± 0.009</td>
<td>116</td>
</tr>
<tr>
<td>322.15</td>
<td>-0.0613 ± 0.0031</td>
<td>-0.06 ± 0.01</td>
<td>124</td>
</tr>
<tr>
<td>323</td>
<td>-0.0614 ± 0.0031</td>
<td>-0.068 ± 0.01</td>
<td>122</td>
</tr>
<tr>
<td>323.15</td>
<td>-0.0614 ± 0.0031</td>
<td>-0.07 ± 0.01</td>
<td>123</td>
</tr>
</tbody>
</table>

$^a$Theoretical error bars assuming the interaction-induced polarizability trace accurate to ±5%.

$^b$The experimental error was not reported.

in $h^2$ is not surprising, since the semiclassical expansion of the pressure virial coefficient is known to diverge as well (see e.g. Ref. 161).

Given the overall pattern of convergence of the semiclassical expansion, it is interesting to find whether any rational approximations involving the low-order quantum corrections will reproduce the converged quantum result. It is well known$^{162}$ that divergent series can be effectively summed by means of Padé approximants. Since we know only three terms in the expansion of $B_2(T)$ as a power series in $h^2$, we could only use the simplest [1/1] approximant. The values of this approximant at various temperatures are reported in the sixth column of Table 1. Except for the lowest temperatures, the simple [1/1] Padé approximant works surprisingly well. For $T = 15$ and 20 K the sum of the classical term and first- and second-order quantum corrections overestimates the exact result by 265% and 58%, respectively, while the [1/1] approximant reproduces the quantum results with errors of the order of 3%. This result is gratifying since the calculation of the quantum corrections is much simpler than full quantum-statistical calculations. It remains to be seen, however, if this optimistic result holds for other systems as well.

In Table 2 and Fig. 3 we compare the computed second dielectric virial coefficients of $^4$He with experimental data.$^{114-118,120,122-124}$ In Chapter 2 we have carefully checked the convergence of the SAPT expansion by comparison with
Numerical results and discussion

FIG. 3. Comparison of the \textit{ab initio} and experimental second dielectric virial coefficients of $^4$He at various temperatures. The solid line represents the second dielectric virial coefficients generated from the \textit{ab initio} polarizability trace of Chapter 2 and the empirical potential of Ref. 137. Crosses label the indirect measurements from Refs. 116, 122, 123, and 124, open circles and squares the measurements from Refs. 120 and 114, respectively, and filled circles and squares represent experimental data from Refs. 115, 117, and 118, respectively.

The exact results from full configuration interaction calculations, as well as the basis-set convergence. We have estimated the residual error in our polarizability trace to be 5% at worst. Since the second dielectric virial coefficient is linear in $\Delta \alpha$, our values for $B_2(T)$ should be accurate to 5% or better. At high temperatures our results agree well with the data from indirect measurements.\textsuperscript{116,122-124} The only exception is the value at $T = 242.95$ K. Here the difference is as large as 25%. Our results suggest that the second dielectric virial coefficient at this temperature should be larger than $-0.55$ cm$^6$ mol$^{-2}$.

At low temperatures the situation is more complex. Our result at 77.4 K agrees very well with the value from indirect measurements reported by Huot and Bose.\textsuperscript{123} Other low temperature data were obtained from direct measurements\textsuperscript{120} and show a lot of scatter. At $T = 13.804$ K our value agrees with the measurement, while at $T = 7.198$ K the theoretical result is almost within the experimental error bars. At other temperatures the disagreement is quite substantial and it is unlikely that the theoretical polarizability trace will change so drastically. Therefore, we suggest that these data should be remeasured.
Chapter 3: Second dielectric virial coefficient of helium

ACKNOWLEDGMENTS

We would like to thank Professor R. J. Le Roy for providing us with his bcont program. This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and Polish Scientific Research Council (KBN), Grant No. 3 T09A 07209.
Chapter 4

A new He–CO interaction energy surface with vibrational coordinate dependence. I. Ab initio potential and infrared spectrum*

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Abstract

The intermolecular potential energy surface of the He–CO complex including the CO bond length dependence has been calculated using symmetry-adapted perturbation theory (SAPT). The potential has a minimum of $\epsilon_m = -23.734 \text{ cm}^{-1}$ with $R_m = 6.53$ bohr at a skew geometry ($\theta_m = 48.4^\circ$) if the molecular bond length is fixed at the equilibrium value of 2.132 bohr. We have applied the potential in the calculation of bound state levels and the infrared spectrum for the $^{3}$He–CO and $^{4}$He–CO complexes. The computed ab initio transition frequencies are found to agree within 0.1 cm$^{-1}$ with experiment. In an accompanying work [J. P. Reid, H. M. Quiney, and C. J. S. M. Simpson, J. Chem. Phys. 107, 9929 (1997)], the potential surface is used to calculate vibrational relaxation cross sections and rate constants.

I. INTRODUCTION

The interaction between the helium atom and the carbon monoxide molecule has been the subject of a variety of experimental and theoretical studies. The system is of interest from an astrophysical point of view on account of the role that the CO molecule plays in dense interstellar clouds. Carbon monoxide is excited mostly by collisions with abundant species such as He and H₂ in that environment. Additionally, the He–CO van der Waals complex shows interesting dynamics which lie between the semirigid and nearly free rotor limits.

The relatively small number of electrons of He–CO permits theoreticians to calculate intermolecular potential energy surfaces by \textit{ab initio} methods. Thomas, Kraemer, and Diercksen (TKD) published a potential in 1980\textsuperscript{163} that was calculated at the singles and doubles configuration interaction (CISD) level. Though their potential was state-of-the-art at that time, the use of rather small basis sets resulted in an underestimated potential well depth. Furthermore, the interaction energy was not corrected for the basis set superposition error (BSSE). The TKD potential was extended later\textsuperscript{164} to include the dependence on the CO bond length. More recently, two \textit{ab initio} potentials were computed by the supermolecular approach using fourth-order many-body perturbation theory (MBPT\textsuperscript{4}).\textsuperscript{165,166} Moszynski \textit{et al.} reported a preliminary potential calculated by applying symmetry-adapted perturbation theory (SAPT).\textsuperscript{80}

A number of spectroscopic studies as well have been devoted to the He–CO complex. Chuaqui \textit{et al.}\textsuperscript{167} recorded high-resolution infrared spectra near the fundamental band region of the CO monomer for the complex with \textsuperscript{3}He and \textsuperscript{4}He. A more powerful spectroscopic technique was applied recently\textsuperscript{168} to detect the “hidden” lines in the spectra, which were obscured by transitions of the CO monomer in the original measurements. The authors of Ref. 167 could not assign all observed transitions using conventional spectroscopic methods and theoretical spectra generated from the \textit{ab initio} TKD potential. Therefore, a two-dimensional potential energy surface named V(3,3,3) was fitted to reproduce the experimental transition frequencies. Subsequently, a potential with a different functional form was determined from a fit to the same set of spectroscopic data.\textsuperscript{169} The starting point of the new potential surface was the exchange-Coulomb (XC) model potential, which is partly based on \textit{ab initio} information on the exchange-repulsion energy and long-range induction and dispersion coefficients. This “XC” potential reproduced the observed spectrum as well as the V(3,3,3) potential. Moreover, because of its sounder theoretical basis the XC potential is expected to be more realistic in the regions not sampled by the spectroscopic data.

The semi-empirical XC and V(3,3,3) potentials and the \textit{ab initio} TKD and
SAPT potentials were used to calculate pressure broadening and shifting cross sections for pure rotational transitions of CO in helium. Good qualitative agreement was obtained for the cross sections computed from the XC, $V_{(3,3,3)}$, and SAPT potentials. The theoretical data, however, are in substantial disagreement with experiment at very low temperatures. This deviation is probably due to experimental errors or the breakdown of the line shape theory, not because of inaccuracies in the potentials. The agreement of the cross sections obtained from the TKD potential with some of the experimental very low temperature data appeared to be fortuitous. Second virial coefficients computed from the SAPT potential and from the XC and $V_{(3,3,3)}$ potentials were in reasonable accord with experimental data. The SAPT potential was also tested against experimental transport properties.

Vibrational relaxation of CO ($v = 1$) by inelastic collisions with helium atoms has been the subject of various theoretical studies (see Ref. 174 and references therein). Vibration relaxation strongly depends on the shape of the intermolecular potential. Rate constants determined at very low temperatures are sensitive to the van der Waals well, while the anisotropy of the repulsive wall is probed at higher temperatures. Most of the studies on vibrational relaxation rate constants of the last decade used the TKD potential. Since comparative studies have shown that this TKD potential suffers from inaccuracies, a high quality He–CO potential including the vibrational coordinate dependence is needed.

The current chapter presents the calculation of an \textit{ab initio} SAPT potential dependent on the CO bond length. In Ref. 80, the two-dimensional SAPT potential was used in dynamical calculations on the frequencies and intensities of the transitions in the infrared spectrum accompanying the fundamental bond of CO. It was found that the line positions agreed within a few tenths of a wave number with the experimental data from Ref. 167. To test the accuracy of the current three-dimensional potential in the region of the Van der Waals minimum a new series of dynamical calculations have been performed. The results are compared with the data from Ref. 167 as well as with the new data from Ref. 168. In an accompanying work the three-dimensional potential is used to calculate rate constants for the vibrational relaxation of the $^4\text{He–CO}$ and $^3\text{He–CO}$ complexes.

\section*{II. OUTLINE OF SAPT CALCULATIONS}

The SAPT approach used here has been described in a number of papers (Refs. 80, 79 and 175, cf. Chapter 6). The interaction energy can be decomposed into terms corresponding to the Hartree–Fock ($E_{\text{HF}}$) and correlated
(E_{\text{int}}^{\text{corr}}) levels of theory,

\[ E_{\text{int}} = E_{\text{int}}^{\text{HF}} + E_{\text{int}}^{\text{corr}}. \]  

The Hartree–Fock interaction energy was obtained from supermolecular self-consistent field calculations and represented as a sum of individual contributions. The SAPT contribution to the interaction energy at the correlated level is represented here as in Ref. 80, except that the electron correlation effects on the exact first-order exchange contribution are approximated by

\[ E_{\text{exch}}^{(1)} = E_{\text{exch}}^{(1)} + E_{\text{exch}}^{(12)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD}). \]  

In the expression for \( E_{\text{exch}}^{(12)} \) the first- and second-order cluster operators are replaced by converged coupled-cluster operators, leading to a sum of higher-order terms (in the intramolecular correlation) denoted \( \Delta_{\text{exch}}^{(1)}(\text{CCSD}) \). Although the CCSD correction was not included in the potential of Ref. 80, it was discussed that it may have a non-negligible effect on the anisotropy.

The interaction energy surface for the He–CO system can be naturally expressed in Jacobi coordinates \((R, r, \theta)\), where \( R \) is the distance between the c.m. of CO and the helium atom, \( r \) is the CO bond length, and \( \theta \) is the angle between the vector pointing from the molecular c.m. to the atom and the vector pointing from the carbon to the oxygen nucleus. Calculations have been performed for intermolecular distances \( R = 5, 6, 7, 8, \) and 10 bohr, and seven equidistant angles \( \theta \) ranging from \( \theta = 0^\circ \) to \( \theta = 180^\circ \). In addition, potential energy curves have been computed for \( \theta = 15^\circ, 75^\circ, 105^\circ, \) and \( 165^\circ \). The CO bond length \( r \) was varied over five values: the equilibrium bond length \( r_e = 2.132 \) bohr, the two values of \( r = 1.898 \) and 2.234 bohr at which Schinke and Diercksen previously calculated a potential energy surface, and two additional values of \( r = 2.050 \) and 2.170 bohr. In total, we calculated 275 points on the three-dimensional surface.

As in the previous work, a \([5s3p2d] \) basis was used for the helium atom. The \( s \) orbitals were represented by the (61111) contraction of Van Duijneveldt’s 10s set, and the exponents of the polarization functions were taken from Ref. 93. For the carbon and oxygen atoms we took the \([8s5p3d1f] \) basis sets of Diercksen and Sadlej optimized for the dipole and quadrupole properties of the CO molecule. In Ref. 80, however, the five steepest \( p \) functions on both C and O were inadvertently contracted to one basis function instead of two. All terms except \( E_{\text{disp}}^{(20)} \) were calculated with this basis set. In the calculation of \( E_{\text{disp}}^{(20)} \) an extended basis set was used with diffuse bond functions from Ref. 179, located at the middle of the intermolecular bond. To investigate the effect of the basis, we performed additional calculations at \( R = 7 \) bohr, \( r = 2.132 \) bohr, and \( \theta = 0^\circ \) and \( 180^\circ \) with the \([9s7p3d2f] \) basis sets for the carbon and oxygen atoms from
Hettema et al.\textsuperscript{180} Polarization functions were applied in their spherical form (five \textit{d} functions and seven \textit{f} functions). Full dimer basis sets were used in the SAPT calculations in order to account for charge-overlap effects.

All calculations were performed employing the \textit{sapt} system of codes.\textsuperscript{95} The \textsc{polcor} package\textsuperscript{73} was used to compute additional long-range induction and dispersion coefficients corresponding to the multipole expanded induction and dispersion energies. These long-range coefficients, calculated with the same basis sets and at the same level of theory, were subsequently used in the analytical fitting of the induction and dispersion energies. The Boys–Bernardi counterpoise correction\textsuperscript{98} was applied to eliminate the BSSE from the supermolecular Hartree–Fock interaction energy.

A two-step procedure was used in fitting the interaction energy. In the first step, one-dimensional fits in \textit{R} were produced for each value of \( \theta \); subsequently we expanded all fit parameters in Legendre polynomials \( P_l(\cos \theta) \). The CO bond length dependence of the potential was represented by expanding the linear parameters in powers of \( r - r_e \), where \( r_e = 2.132 \) bohr is the experimental CO equilibrium bond length. In the second step, we used a global three-dimensional fitting procedure with the parameters from the one-dimensional fits of the first step as starting point. The fitted potential reproduces all \textit{ab initio} calculated points within 2\%. In the region of the potential minimum the difference between the fitted potential energy and its \textit{ab initio} counterpart is typically a few tenths of a wave number and at most 0.5\, cm\textsuperscript{-1}. A \textsc{fortran} subroutine for generating the \textit{ab initio} potential is available from the authors at the electronic mail address avda@theochem.kun.nl.

\section*{III. FEATURES OF THE POTENTIAL ENERGY SURFACE}

We first look at the potential energy surface, fitted to the \textit{ab initio} calculated data points, for \( r \) fixed at the experimental CO equilibrium bond length \( r_e = 2.132 \) bohr. The potential surface shows a single minimum of depth \( \epsilon_m = -23.734 \) cm\textsuperscript{-1} at \( R_m = 6.53 \) bohr and \( \theta_m = 48.4^\circ \). Comparison with the previously published two-dimensional potential energy surface\textsuperscript{80} shows that the current potential predicts a minimum corresponding to the skew symmetry of the complex instead of the linear CO–He configuration. As the potential is very flat in region \( \theta = 0^\circ \) to 120\(^\circ\), small inaccuracies in the basis set or the fit can cause the global minimum to shift from one geometry to the other. For the \( \theta = 0^\circ \) curve at \( r = 2.132 \) bohr, the potential shows a minimal value at \( R = 6.94 \) bohr of \( \epsilon = -21.078 \) cm\textsuperscript{-1}, which is only a few wave numbers above the global minimum. The improvement of the basis set, compared to Ref. 80, has a significant effect on the interaction energies. Two recently computed MBPT4
Chapter 4: Ab initio potential and IR spectrum of He–CO

FIG. 1. Contour plot of the \textit{ab initio} potential (in cm\(^{-1}\)) at \(r = 2.132\) bohr.

potentials predict global minima of \(\epsilon = -20.32\) cm\(^{-1}\) at \(\vartheta_m = 60^\circ\), \(R_m = 6.60\) bohr\(^{166}\) and \(\epsilon_m = -21.95\) cm\(^{-1}\) at \(\vartheta_m = 70^\circ\), \(R_m = 6.43\) bohr,\(^{165}\) i.e., at the skew geometry. By contrast, a linear equilibrium geometry with \(\epsilon_m = -22.331\) cm\(^{-1}\), \(R_m = 6.84\) bohr was predicted by the “XC” model potential,\(^{169}\) which was fitted to the infrared spectrum and was based on an exchange-Coulomb model. How difficult it is to locate the global minimum is illustrated by the fact that the older \(V_{(3,3,3)}\) potential fitted to the same spectroscopic data has its minimum at the skew geometry.\(^{167}\) These \textit{ab initio} and semi-empirical potential surfaces were compared in a recent work by Thachuk \textit{et al.}\(^{170}\) together with our two-dimensional potential. Agreement between the current potential and the semi-empirical XC potential, which has proved to be very accurate, is better than for our old potential surface and is now within 2 cm\(^{-1}\). Figure 1 depicts a contour plot of the \textit{ab initio} potential at \(r = 2.132\) bohr.

In Table 1 we compare the separate components of the interaction energy computed in two different basis sets. In case A, all components were computed with the basis sets from Diercksen and Sadlej\(^{178}\) for the C and O atoms, except for the contribution \(E_{\text{disp}}^{(20)}\) which was calculated in the basis set with additional bond functions. The basis sets from Hettema \textit{et al.}\(^{180}\) for C and O were used in case B, where no bond functions were included (cf. Sec. II). From
Table 1 it is seen that the differences between the two basis sets are manifest in two components, namely, the intramolecular correlation correction to the first-order exchange energy, \(\epsilon_{\text{exch}}^{(1)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD})\), and the dispersion energy \(E_{\text{disp}}^{(2)}\). Since basis B contains more \(s\) and \(p\) functions on the CO monomer, the intramolecular correlation is taken into account to a greater extent than in basis A. It is known that molecules with triple bonds are sensitive to electronic correlation in higher-order levels of perturbation theory. This explains the difference in \(\epsilon_{\text{exch}}^{(1)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD})\), which is as large as 26% for \(\theta = 180^\circ\). In comparison with the results from Ref. 80 we observe that at \(\theta = 0^\circ\) and \(180^\circ\) the Hartree–Fock interaction energies are 0.83 and 6.50 cm\(^{-1}\) higher, respectively, while \(\epsilon_{\text{exch}}^{(1)} + \Delta_{\text{exch}}^{(1)}(\text{CCSD})\) at \(\theta = 0^\circ\) is 1.50 cm\(^{-1}\) higher. These deviations are caused by the incorrect contraction of the steepest \(p\) functions in Ref. 80. Secondly, in basis A, which includes bond functions in the calculation of \(E_{\text{disp}}^{(20)}\), the dispersion energy \(E_{\text{disp}}^{(2)}\) is 1.3 and 5.7 cm\(^{-1}\) lower at \(\theta = 0^\circ\) and \(180^\circ\), respectively, in comparison with basis B (without bond functions). The results for basis B are approximately equal to the results found for \(E_{\text{disp}}^{(20)}\) in Ref. 80: \(-38.81\) and \(-94.48\) cm\(^{-1}\) at \(\theta = 0^\circ\) and \(180^\circ\), respectively. Although the calculation of \(E_{\text{disp}}^{(20)}\) is not strictly variational, it follows in practice that an improvement of the basis implies a lowering of \(E_{\text{disp}}^{(20)}\). If only nucleus-centered basis sets are used, functions with high angular momenta have to be included to describe the dispersion energy properly. This can be avoided by extending the basis set with a series of diffuse bond functions with low angular quantum numbers. The exact origin and exponents of the bond functions hardly affect the energy. As \(E_{\text{disp}}^{(20)}\) constitutes the main contribution to the dispersion energy, calculating this term (at relatively low cost) in a basis with diffuse bond functions causes the dispersion energy and consequently the total interaction energy to be substantially lowered.
IV. BOUND STATES AND INFRARED SPECTRUM OF HE–CO

As is well known, nuclear motions of weakly bound van der Waals complexes can be described in a set of coordinates relative to either a space-fixed or a dimer-embedded frame. When the strength of the anisotropy in the intermolecular potential is small in comparison with the end-over-end rotational constant $1/(2\mu R^2)$ of the dimer, it is convenient to use the space-fixed coordinate system. It is this description that is used here even though the anisotropy of the potential in the van der Waals region is not particularly weak. We did this because the energy levels and infrared transitions of the He–CO complex can be approximately classified by the case (a) coupling of Bratoz and Martin (see Refs. 1 and 183 for a review). Furthermore, the intramolecular vibration can to a good approximation be decoupled from the intermolecular modes because of the high frequency ($\sim 2143 \text{ cm}^{-1}$) of the former. The $r$ dependent rotational constant of CO and potential function can then be replaced by their vibrationally averaged counterparts, $b_v$ and $V_v(R, \vartheta)$, respectively, with $v$ labeling the intramolecular vibrational mode. The nuclear motions of He–CO are thus described by the Hamiltonian

$$H_v = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{l^2}{2\mu R^2} + b_v j^2 + V_v(R, \vartheta),$$

where $\mu$ is the reduced mass of the complex and $j$ and $l$ are the angular momenta associated with the molecular rotation and with the end-over-end rotation of the system, respectively. Most calculations in this work applied this adiabatic decoupling approximation. Additional full three-dimensional $(R, \vartheta, r)$ dynamical computations were performed for the $J = 0$ and 1 states of $^4$He–CO. In these calculations, the ground state potential for the CO molecule from Huxley and Murrell was added to the intermolecular potential function.

In case of an isotropic potential, $j$ and $l$ are good quantum numbers, corresponding to the molecular rotation in the complex and the end-over-end rotation of $R$, respectively. The total angular momentum $J = j + l$ is always conserved but a degenerate $(j, l)$ level splits into sublevels $J = |j - l|, \ldots, j + l$ under the influence of the anisotropy of the potential. It was shown in a previous paper that for most of the eigenstates, the dominant $(j, l)$ contribution to the wave function is of the order of 90%, suggesting that the CO molecule in the dimer behaves like a slightly hindered rotor. This was confirmed by the observation that although most transitions did not obey selection rules corresponding to the case (a) coupling of Bratoz and Martin, the most intense lines did correspond to the free internal rotor limit. Therefore, the states can to be labeled a good approximation by $j$ and $l$. 


TABLE 2. Expectation values in atomic units of \((r - r_e)^k\), \(k = 1, 2, 3\), for the \(v = 0\) and \(v = 1\) vibrational states.

<table>
<thead>
<tr>
<th>(v)</th>
<th>(v = 0)</th>
<th>(v = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle r - r_e \rangle)</td>
<td>0.0074502</td>
<td>0.0224821</td>
</tr>
<tr>
<td>(\langle (r - r_e)^2 \rangle)</td>
<td>0.0041377</td>
<td>0.0127990</td>
</tr>
<tr>
<td>(\langle (r - r_e)^3 \rangle)</td>
<td>0.0001120</td>
<td>0.0007388</td>
</tr>
</tbody>
</table>

When we assume that the CO vibration is decoupled from the intermolecular modes, the transition frequencies are given by

\[
\nu(v = 1, j', l', J' \leftarrow v = 0, j'', l'', J'') = E_{j', l', v = 1}^{j'', l'', v = 0} + Q_1(0),
\]

where \(Q_1(0) = 2143.2712\) cm\(^{-1}\) is the frequency of the CO fundamental stretching mode, determined from a Dunham analysis. The intensities of the infrared transitions in He–CO accompanying the fundamental band of CO were calculated as in Ref. 80, at a temperature of \(T = 50\) K. The intermolecular transitions obey the following selection rules: \(|\Delta p| = 1\) with \((-1)^p \equiv (-1)^{j+l}\), and \(|\Delta J| = 0\) or \(1\). In addition, the selection rules \(\Delta l = 0\) and \(|\Delta j| = 1\) hold approximately since \(j\) and \(l\) are nearly good quantum numbers.

To compute the vibrationally averaged potential surface \(V_v(R, \theta)\) for a given vibrational state \(v\) of the CO monomer, the powers \((r - r_e)^k\) in the analytical expression of the potential energy were replaced by their corresponding expectation values. We have determined the eigenfunctions of the potential from Ref. 184 by using the discrete variable representation (DVR) method with a basis of sinc functions. The expectation values of the powers \((r - r_e)^k\) over the \(v = 0\) and \(v = 1\) vibrational states that were obtained from these eigenfunctions are listed in Table 2.

A radial basis of Morse type oscillator functions was used for the \(R\) coordinate. The parameters \(R_e\), \(D_e\), and \(\omega_e\) were optimized by minimizing the energy of the \(J = 0\) state. This gave \(R_e = 13.050\) and 14.149 bohr for \(^4\)He–CO and \(^3\)He–CO, respectively, \(D_e = 14.3758\) cm\(^{-1}\), and \(\omega_e = 9.9861\) cm\(^{-1}\). The final basis was restricted to the space with \(j \leq 10\) for the angular basis and order \(n \leq 23\) for the radial basis. The vibrationally averaged rotational constants \(b_0\) and \(b_1\) of the CO molecule were fixed at 1.9225125 and 1.9050074 cm\(^{-1}\), respectively. The rotational constant for the vibrational ground state is close to the highly accurate value of 1.922528988 cm\(^{-1}\) reported by Varberg and Evenson. In the full three-dimensional calculations a Morse type basis for \(r\) was used with \(r_e = 2.1597\) bohr, \(D_e = 82.3030\) cm\(^{-1}\), \(\omega_e = 2142.95\) cm\(^{-1}\), and order \(n \leq 4\). We used the following masses: \(^3\)He – 3.01603 amu, \(^4\)He – 4.00260 amu, \(^12\)C – 12 amu, and \(^16\)O – 15.99491 amu. For practical reasons, all calculations were performed by the triatom package, which uses
Chapter 4: Ab initio potential and IR spectrum of He–CO

TABLE 3. Energy levels (in cm$^{-1}$) of the $^4$He–CO complex, relative to the $(J,j,l) = (0,0,0)$ level at $-6.7879$ and $-6.8359$ cm$^{-1}$ (theoretical values) for $v = 0$ and $v = 1$, respectively. “Experimental” values are from Ref. 168.

<table>
<thead>
<tr>
<th>$J$</th>
<th>$(j,l)$</th>
<th>$v = 0$ This work</th>
<th>“Experimental”</th>
<th>$v = 1$ This work</th>
<th>“Experimental”</th>
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<tr>
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<td>7.2441</td>
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<td>7.2209</td>
<td>7.1426</td>
</tr>
<tr>
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<td>9.4878</td>
<td>9.3940</td>
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</tr>
</tbody>
</table>

the dimer-embedded frame, rather than by the atdiatsf package, which is based on a space-fixed coordinate system. Note that both descriptions give exactly the same results, only the approximate quantum numbers labeling the states are different.

In Table 3 we summarize the results of the bound state calculations for $^4$He–CO. There are fourteen bound states, which can be labeled approximately by angular momentum quantum numbers $j$ and $l$. The potential energy surface does not support states excited in the van der Waals stretch. It should be noted that states of positive energy lying below the $j = 1$ rotational level of the CO monomer are truly bound if they have parity $p = (-1)^{J+1}$. These states cannot mix with $j = 0$ continuum states, which have parity $p = (-1)^{J}$, since both $p$ and $J$ are conserved. The $j = 1$ rotational level of CO in its ground state was experimentally determined at 3.8450 cm$^{-1}$. The ground state of $^4$He–CO is bound by 6.788 cm$^{-1}$. Our earlier two-dimensional SAPT potential supports a ground state lying 0.174 cm$^{-1}$ lower, which is in agreement with the observation that the old potential has a slightly deeper well. The “experimental” energy level scheme shown in Table 3 was reported by Chan and McKellar who slightly modified the levels from Chuaqui et al. by including the transition frequencies of the hidden lines. Furthermore, their scheme includes the $(J,j,l) = (4,1,4)$ level.

Full three-dimensional calculations for $^4$He–CO ($J = 0$ and 1) showed that the bound levels are affected by less than 0.001 cm$^{-1}$ by the decoupling.
approximation. For instance, the \((J, j, l) = (1, 1, 1)\) state for \(v = 0\) is decreased from 4.3083 to 4.3079 cm\(^{-1}\) by this approximation, while the \((J, j, l) = (0, 1, 1)\) state for \(v = 1\) is increased from 5.3086 to 5.3087 cm\(^{-1}\). This is in agreement with the result found for the He–HF complex\(^{187}\) that the coupling between inter- and intramolecular modes is very small for atom–diatom systems.

The calculated infrared transition frequencies and intensities for the \(^4\)He–CO complex are reported in Table 4 and graphically illustrated in Fig. 2. Table 4 shows that the agreement of theoretical transition frequencies with the results of the high-resolution measurements\(^{167,168}\) is excellent. All line positions agree within 0.1 cm\(^{-1}\) or better, while the r.m.s. deviation is 0.038 cm\(^{-1}\). The absolute errors of the transition frequencies computed from our previous two-dimensional \textit{ab initio} potential\(^80\) were as large as 0.5 cm\(^{-1}\) for some transitions. Only after scaling the short range contribution to the \(V_3(R)\) component of the potential energy agreement within 0.2 cm\(^{-1}\) for all transitions was reached, whereas the agreement we obtain now is twice as good without any scaling. The transition intensities predicted by the \textit{ab initio} potential also agree reasonably well with the experimental values. One should keep in mind that intensities are determined from experiment with much less accuracy than the corresponding transition frequencies.\(^{167}\)
### TABLE 4

Frequencies $\nu$ (in cm$^{-1}$) and intensities (in arbitrary units, relative to the (3, 1, 2) $\leftrightarrow$ (2, 0, 2) intensity) of the transitions in the infrared spectrum of $^3$He–CO accompanying the fundamental band of CO.

<table>
<thead>
<tr>
<th>Transition</th>
<th>This work</th>
<th>Observed, Ref. 167</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{calc}}$</td>
<td>Intensity</td>
<td>$\nu_{\text{obs}}$</td>
</tr>
<tr>
<td>(1, 1, 1) $\leftrightarrow$ (1, 1, 0)</td>
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<td>2142.9074</td>
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</tr>
<tr>
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<td>4.6</td>
</tr>
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<td>4.6</td>
</tr>
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</tr>
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<td>6.6</td>
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</tr>
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<td>(3, 0, 3) $\leftrightarrow$ (4, 0, 4)</td>
<td>2141.0336</td>
<td>17.8</td>
</tr>
</tbody>
</table>

(Continued on next page)
In Table 5 we report the bound state levels for the $^3$He–CO complex generated from the $ab$ initio potential. The twelve transitions observed in Ref. 167 for $^3$He–CO were insufficient to determine the energy levels accurately. The addition of seven new transitions, however, enabled the authors of Ref. 168 to construct the experimental energy level scheme listed in Table 5. The experimental $(J,j,l) = (3,1,3)$ level is absent since the $(3,0,3) \leftrightarrow (3,1,3)$ transition could not be observed. Table 6 and Fig. 3 show the $ab$ initio transition frequencies and intensities for the $^3$He–CO complex, together with their experimental counterparts from Refs. 167 and 168. Agreement with experiment is equally good as for $^4$He–CO. All line positions are reproduced within 0.06 cm$^{-1}$, the r.m.s. deviation is 0.033 cm$^{-1}$. The infrared intensities are also correctly predicted. The excellent agreement between theoretical and experimental transition frequencies for both $^4$He–CO and $^3$He–CO confirms that the $ab$ initio calculated potential energy surface represents the anisotropy of the potential in the region of the van der Waals minimum very accurately.

The band origin of the $v = 1 \leftrightarrow 0$ transition is lower in the He–CO complex than in the free monomer. The observed red shifts for $^4$He–CO and $^3$He–CO are $-0.024$ and $-0.021$ cm$^{-1}$, respectively,\textsuperscript{168} the theoretical values are $-0.048$ and $-0.044$ cm$^{-1}$, respectively. This overestimation of the red shifts is reflected in the mean difference between calculated and observed transition frequencies which are $-0.019$ and $-0.017$ cm$^{-1}$, respectively. As discussed above, the bound state levels obtained from three-dimensional and decoupled two-dimensional calculations agree within 0.001 cm$^{-1}$. The same result was found for the band origin. Therefore, we conclude that the remaining small disagreements between theoretical and experimental red shifts must be due to minor inaccuracies in the potential function, rather than to the decoupling approximation.
TABLE 5. Energy levels (in cm$^{-1}$) of the $^3$He-CO complex, relative to the $(J,j,l) = (0,0,0)$ level at $-5.5416$ and $-5.5858$ cm$^{-1}$ (theoretical values) for $v = 0$ and $v = 1$, respectively. "Experimental" values are from Ref. 168.

<table>
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<th>&quot;Experimental&quot;</th>
<th>This work</th>
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<td>---$^a$</td>
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<td>7.8232</td>
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</table>

$^a$This level has not been directly observed, it is estimated to be at 7.856 cm$^{-1}$.

FIG. 3. Comparison of the theoretical and experimental infrared spectra of the $^3$He-CO complex accompanying the fundamental band of CO. The temperature is 50 K.
TABLE 6. Frequencies $\nu$ (in cm$^{-1}$) and intensities (in arbitrary units, relative to the (2,1,1) $\leftrightarrow$ (1,0,1) intensity) of the transitions in the infrared spectrum of $^3$He-CO accompanying the fundamental band of CO.

<table>
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</thead>
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<td>$\nu_{\text{obs}}$</td>
<td>$\nu_{\text{calc}} - \nu_{\text{obs}}$</td>
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<td>$\nu_{\text{calc}}$</td>
<td>Intensity</td>
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V. SUMMARY AND CONCLUSIONS

The interaction potential energy surface of the He–CO complex was calculated for a broad range of configurations using symmetry-adapted perturbation theory. In comparison with previous work\textsuperscript{80} the anisotropy of the exchange-repulsion energy was computed by the more advanced SAPT–CCSD method, the basis set was improved, and the CO bond length was varied over five values, which yields a full three-dimensional potential surface. We have shown that the present potential agrees very well with the accurate semi-empirical XC potential of Le Roy \textit{et al.}\textsuperscript{169} better than our earlier \textit{ab initio} potential.

Using the computed potential energy surface we have calculated bound rovibrational states and the infrared spectrum of the He–CO complex corresponding to the simultaneous excitation of the vibration and hindered rotation of the CO molecule within the dimer. Variational characterization of the rovibrational states revealed a ground state of \(^4\)He–CO with a dissociation energy of 6.79 cm\(^{-1}\) and several angularly excited states of the complex. The predicted positions and intensities of lines in the infrared spectrum are in excellent agreement with the experimental spectrum.\textsuperscript{167,168} The good agreement for the transition frequencies shows that the anisotropy of the potential in the well region is correct. The present \textit{ab initio} SAPT potential was used in the calculation of second virial coefficients (see Chapter 8). Very good agreement with the majority of available experimental data was obtained, showing that the potential well depth is also predicted correctly. In an accompanying work\textsuperscript{174} the accuracy of the potential in the repulsive region and the correctness of its vibrational coordinate dependence is tested.

ACKNOWLEDGMENTS

This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and by KBN funds through the Department of Chemistry, University of Warsaw, within the Grant BW-1343/38/96.
Chapter 5

Ab initio potential energy surface and near-infrared spectra of the Ne–C₂H₂ and Ne–C₂HD complexes

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Abstract

Symmetry-adapted perturbation theory has been applied in the calculation of the potential energy surface for the Ne–C₂H₂ complex. The interaction energy is interpreted in terms of the electrostatic, exchange, induction, and dispersion components and the anisotropy of the surface is analyzed in terms of these contributions. Our potential has a global minimum of $\epsilon_m = -52.310$ cm$^{-1}$ for a skew geometry ($R_m = 7.20$ bohr, $\theta_m = 53.1^\circ$) and a local minimum at the linear geometry ($R_m = 8.24$ bohr, $\epsilon_m = -50.542$ cm$^{-1}$). The computed points have been fitted analytically and have been used in converged variational calculations of the rovibrational energy levels and near-infrared transitions and intensities corresponding to the simultaneous excitation of the vibration and hindered rotation of the C₂H₂ and C₂HD monomers within the Ne–C₂H₂ and Ne–C₂HD complexes. The nature of the bound states and the spectrum generated from the ab initio potential are discussed.
Chapter 5: Potential and IR spectrum of Ne–$\text{C}_2\text{H}_2$ and Ne–$\text{C}_2\text{HD}$

I. INTRODUCTION

Over the last decades there has been a considerable interest in theoretical and experimental studies of van der Waals molecules involving the acetylene molecule. One of the reasons for this interest is that acetylene is a trace constituent of the atmospheres of the planets Jupiter and Saturn, and Saturn’s satellite Titan.\textsuperscript{192,193} The temperature profiles of these atmospheres can be accurately monitored provided that spectroscopic and collisional processes involving the acetylene molecule are well understood. It is not surprising then, that van der Waals complexes of $\text{C}_2\text{H}_2$ with rare gas atoms have been thoroughly investigated using high-resolution spectroscopy,\textsuperscript{194–200} scattering techniques,\textsuperscript{201–216} and \textit{ab initio} methods (Refs. 79, 217–223 and Chapters 8 and 9).

In a recent paper\textsuperscript{79} an intermolecular potential energy surface for the He–$\text{C}_2\text{H}_2$ complex was reported which was computed by symmetry-adapted perturbation theory (SAPT). This potential was shown to reproduce all major features of the recorded near-infrared spectrum,\textsuperscript{199} which suggests that its anisotropy is correct, at least in the well region. As a further test of the \textit{ab initio} potential, in Chapter 9 we compute the energy loss spectra and total differential cross sections for the He–$\text{C}_2\text{H}_2$ scattering. The agreement with the experiment\textsuperscript{211} is excellent, which indicates that both the isotropic and the anisotropic parts of the SAPT potential in the repulsive region are accurate. As an additional test of the \textit{ab initio} potential, in Chapter 8 we report second virial coefficients for the He–$\text{C}_2\text{H}_2$ mixtures. The agreement with experiment is again very good.

Surprisingly, theoretical and experimental investigations of the Ne–$\text{C}_2\text{H}_2$ complex are scarce. The experimental studies of Ne–$\text{C}_2\text{H}_2$ were limited to measurements of collisional probabilities for vibrational relaxation of the excited $\text{C}_2\text{H}_2$ and $\text{C}_2\text{D}_2$ molecules by the neon atoms.\textsuperscript{212–216} Only recently, Bemish and Miller\textsuperscript{200} measured the near-infrared spectra of Ne–$\text{C}_2\text{H}_2$ and Ne–$\text{C}_2\text{HD}$ corresponding to the simultaneous excitation of the vibration and hindered rotation of the $\text{C}_2\text{H}_2$ and $\text{C}_2\text{HD}$ monomers within the complexes. To our knowledge, no \textit{ab initio} potential is available for this system. Since the results reported in Ref. 79 and Chapters 8 and 9 suggest that SAPT is a suitable method to establish reliable potential energy surfaces for complexes involving the acetylene molecule, we fill this gap in the present chapter and report SAPT calculations of the potential energy surface for Ne–$\text{C}_2\text{H}_2$. This potential is applied to generate the positions and intensities of the lines in the infrared spectra of the Ne–$\text{C}_2\text{H}_2$ and Ne–$\text{C}_2\text{HD}$ complexes corresponding to the simultaneous excitation of vibration and internal rotation of the $\text{C}_2\text{H}_2$ and $\text{C}_2\text{HD}$ monomers within the complexes.
II. METHODS AND DEFINITIONS

A. Outline of SAPT calculations

In the present chapter we follow the SAPT method introduced and tested in previous work (see Refs. 79, 80 and 175 and Chapter 6 for the most recent applications). The intermolecular interaction energy $E_{\text{int}}$ is represented by the sum of the first- and second-order polarization and exchange contributions,1

$$E_{\text{int}} = E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-def}}^{(2)} + E_{\text{exch-disp}}^{(2)},$$  \hspace{1cm} (1)

where $E_{\text{pol}}^{(1)}$ is the electrostatic energy, fully accounting for the overlap (penetration) of the monomer charge distributions, $E_{\text{ind}}^{(2)}$ and $E_{\text{disp}}^{(2)}$ denote the nonexpanded induction and dispersion energies, and $E_{\text{exch-ind}}^{(2)}$, $E_{\text{exch-def}}^{(2)}$, and $E_{\text{exch-disp}}^{(2)}$ are the second-order exchange-induction, exchange-deformation, and exchange-dispersion energies. In practice, the contributions appearing on the r.h.s. of Eq. (1) were evaluated using the many-body techniques developed in Refs. 61–67 and 224 (see also Ref. 4 for a review). The exchange-deformation term is defined as in Refs. 84 and 85, and was computed from the supermolecule Hartree–Fock interaction energy. We used the Boys–Bernardi98 counterpoise correction to eliminate the basis set superposition error from the supermolecular Hartree–Fock calculations. The computational scheme adopted in this work was the same as in Refs. 79 and 175 and Chapter 6.

The intermolecular potential energy surface for the Ne–C$_2$H$_2$ system, where C$_2$H$_2$ is kept linear and rigid, can be naturally described in the Jacobi coordinates $(R, \vartheta)$, where $R$ is the distance from the center of mass of C$_2$H$_2$ to the Ne atom, and $\vartheta$ is the angle between the molecular axis and the vector pointing from the center of mass of C$_2$H$_2$ to Ne. Calculations have been performed for five intermolecular distances ranging from $R = 5$ to 10 bohr and ten equidistant angles $\vartheta$ from $\vartheta = 0^\circ$ to $90^\circ$. In total, we calculated 50 points on the surface. In all calculations the acetylene molecule was kept at its experimental equilibrium geometry, i.e., $r(\text{CH}) = 2.0042$ bohr and $r(\text{CC}) = 2.2737$ bohr.225

For the neon atom we used a [5s4p3d2f] basis set. The core-valence part of this basis consisted of the cc-pVDZ basis of Woon and Dunning226,227 with the most diffuse s orbital (exponent 0.4869) left uncontracted. For the diffuse part we selected an even-tempered set optimized for the cc-pVTZ basis.228 We augmented this basis with s orbitals with exponents 0.1133 and 0.03394, p orbitals (0.0918 and 0.02552), d orbitals (0.386 and 0.13595) and f orbitals (1.084 and 0.46189) (see Table III of Ref. 228). For the acetylene molecule we used the [4s4p3d2f/3s2p1d] basis set of Maroulis and Thakkar.229
Chapter 5: Potential and IR spectrum of Ne–C$_2$H$_2$ and Ne–C$_2$HD

All calculations were performed with the SAPT system of codes. In addition, long-range induction and dispersion coefficients corresponding to the multipole-expanded induction and dispersion energies have been computed at the same level of theory and with the same basis sets by means of the POLCOR package. These coefficients were subsequently used in the analytical fits of the induction and dispersion energies. The fitting procedure adopted in the present chapter was the same as in Ref. 175. A FORTRAN subroutine for generating the potential is available from the authors on request at the electronic mail address avda@theochem.kun.nl.

B. Outline of dynamical calculations

Depending on the strength of the anisotropy in the interaction potential, nuclear motions in van der Waals complexes are best described in a set of coordinates related to a space-fixed or body-fixed frame. We have checked that for Ne–C$_2$H$_2$ the space-fixed description is most appropriate. This means that the energy levels and infrared transitions in Ne–C$_2$H$_2$ can be approximately classified by the use of the case (a) coupling of Bratoz and Martin (see also Refs. 1 and 183 for reviews). The intramolecular vibrations can be decoupled from the intermolecular modes because of their high frequency [3294.8395 cm$^{-1}$ (Ref. 230) and 3335.602 cm$^{-1}$ (Ref. 231) for the $\nu_3$ modes of C$_2$H$_2$ and C$_2$HD, respectively], so we have the following Hamiltonian describing the intermolecular motion and the overall rotation of the complex:

$$H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{I^2}{2\mu R^3} + b_r j^2 + V_v(R, \theta),$$

where $\mu$ is the reduced mass of the dimer, $b_r$ is the rotational constant of C$_2$H$_2$ in the vibrational state $v$, $V_v(R, \theta)$ is the interaction potential of Ne–C$_2$H$_2$ averaged over the vibrational state $v$ of C$_2$H$_2$, $j$ is the angular momentum of acetylene, and $I$ denotes the angular momentum associated with the end-over-end rotation of the complex. In this work, we assume that the vibrationally averaged potential $V_v$ can be approximated by the potential computed for the experimental equilibrium geometry of C$_2$H$_2$. Furthermore, we assume in first instance that the interaction potentials for Ne–C$_2$H$_2(v = 0)$ and Ne–C$_2$H$_2(v = \nu_3)$ are the same. In order to get agreement with the experimental spectrum of Ne–C$_2$HD, we will then introduce small changes in the potential of the excited state.

The wave function $\Psi^{JM}(R, \hat{R}, \hat{r})$ was expanded in a basis of products of radial functions $\chi_n(R)$ and angular functions which are Clebsch–Gordan coupled spherical harmonics,
Outline of dynamical calculations

\[ [Y^J(\hat{r}) \otimes Y^l(\hat{R})]_M^J = \sum_{m_1,m_j} \langle j,m_1;l,m_1;J,M \rangle Y^J_{m_1}(\hat{R}) Y^l_{m_j}(\hat{r}), \]  
\hspace{1cm} (3)

where \( Y^J_m \) denotes a normalized spherical harmonic, \( \langle j_1,m_1;j_2,m_2|J,M \rangle \) is the Clebsch–Gordan coefficient, \( J = |j - l|, \ldots, j + l \) is the rotational quantum number corresponding to the total angular momentum \( J = J + l \), \( \hat{R} \) stands for the spherical polar angles of \( \hat{R} \) with respect to a space-fixed frame, and an analogous definition holds for \( \hat{r} \).

For the nondeuterated acetylene species the angular basis of Eq. (3) is adapted to the permutation inversion group \( PI(C_{2v}) \).\(^{232}\) The eigenstates with \( j \) even and odd are states of para and ortho acetylene, respectively, in its ground vibrational state in interaction with the Ne atom. Since the \( \nu_3 \) state is antisymmetric under the permutation of identical nuclei, the ortho/para assignment for the dimer with acetylene in the \( \nu_3 \) state is just reversed, i.e., the van der Waals states with \( j \) even and odd correspond here to ortho and para acetylene, respectively, interacting with neon. The angular basis functions of Eq. (3) have also a well defined parity \( p = (-1)^{j+l} \), so for a given parity of \( j \) the full Hamiltonian, Eq. (2), is blocked in both \( p \) and \( J \). Within each block functions with various \( j \) and \( l \) are mixed through the potential.

The radial basis consisted of Morse type oscillator functions\(^{233}\) characterized by three parameters \( R_e, D_e, \) and \( \omega_e \), which served as further variational parameters. We optimized these by minimizing the energy of the lowest \( J = 0 \) state. This gave \( R_e = 7.85 \) bohr, \( D_e = 42.2936 \) cm\(^{-1} \), and \( \omega_e = 16.406 \) cm\(^{-1} \). The final basis was restricted to the space with \( j \leq 20 \) and \( n \leq 28 \). The rotational constants were fixed at 1.176642 and 1.172421 cm\(^{-1} \) for the ground and \( \nu_3 \) states of \( C_2H_2 \), respectively,\(^{234}\) and 0.99152789 cm\(^{-1} \) (Ref. 235) and 0.986697 cm\(^{-1} \) (Ref. 231) for the same states of \( C_2HD \). In the calculations we used the following masses: \(^{20}\)Ne: 19.99244 amu, \(^{12}\)C: 12 amu, \(^{1}\)H: 1.007825 amu, and \(^{2}\)H: 2.0140 amu.\(^{145}\)

In the calculation of the intensities of the intermolecular transitions for Ne–\( C_2H_2 \), accompanied by the monomer transition \( 0 \rightarrow \nu_3 \), we assume that there is no interconversion between ortho and para monomers, so that in effect they can be considered as different molecules. The contribution to the infrared absorption coefficient \( I(0,i'',J'' \rightarrow v',i',J') \) from the transition \( 0,i'',J'' \rightarrow v',i',J' \) is proportional to

\[ g_I \frac{\exp(-E_{v',i',J'}/k_BT) \left( E_{v'',i'',J''}^{J''} - E_{v',i',J'}^{J'} \right) S(0,i'',J'' \rightarrow v',i',J')}{Z(T)}, \]  
\hspace{1cm} (4)

where \( g_I \) is the spin-statistical factor, equal to 3 and 1 for ortho and para acetylene, respectively, \( E_{v',i',J'}^{J'} \) denotes the energy of the state labeled by \( (v,i,J) \), \( k_B \) is the Boltzmann constant, \( T \) is the assumed beam temperature, and \( Z(T) \)
is the partition function for ortho or para Ne–C$_2$H$_2$. In the calculation of the line strength $S(0, i''', J'''' \rightarrow v', i', J')$ we assumed that the transition dipole corresponding to the $0 \rightarrow \nu_3$ transition in free acetylene is not affected by the interaction with the Ne atom.

The infrared transitions in Ne–C$_2$H$_2$ accompanying the $\nu_3$ mode of acetylene will go from ortho to ortho and para to para species, and will obey the following selection rules: $|\Delta p| = 1$, and $|\Delta J| = 0$ or 1. Additionally, if the anisotropy in the potential is weak, the energy levels may be labeled by the quantum numbers $j$ and $l$ and the selection rule $|\Delta l| = 0$ holds approximately.

The calculations for Ne–C$_2$HD were performed with the \textit{ab initio} potential of Ne–C$_2$H$_2$ transformed to the center-of-mass frame of C$_2$HD. The distance between the centers of mass of C$_2$HD and C$_2$H$_2$ was fixed at $\delta = 0.116961$ bohr. For Ne–C$_2$HD there is no ortho/para distinction of the rovibrational states. Consequently, if the energy levels can be labeled with the quantum numbers $j$ and $l$, the infrared transitions obey the additional approximate selection rule $|\Delta j| = 1$.

### III. FEATURES OF THE POTENTIAL ENERGY SURFACE

Our potential energy surface reveals two nonequivalent minima (and two others determined by symmetry). The global minimum corresponds to a skew configuration of the complex ($\vartheta_m = 53.1^\circ$ and $R_m = 7.20$ bohr) and its well depth amounts to $\epsilon_m = -52.310$ cm$^{-1}$. The local minimum is located at the linear Ne–HCCH geometry ($R_m = 8.24$ bohr and $\epsilon_m = -50.542$ cm$^{-1}$).

In order to visualize the shape of the potential energy surface in the regions of the two minima, we report in Fig. 1 angular scans through the potential at $R = 7.20$ and 8.24 bohr for $\vartheta$ ranging from $0^\circ$ to $180^\circ$. An inspection of Fig. 1 shows that the two curves represent double-well potentials with rather small barriers separating the equivalent minima. The global minima at $R = 7.20$ bohr are located between two repulsive walls, and the height of the wall suggests that it may represent a barrier to internal rotations of the C$_2$H$_2$ monomer within the complex. However, when going to larger $R$ the height of this barrier diminishes considerably. One can, thus, expect that the acetylene molecule in the complex behaves as a slightly hindered rotor.

To investigate the importance of the anisotropic contributions to the potential in various regions of the configuration space, it is customary to expand it as a series in Legendre polynomials,

$$V(R, \vartheta) = \sum_{L=0}^{\infty} V_L(R) P_L(\cos \vartheta),$$ (5)
FIG. 1. Angular dependence of the Ne–C₂H₂ interaction potential in the region of the global and local minima at $R = 7.20$ and 8.24 bohr, respectively.

FIG. 2. Expansion coefficients $V_l(R)$ [cf. Eq. (5)] of the anisotropic Ne–C₂H₂ potential as functions of $R$. The dashed curves represent the expansion coefficients for Ne–C₂HD.
where the expansion coefficients $V_L(R)$ are given by

$$V_L(R) = \frac{2L+1}{2} \int_0^{\pi} V(R, \theta) P_L(\cos \theta) \sin \theta \, d\theta.$$  

(6)

Obviously, the radial functions $V_L(R)$ can be evaluated numerically by the use of a Gauss–Legendre quadrature. In the case of Ne–C$_2$H$_2$, the terms with odd $L$ in Eq. (5) vanish because of the symmetry of the potential. The term with $L = 0$ is the isotropic potential. In order to establish the importance of the anisotropic terms at various values of $R$, we report in Fig. 2 the radial dependence of the $V_L(R)$ coefficients for $L \leq 6$. An inspection of Fig. 2 shows that around $R = 7.2$ bohr all terms with $L \leq 6$ are important, and the convergence of the expansion (5) for fixed $R$ and $\theta$ varying from $0^\circ$ to $90^\circ$ is not particularly fast. By contrast, in the region of the local minimum ($R = 8.2$ bohr) the interaction potential is dominated by the isotropic term and the leading anisotropic component $V_2(R)$. Also reported in Fig. 2 are the radial expansion coefficients for the Ne–C$_2$HD isotopomer. Note that the C$_2$HD molecule is not symmetric, so the odd terms in the angular expansion (5) do not vanish in this case. An inspection of Fig. 2 shows that the shift of the center of mass does not introduce important changes in the even terms of the Legendre expansion. However, the odd terms with $L = 1$ and 3 are not negligible, especially around the global minimum.

Tables 1 and 2 list the total interaction energy and its components ($E^{(1)}_{\text{pol}}$, $E^{(1)}_{\text{exch}}$, $E^{(2)}_{\text{exch-ind}}$, $E^{(2)}_{\text{exch-def}}$, $E^{(2)}_{\text{disp}}$, and $E^{(2)}_{\text{exch-disp}}$) for $R = 7.20$ bohr and 8.24 bohr and varying $\theta$. See also Figs. 3(a) and 3(b) for graphical illustrations. The induction, dispersion, and exchange energies are the three major contributions to the interaction potential determining its anisotropy. The electrostatic energy is less important, although not negligible, especially at small values of $\theta$. As expected, the induction and dispersion terms reveal minima at the hydrogen atom ends, and broad maxima in the middle of the C=C bond. Obviously, these components favor the linear minimum in the potential energy surface. However, the exchange energy

$$E_{\text{exch}} = E^{(1)}_{\text{exch}} + E^{(2)}_{\text{exch-ind}} + E^{(2)}_{\text{exch-def}} + E^{(2)}_{\text{exch-disp}}$$

behaves in a reverse manner to $E^{(2)}_{\text{ind}} + E^{(2)}_{\text{disp}}$, and is much more anisotropic. Consequently, the position of the global minimum can be attributed to the strong reduction of the exchange component.

IV. NEAR-INFRARED SPECTRUM OF NE–C$_2$H$_2$ AND NE–C$_2$HD

In Tables 3 and 4 we report the energy levels of the $^{28}$Ne–C$_2$H$_2$ complex for $J \leq 5$. The ground states of the para and ortho species are bound by 34.029 cm$^{-1}$
### Table 1. Angular dependence of the Ne-C$_2$H$_2$ interaction energy components in the region of the global minimum ($R = 7.0$ bohr). Energies are in cm$^{-1}$.

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Angular dependence of the Ne-C₂H₂ interaction energy components in the region of the local minimum \((R = 8.0\) bohr). Energies are in \(\text{cm}^{-1}\).

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</table>
Features of the potential energy surface

(a) \(^{\text{degrees}}\) (b) \(\text{iS} \, (\text{degrees})\)

**FIG. 3.** Angular dependence of the Ne–C\(_2\)H\(_2\) interaction energy components in the region of the global (a) and local (b) minima. The abbreviations exch, elst, ind, and disp refer to \(E_{\text{exch}} = E^{(1)}_{\text{exch}} + E^{(2)}_{\text{exch-ind}} + E^{(2)}_{\text{exch-def}} + E^{(2)}_{\text{exch-disp}}\), \(E^{(1)}_{\text{pol}}, E^{(2)}_{\text{ind}},\) and \(E^{(2)}_{\text{disp}}\), respectively. The dashed lines represent the total interaction energy.
and 32.706 cm$^{-1}$, respectively, relative to the $j = 0$ state of C$_2$H$_2$. The labeling of the states with the approximate quantum numbers $j$ and $l$ is listed in Tables 3 and 4. Also shown in these tables are contributions of the dominant ($j, l$) angular function to the wave function of the $i$th state for a given $J$, defined as

$$\%_{i,j,l} = 100 \sum_n C_{i,j,l,n}^J C_{i,j,l,n}^J.$$  

(7)

For most of the eigenstates, the dominant ($j, l$) contribution to the wave function is larger than 80%, which demonstrates that acetylene in the complex indeed behaves like a slightly hindered rotor. Consequently, the case (a) coupling provides the most appropriate classification of the energy levels and infrared transitions in Ne–C$_2$H$_2$.

The energy levels of $^{20}$Ne–C$_2$HD with $J \leq 5$ are presented in Table 5. The ground state of the Ne–C$_2$HD isotopomer is bound by 35.130 cm$^{-1}$. Also presented in Table 5 is the labeling of the states with the $j$ and $l$ quantum numbers. Since the energy levels are most sensitive to the even terms in the Legendre expansion and since these terms did not change significantly by the shift of the center of mass (cf. Fig. 2), we expect that the pattern of the levels for Ne–C$_2$HD should be qualitatively similar to Ne–C$_2$H$_2$. An inspection of Tables 3–5 shows that this is indeed the case. In particular, the ground state is shifted by only 0.23 cm$^{-1}$, while the first bending state with $(j, l, J) = (1, 1, 0)$
**TABLE 4.** Energy levels of para Ne-C$_2$H$_2$ with $J \leq 5$.

<table>
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<th>$p$</th>
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### TABLE 5. Energy levels of Ne-C₂HD with $J \leq 5$.

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Near-infrared spectrum

is shifted by 0.60 cm$^{-1}$.

Since the rovibrational states of Ne–C$_2$H$_2$ reveal the behavior of a slightly hindered rotor, it is interesting to see the contour plots of the corresponding wave functions. In Fig. 4(a) we present the contour plot of the anisotropic potential, while we depict in Figs. 4(b) and 4(c) the contour plots of the $J = 0$ state wave functions for $j = 0$ and 1, respectively. The wave function for the $j = 0$ state shows two equivalent maxima separated by a small barrier. The position of the maximum is quite close to the position of the global minimum in potential. The state is rather delocalized, which confirms its nearly free rotor character. It is worth noting that in the limit of case (a) coupling the contours for this state should be independent of $\vartheta$, hence Fig. 4(b) shows that the admixture of $j \neq 0$ states, induced by the anisotropy, strongly affects the shape of the wave function. Also presented in Fig. 4(b) is the contour plot of the Ne–C$_2$HD wave function for $j = J = 0$. An inspection of this figure shows that the asymmetry of the wave function caused by the isotopic substitution is small. It is mostly noticeable for the values of $R$ and $\vartheta$ corresponding to the minima of the potential.

The contour plot 4(c) of the wave function for the $J = 0$ state of ortho Ne–C$_2$H$_2(v = 0)$ reveals a single maximum corresponding to the linear Ne–HCCH geometry. The radial position of this maximum is close to the position of the local minimum in the potential. Also this state shows a substantial delocalization, while the presence of a horizontal nodal plane suggests that it can be considered as a bending state.

Finally, in Figs. 5 and 6 we report the near-infrared spectra of Ne–C$_2$H$_2$ and Ne–C$_2$HD, respectively, accompanying the $\nu_3$ band of acetylene, generated from our \textit{ab initio} potential. The rotational temperature in the beam was assumed to be 1 K. A table collecting all transitions can be obtained from the authors on request. As expected, the most intense lines can be identified (within the case (a) coupling) as $\Delta l = 0$ transitions. Thus, the spectra of Ne–C$_2$H$_2$ and its isotopomer may be considered as the spectra of free C$_2$H$_2$/C$_2$HD perturbed by neon. Our synthetic spectra agree qualitatively with the experimental spectra recorded by Bemish and Miller. However, small red/blue shifts occur. These shifts affect not only the origins of the $P$, $Q$, and $R$ subbands in the spectrum, but also the individual transition frequencies. This means that the transition frequencies depend sensitively on the difference between the interaction potentials for Ne–C$_2$H$_2(v = 0)$ and Ne–C$_2$H$_2(v = \nu_3)$, and precise knowledge of the upper state potential is necessary to make definite assignments.

In Fig. 6(a) we depict the near-infrared spectrum of Ne–C$_2$HD obtained by applying the same interaction potential for the ground and excited state. The spectrum of Fig. 6(b) is calculated after scaling the exchange and electrostatic
Chapter 5: Potential and IR spectrum of Ne-C_{2}H_{2} and Ne-C_{2}HD
FIG. 4. (a) Cut through the ab initio Ne–C₂H₂ potential (in cm⁻¹). (b) Cut through the $J = 0$ rovibrational wave function of para Ne–C₂H₂ ($v = 0$). The dashed contours represent the $j = J = 0$ wave function of Ne–C₂HD ($v = 0$). Amplitudes of the wave functions are in $10^{-3}$ (bohr)⁻³/₂. (c) Cut through the $J = 0$ rovibrational wave function of ortho Ne–C₂H₂ ($v = 0$). Amplitudes of the wave functions are in $10^{-3}$ (bohr)⁻³/₂.
FIG. 5. Near-infrared spectrum of the Ne–C$_2$H$_2$ complex accompanying the $\nu_3$ mode of acetylene, calculated from the ab initio potential. The rotational temperature is 1 K. Intensities are in arbitrary units.

(charge-overlap) contributions to the excited interaction potential by 0.98 and the total excited potential by 0.96. Effectively, this results in a shift of the intermolecular distance $R_m$ corresponding to a minimum interaction energy, varying from $-0.03$ bohr at the linear geometry to $-0.06$ bohr at the perpendicular configuration. The scaling decreases the well depth by 0.12 and 0.57 cm$^{-1}$ at the global minimum ($\vartheta_m = 53.1^\circ$) and the linear configuration, respectively. The saddle point at $\vartheta = 90^\circ$ is lowered by 0.12 cm$^{-1}$. It is clear from Figs. 6(a) and (b) that the scaling affects the individual transition frequencies. The results of Fig. 6(b) are in semiquantitative agreement with the experimental spectrum from Ref. 200 so that assignments of the individual lines in this spectrum can now be made. In further work we plan to systematically improve the excited state potential by fitting the experimental frequencies and intensities.

V. SUMMARY AND CONCLUSIONS

The interaction potential energy surface of the Ne–C$_2$H$_2$ complex has been calculated for a broad range of configurations by the use of symmetry-adapted perturbation theory. From the computed potential we have generated bound rovibrational states and the infrared spectrum of the Ne–C$_2$H$_2$ complex
FIG. 6. Near-infrared spectrum of the Ne-C$_2$HD complex accompanying the $\nu_3$ mode of acetylene in the region of the $R(0)$ transition in free C$_2$HD, calculated from the \textit{ab initio} potential. The rotational temperature is 1 K. Intensities are in arbitrary units. (a) Same interaction potential applied for the ground and excited state. (b) Exchange and electrostatic (charge-overlap) contributions to the excited interaction potential scaled by 0.98, total excited interaction potential scaled by 0.96.
corresponding to the simultaneous excitation of the $\nu_3$ vibration and hindered rotation of the $\text{C}_2\text{H}_2$ molecule within the dimer. Variational characterization of the rovibrational states revealed ground states of para and ortho $^{20}\text{Ne}-\text{C}_2\text{H}_2$ with dissociation energies of 34.902 cm$^{-1}$ and 35.059 cm$^{-1}$, respectively. The ground state of $^{20}\text{Ne}-\text{C}_2\text{HD}$ is bound by 35.130 cm$^{-1}$. Due to a relatively weak anisotropy of the potential all rovibrational states could be classified using the case (a) coupling of Bratoz and Martin.$^{182}$ Consequently, the acetylene molecule in the complex behaves as a slightly hindered rotor, and the near-infrared spectra of $\text{Ne-}\text{C}_2\text{H}_2$ and $\text{Ne-}\text{C}_2\text{HD}$ can be considered as the spectra of free $\text{C}_2\text{H}_2/\text{C}_2\text{HD}$ slightly perturbed by neon. The predicted positions and intensities of the lines in the near-infrared spectra are in qualitative agreement with the experimental spectra.$^{200}$ Various features of the experimental data suggest, however, that red/blue shifts occur. These shifts originate from the difference between the interaction potentials for the vibrational ground and excited states and affect the individual transition frequencies to a different extent. Their precise knowledge is necessary to make definite assignments. For the $\text{Ne-}\text{C}_2\text{HD}$ spectrum assignments can be made by scaling the excited interaction potential. Further work in this direction is still in progress.

ACKNOWLEDGMENTS

We wish to thank Professor Roger Miller and Dr. Ray Bemish for providing us with the unpublished near-infrared spectrum of the $\text{Ne-}\text{C}_2\text{H}_2$ complex. This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and by KBN funds through the Department of Chemistry, University of Warsaw, within the Grant BW-1343/38/96.
Chapter 6

Ab initio potential energy surface and rotationally inelastic integral cross sections of the Ar–CH₄ complex*

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Abstract

Symmetry-adapted perturbation theory has been applied to compute the intermolecular potential energy surface of the Ar–CH₄ complex. The interaction energy, including high-level intramonomer correlation effects, is found to be dominated by the first-order exchange contribution and the dispersion energy. The *ab initio* potential has four equivalent minima of $\epsilon_m = -144.30$ cm$^{-1}$ at $R_m = 7.00$ bohr, for structures in which the argon atom approaches the face of the CH₄ tetrahedron. The computed potential energy surface has been analytically fitted and used in converged close-coupling calculations to generate state-to-state integral cross sections for rotational excitation of CH₄ in collisions with argon. The computed cross sections are generally in good agreement with the experimental data [W. B. Chapman et al., J. Chem. Phys. 105, 3497 (1996)]. Some discrepancies for the smallest cross sections can be explained by the influence of sequential collision channels, with the use of a master equation approach.

I. INTRODUCTION

Methane is an active constituent of the atmospheres of the earth, outer planets of the solar system,236 and Saturn's satellite Titan.237 The temperature profiles of these atmospheres can be accurately monitored provided that spectroscopic and collisional processes involving the methane molecule are well understood. It is not surprising, then, that van der Waals complexes of CH\(_4\) with hydrogen and rare gas atoms attracted interest of various experimental groups.

Before the advent of modern spectroscopic and scattering techniques the Ar–CH\(_4\) interaction potential was approximately known from measurements of the bulk and transport properties: second virial coefficients,238–245 viscosities,246–248 diffusion coefficients,249–251 and thermal diffusion factors.250–256 Since these data are not very sensitive to the details of the interaction potential, they could be interpreted in terms of simple isotropic potentials.

Numerous experimental studies have been devoted to collisional processes involving argon atoms and methane molecules.257–264 Early experiments were mainly concerned with the studies of the rotational relaxation processes257,265 and integral266 and differential cross sections.258,267 The rotational relaxation experiments257,265 were interpreted using a classical rough-sphere model, while the molecular beam data258,266,267 could be analyzed using simple isotropic potentials, often incompatible with the isotropic potentials derived from the experimental studies of the bulk and transport properties.

In the late seventies Buck and collaborators measured total differential cross sections259 and (state-unresolved) energy loss spectra260 of the Ar–CH\(_4\) complex. The total differential cross sections showed a pronounced rainbow structure, sensitive to the depth of the potential. The scattering data, together with the second virial coefficients238–245 and the mean-square torque data,268,269 have been used to derive an anisotropic potential energy surface for Ar–CH\(_4\). The isotropic term in this potential has been further refined263 by fitting to measured (state-unresolved) integral cross sections.262

Recently, Nesbitt and collaborators264 reported state-to-state integral cross sections for rotational excitation of methane in collisions with the argon atoms. Using spectroscopic techniques270–272 to monitor the populations of the CH\(_4\) rotational states after collision, the authors of Ref. 264 were able to obtain fully resolved state-to-state integral cross sections. The measured data were analyzed by using the empirical potential of Buck et al.260 The agreement between theory and experiment was reasonable, although several cross sections could not be accurately reproduced.

The Ar–CH\(_4\) complex was also object of several high-resolution spectroscopic studies. The groups of McKellar,273 Miller,6 and Nesbitt274 recorded the infrared spectrum of the complex corresponding to the simultaneous excitation
of the \(\nu_3\) vibration and rotation of the CH\(_4\) subunit within the complex. To our knowledge the recorded spectra are not well understood, and could not be analyzed using the potential of Buck et al.\(^{260}\) (see Ref. 275).

Surprisingly, \textit{ab initio} calculations for the Ar–CH\(_4\) complex are scarce. Fowler et al.\(^{276}\) reported the long-range dispersion coefficients for Ar–CH\(_4\) computed from RPA polarizabilities. More recently, Szczesniak et al.\(^{277}\) reported a few cuts through the potential from MP2 calculations with small basis sets. They determined the position and the depth of the minimum, and estimated that the well depth can be underestimated by 25\%, while the position of the minimum can be overestimated by 0.5 bohr. So an \textit{ab initio} calculation of the full potential energy surface for Ar–CH\(_4\) and its application to study various collisional and spectroscopic processes is now in order.

In the present chapter we report symmetry-adapted perturbation theory (SAPT) calculations of the potential energy surface for Ar–CH\(_4\), and dynamical calculations of the state-to-state integral cross sections for rotational excitation of methane in collisions with argon.

**II. OUTLINE OF SAPT CALCULATIONS**

\textbf{A. Method and definitions}

In the present chapter we follow the approach introduced and tested in previous papers\(^{77–80}\) (see also Ref. 4 for a review). The SAPT interaction energy is represented as sum of the first- and second-order polarization and exchange contributions,\(^4\)

\[
E_{\text{int}} = E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{pol}}^{(2)} + E_{\text{exch}}^{(2)} + \cdots ,
\]

where \(E_{\text{pol}}^{(1)}\) is the classical electrostatic energy calculated with full account of charge-overlap (penetration) effects, \(E_{\text{pol}}^{(2)}\) is the sum of the induction and dispersion energies, \(E_{\text{exch}}^{(2)} = E_{\text{exch-ind}}^{(2)} + E_{\text{exch-disp}}^{(2)}\), rigorously damped by charge-overlap effects, and \(E_{\text{exch}}^{(n)}\) \(n = 1, 2\), are the exchange contributions, which can be physically interpreted as an effect of the resonance tunneling of electrons between the interacting systems. The second-order exchange energy can be decomposed into the induction and the dispersion part, \(E_{\text{exch}}^{(2)} = E_{\text{exch-ind}}^{(2)} + E_{\text{exch-disp}}^{(2)}\). The exchange-induction \(E_{\text{exch-ind}}^{(2)}\) and the exchange-dispersion energies \(E_{\text{exch-disp}}^{(2)}\) can be viewed as the result of the coupling of the electron exchange with the induction and dispersion interactions, respectively.

One has to use the many-body version of SAPT that systematically treats the intramonomer correlation effects\(^8,6^1\) for interactions of many-electron systems.
The interaction energy components of Eq. (1) can be now written in the form of a double perturbation series,

\[ E_{\text{pol}}^{(n)} = \sum_{l=0}^{\infty} E_{\text{pol}}^{(n,l)} \quad \text{and} \quad E_{\text{exch}}^{(n)} = \sum_{l=0}^{\infty} E_{\text{exch}}^{(n,l)}, \quad (2) \]

where the superscripts \( n \) and \( l \) denote the orders in the intermolecular interaction and intramonomer correlation, respectively.

In practice the many-body perturbation expansions of Eqs. (2) must be truncated. In the present study the various first- and second-order contributions to \( E_{\text{int}} \) were approximated as follows:

\[ E_{\text{pol}}^{(1)} = E_{\text{pol}}^{(10)} + E_{\text{pol,resp}}^{(12)} + E_{\text{pol,resp}}^{(13)} \]

\[ E_{\text{exch}}^{(1)} = E_{\text{exch}}^{(10)} + E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)} + \Delta_{\text{exch}}^{(1)} (\text{CCSD}), \]

\[ E_{\text{ind}}^{(2)} = E_{\text{ind,resp}}^{(20)} + \epsilon_{\text{ind}}, \]

\[ E_{\text{exch-ind}}^{(2)} = E_{\text{exch-ind,resp}}^{(20)} + \epsilon_{\text{exch-ind}}, \]

\[ E_{\text{disp}}^{(2)} = E_{\text{disp}}^{(20)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)}, \]

\[ E_{\text{exch-disp}}^{(2)} = E_{\text{exch-disp}}^{(20)}, \]

The electrostatic terms \( E_{\text{pol}}^{(10)} \) and \( E_{\text{pol,resp}}^{(11)} \) are defined as in Ref. 64. The first-order exchange components \( E_{\text{exch}}^{(11)} \) are defined as in Refs. 65 and 66. The quantity \( \Delta_{\text{exch}}^{(1)} \) (CCSD), obtained from coupled cluster singles and doubles calculations, gives first-order exchange contributions which are higher than second-order in the monomer correlation. The dispersion components \( E_{\text{disp}}^{(20)} \) are derived in Ref. 63. The uncorrelated induction and exchange-induction energies, \( E_{\text{ind,resp}}^{(20)} \) and \( E_{\text{exch-ind,resp}}^{(20)} \), are defined as in Refs. 86 and 87, respectively. The induction-correlation term \( \epsilon_{\text{ind}}^{(22)} \) represents the true correlation contribution to the nonrelaxed \( E_{\text{ind}}^{(22)} \) term, as defined in Ref. 67. Finally, \( E_{\text{exch-disp}}^{(20)} \) is the so-called Hartree–Fock exchange-dispersion energy.

The uncorrelated induction energy \( E_{\text{ind,resp}}^{(20)} \) is significantly quenched by its exchange counterpart \( E_{\text{exch-ind,resp}}^{(20)} \) and the same must be true in the case of \( \epsilon_{\text{ind}}^{(22)} \). Since the contribution which accounts for such quenching has not been coded yet, we have estimated it by scaling the uncorrelated quantity with the factor \( \epsilon_{\text{ind}}^{(22)} / E_{\text{ind,resp}}^{(20)} \).
induction and exchange effects is necessary to obtain accurate potential energy surfaces. In the present chapter we follow Refs. 77–80, and include these higher-order contributions from the equation\textsuperscript{84,85}

\[ \delta E_{\text{int}}^{\text{HF}} = E_{\text{int}}^{\text{HF}} - \left( E_{\text{pol}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} \right), \tag{10} \]

where \( E_{\text{int}}^{\text{HF}} \) is the supermolecule Hartree-Fock interaction energy.

\textbf{B. Computational details}

In the literature several systems of axes have been reported to describe the Ar–CH\textsubscript{4} complex.\textsuperscript{275,278,279} We adopted a frame fixed to CH\textsubscript{4} with the CH bonds in the directions defined by the carbon atom located at the origin and the points \((\sqrt{2},0,1), (-\sqrt{2},0,1), (0,\sqrt{2},-1)\), and \((0,-\sqrt{2},-1)\), see Fig. 1. The position of the argon atom in the complex can then be described by spherical coordinates \((R, \Theta, \Phi)\). This system of axes, as noted by Hutson and Thornley,\textsuperscript{275} is most convenient for dynamical calculations on atom–spherical top complexes since the \(xz\) plane is a plane of symmetry. The \(z\) axis of the molecule fixed system is a twofold axis; the \([\sqrt{2},0,1]\) axis is a threefold axis. The methane molecule was kept rigid with the CH bond lengths fixed at the experimental equilibrium.
value,\(^{280}\) \(r(CH) = 2.052\) bohr. Calculations were performed for five intermolecular distances \(R\) ranging from \(R = 5\) to 10 bohr and for six sets of angles. The angular coordinates of the computed grid were obtained by constructing a set of 144 approximately equidistant points on a sphere with \(T_4\) symmetry imposed. The sphere was divided into 24 segments with each segment corresponding to an irreducible section. Six points were attached to each segment in such a manner that with each point also its inversion image is present. The optimal distribution of the points was determined by assuming a hypothetical repulsive exponential pair potential between the points and minimizing the energy without breaking the tetrahedral symmetry. The resulting angle pairs for one irreducible segment are \((\Theta_1, \Phi_1) = (81.9^\circ, 25.4^\circ), (82.6^\circ, 8.6^\circ), (67.9^\circ, 8.4^\circ)\), together with the corresponding inverted points with angles \((180^\circ - \Theta_1, 180^\circ + \Phi_1)\). Each point \((\Theta_1, \Phi_1)\) has four neighbors, and the nearest neighbor distance is about 15°. We have checked that the resulting set of angles was not very sensitive to the form and the parameters of the assumed hypothetical short-range potential. In addition, seven points have been computed in the region of van der Waals minimum. In total, we calculated 37 points on the potential surface.

All calculations were performed with the SAPT system of codes.\(^{95}\) We employed the \([7s4p3d2f1g]\) basis set from Ref. 77 for the argon atom and the \([6s4p3d1f/4s2p1d]\) basis from Maroulis\(^{281}\) for the methane molecule. The Boys–Bernardi counterpoise correction\(^{98}\) was used to eliminate the basis set superposition error from the supermolecular Hartree-Fock calculations. Long-range coefficients corresponding to the multipole expansions of the induction and dispersion energies were used in the analytical fits of these terms. The induction and dispersion coefficients were computed by the POLCOR package,\(^{73,74}\) with the same basis sets and at the same level of theory as the SAPT calculations.

Since a preliminary application of the potential to the calculation of second virial coefficients showed that its well was slightly too shallow (see Chapter 8) we adopted the “asymptotic scaling” technique to improve the \(ab\ initio\) potential. This technique was introduced in the paper on the SAPT potential of He–HF.\(^{78}\) It takes into account that the dispersion and induction contributions to the interaction energy are the terms that suffer most from basis set incompleteness. Therefore, the long-range dispersion and induction coefficients entering the analytical expressions for the dispersion energy \(E^{(2)}_{\text{disp}}\) and the induction energy \(E^{(2)}_{\text{ind}}\) (see the next section) are replaced by the corresponding coefficients computed in a basis of higher quality. Note that this replacement is performed after the fitting procedure. For this purpose the (frequency dependent) polarizabilities of the argon atom were computed in the \([11s9p5d4f3g]\) basis from Ref. 282 and the multipole moments and polarizabilities of the methane molecule were calculated using the \([9s7p5d2f]\) and \([5s4p2d]\)
basis sets from Ref. 180 for the carbon and hydrogen atoms, respectively. In comparison with the long-range coefficients, the short-range penetration contributions to the dispersion and induction energies are less sensitive to the quality of the basis. Therefore, these terms are determined by fitting the \textit{ab initio} values of $E_{\text{disp}}^{(2)}$ and $E_{\text{ind}}^{(2)}$ to analytical expressions using the long-range coefficients computed in the original, smaller basis, cf. Sec. III. The asymptotic scaling method is discussed in more detail in Ref. 78.

III. ANALYTICAL POTENTIAL FITS

A. Multipole expansion of the induction and dispersion energies for atom–spherical top complexes

At large intermonomer distances $R$ the interaction potential $V$ can be represented by an asymptotic expansion of the form\textsuperscript{4}

$$V(R, \Theta, \Phi) \approx \sum_{n=0}^{\infty} C_n(\Theta, \Phi) R^{-n},$$

(11)

where the coefficients $C_n$ are uniquely defined by $V$. Using the multipole expansion of the intermolecular interaction operator\textsuperscript{5,72} we will show that for atom–spherical top complexes the $C_n$ coefficients appearing in Eq. (11) can be represented as finite expansions in the tetrahedral invariant functions $T^l$,

$$C_n(\Theta, \Phi) = \sum_l C_n^l T^l(\Theta, \Phi),$$

(12)

where the constants $C_n^l$ are the long-range coefficients. The authors of Ref. 275 derived a few of the lowest functions invariant under the group $T_d$, which they used in the angular expansion of the potential for Ar–CH$_4$. In the Appendix we briefly sketch the derivation of such functions and in Table 1 explicit expressions are given for the invariant angular functions with $l \leq 10$. Equations (11) and (12) hold separately for the induction and dispersion energies. The corresponding long-range coefficients will be denoted by $C_{n,\text{ind}}^l$ and $C_{n,\text{disp}}^l$, respectively. For atom–spherical top complexes only the induction and dispersion energies do not vanish in the multipole approximation; the long-range induction and dispersion coefficients can be used in the analytical fit of the potential to fix the correct large-$R$ asymptotics.

The expansion coefficients $C_{n,\text{ind}}^l$ and $C_{n,\text{disp}}^l$ can be deduced from general, open-ended formulas (cf. Refs. 5 and 72 and Chapter 1). In the heart of these formulas we find the angular dependence, which is described by an inner product of two irreducible $SO(3)$ (full rotation group) tensors. For the induction energy we have
TABLE 1. Functions $T^l$ carrying the $A_1$ representation of the group $T_d$. The functions $S_{lm}$ are defined as \((C_{lm} + C_{-m})/(1 + \delta_{m0})\), where $C_{lm}$ is a Racah normalized spherical harmonic function with the Condon & Shortley phase convention. The functions are normalized such that the lowest $m$ component has unit coefficient.

<table>
<thead>
<tr>
<th>$T^0(\Theta, \Phi)$</th>
<th>$S_{00}(\Theta, \Phi) = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^3(\Theta, \Phi)$</td>
<td>$S_{33}(\Theta, \Phi)$</td>
</tr>
<tr>
<td>$T^4(\Theta, \Phi)$</td>
<td>$S_{43}(\Theta, \Phi) - \sqrt{\frac{7}{5}} S_{40}(\Theta, \Phi)$</td>
</tr>
<tr>
<td>$T^6(\Theta, \Phi)$</td>
<td>$S_{63}(\Theta, \Phi) + \sqrt{\frac{11}{7}} S_{60}(\Theta, \Phi)$</td>
</tr>
<tr>
<td>$T^8(\Theta, \Phi)$</td>
<td>$S_{83}(\Theta, \Phi) - \sqrt{\frac{91}{44}} S_{81}(\Theta, \Phi) + \sqrt{\frac{445}{1188}} S_{80}(\Theta, \Phi)$</td>
</tr>
<tr>
<td>$T^{10}(\Theta, \Phi)$</td>
<td>$S_{103}(\Theta, \Phi) + \sqrt{\frac{263}{625}} S_{101}(\Theta, \Phi) - \sqrt{\frac{1177}{1300}} S_{100}(\Theta, \Phi)$</td>
</tr>
</tbody>
</table>

\[
W_{\text{ind}}^l = \sum_{m=-l}^{l} (-1)^m \left[ Q^{l\alpha} \otimes Q^{l\alpha} \right]_{-m}^l g C_{m}^{l}(\Theta, \Phi),
\]

where $C_{lm}^{l}$ is a spherical harmonic in the Racah normalization depending on the polar angles of the argon atom and $Q^{l\alpha} = \{Q_{m\alpha}^{l}\}$ is the expectation value of a multipole moment on CH$_4$. The square bracket expression is a Clebsch–Gordan series. In the dispersion energy expansion we find the same type of inner product, and since the procedure of rewriting this expression in terms of the functions $T^l$ is completely analogous to the induction case, we will concentrate on the latter.

By definition $W_{\text{ind}}^l$ is invariant under any simultaneous rotation of methane and the position vector of argon. Under inversion it obtains the parity factor $(-1)^{l\alpha + l\alpha + l}$. On physical grounds we expect the quantity $W_{\text{ind}}^l$ also to be invariant under the operations of the tetrahedral group $T_d$ acting on one monomer. We have a choice, we can either fix the position of the atom and rotate and reflect methane to indistinguishable orientations, or we can move the atom from one equivalent position to the other by the operations in $T_d$. We choose the second option and write

\[
W_{\text{ind}}^l = \sum_{m=-l}^{l} (-1)^m [Q^{l\alpha} \otimes Q^{l\alpha}]_{-m}^l g C_{m}^{l}(\Theta, \Phi) \quad \text{for all } g \in T_d.
\]

After summation of both sides in Eq. (14) over the group and division by the order of $T_d$ the following $A_1$ function appears:

\[
T_{m}^{l} = \frac{1}{24} \sum_{g \in T_d} g C_{m}^{l}.
\]

By elementary group character theory we can easily establish that the multiplicity of $A_1$ in the irrep $l$ of $SO(3)$ is zero for $l = 1, 2, 5$, unity for all other
cases with \( l < 12 \) and two for \( l = 12 \). The first threefold multiplicity occurs for \( l = 24 \). See Ref. 283 for a complete multiplicity table. However, since we will not go as high as \( l = 12 \) in our expansions we ignore the multiplicity problem, so that we can drop the label \( m \) and define

\[
T^l \equiv \begin{cases} 
\frac{N_l}{24} \sum_g g C_0^l & \text{for } l = 0, 4, 6, 8, 10, \\
\frac{N_l}{24} \sum_g g C_2^l & \text{for } l = 3, 7, 9.
\end{cases}
\]  

(16)

The other \( A_2 \) functions are simply proportional to these,

\[ T^l_m = \gamma_m T^l. \]  

(17)

In Table 1 we see that

\[
T^l = \sum_{\text{even } m \geq 0} \gamma^l_m \left[ C^l_m(\Theta, \Phi) + C^l_{-m}(\Theta, \Phi) \right] / (1 + \delta_{m0}),
\]

(18)

where the \( \gamma^l_m \) are simple coefficients. We choose \( N_l \) such that \( \gamma^l_m = 1 \) for the lowest \( m \) value with nonvanishing coefficient. Returning to Eq. (14) and using Eqs. (15) and (17) we find that

\[
W_{\text{ind}}^l = \left\{ \sum_{m=-l}^{l} (-1)^m \left[ Q^l \otimes Q^{l*} \right]_{-m} \gamma^l_m \right\} T^l \equiv \beta^l T^l.
\]

(19)

The expression \( \beta^l \) between curly brackets is independent of \( m \). For \( l = 0, 4, 6, 8, \) and 10 we equate the coefficient of \( C_0^l \) in \( W_{\text{ind}}^l \) and \( \beta^l T^l \) and find

\[ \beta^l = \left[ Q^l \otimes Q^{l*} \right]_{0}^l, \]

(20)

since, due to our normalization condition, \( \tau^l_0 \) is unity. Likewise we find by equating the coefficients of \( C_2^l \) in the case of \( l = 3, 7, 9 \) that

\[ \beta^l = \left[ Q^l \otimes Q^{l*} \right]_{2}^l. \]

(21)

Using this expression for \( W_{\text{ind}}^l \), we finally find from the general expression of Refs. 5 and 72 and Chapter 1 the coefficients with \( l \leq 10 \) in the expansion of Eq. (12),

\[
C_{n,\text{ind}}^l = \frac{(-1)^{l+1}}{2} \sum_{l_A, l'_A} \sum_{l_B, l'_B} \frac{1}{(2l_B)!} \left[ \frac{(2l_A + 2l_B + 1)(2l'_A + 2l_B + 1)}{(2l_B + 1)(2l_A)(2l'_A)!} \right]^{1/2} \times (l_A + l_B, 0; l'_A + l_B, 0|l, 0) \left\{ \begin{array}{ccc} l_A & l'_A \\ l_B & l_B \\ l & l \end{array} \right\} \times
\]
Chapter 6: Potential and integral cross sections of Ar–CH₄

\[ \times [Q^{l_A} \otimes Q^{l_A'}] \alpha_0^{(l_B l_B')} |l(0), \]  

and for the dispersion energy,

\[ C_{n,\text{disp}}^l = \frac{(-1)^{l^2+1}}{2\pi} \sum_{l_A, l_A'} \sum_{l_B=1} \left( \frac{(2l_A + 2l_B + 1)!(2l_A' + 2l_B + 1)!}{(2l_B + 1)!(2l_A + 1)!} \right)^{1/2} \]
\[ \times (l_A + l_B, 0; l_A' + l_B, 0 | l, 0) \left\{ \begin{array}{ccc} l_A & l_A' & l_B \\ l_A + l_B & l_A + l_B & l_B \end{array} \right\} \]
\[ \times \int_0^\infty \alpha_\kappa^{(l_A l_A')l_l}(i\omega) \alpha_0^{(l_B l_B')l_l}(i\omega) d\omega, \]  

where the summation over \( l_A, l_A', \) and \( l_B \) is restricted to indices with \( l_A + l_A' + 2l_B = n - 2, \kappa = 0 \) for \( l = 0, 4, 6, 8, 10 \) and \( \kappa = 2 \) for \( l = 3, 7, 9. \) The quantity \( \alpha_\kappa^{(l_l')l_l}(i\omega) \) denotes the irreducible component of the frequency-dependent polarizability tensor, the quantity in pointed brackets is a Clebsch-Gordan coefficient and the quantity in curly braces is a 6j symbol.  

B. Outline of the fitting procedure

The different contributions to the interaction energy, as computed by SAPT, exhibit different radial dependence, and each component of the interaction energy can be fitted separately. We performed separate fits of the sum of short-range contributions \( E_{\text{short}} \), of the induction energy \( E^{(2)}_{\text{ind}} \), and of the dispersion energy \( E^{(2)}_{\text{disp}} \).

The fitting procedure adopted in the present work was similar to that of previous papers. For a given set of angles \((\Theta, \Phi)\) we performed one-dimensional radial fits of the short-range, induction, and dispersion energies. The parameters obtained from these 1D fits as functions of \( \Theta \) and \( \Phi \) were represented by expansions in tetrahedral harmonics. Since the final analytical representation of the potential obtained in this way showed unphysical oscillations, the parameters from the expansions in \( T^l(\Theta, \Phi) \) were used as starting points for a global three-dimensional fit.

The short-range contribution was fitted to the expression

\[ E_{\text{short}}(R, \Theta, \Phi) = \left[ A_{\text{short}}(\Theta, \Phi) + B_{\text{short}}(\Theta, \Phi) R \right] \times \exp \left[ -\alpha_{\text{short}}(\Theta, \Phi) R \right], \]  

where the parameters \( A_{\text{short}}(\Theta, \Phi) \), \( B_{\text{short}}(\Theta, \Phi) \), and \( \alpha_{\text{short}}(\Theta, \Phi) \) were represented by angular expansions in tetrahedral harmonics,
Outline of the fitting procedure

\[ A^{\text{short}}(\Theta, \Phi) = \sum_{l=0,3,4,6,7} A^l_{\text{short}} T^l(\Theta, \Phi), \]  

(26)

and analogous expressions for \( B^{\text{short}}(\Theta, \Phi) \) and \( a^{\text{short}}(\Theta, \Phi) \).

The induction component \( E_{\text{ind}}^{(2)}(R, \Theta, \Phi) \) was represented by the sum of the damped multipole expansion and an exponential function (the latter representing the short-range charge-overlap contribution to the induction energy),

\[ E_{\text{ind}}^{(2)}(R, \Theta, \Phi) = -\exp \left[ \alpha_{\text{ind}}(\Theta, \Phi) - \beta_{\text{ind}}(\Theta, \Phi) R \right] - f_{10} \left( R; \tilde{\beta}_{\text{ind}} \right) C_{10,\text{ind}}(\Theta, \Phi) R^{-10}. \]  

(27)

The induction constant for a given set of angles \((\Theta, \Phi)\) is defined by Eqs. (12) and (22). The coefficients \( C^l_{10,\text{ind}} \) were computed \textit{ab initio} in the same basis set and at the level of theory corresponding to the fitted function \( E_{\text{ind}}^{(2)} \). For the asymptotically scaled potential, the coefficients \( C^l_{10,\text{ind}} \) were replaced after the fitting by new ones computed in the larger basis set described in Sec. II B. We assumed the damping function \( f_n(R; b) \) in the Tang–Toennies form,

\[ f_n(R; b) = 1 - \exp \left( -b R \right) \sum_{k=0}^n \frac{(b R)^k}{k!}. \]  

(28)

As for the \( E_{\text{short}} \) component, the fitted parameters \( \alpha_{\text{ind}}(\Theta, \Phi) \) and \( \beta_{\text{ind}}(\Theta, \Phi) \) were represented by a series in tetrahedral harmonics, in this case with \( l \) running from 0 up to 6 inclusive. The damping parameter \( \tilde{\beta}_{\text{ind}} \) was not expanded. Note that in Eq. (27) we use atomic units for the energy, as well as for the distance.

The dispersion energy is represented by an analytical expression of the form,

\[ E_{\text{disp}}^{(2)}(R, \Theta, \Phi) = A^{\text{disp}}(\Theta, \Phi) \exp \left[ -\beta^{\text{disp}}(\Theta, \Phi) R \right] - \sum_{n=6}^{10} f_n \left( R; \tilde{\beta}^{\text{disp}}(\Theta, \Phi) \right) C_{n,\text{disp}}(\Theta, \Phi) R^{-n}. \]  

(29)

The fitted parameters \( A^{\text{disp}}(\Theta, \Phi) \), \( \beta^{\text{disp}}(\Theta, \Phi) \), and \( \tilde{\beta}^{\text{disp}}(\Theta, \Phi) \) were expanded in tetrahedral harmonics with \( l \leq 7 \) as in Eq. (26). The long-range dispersion coefficients \( C^l_{n,\text{disp}} \) were computed \textit{ab initio} from Eqs. (12) and (23) in the same basis set and at the level of theory corresponding to the fitted function \( E_{\text{disp}}^{(2)} \). For the asymptotically scaled potential, the coefficients \( C^l_{n,\text{disp}} \) were replaced after the fitting by new ones computed in the larger basis set described in Sec. II B. The damping function was also assumed in the Tang–Toennies form as for the induction term.

The final fitted potential (before asymptotic scaling) is compared with the \textit{ab initio} results on which the fit was based, as well as with the additional \textit{ab initio}
points off the grid. This shows that the typical fitting error is smaller than 1%.
The only exception, for obvious reasons, is the region around the point where
the potential goes through zero. We have not tabulated all the fit parameters;
a **fortran** program that generates the analytical Ar–CH$_4$ potential can be
requested by electronic mail from avda@theochem.kun.nl.

**IV. FEATURES OF THE POTENTIAL ENERGY SURFACE**

In the remainder of the current chapter, we denote by “the potential” the
asymptotically scaled *ab initio* potential, unless explicitly stated otherwise.
Our *ab initio* potential shows four equivalent minima at the facial configura-
tions, where the argon atom is above the midpoint of any of the four triangular
faces of the CH$_4$ molecule. The first minimum corresponds to the geometry
($\Theta_m, \Phi_m$) = (125.26°, 0°) with the equilibrium distance $R_m$ = 7.00 bohr,
and the well depth $\epsilon_m$ = $-144.30$ cm$^{-1}$. The other, equivalent, minima are found
by rotating over 180° around the $C_2$ axes. Figure 2 depicts the intersection
of the three-dimensional potential surface with the $xz$ plane ($\Phi = 0°$). An
inspection of Fig. 2 shows that the minimum of the potential is well defined.
Note that the local minimum at $\Theta = 0°$ corresponds to a saddle point on the
three-dimensional surface. Our potential has six equivalent saddle points at $R_s$
= 7.37 bohr with a depth of $\epsilon_s$ = $-116.17$ cm$^{-1}$ for the edge configurations, i.e.,
for the geometry with ($\Theta_s, \Phi_s$) = (0°, 0°) and for the geometries following from
rotations over 120° around the $C_3$ axes. Before asymptotic scaling was applied,
the potential had a global minimum of $\epsilon_m$ = $-135.20$ cm$^{-1}$ at $R_m$ = 7.04 bohr
for the facial configuration and saddle points with a depth of $\epsilon_s$ = $-110.76$ cm$^{-1}$
at $R_s$ = 7.39 bohr for the edge configurations. Subsequent asymptotic scaling
thus lowered the minimum and the saddle points of the potential by 9.10 and
5.41 cm$^{-1}$, respectively, while the corresponding optimum bond lengths were
shortened by 0.04 and 0.02 bohr, respectively.

The SAPT potential can be compared with the *ab initio* results of Szczesniak
et al.$^{277}$ The authors of Ref. 277 computed three cuts through the potential
energy surface of Ar–CH$_4$ using the supermolecule Møller-Plesset perturba-
tion theory truncated at the second order (MP2) and small basis sets. Their
calculation correctly predicts an equilibrium structure for the facial configu-
ration of the complex, but the parameters of the well, $R_m$ = 7.5 bohr and
$\epsilon_m$ = $-113$ cm$^{-1}$, are rather different from the present results. Szczesniak et al.$^{277}$
estimated that their well depth may be underestimated by as much as
25%, while the equilibrium distance may be overestimated by 0.5 bohr. It is
interesting to note that our values for $R_m$ and $\epsilon_m$ support these estimates of
errors of MP2 calculations with small bases. As a matter of fact, our well depth
represents 128% of the MP2 value, while our equilibrium distance is smaller than the MP2 result by exactly 0.50 bohr.

In Table 2 we report the different contributions to the interaction energy (obtained directly from the SAPT calculations, not via the fitted potential) for the facial, edge, and vertex configurations at \( R = 7.025, 7.4, \) and \( 7.896 \) bohr, respectively, which are nearly optimal intermolecular distances. The vertex configurations, with \((\Theta, \Phi)\) equal or equivalent to \((54.74^\circ, 0^\circ)\), represent maxima on the cuts through the potential surface at fixed \( R \). They correspond to geometries with a linear C–H···Ar configuration. An inspection of Table 2 shows that the interaction energy for Ar–CH\(_4\) is dominated by the first-order exchange and dispersion energies, together with, to a lesser extent, the electrostatic contributions. Although the induction contribution is non-negligible for all configurations, it is almost entirely quenched by its exchange counterpart. By contrast, the exchange quenching of the dispersion energy is rather small. For all configurations the exchange-dispersion energy represents only 6–7% of the large dispersion term.

A more detailed presentation of the angular dependence of the short-range, induction, and dispersion contributions to the potential is given in Fig. 3. From Fig. 3 and Table 2 it is seen that the anisotropy of the potential is dominated by the short range contributions, in particular the first-order exchange energy, and

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**FIG. 2.** Cut through the *ab initio* Ar–CH\(_4\) potential energy surface at \( \Phi = 0^\circ \) (in cm\(^{-1}\)).
Chapter 6: Potential and integral cross sections of Ar–CH₄

### TABLE 2.

Components of the interaction energy for the facial, edge, and vertex configurations. Energies are in cm⁻¹, the intermolecular distances are $R = 7.025$, 7.4, and 7.896 bohr for the facial, edge, and vertex configurations, respectively. The numbers in parentheses denote the values obtained from the asymptotically scaled potential.

<table>
<thead>
<tr>
<th>Components</th>
<th>Facial</th>
<th>Edge</th>
<th>Vertex</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{pol}}^{(1)}$</td>
<td>−56.91</td>
<td>−45.18</td>
<td>−48.83</td>
</tr>
<tr>
<td>$E_{\text{exch}}^{(1)}$</td>
<td>190.83</td>
<td>158.60</td>
<td>169.40</td>
</tr>
<tr>
<td>$E_{\text{ind,resp}}^{(2)}$</td>
<td>−51.64 (−50.90)</td>
<td>−43.92 (−45.64)</td>
<td>−54.07 (−52.63)</td>
</tr>
<tr>
<td>$E_{\text{exch–ind,resp}}^{(2)}$</td>
<td>50.21</td>
<td>42.82</td>
<td>50.15</td>
</tr>
<tr>
<td>$E_{\text{disp}}^{(2)}$</td>
<td>−277.54 (−287.92)</td>
<td>−231.00 (−235.83)</td>
<td>−206.75 (−210.84)</td>
</tr>
<tr>
<td>$E_{\text{exch–disp}}^{(2)}$</td>
<td>16.81</td>
<td>13.79</td>
<td>13.45</td>
</tr>
<tr>
<td>$\delta E_{\text{HF}}^{\text{int}}$</td>
<td>−6.90</td>
<td>−5.46</td>
<td>−8.39</td>
</tr>
<tr>
<td>$E_{\text{int}}$</td>
<td>−135.15 (−144.25)</td>
<td>−110.33 (−116.07)</td>
<td>−85.00 (−84.48)</td>
</tr>
</tbody>
</table>

**FIG. 3.** Dependence of the different contributions to the Ar–CH₄ interaction energy on the angle $\Theta$ at $R = 7.5$ bohr, $\Phi = 0°$. Depicted are the sum of short-range contributions, $E_{\text{short}}$, the induction energy $E_{\text{ind}}^{(2)}$, and the dispersion energy $E_{\text{disp}}^{(2)}$. The dashed line shows the total interaction energy. Energies are in cm⁻¹.
FIG. 4. Expansion coefficients $V_l(R)$, cf. Eq. (30), of the *ab initio* Ar–CH$_4$ interaction potential. Racah normalization has been applied, see text for details.

the dispersion term. The anisotropy of the induction energy only becomes important in the region near the vertex configuration where its effect is a lowering of the interaction energy.

To investigate the importance of the anisotropic contributions to the potential in various regions of the configuration space it is useful to expand it as a series in tetrahedral harmonics,

$$V(R, \Theta, \Phi) \approx \sum_{l=0}^{l_{\text{max}}} V_l(R) T^l(\Theta, \Phi),$$

(30)

where $V$ is the sum of contributions in Eqs. (25), (27), and (29). The expansion coefficients $V_l(R)$ can be easily evaluated numerically by the use of Gauss–Legendre and Gauss–Chebyshev quadratures. The advantage of expansion (30) is that it shows explicitly the anisotropy of the potential, the term with $l = 0$ being the isotropic potential. In order to establish the importance of various anisotropic terms at various $R$, we report in Fig. 4 the radial dependence of the expansion coefficients for $l \leq 7$. Since it is common to expand potentials in angular functions normalized to $4\pi/(2l + 1)$, i.e., Racah normalization, we have multiplied the coefficients $V_l(R)$ in Fig. 4 by the inverse of the normalization factor, $\left[ (T^l|T^l)(2l + 1)/4\pi \right]^{1/2}$. Around the minimum $R = 7.00$ bohr the interaction potential is dominated by the isotropic term and
Chapter 6: Potential and integral cross sections of Ar–CH₄

the leading anisotropic components $V_3(R)$ and $V_4(R)$. By contrast, in the repulsive region higher anisotropic terms are very important and the convergence of expansion (30) for fixed $R$ and $(\Theta, \Phi)$ varying is not particularly fast.

V. OUTLINE OF DYNAMICAL CALCULATIONS

In the space-fixed coordinate system the Hamiltonian for an atom–spherical top system can be written as

$$H = -\frac{\hbar^2}{2\mu R} \left( \frac{\partial^2}{\partial R^2} \right) R + \frac{\hat{J}^2}{2\mu R^2} + V(R, \Theta, \Phi) + H_{\text{mon}},$$

where $\mu$ is the reduced mass of the complex, $\hat{J}^2$ denotes the square of the end-over-end angular momentum operator, and $H_{\text{mon}}$ is the Hamiltonian for the spherical top monomer. The total wave function of the collisional complex can be expanded in terms of angular basis functions that are eigenfunctions of the end-over-end angular momentum $\hat{J}^2$, the total angular momentum $\hat{J}$, and of the monomer Hamiltonian $H_{\text{mon}}$.

$$\Psi^{JM}_{j_{E}} = R^{-1} \sum_{j_{L}, \tau} \chi^{j}_{j_{L}}(R) \left[ Y^{j}(\alpha_R, \beta_R) \otimes \Phi^{j_{E}}(\alpha_{R}, \beta_{R}, \gamma_{R}) \right]_{M}^{j},$$

where $\Phi^{j_{E}}_{m_{E}}$ is the rotational wave function of the monomer with angular momentum $j$, depending on the Euler angles $(\alpha_{R}, \beta_{R}, \gamma_{R})$ of the monomer in the space-fixed coordinate system; $(\alpha_R, \beta_R)$ denote the spherical polar angles of the intermolecular vector $R$ in the space-fixed frame. The index $\tau$ contains additional information about the symmetry of the monomer state ($A, E, F$ symmetry).

The rovibrational levels of CH₄ can be classified under the molecular symmetry group $T_d(M)$. If the centrifugal distortion terms are neglected, the rotational levels of CH₄ are given by $bj(j + 1)$, where $b$ is the rotational constant. The inclusion of the tetrahedral distortion introduces additional splittings, and the energy levels are classified according to the irreducible representations of $T_d(M)$. The multiplicities of the $A_1, A_2, E, F_1,$ and $F_2$ representations of $T_d(M)$ occurring for a given $j$ have been given by Hougen. Note that the same symmetry may occur more than once for a given $j$; in accordance with Ref. 283 we label such quasi-degenerate states with the superscripts (1), (2), etc.

If the tetrahedral centrifugal distortion terms are included, the monomer’s wave functions $\Phi^{j_{E}}_{m_{E}}$ are linear combinations of the normalized rotation matrices $D^{j}_{m_{E}}$. The expansion coefficients can be obtained by diagonalizing the monomer Hamiltonian $H_{\text{mon}}$ for a given $j$, and taking linear combinations.
of the degenerate eigenvectors to ensure specific symmetries with respect to the coordinate system. The matrix elements of $H_{\text{mon}}$ in the basis of symmetric top functions are given by:

$$\langle jk | H_{\text{mon}} | jk \rangle = bj(j + 1) - dj(j + 1)^2 + \frac{1}{2} dt \left[ -3j(j-1)(j+1)(j+2) + 5k^2(6j^2 + 6j - 5) - 35k^4 \right],$$

$$\langle jk | H_{\text{mon}} | jk \pm 4 \rangle = \frac{5}{4} dt \left\{ [j(j + 1) - k(k \pm 1)] \left[ j(j + 1) - (k \pm 1)(k \pm 2) \right] \right\}^{1/2},$$

where $b$, $d_j$, and $d_t$ denote the rotational constant, centrifugal distortion constant, and the tetrahedral centrifugal distortion term, respectively. In the current chapter we have adopted the following values for these constants: $b = 5.241 \text{ cm}^{-1}$, $d_j = 1.108 \times 10^{-4} \text{ cm}^{-1}$, and $d_t = 4.425 \times 10^{-6} \text{ cm}^{-1}$.288

The radial functions $\chi_{j\tau}(R)$ are solutions of the system of close-coupling equations. In our calculations these equations were solved using the log-derivative propagator289 as modified by Alexander and Manolopoulos. The log-derivative algorithm of Mrugala and Secrest289 was used to propagate from $R_{\text{min}} = 5 \text{ bohr}$ to $R_{\text{end}} = 15.0 \text{ bohr}$ with a constant step (10 steps per half wavelength for the open channel of highest kinetic energy in the asymptotic region). The Airy propagator was used to propagate from $R_{\text{end}}$ to $R_{\text{max}} = 100 \text{ bohr}$. The angular basis included all channels with $j$ values up to and including $j_{\text{max}} = 10$ for all symmetries. Partial wave components with increasing $J$ were included in the calculations until the inelastic state-to-state cross sections were converged within 0.001 A². The highest value of $J$ was $J_{\text{max}} = 87, 99, \text{ and } 78$ for the $A, F, \text{ and } E$ symmetries, respectively. For the dynamical calculations the potential was expanded in real harmonics with $l \leq 18$ by means of 25-point Gauss–Legendre and Gauss–Chebyshev quadratures. The integration parameters ($R_{\text{min}}, R_{\text{end}}, \text{ and } R_{\text{max}}$), the number of channels included in the calculation, and the potential expansion were chosen to yield the state-to-state cross sections converged to 1% at worst. The reduced mass of Ar–CH$_4$ was 11.441 478 amu.145 All calculations were performed with the MOLSCAT system of codes.291

VI. ROTATIONALLY INELASTIC CROSS SECTIONS FOR AR–CH$_4$: CONFRONTATION WITH EXPERIMENT

In Table 3 we compare the computed state-to-state integral cross sections for Ar–CH$_4$ with the experimental data.264 Initially, the CH$_4$ molecules are in the lowest permissible rotational state for each of the symmetry types: $j'' = 0, 1, \text{ and } 2$ for $A, F, \text{ and } E$ symmetries, respectively. An inspection of Table 3
Chapter 6: Potential and integral cross sections of Ar–CH₄

TABLE 3. Comparison of the computed and measured state-to-state scattering cross sections (in Å²) and populations (in %) for Ar–CH₄. Initial rotational states are \( j'' = 0, 1, \) and 2 for \( A, F, \) and \( E \) symmetries, respectively.

<table>
<thead>
<tr>
<th>( j' )</th>
<th>( A ) states</th>
<th>( \sigma_{j'' \rightarrow j'} )</th>
<th>( F_{j'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Computedᵃ</td>
<td>Observedᵇ</td>
<td>Ref. 264ᶜ</td>
</tr>
<tr>
<td>3, ( A₂ )</td>
<td>26.685</td>
<td>26.685</td>
<td>29(7)</td>
</tr>
<tr>
<td>4, ( A₁ )</td>
<td>20.661</td>
<td>20.661</td>
<td>20(5)</td>
</tr>
<tr>
<td>6, ( A₂ )</td>
<td>0.428</td>
<td>0.428</td>
<td>1.4(2)</td>
</tr>
<tr>
<td>6, ( A₁ )</td>
<td>0.737</td>
<td>0.737</td>
<td>2.0(3)</td>
</tr>
<tr>
<td>7, ( A₂ )</td>
<td>0.364</td>
<td>0.364</td>
<td>0.3(2)</td>
</tr>
<tr>
<td>Total</td>
<td>48.875</td>
<td>48.875</td>
<td>52(9)</td>
</tr>
<tr>
<td>2, ( F₂ )</td>
<td>12.209</td>
<td>12.209</td>
<td>18(4)</td>
</tr>
<tr>
<td>3, ( F₁ )</td>
<td>12.566</td>
<td>12.566</td>
<td>13(3)</td>
</tr>
<tr>
<td>3, ( F₁ )</td>
<td>9.997</td>
<td>9.997</td>
<td>11(3)</td>
</tr>
<tr>
<td>4, ( F₁ )</td>
<td>6.696</td>
<td>6.696</td>
<td>6(1)</td>
</tr>
<tr>
<td>4, ( F₂ )</td>
<td>4.369</td>
<td>4.369</td>
<td>4.9(9)</td>
</tr>
<tr>
<td>5, ( F₁ )</td>
<td>2.562</td>
<td>2.562</td>
<td>1.7(3)</td>
</tr>
<tr>
<td>5, ( F₂ )</td>
<td>0.928</td>
<td>0.928</td>
<td>1.8(3)</td>
</tr>
<tr>
<td>5, ( F₁ )</td>
<td>1.011</td>
<td>1.011</td>
<td>2.3(4)</td>
</tr>
<tr>
<td>6, ( F₁ )</td>
<td>1.057</td>
<td>1.057</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>6, ( F₂ )</td>
<td>0.729</td>
<td>0.729</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>7, ( F₁ )</td>
<td>0.247</td>
<td>0.247</td>
<td>0.3(1)</td>
</tr>
<tr>
<td>7, ( F₁ )</td>
<td>0.214</td>
<td>0.214</td>
<td>—</td>
</tr>
<tr>
<td>7, ( F₁ )</td>
<td>0.187</td>
<td>0.187</td>
<td>—</td>
</tr>
<tr>
<td>7, ( F₁ )</td>
<td>0.074</td>
<td>0.074</td>
<td>0.05(9)</td>
</tr>
<tr>
<td>7, ( F₂ )</td>
<td>0.180</td>
<td>0.180</td>
<td>0.0(2)</td>
</tr>
<tr>
<td>Total</td>
<td>52.113</td>
<td>52.113</td>
<td>60(11)</td>
</tr>
<tr>
<td>4, ( E )</td>
<td>16.997</td>
<td>16.997</td>
<td>20(4)</td>
</tr>
<tr>
<td>5, ( E )</td>
<td>6.540</td>
<td>6.540</td>
<td>7(1)</td>
</tr>
<tr>
<td>6, ( E )</td>
<td>4.449</td>
<td>4.449</td>
<td>6(1)</td>
</tr>
<tr>
<td>7, ( E )</td>
<td>0.454</td>
<td>0.454</td>
<td>1.0(3)</td>
</tr>
<tr>
<td>8, ( E₁ )</td>
<td>0.037</td>
<td>0.037</td>
<td>—</td>
</tr>
<tr>
<td>8, ( E₂ )</td>
<td>0.028</td>
<td>0.028</td>
<td>0.0(1)</td>
</tr>
<tr>
<td>Total</td>
<td>27.716</td>
<td>27.716</td>
<td>33(7)</td>
</tr>
</tbody>
</table>

ᵃFrom close-coupling calculations on the \( ab \) \( initio \) SAPT potential. The reported values represent a weighted average around the mean collision energy \( E_{CM} = 300 \) cm⁻¹.
ᵇExperimental data, Ref. 264.
ᶜComputed from close-coupling calculations on the empirical potential of Buck et al. (Ref. 260). The reported values represent a weighted average around the mean collision energy \( E_{CM} = 300 \) cm⁻¹.
ᵈDefined as the ratio of the state-to-state cross section to the total inelastic cross section, \( \sigma_{j'' \rightarrow j'}/\sigma_{Tot}^{inel}(j'') \).
ᵉComputed from the master equation at 20% depletion of the initial state.
ᶠTotal inelastic cross section for a given initial state \( j'' \), \( \sigma_{Tot}^{inel}(j'') \).
shows that the overall agreement between theory and experiment is rather satisfactory. The \textit{ab initio} SAPT potential reproduces correctly most of the features governing inelastic events in the Ar–CH\textsubscript{4} collisions, although some deficiencies are also evident. First we note that the cross sections larger than 3 \(\text{Å}^2\) are very well reproduced. Except for the 1 \(\rightarrow\) 2 transition in the \(F\) manifold, and the 2 \(\rightarrow\) 6 transition in the \(E\) manifold, the theoretical values are well within the estimated experimental error bars. The reproduction of smaller cross sections which do not involve quasi-degenerate final states is also rather good. The agreement with experiment for the cross sections with quasi-degenerate final states is less satisfactory, but this disagreement may be partly due to sequential collisions (cf. the discussion below). However, even in this case the \textit{ab initio} potential predicts the correct ordering of the cross sections. For instance, the ratio of the theoretical cross sections with \(j' = 6\) in the \(A\) manifold is 0.58, while the corresponding experimental value is 0.7. The ordering of the cross sections with \(j' = 6\) in the \(F\) manifold is also reasonably well reproduced. The only exception are the values of the cross sections for the 1 \(\rightarrow\) 5 transitions. The final states for these transitions correspond to \(F^1_1\), \(F^2_2\), and \(F^1_2\) symmetries, respectively. An inspection of Table 3 shows the ordering of the cross sections predicted by the theory \((F^1_1 > F^2_2 > F^1_2)\) is different from the ordering observed in the experiments \((F^1_1 > F^1_2 > F^2_2)\).

The total inelastic cross sections \(\sigma_{\text{tot}}^{\text{inel}}(j'')\) also agree well with the measured values. The total inelasticities for the \(F\) and \(E\) manifolds are somewhat underpredicted, but they are still within the experimental error bars. The theory predicts the correct ordering of the total inelastic cross sections for different symmetries, \(F > A > E\). Also the theoretical ratio of the total inelastic cross sections for different nuclear spin species, \(F : A : E = 1.9 : 1.8 : 1.0\), compares well with the experimental ratio \(F : A : E = 1.8(3) : 1.6(3) : 1.0(2)\).

It is gratifying to observe that the inelastic cross sections generated from the present \textit{ab initio} potential are in a better agreement with the experimental data\textsuperscript{264} than those computed from the empirical potential of Buck et al.\textsuperscript{260} fitted to reproduce the (state-unresolved) differential molecular beam data. This better agreement holds not only for the absolute values of the cross sections \(\sigma_{j''\rightarrow j'}\), but also for the ordering of the cross sections.

Integral state-to-state cross sections were also calculated from the potential before the asymptotic scaling was applied, i.e., with long-range induction and dispersion coefficients computed in the same basis as used in the SAPT calculations. It was found that the results were quite similar to the computed data listed in Table 3, but that the agreement with experiment is less good than with the asymptotic scaling. The cross sections larger than 3 \(\text{Å}^2\) differ by 0.7 \(\text{Å}^2\) or less from the data computed with the asymptotically scaled potential, for
the other cross sections the differences are typically smaller than 0.1 Å². The largest difference was found for the cross section with \( j' = 2 \) in the \( F \) manifold which was 6 % smaller than the corresponding value in Table 3, namely 11.546 Å². This close agreement supports the idea that rotationally inelastic state-to-state cross sections are less sensitive to the depth of the potential than to its anisotropy, which is much less affected by the asymptotic scaling. However, since the computed data given in Table 3 are systematically in better agreement with experiment than the corresponding results before the asymptotic scaling, we may conclude that the asymptotic scaling of the potential has a small but positive effect on the calculated integral cross sections.

As discussed in Ref. 264 the smallest measured populations of the rotational states after collision may be contaminated by contributions from sequential collisions. This would mean that some of the measured rotational populations are not the measure of the cross sections for a single transition \( j'' \rightarrow j' \), but rather for sequential transitions \( j'' \rightarrow j_1 \rightarrow j' \). This mechanism will be especially important when the cross section \( \sigma_{j_1 \rightarrow j'} \) is large compared to \( \sigma_{j'' \rightarrow j'} \). To get more insight into the possible influence of the sequential collision channels on the smallest populations of the final rotational states of methane one can apply a master equation approach, cf. the appendix of Ref. 264. The final population of molecules in state \( j' \) is due to two types of processes: the gain processes in which molecules in states \( j \) are (de)excited to the state \( j' \), and the loss processes, in which the molecules in state \( j' \) are removed by collision. The time evolution of the populations of rotational states in a nonequilibrium gas can be monitored via the master equation

\[
\frac{dP_f}{dt} = \sum_{i \neq f} \sigma_{i \rightarrow f} P_i - \sum_{i \neq f} \sigma_{f \rightarrow i} P_f, \tag{34}
\]

where \( P_f \) denotes the population of the \( f \)th rotational state of CH\(_4\) of a given symmetry. The initial populations are obviously \( P_f(t = 0) = \delta_{f, j''} \), and the solution of Eq. (34) is propagated until the population of the initial state, \( P_{j''} \), is reduced by 20%. The final populations predicted in this way can be compared with the populations measured at 20% depletion of the initial state.

The results of the master equation analysis are presented in Table 3. Also reported in this table are the experimental populations of the final rotational states of CH\(_4\), and the theoretically predicted populations neglecting the possible influence of the sequential collisions, i.e., computed as the ratios \( \sigma_{j'' \rightarrow j'}/\sigma_{\text{tot}}^{\text{inel}}(j'') \). An inspection of Table 3 shows that most of the final populations computed from the master equation are very close to the populations obtained by neglecting sequential collisions. However, the populations of the nearly degenerate states are very different from those predicted from the simple
ratio $\sigma_{j' \to j'}/\sigma_{\text{tot}}^{\text{inel}}(j')$. For instance, the ratio of the theoretical cross sections with $j' = 6$ in the $A$ manifold is 0.58. If we take into account the sequential collisions, the corresponding ratio is 0.72, in very good agreement with the experimental value of 0.70. Similarly, the populations of the $j' = 6$ states in the $F$ manifold are in the ratio of 4.27 : 2.94 : 1.0. If we correct the theoretical values for the effect of sequential collisions the ratio is 2.55 : 1.79 : 1.0 in rather good agreement with the measured ratio of 2.57 : 1.29 : 1.0.

One may note that despite the use of the master equation analysis some differences between theory and experiment remain. In particular, the correct ordering of the rotational populations for $j' = 5$ in the $F$ manifold is not reproduced, and the absolute values of some predicted final populations are outside the experimental error bars. This suggests that the anisotropy of the ab initio potential in the repulsive region may be slightly incorrect. Further application of this potential in calculating differential scattering cross sections and infrared spectra will give more information about its reliability.

VII. SUMMARY AND CONCLUSIONS

The interaction potential energy surface of the Ar–CH$_4$ molecule has been calculated for a broad range of configurations using symmetry-adapted perturbation theory. Our calculation provides separate values for the fundamental components of the interaction energy. As expected, the Ar–CH$_4$ complex was found to be bound mainly by dispersion forces. However, other contributions to the interaction energy, e.g. the electrostatic energy, were shown to be non-negligible. The ab initio potential has four equivalent minima of $e_m = -144.30$ cm$^{-1}$ at $R_m = 7.00$ bohr, for structures in which the argon atom approaches the face of the CH$_4$ tetrahedron. It appears that the depth of the van der Waals minimum and the anisotropy of the interaction result from a subtle balance of the electrostatic, exchange, and dispersion contributions.

Using the computed potential energy surface we have calculated the state-to-state scattering cross sections for rotational excitation of methane in collisions with argon. The ab initio SAPT potential reproduces correctly most of the observed features governing inelastic Ar–CH$_4$ collisions. The largest cross sections agree very well with the experimental data. Some discrepancies in the smallest cross sections involving quasi-degenerate final states can be partly explained by the sequential collision mechanism using a master equation analysis. The computed total inelastic cross sections for the $A$, $F$, and $E$ symmetries also agree well with the experiment, suggesting that the present ab initio potential may be useful for the computation of other observable quantities.
like second virial coefficients, differential scattering cross sections and infrared spectra. Work in this direction is reported in Chapters 7 and 8.

ACKNOWLEDGMENTS

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APPENDIX A: THE CONSTRUCTION OF TETRAHEDRAL A_1 FUNCTIONS.

Our goal is to find angular functions T_{l m}^I that transform according to the A_1 irrep of the tetrahedral group T_d, cf. Eq. (15). It is most convenient to obtain these functions by induction from the A_1 irrep (irreducible representation) of D_{2d} ⊂ T_d, because functions that are invariant under D_{2d} are easily written down. Indeed, these functions are the tesseral (real) harmonics of the cosine type,

\[ S_{m}^{l} = \frac{(-1)^{m}C_{m}^{l} + C_{-m}^{l}}{1 + \delta_{m0}}, \quad m \geq 0, \quad (A1) \]

that satisfy the condition that \( l + m/2 \) is an even integer. This has the consequence that for odd values of \( l \) functions \( S_{m}^{l} \) with \( m < 2 \) cannot be invariant under \( D_{2d} \).

The induced rep is generated by the action of the left coset generators \( C_3 \) and \( C_3^2 \) of \( D_{2d} \) in \( T_d \), where \( C_3 \) is the rotation over \( 2\pi/3 \) around the axis \( n = [\sqrt{2}, 0, 1] \) and \( C_3^2 \) is the rotation over \( 4\pi/3 \) around the same axis. A function carrying the A_1 irrep of \( T_d \) is then obtained by simply summing

\[ T_{l}^{I} \propto (1 + C_3 + C_3^2) S_{\kappa}^{l}, \quad (A2) \]

where \( \kappa = 0 \) or 2 depending on \( l \), cf. Sec. III.A. In order to determine the action of a coset generator \( g \) on the tesseral harmonics we observe that \( g \in T_d \subset SO(3) \), so that

\[ gS_{\kappa}^{l} = \sum_{m'} C_{m'}^{l} \left[ D_{m',\kappa}^{l}(g) + D_{m',-\kappa}^{l}(g) \right] / (1 + \delta_{\kappa0}), \quad (A3) \]

where \( D_{m',\kappa}^{l} \) is an element of the Wigner rotation matrix.\(^{89}\)

The Euler angles associated with the rotation \( C_3 \) are given by
and those describing $C_2^2$ are

$$(\alpha, \beta, \gamma) = \left(\frac{\pi}{4}, \frac{\pi}{2}, \frac{5\pi}{4}\right).$$

The following relations were found useful in deriving the expressions in Table 1:

$$D^l_{m'm'}(C_3) + D^l_{m'm'}(C_3^2) = 2 d^l_{m'm'}(\pi/2) (-1)^{(m'-3m)/4},$$

$$d^l_{m'm'}(\pi/2) = \frac{(-1)^{m-m'}}{2^l} \frac{(l+m')!(l-m')!}{(l+m)!(l-m)!} \sum_k (-1)^k \binom{j+m}{k} \binom{j-m}{k+m'-m},$$

where $d^l_{m'm'}$ are Wigner’s functions.\(^{89,202}\)

Finally we wish to remark that the tetrahedral harmonics of even $l$ are identical to octahedral harmonics, since the groups $T_d$ and $O$ are closely related. For odd $l$ the $A_2(A_1)$ octahedral harmonics are $A_1(A_2)$ tetrahedral harmonics. A complete table of octahedral harmonics up to and including $l = 12$ can be found in Ref. 293.
Total differential cross sections for Ar–CH₄ from an ab initio potential*

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Abstract

Total differential cross sections for the Ar–CH₄ scattering complex at $E_{CM} = 90.1$ meV were obtained from converged close-coupling calculations based on a recent ab initio potential computed by symmetry-adapted perturbation theory (SAPT). Agreement with experiment is good, which demonstrates the accuracy of the SAPT potential.

Chapter 7: Differential cross sections of Ar–CH₄

I. INTRODUCTION

During the last few decades a number of experimental and theoretical studies have been devoted to the rotationally elastic and inelastic scattering of Ar–CH₄. In their pioneering work 278–279, 294 Secrest and coworkers applied both the close-coupling (CC) and coupled-states (CS) formalisms in the calculations of differential cross sections (DCS). Buck et al. 259 measured total differential cross sections in a crossed-beam experiment at $E_{CM} = 90.1$ meV. These results were used to derive an empirical potential of the Morse-spline-van der Waals type including the leading anisotropic contribution with tensor order $l = 3$. Time-of-flight (TOF) spectra were reported 260 and compared with CS calculations that used the potential from Ref. 259. Total differential cross sections for Ar–CH₄ were also measured at slightly different collision energies 261. Liuti et al. 263 reported total integral cross sections for rare gas–methane scattering as functions of the velocity. These data were used to further improve the isotropic term in the potential of Ref. 259.

In Chapter 6 we reported an ab initio intermolecular potential energy surface for Ar–CH₄ calculated using symmetry-adapted perturbation theory (SAPT). After performing an analytical fit to the computed points, the long range dispersion and induction coefficients in the fit were replaced by coefficients calculated in a larger basis set. See Ref. 78 for a more detailed description of this asymptotic scaling procedure. We applied this ab initio potential in CC calculations of state-to-state integral cross sections for A, E, and T states of methane rotationally excited by collisions with argon. The results were generally in good agreement with experimental data 264. In Chapter 8 the ab initio SAPT potential is used to generate second virial coefficients for the Ar–CH₄ complex. Virial coefficients computed from the asymptotically scaled potential are found to agree well with experiment, substantially better than those calculated from the original nonscaled potential.

In Chapter 9 total differential cross sections and TOF spectra for He–C₂H₂ computed from a SAPT potential 79 are found to be in excellent agreement with experiment. In the current chapter we present total differential cross sections for Ar–CH₄, computed at the collision energy $E_{CM} = 90.1$ meV, from converged CC scattering calculations. We compare the results obtained from the asymptotically scaled and the nonscaled SAPT potentials with the experimental data from Ref. 259.

II. COMPUTATIONAL DETAILS

The CC equations for atom–spherical top scattering were given in Ref. 275 and Chapter 6. The monomer wave functions for methane are expressed as linear
Computational details

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combinations of symmetric top functions (normalized rotation matrix elements). The coefficients in these combinations are obtained by constructing and diagonalizing for each angular momentum \( j \) a rotational Hamiltonian matrix that includes the tetrahedral centrifugal distortion (see Ref. 275 and Chapter 6. The following values were assigned to the rotational constant \( b \), the centrifugal distortion constant \( d_j \), and the tetrahedral centrifugal distortion constant \( d_t \):

\[
b = 5.2410356 \text{ cm}^{-1}, \quad d_j = 1.10864 \times 10^{-4} \text{ cm}^{-1}, \quad d_t = 4.425 \times 10^{-6} \text{ cm}^{-1}.
\]

The CC equations were solved applying the modified log-derivative – Airy integrator. The log-derivative propagator was used from \( R_{\text{min}} = 4.5 \text{ bohr} \) to \( R_{\text{mid}} = 15 \text{ bohr} \) with a constant step size corresponding to 5 steps per half wavelength for the open channel of highest kinetic energy in the asymptotic region. From \( R_{\text{mid}} \) to \( R_{\text{max}} = 100 \text{ bohr} \) the Airy propagator was used. Partial wave contributions with increasing values of the total angular momentum \( J \) were included until both the elastic and inelastic state-to-state cross sections were converged within 0.001 Å. With the asymptotically scaled potential, the highest values of \( J \) included for the \( A \), \( E \), and \( T \) symmetries were 309, 310, and 297, respectively. If the lengths of the partial wave expansions were smaller, the elastic contributions showed unphysical oscillations, especially at large angles. The angular basis contained all channels with monomer angular momentum \( j \) up to 14 inclusive. However, for the \( E \) and \( T \) symmetries the components with \( J > 190 \) and 182, respectively, were calculated in a basis including only channels with \( j \leq 11 \). The total number of channels for the bases with \( j \leq 14 \) and \( j \leq 11 \) were \( \approx 385 \) and 190, respectively, for the \( E \) symmetry, and \( \approx 360 \) and 290, respectively, for the \( T \) symmetry. Thus, decreasing the maximum value of the monomer angular momentum \( j \) from 14 to 11 caused the sizes of the basis sets to be reduced by approximately a factor of two. For the \( A \) symmetry, the total number of channels was \( \approx 90 \). We tested that the deviations caused by the reduction of the monomer basis at large \( J \) were negligible. We performed additional calculations for the \( A \) states with the nonscaled potential and the same set of parameters. The highest value of \( J \) included was 307 in this case.

The \( \text{Ar–CH}_4 \) interaction potential, which is a function of the distance \( R \) between the CH\(_4\) center-of-mass (c.m.) and the Ar atom and of the polar angles \((\theta, \phi)\) of the vector \( \mathbf{R} \), was expanded in real combinations of spherical harmonics \( Y_{\ell}^{m}(\theta, \phi) \) with \( \ell \leq 18 \). The expansion coefficients were computed by means of 25-point Gauss–Legendre and Gauss–Chebyshev quadratures in \( \theta \) and \( \phi \), respectively. The reduced mass of \( \text{Ar–CH}_4 \) is 11.441478 amu. The integration parameters, the size of the monomer basis, the number of partial waves, and the length of the expansion of the potential were chosen such that the state-to-state cross sections were converged within 1% at worst. All scattering calculations
w ere performed using the MOLSCAT system of codes. Differential cross sections in the c.m. frame were generated from the calculated $S$ matrix elements using the DCS program. This program was extended such that it can be applied to atom-spherical top systems. The c.m. scattering angle $\Theta_{CM}$ was varied from 0° to 180° with steps of 0.5°. It was assumed that initially the methane molecules are in the lowest rotational state permitted for each of the symmetry types, i.e., $j'' = 0, 1, \text{ and } 2$ for $A, T, \text{ and } E$ symmetries, respectively.

In order to compare the ab initio total differential cross sections, summed over all elastic and inelastic channels, with experiment, the calculated values were transformed from the c.m. frame to the laboratory-fixed (lab) frame and averaged over the velocity and angular distributions of the methane and argon beams. Furthermore, corrections were made for the energy response and physical size of the detector. The averaging procedure is described in detail elsewhere. The key parameters are the full width at half maximum of the c.m. angular and velocity distributions, $\delta = 1.46° \text{ and } \Delta v/v = 0.13$, respectively. They are calculated using a Monte-Carlo procedure with the quantities mentioned above as input information. The actual calculations are then performed on a 12 x 12 point grid in the two variables. The energy dependence of the cross sections is explicitly taken into account with the help of a scaling law which has been checked against exact calculations.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) depict the state-to-state, total inelastic, and total differential cross sections for the $A$ symmetries of Ar–CH$_4$ as functions of the c.m. angle $\Theta_{CM}$. The same results for the $T$ species are presented in Figs. 2(a) and (b) and for the $E$ states in Figs. 3(a) and (b). Only cross sections for the transitions with $j' \leq 7$ are shown ($j'$ denotes here the rotational quantum number of the final state). Cross sections with higher $j'$ are not reported since their contribution to the total differential cross sections is very small. An inspection of these figures shows that at small angles the elastic component dominates the total differential cross sections. At larger angles the inelastic transitions become increasingly important, especially for the $A$ and $T$ symmetries. For these symmetries the elastic term has a deep minimum around $\Theta_{CM} = 60°$. It is interesting to note that although various state-to-state differential cross sections show very different dependence on the c.m. deflection angle, the total cross sections (i.e., the cross sections summed over the elastic and all inelastic channels) are almost identical.

The theoretical total differential cross section for the $A$ states of Ar–CH$_4$, transformed to the lab frame and averaged over the experimental conditions,
FIG. 1. State-to-state inelastic (a) and elastic, total inelastic, and total (b) differential cross sections for the $A$ symmetries of Ar–CH$_4$ calculated with the asymptotically scaled SAPT potential as functions of the c.m. angle. The molecular rotational quantum numbers of the final states are indicated.
FIG. 2. State-to-state inelastic (a) and elastic, total inelastic, and total (b) differential cross sections for the $T$ symmetries of Ar–CH$_4$ calculated with the asymptotically scaled SAPT potential as functions of the c.m. angle. The molecular rotational quantum numbers of the final states are indicated.
Results and discussion

(a) Experimental results for state-to-state inelastic differential cross sections for the $E$ symmetries of Ar–CH$_4$ calculated with the asymptotically scaled SAPT potential as functions of the c.m. angle. The molecular rotational quantum numbers of the final states are indicated.

(b) Theoretical predictions for elastic, total inelastic, and total differential cross sections as a function of the c.m. angle.
FIG. 4. Total differential cross sections (multiplied by $\Theta^{7/3}$) computed from the asymptotically scaled SAPT potential (solid line) and the nonscaled SAPT potential (dashed line) as functions of the lab angle. Circles denote experimental data from Ref. 259, the error bars represent ±1 standard deviation of the mean.
FIG. 5. Total differential cross section (multiplied by $\Theta^{7/2}$) computed from the semi-empirical $V_S + V_T$ potential of Ref. 259 as a function of the lab angle. Circles denote experimental data from Ref. 259, the error bars represent ±1 standard deviation of the mean.
is reported as a function of the laboratory angle in Fig. 4. It was essential that
different inelastic contributions were transformed individually, since they have
different final velocities. The use of the purely elastic transformation would
substantially underestimate the theoretical differential cross sections at large
lab angles. The experimental cross sections from Ref. 259 are displayed in
this figure as well. In order to remove the strong angular dependence of the
elastic differential cross section the data are multiplied by $\Theta^{7/3}$. Although the
state-to-state differential cross sections for the $E$ and $T$ states of Ar--CH$_4$
do not come from those of the $A$ species (cf. Figs. 1-3), the total differential cross
sections in the lab frame were found to be almost identical. Therefore, these
results are not shown. The position of the maximum of the total differential
cross sections, the rainbow angle, is very well reproduced, but the slope of the
theoretical curve beyond the rainbow angle is somewhat different from
experiment. These two features of the total differential cross sections are mainly
sensitive to the well depth of the potential, so the results presented in Fig. 4
suggest that the well depth of the $ab\ initio$ potential is underestimated, but
only by a very minor amount. Furthermore, the positions and amplitudes of the
diffraction oscillations, which modulate the maximum of the curve, agree well
with experiment. This result indicates that both the onset of the repulsive wall
($R_0$) and the anisotropy of the minimum distance $R_{\text{m}}(\Theta)$ of the potential are
realistic. On the other hand, the coarse structure amplitude of the curve, which
represents the rainbow maximum, slightly deviates from the experimental data.
Test calculations of the averaging process show that the rainbow amplitude is
not influenced by small changes of the resolution.

A possible reason for such a behavior could be too weak a damping of the
rainbow amplitude due to the anisotropy of the well depth. However, a careful
inspection of the total differential cross sections in the rainbow region shows
that they are completely dominated by the elastic contributions. This is also
reflected in the potential terms in the attractive part near the inflection point
which is the part of the potential that is most sensitively probed in rainbow
scattering. Here $V_0$ is much larger than the anisotropic $V_3$ and $V_4$ terms (see
Chapter 6). Therefore, we attribute the small discrepancy in the rainbow
amplitude to a small error in the shape of the potential near the inflection point: the rainbow impact parameter is slightly too large, which influences
the rainbow amplitude.\textsuperscript{298} Indeed the best fit isotropic potentials of Refs. 259
and 263 exhibit smaller rainbow impact parameters and thus slightly smaller
amplitudes.

For comparison, we have plotted in Fig. 5 the total differential cross sections
for the $A$ states of Ar--CH$_4$, calculated from the semiempirical potential $V_0^A + V_3^A$
reported by Buck \textit{et al.}\textsuperscript{259} This figure is not identical with Fig. 8 of Ref. 259,
which was obtained from the same potential, because in the present work we applied the close-coupling instead of the coupled-states formalism and did not retransform the results to the c.m. frame. The agreement of the present curve with experiment is worse between 5° and 6° (lab angles), the same up to 20°, and better for larger angles. The ab initio results of Fig. 4 agree somewhat better with experiment than the semiempirical results for angles smaller than 12°, somewhat worse between 12° and 23°, and are comparable for larger angles. On the average, agreement with the experimental results is equally good for the SAPT potential and for the semiempirical potential of Ref. 259 that was mainly fitted to these data.

Also reported in Fig. 4 are the theoretical total differential cross sections calculated from the nonscaled SAPT potential. An inspection of the figure shows that the agreement with experiment is considerably worse. The predicted rainbow angle is too small, indicating that the well of this potential is too shallow. A change in the well depth of the potential also affects the onset of the repulsive wall. Consequently, the oscillations on the curve for the nonscaled potential in Fig. 4 are slightly out of phase with respect to the experimental data. A similar result concerning the well depth was found from the analysis of the second virial coefficients calculated with the asymptotically scaled and the nonscaled SAPT potentials, see Chapter 8.

We conclude that the asymptotically scaled SAPT potential reported in Chapter 6 is able to reproduce well the total differential cross sections for Ar-CH₄. The only deviation from experiment is in the rainbow amplitudes suggesting that there are small inaccuracies in the shape of the potential near the inflection point. The well depth of the potential, however, is very realistic, since the position of the rainbow angle is accurately reproduced. Comparison with the results obtained from the semiempirical potential of Ref. 259, which was fitted to the measured differential cross sections, shows that the results from the SAPT potential agree about equally well with these experimental data. Work on the application of this ab initio potential to generate the infrared spectrum of the Ar-CH₄ complex in the region of the ν₂ mode is in progress. Comparison with the experimental spectrum will provide a further check of the accuracy of the potential.

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Chapter 8

Second virial coefficients for atom–molecule complexes from ab initio SAPT potentials*

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Abstract

Ab initio potentials, calculated by symmetry-adapted perturbation theory, are applied to compute second virial coefficients (including first-order quantum corrections) for He–CO, Ne–CO, Ar–H₂, He–C₂H₂, and Ar–CH₄ mixtures over a wide range of temperatures. The experimental methods are briefly outlined and the errors in the procedure to obtain mixed virial coefficients from the experimental data are discussed. Very good agreement with the majority of the available experimental data is observed for all systems except Ar–CH₄ where calculated virial coefficients are slightly too high in comparison with measured data. Possible reasons for discrepancies between theory and experiment at very low temperatures are discussed.

I. INTRODUCTION

The knowledge of the interaction potential of a group of molecules as a function of their mutual separations and orientations is sufficient to determine all microscopic and macroscopic properties of gases, liquids, and solids. Before the advent of modern spectroscopic and scattering techniques, measurements of the macroscopic properties were a unique source of knowledge about intermolecular forces. Nowadays high-resolution spectra of molecular complexes and molecular beam scattering data are available which are very sensitive to the details of the potential energy surfaces, but macroscopic properties still provide additional information about intermolecular forces.

In principle, all macroscopic properties are influenced by intermolecular forces, and probe the potential energy surface. In practice, only few of them are suitable for studies of interactions between molecules. First of all, a sound and accurate quantum-statistical theory connecting the interaction potential and the macroscopic property must be available. Moreover, the interaction potential should not be buried under too many layers of theory or too much statistical averaging, otherwise the sensitivity will be lost. Finally, the macroscopic property must be measurable with good precision.

Among various macroscopic properties the second virial coefficients of pure gases and mixtures meet all these requirements. The quantum-statistical theory of the virial equation of state is well understood, and semi-classical expressions for this quantity have been derived.\textsuperscript{160,299} At moderately low and high temperatures the dependence of the second virial coefficient on the interaction potential is given by a simple integral.\textsuperscript{160,300} Finally, a wealth of accurate experimental data are available for various atom–molecule systems (see Refs. 301-303 for critical compilations).

In recent years intermolecular potentials of several atom–molecule dimers were computed: Ar–H\textsubscript{2} (Ref. 77), He–HF (Ref. 78), He–CO (Ref. 80 and Chapter 4), Ne–CO (Ref. 175), He–C\textsubscript{2}H\textsubscript{2} (Ref. 79), Ne–C\textsubscript{2}H\textsubscript{2} (Chapter 5), and Ar–CH\textsubscript{4} (Chapter 6) by \textit{ab initio} symmetry-adapted perturbation theory (SAPT),\textsuperscript{4} with the inclusion of the intramonomer electron correlation effects. We believe that these potentials are accurate to within 2 to 4% over the full range of distances and angles. For most of these systems the accuracy of the SAPT potentials has already been proven by comparison of the computed and measured (high-resolution) infrared spectra (Refs. 79,80,82,83, and 175, and Chapters 4 and 5), and state-to-state scattering cross sections and rate constants (Ref. 304 and Chapters 6, 7, 9, and 10). The results of dynamical studies showed that the SAPT potentials for these systems are indeed accurate both in the repulsive region and around the van der Waals minimum (see Refs. 1,305, and 306 for recent reviews of dynamical calculations).
Except for the He–CO complex\textsuperscript{79,173} the accuracy of the SAPT potentials was not demonstrated in calculations of the bulk properties of gases. In the present chapter we fill this gap and report calculations of the second virial coefficients of various atom–molecule complexes for a wide range of temperatures. The theoretical values are critically compared with the existing experimental data. We restrict ourselves to the He–CO, Ne–CO, Ar–H\textsubscript{2}, He–C\textsubscript{2}H\textsubscript{2}, and Ar–CH\textsubscript{4} mixtures, since only for these systems the experimental data are available.\textsuperscript{238–245,301–303,307–315} The plan of the chapter is as follows: in Sec. II we briefly describe the method of calculations. In Sec. III we present a critical overview of the available experimental data. In Sec. IV we discuss the numerical results, and compare our data with various experiments. Finally, in Sec. V we present conclusions.

II. METHOD OF CALCULATIONS

Exact quantum-statistical calculations of the second virial coefficients require the solution of the close-coupling scattering equations at various energies followed by Boltzmann averaging. Except for atomic gases or molecular gases at very low temperatures this procedure is very computer time demanding. Since for atom–molecule complexes very few experimental data are available for temperatures below 100 K, we assume that the second virial coefficient \(B(T)\) can be approximated by the sum of the classical term \([B^{(0)}(T)]\) and the first quantum correction \([B^{(1)}(T)]\),

\[
B(T) = B^{(0)}(T) + B^{(1)}(T).
\]

The expression for the classical term has been known for a long time.\textsuperscript{160} For the interaction of nonspherical systems closed formulas for the first quantum correction have been derived\textsuperscript{300} by expanding the exact quantum-statistical expression for \(B(T)\)\textsuperscript{299} as a power series in \(\hbar^2\) (\(\hbar\) is Planck’s constant). It is worth noting that the classical term \(B^{(0)}(T)\) is a lower bound to the exact \(B(T)\),\textsuperscript{316,317} and that the first quantum correction \(B^{(1)}(T)\) is positive definite, i.e., \(B^{(1)}(T) \geq 0\).\textsuperscript{300}

For atom–linear molecule complexes the expression for \(B^{(0)}(T)\) can be written as\textsuperscript{300}

\[
B^{(0)}(T) = \pi N_A \int_0^\infty \int_0^\pi \{1 - \exp\left[-\beta V(R,\theta)\right]\} R^2 \sin \theta dR d\theta,
\]

where \(V(R,\theta)\) is the interaction potential depending on the distance \(R\) from the atom to the center of mass of the molecule and on the angle \(\theta\) between the molecular axis and the line connecting the atom with the center of mass
Chapter 8: Second virial coefficients from SAPT potentials

of the molecule, \( N_A \) is Avogadro’s constant, and \( \beta \equiv 1/k_B T \), where \( k_B \) is the Boltzmann constant. The first quantum correction \( B^{(1)}(T) \) is represented by the sum of contributions due to the radial \([B_R^{(1)}(T)]\), rotational (angular) \([B_A^{(1)}(T)]\), and Coriolis \([B_C^{(1)}(T)]\) terms in the Hamiltonian,

\[
B^{(1)}(T) = B_R^{(1)}(T) + B_A^{(1)}(T) + B_C^{(1)}(T).
\]  (3)

The contributions appearing on the r.h.s. of Eq. (3) are defined for atom–linear molecule complexes as follows:

\[
B_R^{(1)}(T) = \frac{N_A \pi \hbar^2 \beta^3}{24 \mu} \int_0^\infty \int_0^\pi \exp[-\beta V(R, \theta)] \left( \frac{\partial V}{\partial R} \right)^2 R^2 \sin \theta \, dR \, d\theta, \]  (4)

\[
B_A^{(1)}(T) = -\frac{N_A \pi \beta^2 b_0}{12} \int_0^\infty \int_0^\pi \exp[-\beta V(R, \theta)] \times \sum_{l=0}^\infty l(l+1) V_l(R) P_l(\cos \theta) R^2 \sin \theta \, dR \, d\theta, \]  (5)

\[
B_C^{(1)}(T) = -\frac{N_A \pi \hbar^2 \beta^2}{24 \mu} \int_0^\infty \int_0^\pi \exp[-\beta V(R, \theta)] \times \sum_{l=0}^\infty l(l+1) V_l(R) P_l(\cos \theta) \sin \theta \, dR \, d\theta. \]  (6)

Here \( b_0 \) is the rotational constant of the molecule, \( \mu \) denotes the reduced mass of the complex, and the \( V_l(R) \) are the radial coefficients in the expansion of the potential in Legendre polynomials \( P_l \),

\[
V(R, \theta) = \sum_{l=0}^\infty V_l(R) P_l(\cos \theta). \]  (7)

Similar expressions for atom–spherical top complexes are given by:

\[
B^{(0)}(T) = \frac{N_A}{2} \int (1 - \exp[-\beta V(R)]) \, dR, \]  (8)

\[
B_R^{(1)}(T) = \frac{N_A \hbar^2 \beta^3}{48 \mu} \int \exp[-\beta V(R)] \left( \frac{\partial V}{\partial R} \right)^2 \, dR, \]  (9)

\[
B_A^{(1)}(T) = -\frac{N_A \beta^2 b_0}{24} \int \exp[-\beta V(R)] \times \sum_{l=0}^{\infty} l(l+1) \sum_{\nu=1}^{m_l} V_{l\nu}(R) T_{l\nu}(\Theta, \Phi) \, dR. \]  (10)
Method of calculations

TABLE 1. Parameters used in the calculations. Distances are in bohr, rotational constants in cm$^{-1}$, and masses in amu.

<table>
<thead>
<tr>
<th>System</th>
<th>$R_{\text{min}}$</th>
<th>$R_{\text{max}}$</th>
<th>$l_{\text{max}}$</th>
<th>$N_\theta$</th>
<th>$N_\phi$</th>
<th>$b_0$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He–CO</td>
<td>3.0</td>
<td>150.0</td>
<td>14</td>
<td>16</td>
<td>–</td>
<td>1.92252</td>
<td>3.50191</td>
</tr>
<tr>
<td>Ne–CO</td>
<td>2.0</td>
<td>150.0</td>
<td>14</td>
<td>20</td>
<td>–</td>
<td>1.90528</td>
<td>11.66321</td>
</tr>
<tr>
<td>Ar–H$_2$</td>
<td>2.0</td>
<td>150.0</td>
<td>4</td>
<td>10</td>
<td>–</td>
<td>59.0654</td>
<td>1.91887</td>
</tr>
<tr>
<td>He–C$_2$H$_2$</td>
<td>4.0</td>
<td>150.0</td>
<td>18</td>
<td>24</td>
<td>–</td>
<td>1.17664</td>
<td>3.46890</td>
</tr>
<tr>
<td>Ar–CH$_4$</td>
<td>4.0</td>
<td>100.0</td>
<td>18</td>
<td>25</td>
<td>25</td>
<td>5.24104</td>
<td>11.44148</td>
</tr>
</tbody>
</table>


\[
B_{C}^{(1)}(T) = -\frac{N_A \hbar^2}{48\mu} \int \exp[-\beta V(R)] R^{-2} \times \sum_{l=0}^{\infty} \sum_{v=1}^{m_{l,A_1}} l(l+1) V^l_v(R) T^l_v(\Theta, \Phi) \ dR. \tag{11}
\]

The (multiple) integrals in these expressions are over $R = (R, \Theta, \Phi)$, with $dR = R^2 \sin \Theta dR d\Theta d\Phi$, where $\Theta$ and $\Phi$ are the orientation angles of the atom with respect to the molecule fixed frame. The radial coefficients $V^l_v(R)$ correspond to the expansion of the potential in tetrahedral harmonics $T^l_v(\Theta, \Phi)$ of $A_1$ symmetry, cf. Chapter 6.

\[
V(R) = \sum_{l=0}^{\infty} \sum_{v=1}^{m_{l,A_1}} V^l_v(R) T^l_v(\Theta, \Phi), \tag{12}
\]

where $m_{l,A_1} = \lfloor l/12 \rfloor + 1$ represents the multiplicity of the $A_1$ irreducible representation of $T_d$ in the $2l+1$ dimensional space spanned by the spherical harmonics $Y^l_{m}$. One may note that in Eq. (12) the subscript $l$ runs over selected values: $l = 0, 3, 4, 6, 7, \ldots$ (cf. Chapter 6) for molecules of tetrahedral ($T_d$) symmetry, $l = 0, 4, 6, 8, \ldots$ for molecules of octahedral ($O_h \supset T_d$) symmetry, and $l = 0, 6, 10, 12, \ldots$ for molecules of icosahedral ($I_h \supset T_d$) symmetry.

It is assumed in these formulas that at the temperatures considered the vibrations of the monomers are not excited, so that the molecules can be treated as rigid bodies. In some cases the theoretical potentials were given as explicit functions of the internal coordinates of the monomers (Ar–H$_2$, Ref. 77, and He–CO, Chapter 4). For these systems we have used in our calculations interaction potentials averaged over the ground state vibrational wave functions of the monomers (see Ref. 82 and Chapter 4 for details). For Ar–CH$_4$ we used the potential from Chapter 6 in which the asymptotic scaling of the dispersion and induction energies was applied.

In practice Eqs. (2), (4)–(6), and (8)–(11) were evaluated by numerical integration techniques. For the integration over $R$ we used the Romberg scheme, in the range from $R_{\text{min}}$ to $R_{\text{max}}$. The values of $R_{\text{min}}$ and $R_{\text{max}}$ were chosen such
that in the inner region, $R < R_{\text{min}}$, the function $\exp(-\beta V)$ is effectively zero, while in the outer region, $R > R_{\text{max}}$, all contributions are negligibly small. The number of radial grid points was $N = 2^{n-1} + 1$. We increased $n$ by 1 in each iteration and stopped when the relative error was smaller than $10^{-3}$. The integration over $\theta$ (in the case of Ar–CH$_4$) was performed by using a $N_\theta$-point Gauss–Legendre quadrature. The angular expansion of the potential, Eq. (7) or (12) was truncated at $l_{\text{max}}$ terms. For the integration over $\Phi$ we used a Gauss–Chebyshev quadrature with $N_\Phi$ points. We checked that our results are stable against changes in the boundaries and/or integration parameters. In Table 1 we summarize all relevant parameters used in our calculations.

We tested for Ar–CH$_4$ the outer integration limit $R_{\text{max}}$ and found that a value of 100 bohr is necessary for the classical term $B^{(0)}(T)$ to be converged within 0.001 cm$^3$ mol$^{-1}$. Classical contributions obtained with $R_{\text{max}}$ is 50 bohr differed approximately 0.5% from the converged values. For the Ar–CH$_4$ system this corresponds to an error of 0.1 – 0.5 cm$^3$ mol$^{-1}$. When $R_{\text{max}}$ was set to 50 bohr the first quantum corrections $B^{(1)}(T)$ were converged within 0.001 cm$^3$ mol$^{-1}$. In fact, deviations from the converged results for $B^{(1)}(T)$ were smaller than 1% for an $R_{\text{max}}$ of 10 bohr.

### III. EXPERIMENTAL DETERMINATION OF SECOND VIRIAL COEFFICIENTS

Almost all the virial coefficients that we discuss in the present chapter have been measured by one of the two methods described briefly in this section. The method used in Heidelberg$^{307,309,310,312}$ is a relative method, in which the thermophysical properties of the unknown gas or gas mixture are compared to the properties of a well known gas. Two glass vessels of (almost) equal volumes are filled with these two gases at the same pressure and the same temperature. Then either their volumes can be doubled by expansion into evacuated vessels or their temperature can be changed by heating or cooling. In both cases a small pressure difference builds up because of geometric differences in the apparatus and because of the different virial coefficients of the two gases under comparison. With the help of the expansion method the difference of the virial coefficients of the gases under consideration is determined at room temperature ($T_0 = 296.2$ K) and with the temperature changing method it is measured how much this difference changes with temperature. These methods are easy, in principle, and should give reliable results. But, in practice, there are some hidden error sources that must be known. For example, it is crucial to have a homogeneous temperature bath. Not even a difference of a hundredth of a degree is allowed. In the Heidelberg group this homogeneity is reached by
Experimental determination

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heavily stirring the fluid bath. Furthermore, the vessels have to keep their volumes constant even when pressure changes because of the temperature change. It is learned by experience that a wall thickness of the glass vessels of at least 6 mm is needed in order to overcome this problem. It is possible to perform reproducible measurements of virial coefficients with an apparatus that has some of these hidden faults. In Heidelberg measurements are therefore always performed under different conditions (different pressures, different mole fractions of the gas mixtures, interchange of the known and the unknown gas in the vessels) and the error bounds arise from these results. In the case of a gas mixture a virial coefficient $B_m$ is measured that is mole fraction dependent. With the help of the statistical formula $B_m(x_1, T) = x_1^2 B_1(T) + 2x_1 x_2 B_{12}(T) + x_2^2 B_2(T)$ the interaction second virial coefficient $B_{12}$ can be calculated from the experiments. Here $x_1$ and $x_2 = 1 - x_1$ denote the mole fractions, while $B_1$ and $B_2$ are the virial coefficients of the pure components. As can be seen from the coefficient of $B_{12}$ the error in $B_{12}$ is at least twice as large (for $x_1 = 1/2$) as the error in $B_m$. Additionally the uncertainty of the virial coefficients of the pure components has to be taken into account. Therefore the uncertainty of an interaction second virial coefficient $B_{12}$ near room temperature normally is at least 2 cm$^3$ mol$^{-1}$, and it grows with temperatures further remote from room temperature, since the measurements are more complicated at these temperatures and the reference values are less well known.

Similar arguments hold for the other method applied to measurements of interaction second virial coefficients $B_{12}$. The fact that pressure changes by mixing two pure gases at constant temperature and volume. The pressure difference, which is proportional to an excess quantity $E$ given by $E = B_{12} - (B_1 + B_2)/2$, can be measured very reliably. In order to calculate $B_{12}$ from the measured quantity $E$ the virial coefficients of the pure components of the mixture must be known and this often causes problems at least at very low temperatures. An example shall explain this. In an early paper Knobler et al. reported measurements of interaction second virial coefficients at liquid oxygen temperature (90.2 K). They calculated from their excess quantity $E$ the $B_{12}$ interaction virial coefficient for Ar–H$_2$ to be $B_{12} = -52.1$ cm$^3$ mol$^{-1}$ using an argon virial coefficient $B$(Ar) = $-209$ cm$^3$ mol$^{-1}$ that they had calculated with the help of an empirical Lennard–Jones potential, since no experimental value was known at that time. Meanwhile this value is measured to be $B$(Ar,90.2K) = $-222$ cm$^3$ mol$^{-1}$. Therefore, the value of $-52.1$ cm$^3$ mol$^{-1}$ for $B_{12}$ has to be 6.5 cm$^3$ mol$^{-1}$ more negative and the corrected value is $B_{12}$(Ar–H$_2$, 90.2K) = $-59$ cm$^3$ mol$^{-1}$, in excellent agreement with the value given in Ref. 310.
Chapter 8: Second virial coefficients from SAPT potentials

### TABLE 2.

Comparison of the theoretical and experimental second virial coefficients for He–CO (in cm³ mol⁻¹) as functions of the temperature (in K).

<table>
<thead>
<tr>
<th>T</th>
<th>$B^{(0)}(T)$</th>
<th>$B^{(1)}_R(T)$</th>
<th>$B^{(1)}_L(T)$</th>
<th>$B^{(1)}_T(T)$</th>
<th>$B^{\text{calc}}(T)$</th>
<th>$B^{\text{obs}}(T)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.3</td>
<td>−1.473</td>
<td>2.170</td>
<td>0.192</td>
<td>0.049</td>
<td>0.937</td>
<td>−8.9 ± 8.0</td>
<td>307</td>
</tr>
<tr>
<td>90.1</td>
<td>3.871</td>
<td>1.679</td>
<td>0.148</td>
<td>0.038</td>
<td>5.736</td>
<td>−2.1 ± 7.0</td>
<td></td>
</tr>
<tr>
<td>143.0</td>
<td>14.603</td>
<td>0.816</td>
<td>0.070</td>
<td>0.019</td>
<td>15.508</td>
<td>11.5 ± 6.0</td>
<td></td>
</tr>
<tr>
<td>173.0</td>
<td>17.335</td>
<td>0.616</td>
<td>0.053</td>
<td>0.015</td>
<td>18.018</td>
<td>15.6 ± 5.0</td>
<td></td>
</tr>
<tr>
<td>213.0</td>
<td>19.518</td>
<td>0.457</td>
<td>0.039</td>
<td>0.011</td>
<td>20.025</td>
<td>20.5 ± 5.0</td>
<td></td>
</tr>
<tr>
<td>242.0</td>
<td>20.519</td>
<td>0.382</td>
<td>0.032</td>
<td>0.010</td>
<td>20.942</td>
<td>22.4 ± 5.0</td>
<td></td>
</tr>
<tr>
<td>273.0</td>
<td>21.263</td>
<td>0.323</td>
<td>0.027</td>
<td>0.008</td>
<td>21.621</td>
<td>24.5 ± 5.0</td>
<td></td>
</tr>
<tr>
<td>296.2</td>
<td>21.669</td>
<td>0.288</td>
<td>0.024</td>
<td>0.007</td>
<td>21.989</td>
<td>24.6 ± 4.0</td>
<td></td>
</tr>
<tr>
<td>77.3</td>
<td>−1.473</td>
<td>2.170</td>
<td>0.192</td>
<td>0.049</td>
<td>0.937</td>
<td>−11.0 ± 6.0</td>
<td>308</td>
</tr>
<tr>
<td>90.1</td>
<td>3.871</td>
<td>1.679</td>
<td>0.148</td>
<td>0.038</td>
<td>5.736</td>
<td>−4.0 ± 5.0</td>
<td></td>
</tr>
<tr>
<td>150.0</td>
<td>15.364</td>
<td>0.760</td>
<td>0.065</td>
<td>0.018</td>
<td>16.207</td>
<td>16.5 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>200.0</td>
<td>18.035</td>
<td>0.500</td>
<td>0.042</td>
<td>0.012</td>
<td>19.489</td>
<td>19.5 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>250.0</td>
<td>20.738</td>
<td>0.365</td>
<td>0.031</td>
<td>0.009</td>
<td>21.142</td>
<td>21.0 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>300.0</td>
<td>21.726</td>
<td>0.283</td>
<td>0.024</td>
<td>0.007</td>
<td>22.040</td>
<td>22.5 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>123.15</td>
<td>11.855</td>
<td>1.023</td>
<td>0.089</td>
<td>0.024</td>
<td>12.990</td>
<td>14.31 ± 3.0a</td>
<td>239</td>
</tr>
<tr>
<td>148.15</td>
<td>15.171</td>
<td>0.774</td>
<td>0.067</td>
<td>0.018</td>
<td>16.030</td>
<td>16.64 ± 3.0a</td>
<td></td>
</tr>
<tr>
<td>173.15</td>
<td>17.346</td>
<td>0.615</td>
<td>0.053</td>
<td>0.015</td>
<td>18.028</td>
<td>18.41 ± 3.0a</td>
<td></td>
</tr>
<tr>
<td>223.15</td>
<td>19.910</td>
<td>0.428</td>
<td>0.036</td>
<td>0.011</td>
<td>20.385</td>
<td>20.62 ± 2.0a</td>
<td></td>
</tr>
<tr>
<td>273.15</td>
<td>21.266</td>
<td>0.322</td>
<td>0.027</td>
<td>0.008</td>
<td>21.624</td>
<td>21.53 ± 2.0a</td>
<td></td>
</tr>
</tbody>
</table>

*aExperimental errors are estimated in accordance with Ref. 321.

### IV. NUMERICAL RESULTS AND DISCUSSION

The results of our calculations are presented in Tables 2–6 (see also Figs. 1–4 for graphical illustrations). To facilitate the comparison of the calculated values with the experimental data, we report—in Table 7—root mean square deviations ($\sigma$) for each set of data and for all data pertaining to a given system. 

The quantity $\sigma$ is defined by

$$\sigma = \left[ \frac{1}{N} \sum_{i=1}^{N} \frac{(B^{\text{calc}}_i - B^{\text{obs}}_i)^2}{\delta_i^2} \right]^{1/2}, \quad (13)$$

where $N$ is the number of data points, $B^{\text{calc}}_i$ and $B^{\text{obs}}_i$ denote the calculated and observed second virial coefficients, respectively, and $\delta_i$ is the experimental uncertainty associated with $B^{\text{obs}}_i$ estimated by considering the temperature and the applied measuring method. This quantity indicates that, on average, the calculated values deviate from experiment by $\sigma$ times the experimental uncertainty of the data.
FIG. 1. Comparison of the theoretical and experimental second virial coefficients for He–CO as functions of the temperature. Squares, circles, and triangles denote experimental data from Refs. 307, 308, and 239, respectively.

Before we start a detailed comparison between theory and experiment let us discuss the validity of our theoretical ansatz for the second virial coefficient, Eq. (1). An inspection of Tables 2–6 shows that the quantum effects are small for temperatures larger than 100 K. An exception are complexes containing light systems like helium or hydrogen. Even for these mixtures, however, the first quantum correction usually represents less than 15% of the classical value. Only around the Boyle temperature $T_B$ [defined by the equation $B(T_B) = 0$] the first quantum correction is relatively large, but for $T_B \geq 100$ K the second quantum correction should represent a few percent of $B^{(1)}(T)$ at worst. These observations suggest that the truncation of the semi-classical expansion after the first-order term is fully legitimate for $T \geq 100$ K. At lower temperatures the situation is more complex, and the inclusion of the second quantum correction or the use of quantum mechanical (close-coupling) scattering theory may be necessary. Below we present a detailed comparison of the theoretical and experimental data for the atom–molecule complexes studied in the current chapter.
TABLE 3. Comparison of the theoretical and experimental second virial coefficients for Ne–CO (in cm³ mol⁻¹) as functions of the temperature (in K).

<table>
<thead>
<tr>
<th>T</th>
<th>B⁰(T)</th>
<th>B₁(T)</th>
<th>B₂(T)</th>
<th>B₃(T)</th>
<th>B₄(T)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>123.15</td>
<td>-18.020</td>
<td>0.553</td>
<td>0.197</td>
<td>0.014</td>
<td>-17.256</td>
<td>-14.71 ±3.0⁺</td>
</tr>
<tr>
<td>148.15</td>
<td>-8.041</td>
<td>0.393</td>
<td>0.138</td>
<td>0.010</td>
<td>-7.499</td>
<td>-5.64 ± 3.0⁺</td>
</tr>
<tr>
<td>173.15</td>
<td>-1.373</td>
<td>0.299</td>
<td>0.104</td>
<td>0.008</td>
<td>-0.961</td>
<td>0.42 ± 3.0⁺</td>
</tr>
<tr>
<td>223.15</td>
<td>6.876</td>
<td>0.196</td>
<td>0.067</td>
<td>0.005</td>
<td>7.145</td>
<td>7.83 ± 2.0⁺</td>
</tr>
<tr>
<td>273.15</td>
<td>11.683</td>
<td>0.143</td>
<td>0.048</td>
<td>0.004</td>
<td>11.878</td>
<td>12.23 ± 2.0⁺</td>
</tr>
<tr>
<td>296.15</td>
<td>13.429</td>
<td>0.126</td>
<td>0.042</td>
<td>0.003</td>
<td>13.429</td>
<td>14.1 ± 1.5</td>
</tr>
<tr>
<td>353.15</td>
<td>16.110</td>
<td>0.097</td>
<td>0.032</td>
<td>0.003</td>
<td>16.242</td>
<td>17.2 ± 2.0</td>
</tr>
<tr>
<td>463.15</td>
<td>19.250</td>
<td>0.066</td>
<td>0.021</td>
<td>0.002</td>
<td>19.338</td>
<td>20.6 ± 3.0</td>
</tr>
</tbody>
</table>

⁺Experimental errors are estimated in accordance with Ref. 321.

A. He–CO

*Ab initio* second virial coefficients of He–CO for temperatures ranging from 77.3 to 300 K are compared with the experimental data²₃⁹,³₀⁷,³₀₈ in Table 2 (see also Fig. 1). The SAPT potential reported in Chapter 4 was employed in the calculations. The data of Ref. 308 are extracted from the measurements of Ref. 307 by taking into account that the reference value at room temperature (296.2 K) has been determined more accurately. Furthermore, the data for He–CO have been compared with data for mixtures of helium and neon with argon, N₂, and O₂. From this comparison corrected values for the virial coefficients of He–CO have been estimated. Virial coefficients B(T) at round temperature numbers are shown in Table 2 and Fig. 1.

An inspection of Table 2 shows that there is very good agreement between theory and all three sets of experimental data, except for the lowest two temperatures. This good agreement for intermediate and high temperatures is also supported by small values of the root mean square deviations: σ = 0.505 for the 1986 data of Schramm and collaborators,³₀⁷ 0.113 for the most recent data of Schramm,³₀₈ and 0.231 for the older data of Brewer²₃⁹ (see the second, fourth, and fifth rows of Table 7).

At the lowest two temperatures (77.3 and 90.1 K) there is substantial disagreement between theory and experiment. Table 2 shows that the classical term B⁰(T), which is a lower bound to the exact B(T), is outside the error bars of the new experimental data and only just inside the error bars of the old measurements. The substantial disagreement between experimental and *ab initio* data therefore cannot be explained by the fact that higher-order quantum corrections are neglected. The large difference between the observed and calculated data is quite surprising considering the good agreement for
higher temperatures. Indeed, if the data of Ref. 308 at very low temperatures are compared with corresponding data for He–Ar, Ne–Ar, and Ne–CO complexes, one would estimate the virial coefficients for He–CO at $T = 77.3$ and 90.1 K to be 4 or 5 cm$^3$ mol$^{-1}$ more positive. This would bring the data of Ref. 308 up to $6$ and 1 cm$^3$ mol$^{-1}$ at $T = 77.3$ and 90.1 K, respectively, which is still 7 and 5 cm$^3$ mol$^{-1}$, respectively, below the ab initio data. However, inclusion of the second-order quantum correction could possibly yield virial coefficients that agree with the measured data within the experimental error bars.

**B. Ne–CO**

The comparison of the theoretical and experimental second virial coefficients for Ne–CO is presented in Table 3 and Fig. 2. Two sets of data are available for this system. Brewer$^{239}$ measured $B(T)$ for five temperatures $123.15$ K $\leq T \leq 273.15$ K. Very recently Vatter et al.$^{309}$ reported high temperature values at $T = 296.15, 353.15,$ and 463.15 K. The accuracy of Brewer’s data is not known, but the experimental uncertainty has been estimated by Trengove et al.$^{321}$ to be $\pm 2 – 3$ cm$^3$ mol$^{-1}$. Our computed values agree with the experiment$^{239}$ well
FIG. 3. Comparison of the theoretical and some of the experimental second virial coefficients for Ar–H₂ as functions of the temperature. Circles and triangles denote experimental data from Refs. 310 and 312, respectively.

within the estimated error bars. The agreement with the new data of Ref. 309 is very satisfactory. The overall agreement between theory and experiment is very satisfactory as well: the root mean square deviation is \( \sigma = 0.509 \) (see Table 7). Table 3 shows that all the calculated values are lower than the measured data, suggesting that a very small change in the potential could bring experimental and calculated values to even better agreement.

C. Ar–H₂

The Ar–H₂ van der Waals molecule is one of the most thoroughly investigated atom–diatom complexes. It is not surprising, then, that several sets of the experimental second virial coefficients at various temperatures are available for this system. At intermediate and high temperatures the theoretical values of \( B(T) \) agree very well with the majority of the experimental data (see Table 4 and Fig. 3). The overall good agreement between theory and experiment is also illustrated by the root mean square deviations for all sets of the experimental data. The values of \( \sigma \) reported in Table 7 are always smaller than unity, and range from 0.154 to 0.460.

At low temperatures the agreement between the \textit{ab initio} results and the
TABLE 4. Comparison of the theoretical and experimental second virial coefficients for Ar–H₂ (in cm³ mol⁻¹) as functions of the temperature (in K).

<table>
<thead>
<tr>
<th>T</th>
<th>B⁰(T)</th>
<th>B¹(A)</th>
<th>B¹(C)</th>
<th>B¹(calc)(T)</th>
<th>B¹(obs)(T)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.30</td>
<td>-80.988</td>
<td>9.200</td>
<td>0.222</td>
<td>-71.564</td>
<td>-84.5 ± 6.0</td>
<td>310</td>
</tr>
<tr>
<td>87.10</td>
<td>-64.693</td>
<td>6.965</td>
<td>0.153</td>
<td>-57.574</td>
<td>-65.8 ± 6.0</td>
<td></td>
</tr>
<tr>
<td>90.10</td>
<td>-60.597</td>
<td>6.453</td>
<td>0.138</td>
<td>-54.904</td>
<td>-60.5 ± 6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>123.15</td>
<td>-31.123</td>
<td>3.345</td>
<td>0.059</td>
<td>-27.718</td>
<td>-26.87 ± 3.0</td>
<td>311</td>
</tr>
<tr>
<td>148.15</td>
<td>-18.961</td>
<td>2.347</td>
<td>0.038</td>
<td>-16.576</td>
<td>-16.82 ± 3.0</td>
<td></td>
</tr>
<tr>
<td>173.15</td>
<td>-10.844</td>
<td>1.768</td>
<td>0.027</td>
<td>-9.048</td>
<td>-9.58 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>198.15</td>
<td>-5.078</td>
<td>1.398</td>
<td>0.021</td>
<td>-3.658</td>
<td>-4.16 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>223.15</td>
<td>-0.793</td>
<td>1.145</td>
<td>0.017</td>
<td>-0.369</td>
<td>-0.48 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>248.15</td>
<td>2.498</td>
<td>0.962</td>
<td>0.014</td>
<td>3.474</td>
<td>2.63 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>273.15</td>
<td>5.093</td>
<td>0.825</td>
<td>0.012</td>
<td>5.930</td>
<td>5.31 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>7.182</td>
<td>0.719</td>
<td>0.010</td>
<td>7.911</td>
<td>7.80 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>323.15</td>
<td>8.892</td>
<td>0.635</td>
<td>0.009</td>
<td>9.536</td>
<td>9.41 ± 2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>0.027</td>
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</tr>
<tr>
<td>200.0</td>
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<td>1.376</td>
<td>0.020</td>
<td>-3.320</td>
<td>-4.5 ± 3.0</td>
<td></td>
</tr>
<tr>
<td>250.0</td>
<td>2.711</td>
<td>0.951</td>
<td>0.014</td>
<td>3.676</td>
<td>3.3 ± 3.0</td>
<td></td>
</tr>
<tr>
<td>300.0</td>
<td>7.320</td>
<td>0.712</td>
<td>0.010</td>
<td>8.042</td>
<td>8.1 ± 3.0</td>
<td></td>
</tr>
<tr>
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<td>0.562</td>
<td>0.008</td>
<td>10.977</td>
<td>11.4 ± 3.0</td>
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</tr>
<tr>
<td>400.0</td>
<td>12.584</td>
<td>0.460</td>
<td>0.007</td>
<td>13.051</td>
<td>13.8 ± 3.0</td>
<td></td>
</tr>
<tr>
<td>450.0</td>
<td>14.179</td>
<td>0.387</td>
<td>0.006</td>
<td>14.572</td>
<td>15.6 ± 3.0</td>
<td></td>
</tr>
<tr>
<td>500.0</td>
<td>15.380</td>
<td>0.332</td>
<td>0.005</td>
<td>15.717</td>
<td>16.7 ± 3.0</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>170.0</td>
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<td>-10.3 ± 2.0</td>
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<tr>
<td>180.0</td>
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<td>1.651</td>
<td>0.025</td>
<td>-7.400</td>
<td>-7.8 ± 2.0</td>
<td></td>
</tr>
<tr>
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<td>-6.763</td>
<td>1.503</td>
<td>0.023</td>
<td>-5.237</td>
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</tr>
<tr>
<td>200.0</td>
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<td>1.376</td>
<td>0.020</td>
<td>-3.320</td>
<td>-4.0 ± 2.0</td>
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</tr>
<tr>
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<td>0.019</td>
<td>-1.612</td>
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<td>220.0</td>
<td>-1.271</td>
<td>1.172</td>
<td>0.017</td>
<td>-0.081</td>
<td>-0.9 ± 2.0</td>
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</tr>
<tr>
<td>230.0</td>
<td>0.192</td>
<td>1.089</td>
<td>0.016</td>
<td>1.297</td>
<td>0.3 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>240.0</td>
<td>1.513</td>
<td>1.016</td>
<td>0.015</td>
<td>2.544</td>
<td>1.5 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>250.0</td>
<td>2.711</td>
<td>0.951</td>
<td>0.014</td>
<td>3.676</td>
<td>2.5 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>260.0</td>
<td>3.801</td>
<td>0.893</td>
<td>0.013</td>
<td>4.707</td>
<td>3.5 ± 2.0</td>
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</tr>
<tr>
<td>270.0</td>
<td>4.797</td>
<td>0.840</td>
<td>0.012</td>
<td>5.650</td>
<td>4.2 ± 2.0</td>
<td></td>
</tr>
</tbody>
</table>

(Continued on next page)
measurement of Schramm et al. is less satisfactory. Two explanations for this disagreement are possible. First of all, at these temperatures the quantum effects are rather important, and the second quantum correction may be responsible for the 10–15% disagreement. The authors of Ref. 310 suggest another possibility. Due to slightly different temperatures and unequal ambient pressures in different experiments, the experimental values for $B(T)$ were interpolated to the same temperature. After the interpolation all values agreed within ±9 cm$^3$ mol$^{-1}$, although more than 90% of the measurements agreed within ±6 cm$^3$ mol$^{-1}$. If we tentatively assume that the experimental error bars are ±9 cm$^3$ mol$^{-1}$ we get agreement between theory and experiment for $T = 87.1$ and 90.1 K, and a small disagreement for $T = 77.3$ K which may very well be due to higher quantum effects neglected in the present study. At this point we should note, however, that the experimental value for $T = 90.1$ K is in excellent agreement with the value of $-59 \pm 3$ cm$^3$ mol$^{-1}$ obtained from analyzing the independent measurement of Ref. 318 as discussed in section III.

Because of the “atomic” character of the H$_2$ molecule the intermolecular potential of Ar–H$_2$ is dominated by the isotropic contribution $V_0$ in Eq. (7). This can also be demonstrated by replacing the potential by its isotropic term in the calculation of virial coefficients and comparing the results with the data obtained with the fully expanded potential. Then the difference between the two sets of virial coefficients is less than 0.1 cm$^3$ mol$^{-1}$ for all temperatures listed in Table 4. Complexes containing H$_2$ are exceptional in this context, in general inclusion of anisotropic terms in the potential is necessary to obtain converged results as was demonstrated e.g. for the He–CO complex.

### Table 4. Continued

<table>
<thead>
<tr>
<th>$T$</th>
<th>$B^{(0)}(T)$</th>
<th>$B^{(1)}_R(T)$</th>
<th>$B^{(1)}_A(T)$</th>
<th>$B^{(1)}_S(T)$</th>
<th>$B^{calc}(T)$</th>
<th>$B^{obs}(T)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.2</td>
<td>7.185</td>
<td>0.719</td>
<td>0.010</td>
<td>0.000</td>
<td>7.915</td>
<td>7.93 ± 1.0$^a$</td>
<td>314</td>
</tr>
<tr>
<td>322.2</td>
<td>8.832</td>
<td>0.638</td>
<td>0.009</td>
<td>0.000</td>
<td>9.480</td>
<td>9.30 ± 1.0$^a$</td>
<td></td>
</tr>
<tr>
<td>348.2</td>
<td>10.314</td>
<td>0.567</td>
<td>0.008</td>
<td>0.000</td>
<td>10.889</td>
<td>10.98 ± 1.0$^a$</td>
<td></td>
</tr>
<tr>
<td>373.2</td>
<td>11.506</td>
<td>0.510</td>
<td>0.007</td>
<td>0.000</td>
<td>12.024</td>
<td>12.53 ± 1.5$^a$</td>
<td></td>
</tr>
<tr>
<td>398.2</td>
<td>12.517</td>
<td>0.463</td>
<td>0.007</td>
<td>0.000</td>
<td>12.988</td>
<td>13.78 ± 1.5$^a$</td>
<td></td>
</tr>
<tr>
<td>423.2</td>
<td>13.383</td>
<td>0.423</td>
<td>0.006</td>
<td>0.000</td>
<td>13.813</td>
<td>14.88 ± 2.0$^a$</td>
<td></td>
</tr>
<tr>
<td>447.2</td>
<td>14.101</td>
<td>0.391</td>
<td>0.006</td>
<td>0.000</td>
<td>14.498</td>
<td>15.82 ± 2.0$^a$</td>
<td></td>
</tr>
<tr>
<td>290.0</td>
<td>6.547</td>
<td>0.751</td>
<td>0.011</td>
<td>0.000</td>
<td>7.309</td>
<td>7.2 ± 1.0$^a$</td>
<td>245</td>
</tr>
<tr>
<td>300.0</td>
<td>7.320</td>
<td>0.712</td>
<td>0.010</td>
<td>0.000</td>
<td>8.042</td>
<td>7.8 ± 1.0$^a$</td>
<td></td>
</tr>
<tr>
<td>320.0</td>
<td>8.694</td>
<td>0.644</td>
<td>0.009</td>
<td>0.000</td>
<td>9.348</td>
<td>9.3 ± 1.0$^a$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Estimated errors.
$^b$Smoothed values from Ref. 312.
$^c$Smoothed values from Ref. 313.
Numerical results for Ar–CH₄

TABLE 5. Theoretical second virial coefficient for He–C₂H₂ (in cm³ mol⁻¹) as a function of the temperature (in K) and comparison with experiment for \( T = 296.15 \) K.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( B^{(0)}(T) )</th>
<th>( B^{(1)}_{R}(T) )</th>
<th>( B^{(1)}_{A}(T) )</th>
<th>( B^{(1)}_{C}(T) )</th>
<th>( B^{calc}(T) )</th>
<th>( B^{obs}(T) )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>150.0</td>
<td>18.368</td>
<td>0.839</td>
<td>0.075</td>
<td>0.029</td>
<td>19.331</td>
<td></td>
<td></td>
</tr>
<tr>
<td>175.0</td>
<td>21.180</td>
<td>0.685</td>
<td>0.060</td>
<td>0.024</td>
<td>21.949</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200.0</td>
<td>23.134</td>
<td>0.565</td>
<td>0.050</td>
<td>0.020</td>
<td>23.769</td>
<td></td>
<td></td>
</tr>
<tr>
<td>225.0</td>
<td>24.538</td>
<td>0.478</td>
<td>0.043</td>
<td>0.017</td>
<td>25.076</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250.0</td>
<td>25.572</td>
<td>0.413</td>
<td>0.037</td>
<td>0.015</td>
<td>26.038</td>
<td></td>
<td></td>
</tr>
<tr>
<td>275.0</td>
<td>26.347</td>
<td>0.362</td>
<td>0.033</td>
<td>0.014</td>
<td>26.756</td>
<td></td>
<td></td>
</tr>
<tr>
<td>296.15</td>
<td>26.855</td>
<td>0.327</td>
<td>0.030</td>
<td>0.013</td>
<td>27.225</td>
<td>28.5 ± 2.0</td>
<td>315</td>
</tr>
<tr>
<td>300.0</td>
<td>26.935</td>
<td>0.321</td>
<td>0.029</td>
<td>0.013</td>
<td>27.299</td>
<td></td>
<td></td>
</tr>
<tr>
<td>325.0</td>
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<td>0.288</td>
<td>0.027</td>
<td>0.011</td>
<td>27.711</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350.0</td>
<td>27.729</td>
<td>0.261</td>
<td>0.024</td>
<td>0.011</td>
<td>28.024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>375.0</td>
<td>27.992</td>
<td>0.238</td>
<td>0.022</td>
<td>0.010</td>
<td>28.261</td>
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<td></td>
</tr>
<tr>
<td>400.0</td>
<td>28.192</td>
<td>0.218</td>
<td>0.020</td>
<td>0.009</td>
<td>28.439</td>
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<td></td>
</tr>
</tbody>
</table>

D. He–C₂H₂

Calculated second virial coefficients for the He–C₂H₂ complex are listed as a function of temperature in Table 5. Recently, \( B(T) \) has been measured for a single temperature \( T = 296.15 \) K. The agreement between the \textit{ab initio} and experimental data is very good and the value of \( \sigma \) reported in Table 7 suggests that the experimental error bars may be too large.

E. Ar–CH₄

In the last few decades, several measurements of second virial coefficients have been reported for the Ar–CH₄ complex. In Table 6 we present \textit{ab initio} and experimental data for this system in the temperature range \( T = 107.1 \) up to 550 K. The calculated virial coefficients and a selection of the experimental data are also depicted in Fig. 4.

The data quoted in Table 6 were measured with two types of experiments. In Refs. 239 and 245 pressure differences were measured after mixing two pure gases. Both sets of experiments cover different but neighboring temperature regions and agree very well. We believe these measurements to be the most reliable ones and we extract from these measurements the interaction second virial coefficient at 296.2 K: \( B_{12} = -25.2 \) cm³ mol⁻¹. All the other measurements were performed using the temperature changing method described in Sec. III. For this method a starting value is needed. In Ref. 240 it was calculated using a Lennard–Jones potential and simple combination rules. In Heidelberg it was measured twice with a compression method. In these
TABLE 6. Comparison of the theoretical and experimental second virial coefficients for Ar—CH₄ (in cm³ mol⁻¹) as functions of the temperature (in K). The second virial coefficient of −25.2 cm³ mol⁻¹ at $T = 296.15$ K is taken as a reference point. All other values have been corrected accordingly: data from Ref. 238 have been shifted 1.4 cm³ mol⁻¹ more positive, data from Ref. 240 have been shifted 3.1 cm³ mol⁻¹ more positive, data from Ref. 241 have been shifted 3.3 cm³ mol⁻¹ more positive, data from Ref. 242 have been shifted 4.1 cm³ mol⁻¹ more negative, data from Ref. 243 have been shifted 3.2 cm³ mol⁻¹ more negative, and data from Ref. 244 have been shifted 3.7 cm³ mol⁻¹ more positive.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$B^{(0)}(T)$</th>
<th>$B^{(1)}_R(T)$</th>
<th>$B^{(1)}_A(T)$</th>
<th>$B^{(1)}_C(T)$</th>
<th>$B^{\text{calc}}(T)$</th>
<th>$B^{\text{obs}}(T)$</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>123.15</td>
<td>−171.384</td>
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<td>1.873</td>
<td>0.041</td>
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<td>−149.07 ± 3.0</td>
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<tr>
<td>148.15</td>
<td>−120.874</td>
<td>1.142</td>
<td>1.091</td>
<td>0.024</td>
<td>−118.618</td>
<td>−123.05 ± 3.0</td>
<td></td>
</tr>
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<td>173.15</td>
<td>−89.176</td>
<td>0.778</td>
<td>0.716</td>
<td>0.016</td>
<td>−87.666</td>
<td>−90.89 ± 2.5</td>
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</tr>
<tr>
<td>223.15</td>
<td>−51.818</td>
<td>0.440</td>
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<td>−50.987</td>
<td>−53.80 ± 2.5</td>
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</tr>
<tr>
<td>273.15</td>
<td>−30.683</td>
<td>0.291</td>
<td>0.241</td>
<td>0.006</td>
<td>−30.145</td>
<td>−32.55 ± 2.0</td>
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<td>0.005</td>
<td>−25.035</td>
<td>−27.0 ± 2.0</td>
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<td>0.005</td>
<td>−22.324</td>
<td>−24.2 ± 2.0</td>
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</tr>
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<td>320.0</td>
<td>−17.893</td>
<td>0.215</td>
<td>0.172</td>
<td>0.004</td>
<td>−17.502</td>
<td>−19.0 ± 2.0</td>
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</tr>
<tr>
<td>108.61</td>
<td>−217.158</td>
<td>2.695</td>
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<td>−211.616</td>
<td>−251.5 ± 8.0</td>
<td>238</td>
</tr>
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<td>142.6</td>
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<td>1.260</td>
<td>1.215</td>
<td>0.027</td>
<td>−127.492</td>
<td>−137.2 ± 5.0</td>
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</tr>
<tr>
<td>176.7</td>
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<td>0.679</td>
<td>0.015</td>
<td>−84.178</td>
<td>−85.2 ± 3.0</td>
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</tr>
<tr>
<td>239.8</td>
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<td>0.379</td>
<td>0.323</td>
<td>0.008</td>
<td>−42.868</td>
<td>−46.7 ± 2.0</td>
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<td>295.0</td>
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<td>0.205</td>
<td>0.005</td>
<td>−23.652</td>
<td>−25.5 ± 2.0</td>
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</tr>
<tr>
<td>107.10</td>
<td>−223.001</td>
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<td>0.063</td>
<td>−217.209</td>
<td>−230.0 ± 8.0</td>
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</tr>
<tr>
<td>109.69</td>
<td>−213.128</td>
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<td>0.045</td>
<td>−177.270</td>
<td>−186.3 ± 7.0</td>
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<td>0.037</td>
<td>−156.844</td>
<td>−165.3 ± 7.0</td>
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<td>−133.783</td>
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<td>−116.1 ± 5.0</td>
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<td>0.016</td>
<td>−86.615</td>
<td>−90.9 ± 4.0</td>
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<td>−71.774</td>
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<td>208.79</td>
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<td>0.010</td>
<td>−59.291</td>
<td>−63.0 ± 3.0</td>
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</tr>
<tr>
<td>228.96</td>
<td>−48.774</td>
<td>0.417</td>
<td>0.360</td>
<td>0.008</td>
<td>−47.989</td>
<td>−51.0 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>240.95</td>
<td>−39.208</td>
<td>0.348</td>
<td>0.294</td>
<td>0.007</td>
<td>−38.559</td>
<td>−40.8 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>274.15</td>
<td>−30.355</td>
<td>0.289</td>
<td>0.240</td>
<td>0.006</td>
<td>−29.821</td>
<td>−32.1 ± 2.0</td>
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</table>

(Continued on next page)
**TABLE 6. Continued**

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<th>$T$</th>
<th>$B^{(0)}(T)$</th>
<th>$B_{ii}^{(1)}(T)$</th>
<th>$B_{11}^{(1)}(T)$</th>
<th>$B_{12}^{(1)}(T)$</th>
<th>$B^{\text{calc}}(T)$</th>
<th>$B^{\text{obs}}(T)$</th>
<th>Ref.</th>
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<td>0.203</td>
<td>0.005</td>
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<td>0.002</td>
<td>9.881</td>
<td>5.5 ± 9.0$^b$</td>
<td></td>
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</tbody>
</table>

$^a$Experimental errors are estimated in accordance with Ref. 251.

$^b$Estimated errors.
Chapter 8: Second virial coefficients from SAPT potentials

experiments the gas mixture and a well known gas for comparison were compressed with mercury to half of their volumes and a small pressure difference was measured that builds up because of the nonideal behavior of the gases. The different results, being about $-22$ and $-28$ cm$^3$ mol$^{-1}$ for the measurements reported in Refs. 241 and 244, respectively, show that this method is not very reliable, probably because of some solubility of the gases in mercury. (Therefore the expansion method was used in later experiments.) A shift in the room temperature virial coefficient has a simple consequence for all the other data that were gained with the help of the temperature changing method: It shifts the data with the same amount. In Table 6 we have shifted the experimental data in accordance with the corrected value of the virial coefficient at room temperature.

All experimental data agree well within the estimated error bounds given in Table 6, except that the values of Ref. 239 at $T = 123.15$ K and of Ref. 238 at $T = 108.61$ K do not agree with the data of Ref. 240. At very low temperatures such deviations are easily caused by inhomogeneities in the temperature bath, as was also discussed by Byrne et al.$^{240}$ Another exception is the measurement at $T = 159.88$ K from Ref. 240 which does not agree with the other data.

FIG. 4. Comparison of the theoretical and some of the experimental second virial coefficients for Ar–CH$_4$ as functions of the temperature. Full squares, full circles, open squares, and open circles denote experimental data from Refs. 239, 245, 243, and 244, respectively.
Numerical results for Ar–CH$_4$

from this work. The experimental data at other than the lowest temperatures show a clear relation compared to the calculations. Except for the data at $T = 123.15$ K$^{239}$ and 211.4 K$^{243}$ the calculated virial coefficients are more positive than the experimental values. The theoretical coefficients are within the experimental error bars of the data from Refs. 241–245, except for the data at the two lowest temperatures from Ref. 244, and the data from Ref. 238 at $T = 176.7$ K and 295 K. The computed values do not agree within the error bars of the other data from Ref. 238 and of the data from Refs. 239 and 240. Consequently, Table 7 shows that the values of $\sigma$ for Ar–CH$_4$ are smaller than unity for the sets of data from Refs. 241–245 and equal to 2.990, 2.579, and 1.429 for the data from Refs. 239, 238, and 240, respectively, which include low temperature measurements. The latter three data sets greatly affect the overall value of $\sigma$ which is larger than unity, in contrast with the root mean square deviations for the other systems considered in this work.

The disagreement between measurement and calculation at low temperatures may well be caused by inaccuracies in the experimental methods. In view of the nature of the Ar–CH$_4$ complex quantum corrections beyond the first order are probably small at the temperatures above 100 K. Calculated second virial coefficients are mainly sensitive to the potential well depth. Consequently, the fact that the theoretical virial coefficients are in general more positive than the experimental values suggests that the well of the applied SAPT potential is slightly too shallow. The potential of the Ar–CH$_4$ complex is dominated by the dispersion contribution more than the other potentials regarded in this work because of the large (dynamic) polarizabilities of the monomers. It is the dispersion term which suffers most from basis set incompleteness since basis functions with large angular momenta and small exponents are required. To study the effect of the basis set we also computed second virial coefficients for Ar–CH$_4$ mixtures using the unscaled SAPT potential, cf. Chapter 6. It was found that the agreement with the observed data was considerably worse than for the asymptotically scaled potential, the calculated data being more positive than the experimental values by 16 ± 4, 10 ± 3, and 6 ± 2 cm$^3$ mol$^{-1}$ for temperatures around 150, 200, and 300 K, respectively. Clearly, the quality of the basis set employed in the ab initio calculations is of great importance for the theoretical second virial coefficients. Therefore we conclude that the slightly worse agreement with experiment compared to the other systems is due to inaccuracies in the basis rather than to shortcomings of the SAPT method.
### Table 7

Dimensionless root mean square deviations of various experimental data from the second virial coefficients computed with the *ab initio* SAPT potentials.

<table>
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<tr>
<th>System</th>
<th>Ref.</th>
<th># values</th>
<th>$T$ range (K)</th>
<th>$\sigma$</th>
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<td>8</td>
<td>77.30–296.20</td>
<td>0.733</td>
</tr>
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<td>307</td>
<td>6</td>
<td>143.00–296.20</td>
<td>0.505</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>6</td>
<td>77.30–300.00</td>
<td>1.140</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>4</td>
<td>150.00–300.00</td>
<td>0.113</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>5</td>
<td>123.15–273.15</td>
<td>0.231</td>
</tr>
<tr>
<td></td>
<td>239,307,308</td>
<td>19</td>
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<td>239</td>
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<td>123.15–273.15</td>
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</tr>
<tr>
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<td>296.15–403.15</td>
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</tr>
<tr>
<td></td>
<td>239,309</td>
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<td>123.15–403.15</td>
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<tr>
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<td>129</td>
<td>77.30–550.00</td>
<td>1.120</td>
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V. CONCLUSIONS

Virial coefficients computed \textit{ab initio} from SAPT potentials are in excellent agreement with experimental data for the He–CO, Ne–CO, Ar–H\textsubscript{2}, and He–C\textsubscript{2}H\textsubscript{2} complexes over a wide temperature range. At very low temperatures inhomogeneities in the temperature bath can occur and virial coefficients for the pure components of the mixture are not always accurately known. These problems can cause large deviations in the observed virial coefficients which impede a significant comparison with \textit{ab initio} values. From a computational point of view this implies that the influence of quantum corrections on the virial coefficients cannot be determined very accurately since $B(T)$ is dominated by the classical contribution for temperatures where comparison with experiment is meaningful. More accurate measurements would be necessary to compare between theory and experiment in the very low temperature range.

In contrast with the other complexes discussed in this work, theoretical virial coefficients for Ar–CH\textsubscript{4} lie outside the experimental error bounds for some of the measured data sets, even at other than very low temperatures. This can be explained by inaccuracies in the dispersion contribution to the SAPT potential, which are small on an absolute scale but relatively large in comparison with the other complexes. As a consequence, the relative root mean square deviation, as defined in Sec. IV, is 1.434 for the Ar–CH\textsubscript{4} complex where it is smaller than unity for all other systems.

In general, we conclude that SAPT potentials applied to calculate second virial coefficients give results which are in very good agreement with the majority of the experimental data available.

ACKNOWLEDGMENTS

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Chapter 9

Total differential cross sections and differential energy loss spectra for He–C2H2 from an ab initio potential*

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Abstract

State-to-state elastic and rotationally inelastic differential cross sections for He + C2H2 scattering have been obtained by means of converged close-coupling calculations. An ab initio potential computed by symmetry-adapted perturbation theory (SAPT) was used. From these state-resolved data total differential cross sections at $E_{cm} = 71.3$ meV and energy loss spectra at $E_{cm} = 62.0$ and 102.9 meV have been determined by transformation to the laboratory frame and accounting for the experimental conditions via a Monte-Carlo averaging procedure. The results are in excellent agreement with experiment [U. Buck et al., J. Chem. Phys. 99, 3494 (1993)], which proves that the SAPT potential is indeed very accurate.

I. INTRODUCTION

The most sensitive probes of intermolecular potential energy surfaces (IPSs) are high-resolution spectra of van der Waals molecules and molecular beam scattering data. While the infrared spectra are mainly sensitive to the interaction potential in the region of the van der Waals well, the scattering experiments yield information about the interaction both in the attractive and repulsive regions. The most detailed beam scattering data are provided by state-to-state experiments. However, also total differential cross sections and (state-unresolved) differential energy loss spectra contain useful information about the anisotropy of the interaction, especially about the repulsive wall region.

In principle the total differential cross sections measurements can be used to extract intermolecular potential energy surfaces. The inversion procedure is well understood for atomic systems, but the determination of anisotropic potentials remains still nontrivial, and may be highly nonunique. Moreover, since the scattering data probe mainly the repulsive region in the potential, the IPSs derived from these data may be incompatible with spectroscopic information. On the other hand, ab initio potential energy surfaces that maintain good accuracy both in the attractive and repulsive regions are becoming available. Since nowadays accurate quantum close-coupling calculations have become feasible, theoretical studies of elementary collisional processes based on accurate ab initio potentials and exact description of the quantum dynamics become important for the interpretation of the growing body of experimental data obtained by more and more sophisticated experimental techniques.

Van der Waals complexes containing the acetylene molecule have been object of many molecular beam experiments. In particular, the He-C$_2$H$_2$ complex has been almost exclusively investigated using scattering techniques. Danielson et al. measured total differential cross sections and diffusion coefficients for this system. The cross sections showed pronounced oscillatory structure, suggesting a rather small anisotropy of the potential energy surface. Indeed, the scattering and bulk data could be accurately reproduced by an analytical potential fit with parameters expanded up to and including the second Legendre polynomial $P_2$. These results were in a sharp contrast to results obtained for the He-CO$_2$ complex. The differential scattering data for the latter system showed a pronounced rotational rainbow, suggesting a large anisotropy in the interaction mainly due to the linear extension of the CO$_2$ molecule.

Recently, Schlemmer, Faubel, and Buck et al. reported total differential cross sections and differential energy loss spectra for the He-C$_2$H$_2$ complex at various collision energies. While the total differential cross sections could be
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successfully reproduced by the potential of Danielson et al.,\textsuperscript{208} this potential failed to reproduce the measured differential energy loss spectra, especially at larger collision energies.\textsuperscript{209-211} Schlemmer,\textsuperscript{209} Faubel,\textsuperscript{210} and Buck et al.\textsuperscript{211} demonstrated that the energy loss spectra are much better reproduced by a potential revealing a spindle-shaped contour\textsuperscript{330} in the repulsive region rather than the more usual ellipsoidal shape. This suggests that the anisotropy of the scattering potential of Ref. 208 is not entirely correct, at least in the repulsive wall region. Recently, Bemish and Miller\textsuperscript{199} measured the near-infrared spectrum of the He–C\textsubscript{2}H\textsubscript{2} molecule corresponding to the simultaneous excitation of the asymmetric stretch vibration and hindered rotation of the C\textsubscript{2}H\textsubscript{2} monomer within the complex. The experimental spectrum could not be successfully assigned\textsuperscript{217} by the use of the potential derived from scattering and bulk data.\textsuperscript{208}

In a recent paper an intermolecular potential energy surface for the He–C\textsubscript{2}H\textsubscript{2} complex was reported,\textsuperscript{79} which was computed using the symmetry-adapted perturbation theory (SAPT).\textsuperscript{4,63-67,95} Each contribution to the interaction energy was fitted to an analytical form with physically interpretable parameters. This potential was shown\textsuperscript{79} to reproduce all major features of the recorded near-infrared spectrum.\textsuperscript{199} These results suggested that the anisotropy of the SAPT potential for this system is correct, at least in the potential well region. Since experimental total differential cross sections and differential energy loss spectra are available for this system as well, one can use these data to further test the accuracy of the \textit{ab initio} SAPT potential.

The concept of spindle-shaped potentials was introduced into the field of molecular physics by Kihara and coworkers\textsuperscript{330} to determine orientation dependent Lennard–Jones intermolecular potentials that reproduce the observed second virial coefficients of molecular gases. Nowadays, more advanced models are used to describe interactions between molecules. As a matter of fact, both the perturbational\textsuperscript{4} and supermolecule\textsuperscript{331} approaches interpret the interaction energies in terms of four fundamental components: electrostatics, exchange, induction, and dispersion, as defined by the symmetry-adapted perturbation theory. Since for He–C\textsubscript{2}H\textsubscript{2} a spindle-shaped potential was necessary to reproduce the observed differential energy loss spectra,\textsuperscript{209-211} it is interesting to see to what extent an \textit{ab initio} potential — computed using a high-level treatment of the electron correlation effects — reveals spindle-shaped contours in the repulsive region. If there are any, our \textit{ab initio} results will tell us which physical contributions are responsible for them.

In the present chapter we report the results of exact close-coupling (CC) calculations of differential cross sections for He–C\textsubscript{2}H\textsubscript{2} at collision energies of $E_{cm} = 62.0, 71.3,$ and 102.9 meV. These calculations are based on the recent
Chapter 9: Differential cross sections for \( \text{He} - \text{C}_2\text{H}_2 \)

SAPT potential. The total differential cross sections at \( E_{\text{cm}} = 71.3 \) meV are compared with the recent experimental results, while the state-to-state differential cross sections at \( E_{\text{cm}} = 62.0 \) and 102.9 meV are used to generate the (state-unresolved) energy loss spectra. The latter are again compared with the results of measurements.

II. OUTLINE OF CLOSE-COUPLING SCATTERING CALCULATIONS

The coordinate system used in the CC method is a space-fixed frame. The wave function \( \Psi_E^{J,M}(\vec{R}, \vec{r}, \vec{R}) \) for an atom-rigid linear molecule system corresponding to the total energy \( E \), total angular momentum \( J \), its projection \( M \) on the space-fixed \( z \) axis, and parity \( p \) can be written as an expansion,

\[
\Psi_E^{J,M}(\vec{R}, \vec{r}, \vec{R}) = \sum_{j,l} \chi_{jl}(\vec{R}) \left[ Y_j(\vec{r}) \otimes Y_l(\vec{R}) \right]^J_M,
\]

where \( \vec{r} \) specifies the orientation of the molecule and \( \vec{R} \) stands for the polar angles of the intermolecular vector \( \vec{R} \), both with respect to the space-fixed frame. The angle between the vector \( \vec{R} \) and the molecular axis is denoted \( \gamma \). The angular functions are Clebsch–Gordan coupled products of spherical harmonics \( Y_{m_j}^{j}(\vec{r}) \) and \( Y_{m_l}^{l}(\vec{R}) \),

\[
[Y_j(\vec{r}) \otimes Y_l(\vec{R})]^J_M = \sum_{m_j,m_l} \langle j, m_j; l, m_l | J, M \rangle Y_{m_j}^{m_j}(\vec{R}) Y_{m_l}^{m_l}(\vec{r}),
\]

where \( \langle j, m_j; l, m_l | J, M \rangle \) denotes the standard Clebsch–Gordan coefficient. The radial functions \( \chi_{jl}(\vec{R}) \) are solutions of the system of coupled differential equations (close-coupling equations).

The angular basis of Eq. (2) is adapted to the permutation inversion group \( \mathcal{P}(C_2v) \). In other words, the scattering states with even and odd \( j \) correspond to states of para and ortho acetylene in the ground vibrational state, respectively. The asymptotic form of the functions \( \chi_{jl}(\vec{R}) \) determines the \( S \) matrix elements \( S_{jl,j'j''}^{Jp} \). These in turn define the state-to-state differential cross section by the usual expression (see e.g. Ref. 333).

The close-coupling scattering equations were solved using the hybrid integrator of Alexander. The log-derivative algorithm of Mrugala and Secrest was used to propagate from \( R_{\text{min}} \) to \( R_{\text{end}} = 11.0 \) bohr with a constant step of \( \Delta R = 0.08 \) bohr, and the Airy propagator was used to propagate from \( R_{\text{end}} \) to \( R_{\text{max}} \). The starting point of the integration \( R_{\text{min}} \) was fixed at 4.5, 4.5, and 4.25 bohr for collision energies of 62.0, 71.3, and 102.9 meV, respectively. The corresponding end points were 80.0 bohr for all three collision energies. For \( E_{\text{cm}} \)
III. NUMERICAL RESULTS AND DISCUSSION

A. Total differential cross sections

Experimental data for the total (i.e., summed over all inelastic and elastic channels) differential cross sections of He + C₂H₂ are given in Fig. 1 for the collision energy of \( E_{\text{cm}} = 71.3 \text{ meV} \). In order to enable comparison with experiment, the calculated data were averaged over the angular and velocity distributions of the two beams and were corrected for the energy response and
physical size of the detector. Furthermore, they were transformed from the center-of-mass (c.m.) to the laboratory (lab) frame. The result is displayed in Fig. 1. The agreement between theoretical and experimental data is nearly perfect. The positions as well as the amplitudes of the diffraction oscillations are reproduced by the calculations in all detail, which indicates that both the onset of the repulsive wall $R_0$ and the anisotropy of the minimum distance $R_m(\gamma)$ of the calculated potential surface are realistic.

**B. Energy loss spectra**

The second set of observables, the differential energy loss spectra, are essentially sensitive to the anisotropy of the interaction potential. They are measured with high angular, but low energy, resolution and thus contain information that makes it possible to distinguish between forward and backward scattering.
That is, the spectra discriminate between attractive and repulsive forces at the expense of the state selectivity. The experiment of Ref. 211, however, was conducted with C$_2$H$_2$ as primary beam and He as secondary beam. This leads to a reduction of the angular resolution, since the c.m. angular range of 180° is squeezed to 15° and 23° for the two collision energies $E_{cm} = 62.0$ and 102.9 meV, respectively. In addition, the Newton diagram is double-valued, so that the measured time-of-flight (TOF) spectra consist generally of a fast and a slow peak which correspond to one lab angle but two different c.m. angles. The results for different lab angles $\Theta$ and the two energies are shown in Figs. 2 and 3. In both cases the two peaks coalesce into one when the limiting scattering angle is approached, which occurs at 14° and 21.5° for $E_{cm} = 62.0$ and 102.9 meV, respectively. The c.m. angular range covers 60° to 180°. This means that mainly backward scattered particles were measured which probe the repulsive part of the potential.
A complicated averaging procedure is needed to compare these data with the computational results. The details of this procedure were described in Ref. 337. The intensity of the TOF spectrum at the lab angle $\Theta$ is given by

$$I(t, \Theta) = \sum_{l=1,2} \sum_{i \rightarrow f} p_i \left( \frac{d\sigma}{d\omega} \right)_{if} (g, \bar{\theta}) f(\Delta E_{if}, \Theta, t),$$

where $p_i$ is the relative initial state population and $(d\sigma/d\omega)_{if}$ is the c.m. differential cross section for a single rotational transition $i \rightarrow f$ which depends on the relative velocity $g$ and the c.m. scattering angle $\bar{\theta}$. The $l$ summation is over the fast and slow contribution mentioned above and the $i \rightarrow f$ summation contains all possible transitions which lead to the energy loss $\Delta E_{if}$ measured at the flight time $t$. The distribution function $f$ contains all the information concerning the averaging process and the transformation from the c.m. to the lab system.\textsuperscript{337} It was calculated by a Monte Carlo procedure, using as input information the measured angular and velocity distributions of the two beams. The critical region for this averaging process is the limiting angle. At this angle, the Jacobian of the transformation from the c.m. to the lab frame becomes singular. In practice, even the smallest spread in some of the variables leads to a finite intensity in the energy loss spectra. On the other hand, the actual values of this distribution depend critically on very small changes in velocity and position space. Therefore the calculation had to be performed very accurately, with hardly any approximations.\textsuperscript{338}

The initial state distribution in the experiment with 75\% ortho $C_2H_2$ and 25\% para $C_2H_2$ was 0.42 for $j = 1$, 0.28 for $j = 3$, 0.05 for $j = 5$, 0.13 for $j = 0$, 0.10 for $j = 2$, and 0.02 for $j = 4$.\textsuperscript{211} In the calculation we included therefore the initial states with $j = 1$, 3, 0, and 2. The final states are determined by the maximal possible energy transfer $\Delta E_{\text{max}}$ at each lab angle. These numbers were listed in Table III of Ref. 211. But also in this case we had to extend this range according to the calculated distribution $f$ in Eq. (3) because of the finite resolution.

An example is shown in Fig. 4. Here we compare the calculated energy loss spectrum with the measured one taken at $\Theta = 15^\circ$ and $E_{\text{cm}} = 62$ meV. According to the nominal, possible energy transfer $\Delta E_{\text{max}} = 17$ meV we included all transitions up to $j = 0 \rightarrow 10$ (16.07 meV) and $j = 2 \rightarrow 10$ (15.19 meV). The results in Fig. 4 show an appreciable deviation between measured and calculated values in the region of large energy transfer. If we, however, extend the range to 19.5 meV, a value which was calculated from the averaging procedure, and include the transitions $1 \rightarrow 11$ (18.99 meV) and $2 \rightarrow 12$ (17.53 meV) the agreement between experiment and theory is nearly perfect, as is shown in Fig. 2. This also exemplifies the influence of the transformation near the critical values of the Newton diagram, where two relatively small inelastic cross
Numerical results and discussion

Section contributions significantly to the energy loss spectra in the lab frame. All other spectra were generated in a similar way.

In general, we can state that the agreement between the calculated and the measured energy loss spectra in Figs. 2 and 3 is very good. This is valid for both collision energies. Not only do we find good agreement for the lab angles $\Theta = 12^\circ$ to $19^\circ$ at $E_{cm} = 102.9$ meV, equally good as found in Ref. 211 with an empirical potential, but also at the angles $\Theta = 20^\circ$, $21.5^\circ$, and $23^\circ$ nearly complete agreement is achieved. The same is true for the lower energy $E_{cm} = 62.0$ meV. Here, the disagreement at the small angles $\Theta = 8^\circ$ and $10^\circ$ found in Ref. 211, which was attributed to the failure of theIOS approximation, is completely removed in the new close-coupling calculations. The remaining small discrepancies at the larger deflection angles for $E_{cm} = 102.9$ meV could be caused by the omitted small contributions starting from the initial states with $j = 4$ and 5.

In any case, the good agreement between measurements and calculations indicates that the ab initio potential of Ref. 79 has also the correct anisotropy in the repulsive region. This anisotropy is larger than that of the empirical potential of Ref. 209. This is demonstrated in the upper part of Fig. 5 which shows the contour line $R(\gamma)$ for the energy $V = 62$ meV as a function of the orientation angle $\gamma$. The $R$ values of the ab initio potential are larger in the linear and smaller in the perpendicular approach than those of the spindleshaped empirical potential leading to a difference $\Delta R$ of 0.83 Å. For comparison, the values for the potential of Ref. 209 are 0.66 and those of Ref. 208 are 0.54 Å. The orientation angle with the steepest slope, which is a measure of the asymmetry of the potential surface, is $37^\circ$ for the ab initio, $22^\circ$ for the spindle-shape, and $41^\circ$ for the elliptical shaped potential surfaces. Apparently, the ab initio potential, though the potential with the largest anisotropy, does not

![Graph](image_url)

**FIG. 4.** Comparison of measured time-of-flight spectra at $\Theta = 15^\circ$ and $E_{cm} = 62.0$ meV with CC calculations based on the potential of Ref. 79. Inelastic transitions were included only up to the nominal maximum energy transfer.
IV. CONCLUSIONS

We calculated state-to-state differential scattering cross sections for He–C$_2$H$_2$ at three collision energies using the exact close-coupling formalism. The interaction potential is based on recent calculations applying symmetry-adapted perturbation theory with a high-level treatment of the electron correlation. The results were summed and averaged for comparison with the measured total differential cross sections at 71.3 meV and differential energy loss spectra taken at 62.0 and 102.9 meV. All three experimental data sets were reproduced.
very well, indicating that both the isotropic and the anisotropic part of the near repulsion are realistic. Since this potential is also able to reproduce the major features of the recorded near-infrared spectrum, which are essentially sensitive to the attractive part of the potential, we have one of the very few cases in which detailed scattering and spectroscopic data are completely reproduced by the same potential. While the potential has a global minimum near the linear configuration at $\gamma = 14.16^\circ$ and a local one at $\gamma = 48.82^\circ$ with rather small anisotropy in the attractive region, the shape of the repulsive part is quite anisotropic. At $V = 62$ meV, the difference between the linear and perpendicular approach is 0.83 Å and the largest slope is found at $\gamma = 37^\circ$. The characteristic feature of this potential surface is not a special shape but the fact that the anisotropy changes appreciably when going from the attractive to the repulsive part of the potential. This explains also the seemingly contradictory experimental results of scattering experiments. Those experiments which are mainly sensitive to the attractive part of the interaction potential like the damping of the diffraction oscillations in the total differential cross sections and the rotational energy transfer at small angles and low energy can be fitted by potentials with small anisotropy. The experimental results presented in Ref. 211, which mainly probe the repulsive part of the interaction, require potentials with a relatively large anisotropy.

In order to achieve the results of the current chapter, the interaction potential is of crucial importance. The other ingredients of the data evaluation are the exact close-coupling method for the scattering dynamics and the nearly approximation-free Monte-Carlo procedure for the averaging process.

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Chapter 10

Pressure broadening coefficients and rotational state-to-state rate constants for He–C$_2$H$_2$ from an ab initio potential

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Abstract

Pressure broadening coefficients and state-to-state rate constants for the rotational (de-)excitation of He–C$_2$H$_2$ were obtained by means of converged close-coupling and coupled-states calculations. The ab initio potential used in these calculations was computed previously by symmetry-adapted perturbation theory. The computed pressure broadening coefficients and total rate constants agree well with the available experimental data. Strong disagreement is found for the individual state-to-state rate constants, however. Possible reasons for this discrepancy are discussed.
Chapter 10: Pressure broadening coefficients for He–C₂H₂

I. INTRODUCTION

Over the last two decades important developments have been taking place in the theoretical and experimental studies of the collision-induced broadening of lines in the rovibrational spectra of small molecules. The knowledge of spectral line shapes as functions of pressure and temperature is of considerable interest for both fundamental and practical reasons. On the practical side, the understanding of the collision-broadening of rovibrational lines improves greatly the modeling of the distributions of concentration and temperature in the atmospheres of the earth and outer planets, and in other complex environments such as combustion flames. Pressure broadening and shifting coefficients for different perturbing gases and at different temperatures are of interest in themselves, since they provide important information on molecular relaxation phenomena. In particular, pressure broadening coefficients are closely related to the rates of population transfer between rovibrational states. It is not surprising, then, that the spectral line shapes of various gases have been object of several experimental and theoretical studies.

Theoretical and experimental characterization of the collision-induced line broadening of acetylene by helium as a perturber is of considerable interest for interstellar chemistry because acetylene was found to be a trace constituent of the atmospheres of the planets Jupiter, Saturn, and Neptune while spectral lines are broadened predominantly in these atmospheres by H₂ and, to some degree, by helium. The temperature profiles of these atmospheres can be accurately monitored provided that, among others, the spectroscopic and collisional processes of the He–C₂H₂ complex are well understood. Consequently, the measurement of the pressure broadening coefficients of He–C₂H₂ received particular attention in recent years. The acetylene molecule has two low-energy doubly degenerate bending modes, ν₄ (Π₀) and ν₅ (Π₀). In Ref. 344 the R branch transitions of the (ν₄ + ν₅)⁰ combination band were measured, while in Refs. 345 and 346 line broadening coefficients were obtained from R lines in the ν₅ band. Note that the subscript 0 on (ν₄ + ν₅)⁰ indicates that this combination mode is coupled to vibrational angular momentum l = 0. In addition, closely connected experiments such as the measurement of vibrational and rotational relaxation of acetylene in collisions with helium were conducted recently. The rotational rate constants of Refs. 347 and 348 were measured for acetylene in the vibrationally excited ν₂ stretch mode. It is worth noting that the He–C₂H₂ complex was also thoroughly investigated by other techniques, viz., high-resolution spectroscopy, scattering experiments in crossed molecular beams, and ab initio methods (see also Chapters 8 and 9).

In a recent paper we reported an intermolecular potential energy surface
for the He–C\(_2\)H\(_2\) complex computed by symmetry-adapted perturbation theory (SAPT). This potential was shown to reproduce all major features of the recorded near-infrared spectrum,\(^{199}\) which suggests that its anisotropy is correct, at least in the well region. As an additional test of the \textit{ab initio} potential we computed in Chapter 9 energy loss spectra and total differential cross sections for He–C\(_2\)H\(_2\) scattering. The agreement with the experiment\(^{211}\) was excellent, indicating that both the isotropic and the anisotropic parts of the SAPT potential in the lower-energy repulsive region are accurate. We further tested the \textit{ab initio} potential in Chapter 8 where second virial coefficients for the He–C\(_2\)H\(_2\) mixture were reported. The agreement with the experiment was again very good.

Somewhat surprisingly, pressure broadening and rotational relaxation data for He–C\(_2\)H\(_2\) were not yet analyzed in terms of an interaction potential for this system. As our recent results show that the \textit{ab initio} potential for He–C\(_2\)H\(_2\) is quite accurate in both the repulsive and well regions, we will fill this gap in the current paper and report converged close-coupling and coupled-states calculations of pressure broadening coefficients and state-to-state rotational rate constants obtained from our recent SAPT potential.\(^{79}\) The computed pressure broadening coefficients and state-to-state rotational rate constants are compared with the experimental data of Refs. 344–346 and,\(^{348}\) respectively. In Sec. II we will briefly describe the computational methods used in the present work. In Sec. III we discuss the accuracy of the theoretical results and compare them with the available experimental data. Possible reasons for the discrepancy between theory and experiment for the state-resolved rotational rate constants are discussed and the applicability of the statistically based scaling laws to describe the dependence of the state-to-state rate constants on the rotational energy transfer is investigated. We will end by summarizing the present work.

**II. THEORY AND COMPUTATIONAL METHODS**

State-to-state rate constants for the population transfer between rotational levels \(i\) and \(f\) by collisions at temperature \(T\) are given by the well-known expression

\[
k_{if}(T) = \langle v \sigma_{if} \rangle = \left( \frac{8 k_B T}{\pi \mu} \right)^{1/2} \int_0^\infty \left( \frac{E_{CM}}{k_B T} \right) \exp \left( - \frac{E_{CM}}{k_B T} \right) \sigma_{if}(E_{CM}) \frac{E_{CM}}{k_B T} \, d\left( \frac{E_{CM}}{k_B T} \right),
\]

where \(v\) denotes the relative velocity, \(\sigma_{if}\) is the state-to-state integral collision cross section, \(k_B\) is the Boltzmann constant, \(\mu\) is the reduced mass, and \(E_{CM}\)
stands for the collisional energy. In the derivation of Eq. (1) the colliding particles are assumed to have a (Maxwellian) thermal translational distribution.

Rate constants for the (de)population of rotational levels of $\text{C}_2\text{H}_2$ by collisions with He atoms were calculated for initial rotational states with quantum number $j_i$ varying from 1 up to and including 13, with additional rate constants computed for $j_i = 19$. Rate constants for final rotational quantum numbers $j_f < j_i$ were generated directly from ab initio computed state-to-state integral cross sections. From these we obtained the rate constants with $j_f > j_i$ by assuming a steady state with Boltzmann distribution for the rotational levels in equilibrium:

$$k_{if} = k_{ji} \frac{2j_i + 1}{2j_f + 1} \exp\left(-\frac{\Delta E_{if}}{k_BT}\right), \quad (2)$$

where $\Delta E_{if} \equiv E_f - E_i$ stands for the energy difference between the final and initial states. By comparison of the values of $k_{if}$ obtained from Eqs. (1) and (2) for $j_i = 3$ and $j_f = 1$ we found that this detailed balance approximation is accurate within a few percent.

In the calculation of the state-to-state integral cross sections we applied the close-coupling (CC) method in a space-fixed coordinate system. The wave function $\Psi_E^{J M p}(R, \hat{r}, \hat{R})$ for the He–$\text{C}_2\text{H}_2$ complex with total energy $E$, total angular momentum $J$ with projection $M$ on the space-fixed $z$ axis, and parity $p$ is expressed as

$$\Psi_E^{J M p}(R, \hat{r}, \hat{R}) = \sum_{j,l} \chi_{j l}^{J p}(R) \sum_{m_j, m_l} \langle j, m_j; l, m_l | J, M \rangle Y_{m_l}^j(\hat{R}) Y_{m_j}^j(\hat{r}), \quad (3)$$

where the unit vector $\hat{r}$ specifies the orientation of the (rigid) molecule, $\hat{R}$ corresponds to the polar angles of the intermolecular vector $R$, and $\langle j, m_j; l, m_l | J, M \rangle$ denotes a Clebsch–Gordan coefficient. The radial functions $\chi_{j l}^{J p}(R)$ are solutions of the close-coupling equations, a set of coupled differential equations in $R$. The angular basis of Eq. (3) is automatically adapted to the permutation inversion group $PI(C_{2v})$, i.e., the scattering states with even and odd $j$ correspond to para and ortho acetylene in the vibrational ground state, respectively. As is well known, the elements of the $S$ matrix are determined by the asymptotic form of the functions $\chi_{j l}^{J p}(R)$ and, in turn, they yield the state-to-state integral cross sections.

The MOLSCAT system of codes was applied to determine the solutions of the close-coupling equations, with the aid of the modified log-derivative–Airy propagator. From $R = 4.25$ to 11 bohr the log-derivative propagator was used with a constant step size corresponding to five steps per half wavelength for the open channel of highest kinetic energy in the asymptotic region; the
Airy propagator was used from $R = 11$ to $80$ bohr. The angular basis for the calculations on ortho $\text{C}_2\text{H}_2$ included all channels with $j$ values up to and including $j_{\text{max}} = 15$ for $j_i = 3$ and 5, $j_{\text{max}} = 25$ for $j_i = 7, 9$, and 11, $j_{\text{max}} = 31$ for $j_i = 13$, and $j_{\text{max}} = 35$ for $j_i = 19$, respectively. For para $\text{C}_2\text{H}_2$ the maximum value of $j$ included in the monomer basis was $j_{\text{max}} = 14$ for $j_i = 2, 4$, and 6, $j_{\text{max}} = 24$ for $j_i = 8$ and 10, and $j_{\text{max}} = 30$ for $j_i = 12$. Partial wave components with increasing values of the total angular momentum $J$ were included until convergence within 0.001 Å$^2$ was reached for the elastic as well as the inelastic cross sections. The highest value of $J$ included for $E_{\text{CM}} = 2000$ cm$^{-1}$ was about 120. For lower collisional energies considerably less partial wave components had to be included. Typically, for $E_{\text{CM}} = 1$ cm$^{-1}$ the highest value of $J$ included varied from 12 (for $j_i = 2$) to 66 (for $j_i = 19$). The maximum total number of channels was about 350 in these calculations.

The He-$\text{C}_2\text{H}_2$ intermolecular potential, which is a function of the distance $R$ between the $\text{C}_2\text{H}_2$ center-of-mass (c.m.) and the He atom and of the angle $\theta$ between the vector $\mathbf{R}$ and the molecular axis, was expanded in Legendre polynomials $P_l(\cos \theta)$ with $l \leq 18$. The expansion coefficients were computed by means of a 25-point Gauss-Legendre quadrature. The reduced mass of He-$\text{C}_2\text{H}_2$ is 3.4689 amu.$^{145}$ The integration parameters, the size of the monomer basis, the number of partial waves, and the length of the expansion of the potential were chosen such that the state-to-state cross sections were convergent within 1% at worst.

State-to-state integral cross sections were calculated for 70 collisional energies $E_{\text{CM}}$. An energy step size of 1 cm$^{-1}$ was used for $E_{\text{CM}}$ varying from 1 to 50 cm$^{-1}$, in the range $E_{\text{CM}} = 50$ to 250 cm$^{-1}$ the step size was 10 cm$^{-1}$, and additional calculations were performed for $E_{\text{CM}} = 300, 400, 500, 600, 800, 1000, 1500$, and $2000$ cm$^{-1}$. This set of collisional energies is denoted grid I in the following. The integral in Eq. (1) was determined by numerical integration in two parts. For $E_{\text{CM}} \leq 150$ cm$^{-1}$ the integrand was interpolated by a cubic spline and the trapezium rule was applied with a step size of 0.01 cm$^{-1}$. The value of the integral with boundaries $E_{\text{CM}} = 150$ and 2000 cm$^{-1}$ was obtained by splining the logarithm of the integrand and using the trapezium rule with a step size of 1 cm$^{-1}$. For collision energies below 50 cm$^{-1}$ we found a series of rotational resonances. Especially the lower ones of these are rather narrow, but we found that their contributions to the rate constants are negligible.

If again a thermal distribution for the translational motions of the collisional partners is assumed, pressure broadening coefficients $\gamma_0$ can be expressed as

$$\gamma_0 = \langle v \sigma_{i,ff} \rangle / 2\pi c k_B T,$$

where the average over the relative velocity distribution on the rhs is defined as in Eq. (1), $c$ is the speed of light, and $\sigma_{i,ff}$ denotes the pressure broadening...
cross section, which is obtained from the $S$ matrix elements.\textsuperscript{349} For practical reasons pressure broadening cross sections were generated by applying the coupled-states (centrifugal sudden) approximation\textsuperscript{333,350} instead of the CC method. This coupled-states (CS) approach uses a body-fixed coordinate frame, with its $z$ axis parallel to the intermolecular axis $R$, and consists essentially in replacing the orbital angular momentum operator $\hat{l}^2 = (\hat{J} - \hat{j})^2$ by a constant parameter $L(L + 1)$. The resulting equations are decoupled in $L$ and $\Omega$, where $\Omega$ is the projection of the monomer rotational angular momentum $j$ and of the total angular momentum $J$ on the intermolecular axis. As a consequence, a given monomer basis leads to much smaller sets of coupled equations. The CS method was used to generate pressure broadening cross sections for the rotational transitions accompanying the $\nu_5$ fundamental\textsuperscript{344} and $(\nu_4 + \nu_5)^0$ combination\textsuperscript{345,346} bands of $C_2H_2$. The $\nu_4$ and $\nu_5$ vibrational levels of $C_2H_2$ are $\Pi$ modes and both have a symmetric and an antisymmetric submode with respect to the permutation of identical nuclei.\textsuperscript{351} Therefore, $\Delta j = 1$ ($R$ branch) transitions from the ground vibrational state are allowed provided that the excited vibrational submode is antisymmetric. In this work we consider $R(j)$ lines for $j = 0, 1, \ldots, 29$. The accuracy of the CS formalism in the calculation of pressure broadening cross sections was tested by performing additional CC calculations. Pressure broadening coefficients were obtained from CC cross sections for the $R(1)$, $R(4)$, $R(7)$, and $R(11)$ spectral lines.

We used a grid of collisional energies with step sizes of $\Delta E = 10$ cm$^{-1}$ in the range $E_{\text{CM}} = 0$ to 50 cm$^{-1}$ and $\Delta E = 50$ cm$^{-1}$ in the range $E_{\text{CM}} = 50$ up to 400 cm$^{-1}$ inclusive, and additional energies of 500, 600, 800, 1000, 1500, and 2000 cm$^{-1}$ (grid II). We tested that pressure broadening coefficients generated on grid II agreed within 0.1\% or better with coefficients obtained from grid I, described above. The details of the scattering calculations and the numerical integrations were the same as in the calculation of rate constants. However, since the $R$ branch lines correspond to transitions from monomer rotational states with odd quantum number $j$ to states with even $j$, or vice versa, both species of angular functions had to be included in the monomer basis. This effectively doubles the size of the basis which makes the application of the CC method very expensive. Therefore, most of the calculations were performed using the CS approximation. For each transition $R(j)$ the dimension of the monomer basis was chosen such that convergence within a few tenths of a percent was yielded. For instance, angular functions with $j$ values up to $j_{\text{max}} = 41$ inclusive were included in the calculation of pressure broadening coefficients for the $R(29)$ line.
FIG. 1. Pressure broadening coefficients (full line) for the rotational lines in the \( R \) branch of acetylene perturbed by helium calculated by the CS method. The experimental results from Refs. 344, 345, and 346 are represented by filled circles, squares, and triangles, respectively. The theoretical CC results are represented by open circles. The temperature is 296 K.

III. NUMERICAL RESULTS AND DISCUSSION

In Table 1 the results are presented of the CS calculations on the pressure broadening coefficients \( \gamma_0 \) for the spectral lines in the \( R \) branch of acetylene perturbed by helium. See also Fig. 1 for a graphical illustration of the dependence of \( \gamma_0 \) on the rotational quantum number \( j \) of \( \text{C}_2\text{H}_2 \). Inspection of Table 1 shows that the agreement between theory and experiment is good. Our CS results reproduce all the data of Refs. 344 and 345 within the experimental error bars. The agreement with the experimental data of Varanasi\(^{346}\) is somewhat less good and our results are slightly outside the experimental error bars. The reasons for this discrepancy are twofold. Collision-induced broadening was measured for the rovibrational lines corresponding to the \( \nu_5 \) and \( (\nu_4 + \nu_5)^0 \) modes of acetylene. In our calculations we assumed the same potential for the interaction between the helium atom and the acetylene molecule in its ground and vibrationally excited states, respectively. Although we believe that this assumption is reasonable, it may introduce errors of a few percent. Another source of errors in our calculations is the use of the CS approximation. In order
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<sup>a</sup>Ref. 344  
<sup>b</sup>Ref. 346  
<sup>c</sup>Ref. 345
to check the validity of this decoupling scheme we performed CC calculations for selected lines of C$_2$H$_2$. The results of these additional calculations are also reported in Table 1. Comparison of the CS and CC results for $j = 1, 2, 7,$ and 11 clearly shows that the CS approximation does not lead to large deviations. Still, the CC values are slightly higher than the CS results and tend to improve the agreement between theory and the experiment of Ref. 346.

In Tables 2 and 3 we report theoretical rate constants for the depopulation of rotational levels of ortho and para acetylene, respectively, during collisions with He atoms. Also the experimental data of Rudert and Zacharias$^{348}$ are presented. Since the \textit{ab initio} potential$^{379}$ performed well in the reproduction of experimental total differential cross sections (Chapter 9), energy loss spectra (Chapter 9), and pressure broadening coefficients (see above), we expected to be able to determine rotational state-to-state rate constants and to explain the somewhat unusual behavior of some of the experimental results (e.g. the experimental data for $j_i = 4, 12,$ and 19). It is surprising, therefore, that large discrepancies exist between the computed and measured values, cf. Tables 2 and 3. Unfortunately, it is not easy to find the reasons of such a strong disagreement, as a more detailed inspection of Tables 2 and 3 shows that there is no systematic behavior in the differences between the theoretical and experimental rate constants as functions of the initial state ($j_i$) and final state ($j_f$) rotational quantum numbers. In general, the theoretical values are much higher than the experimental results, although the reverse is true for some of the transitions with $j_i = 12$ and 19. One should note that the theoretical results were obtained from converged CC calculations, so the disagreement between theory and experiment cannot be explained by the application of the decoupling approximation.

The authors of Ref. 348 also reported independent measurements of total rate constants, i.e., summed over the final state rotational quantum number. In Table 4 we compare the theoretical results with the experimental values. The theoretical data were obtained as sums over the state-to-state rate constants up to and including $j_f = 13$. Also reported in Table 4 are the total rate constants obtained by summing the experimental state-to-state rate constants up to and including $j_f = 14$. Inspection of Table 4 shows that the agreement between the theoretical results and measured total rate constants is excellent. Actually, this good agreement may be expected since in the infinite-order sudden (IOS) approximation$^{333}$ the total rate constants are directly proportional to the pressure broadening coefficients and the latter were found above to agree well with the experimental data. In this IOS approximation the total rate constants should be the same for all $j_i$, and equal to the pressure broadening coefficient for the $R(0)$ line, which is $12.82 \mu s^{-1} \text{ Torr}^{-1}$ in the present work.
TABLE 2. Theoretical rate constants divided by $k_B T$ (in μs$^{-1}$ Torr$^{-1}$) for the population transfer between the rotational levels of ortho $C_2H_2$ by collisions with He atoms at $T = 298.15$ K. The results in the upper half of the table are obtained from the results in the lower half by applying the principle of detailed balance, cf. Eq. (2). The experimental values from Ref. 348 are between parentheses.

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TABLE 3. Theoretical rate constants divided by $k_B T$ (in $\mu s^{-1}$ Torr$^{-1}$) for the population transfer between the rotational levels of para C$_2$H$_2$ by collisions with He atoms at $T = 298.15$ K. The results in the upper half of the table are obtained from the results in the lower half by applying the principle of detailed balance, cf. Eq. (2). The experimental values from Ref. 348 are between parentheses.

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Inspection of Table 4 shows that this value agrees very well with the theoretical sum-over-states results and the experiment. By contrast, the total rate constants computed from the experimental state-to-state rate constants are three to four times smaller than the theoretical values. One possible explanation of this fact is the importance of vibrational deactivation. As mentioned in the introduction, the measurements of Ref. 348 were performed for rotational levels of acetylene in the ν3 vibrational state. However, experimental studies on the vibrational depopulation of acetylene in collisions with helium\(^{214-216}\) do not support this conclusion. In fact, the vibrational depopulation rate constants for various vibrational states of C\(_2\)H\(_2\) that were measured in that work are a few orders of magnitude smaller than the total rate constants of Ref. 348. This strongly suggests that the latter are dominated by purely rotational transitions, and that the experimental state-resolved data of Ref. 348 are inaccurate.

This latter conclusion is also supported by the dependence of the (de-excitation) rate constants on the rotational energy transfer. In Figs. 2 (a) and (b) this energy transfer dependence is graphically illustrated for the present theoretical results for ortho and para He–C\(_2\)H\(_2\), respectively. These figures show that the theoretical rate constants are nearly exponential functions of \(\Delta E_{ij}\). This result is in agreement with the findings of Green\(^{352}\) who showed that the rotational (de-excitation) rate constants of systems involving light atoms are well described by the exponential-gap scaling law.\(^{353}\) The experimental results, however, show an erratic dependence on \(j_f\) (see Tables 2 and 3) and, consequently, on the rotational energy transfer. In fact, the experimental values for a given \(j_i\) show an oscillatory behavior that cannot be represented by any simple scaling law. This supports our conclusion that the measurements of the state-resolved rate constants\(^{348}\) should be reconsidered.
FIG. 2. Dependence of the state-to-state de-excitation rate constants on the rotational energy transfer for ortho (a) and para (b) He–C₂H₂, respectively.
IV. CONCLUSIONS

We generated pressure broadening coefficients and state-to-state rate constants for the rotational (de-)excitation of He–C$_2$H$_2$. An ab initio SAPT potential\textsuperscript{79} was applied. Pressure broadening coefficients obtained from calculations based on the CS approximation were found to be in good agreement with measured values\textsuperscript{344-346}. The CS results agreed within a few percent with values from CC calculations for selected $R(j)$ transitions. The latter were found to be slightly higher and in even better agreement with the experiment, at least for small values of $j$. Small deviations from the experimental results reported in Ref. 346 can be explained by the use of the CS approximation and our assumption that our He–C$_2$H$_2$ potential for the vibrational ground state of C$_2$H$_2$ is applicable to He–C$_2$H$_2$ with C$_2$H$_2$ vibrationally excited.

The computed state-to-state rate constants showed large discrepancies compared with the experimental data\textsuperscript{348}. We concluded that this disagreement must be caused by inaccuracies on the experimental side, since the total rate constants which were also reported in Ref. 348 agree with our theoretical state-to-state results summed over the final state rotational quantum number, but disagree with the sum over the experimental state-to-state rate constants. In addition, our calculated total rate constants are close to the pressure broadening coefficient for the $R(0)$ line, to which they should be equal in the IOS approximation. Furthermore, the theoretical rate constants showed a nearly exponential dependence on the rotational energy transfer while the measured data showed unphysical oscillations. We therefore conclude that the state-resolved rate constants of Ref. 348 are inaccurate.

ACKNOWLEDGEMENTS

This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and by the Polish Scientific Research Council (KBN), Grant no. 3 T09A 072 09.
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[5] A. van der Avoird, P. E. S. Wormer, F. Mulder, and R. M. Berns, Top. Curr. Chem. 93, 1 (1980), in the course of this work we found a phase error in Eq. (24) of this reference: the factor \((-1)^{l_a+l_B+l_c}\) was inadvertently omitted.
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Summary

The present thesis contains theoretical and computational studies of intermolecular interactions and properties of weakly interacting atom–molecule complexes. The Born–Oppenheimer approximation is applied, i.e., the fast electronic and the slow nuclear motions are separated. As the intra- and inter-molecular vibrations are also largely decoupled, the molecular constituent of the dimer is often assumed to be in a vibrationally averaged state.

The intermolecular interactions are calculated by symmetry-adapted perturbation theory (SAPT). In the SAPT approach the different contributions to the interaction energy, viz., the electrostatic, induction, dispersion, and exchange components, are computed separately and with high accuracy. Intramolecular electronic correlation effects are included by means of a double perturbation formalism. For large intermolecular distances, multipole expansions can be used to approximate the electrostatic, induction, and dispersion components from the multipole moments and polarizabilities of the isolated monomers.

The first three chapters of the current thesis present studies on properties of collisional complexes. In Chapter 1 interaction-induced dipole moments and polarizabilities are obtained from finite-field calculations based on the SAPT method. Asymptotic (large $R$) expressions are derived by extending the multipole expansion formalism to collision-induced properties. The accuracy of the SAPT approach is tested by comparing numerical results for the dipole moment of $\text{He-H}_2$ and the polarizability of $\text{He}_2$ with results from full configuration interaction calculations. The role of short-range penetration effects is discussed. The convergence of the SAPT expansion for collision-induced properties appears to be satisfactory, at least for the four-electron systems considered in Chapter 1.

Interaction-induced polarizabilities for the helium dimer, obtained from SAPT calculations, are applied in quantum-dynamical studies of binary collision-induced Raman spectra in Chapter 2. The theoretical depolarized spectrum is in good agreement with experiment. The experimental uncertainties in the polarized spectrum, however, are too large to significantly compare theory with experiment. \textit{Ab initio} calculated dielectric virial coefficients, including first and second order quantum corrections, are found to be in good agreement with experimental results from indirect measurements.

A full quantum-statistical expression for the second dielectric virial coefficient is derived in Chapter 3. The importance of quantum effects and the convergence of the semiclassical expansion used in Chapter 2 are discussed. Comparison
with experiment shows quantitative agreement at temperatures above 50 K. At lower temperatures the semiclassical expansion starts to diverge and the theoretical results disagree substantially with experimental data obtained from direct measurements. However, the disagreement of the full quantum-statistical results appears to be mainly caused by experimental inaccuracies.

An \textit{ab initio} potential energy surface for He–CO including vibrational coordinate dependence is reported in Chapter 4. The potential is applied in the calculation of bound state levels and infrared spectra accompanying the fundamental CO transition for the $^3$He–CO and $^4$He–CO complexes. All computed line positions agree within 0.1 cm$^{-1}$ or better with results from high-resolution infrared experiments.

A similar study of the Ne–C$_2$H$_2$ and Ne–C$_2$HD complexes is presented in Chapter 5. An \textit{ab initio} potential is generated and applied in the calculation of bound state levels and infrared transition frequencies and intensities accompanying the fundamental $\nu_3$ transition in (deuterated) acetylene. The theoretical line positions and intensities are in qualitative agreement with experiment but small scalings of the potential for the excited dimer are necessary to obtain quantitative agreement and to assign quantum numbers to the transitions.

In Chapter 6 the \textit{ab initio} calculation of an Ar–CH$_4$ potential is reported. Tetrahedral invariant functions are used in the analytical representation of the potential. State-to-state integral cross sections are generated from the SAPT potential by means of converged close-coupling (CC) calculations and are compared with experimental results. Although the larger cross sections agree quite well with experiment, some of the smaller cross sections involving quasi-degenerate states show discrepancies. This can be partly explained by the occurrence of sequential collisions, as is shown by a master equation analysis.

The SAPT potential for Ar–CH$_4$ is further tested in Chapter 7, where state-to-state and total differential cross sections obtained from CC calculations are reported. For comparison with experiment, the cross sections are transformed from the center-of-mass to the laboratory frame and corrections for experimental conditions are made. The good agreement with experimental cross sections shows that the well depth of the potential and the onset of the repulsive wall are realistic. On the other hand, small deviations in the slope of the theoretical curve suggest that there is a minor inaccuracy in the anisotropy of the potential near the inflection point.

Intermolecular potentials can also be applied in the calculation of macroscopic properties of gas mixtures. The accuracy of five \textit{ab initio} potentials, calculated by the SAPT method, is tested by generating second virial coefficients for a wide range of temperatures in Chapter 8. First and second order quantum corrections are included. Theoretical results for the He–CO, Ne–CO,
Ar–H₂, and He–C₂H₂ complexes agree very well with the best available experimental data. The calculated virial coefficients for Ar–CH₄, however, are somewhat too high with respect to experiment. This result suggests that the well of the Ar–CH₄ potential is slightly too shallow.

In Chapter 9 differential cross sections and energy loss spectra for He + C₂H₂ scattering are generated from a SAPT potential using the CC method. Averaging procedures are performed in order to compare computational and experimental results. Theory and experiment are in excellent agreement here, indicating that especially the lower energy repulsive part of the potential is very accurate.

The SAPT potential for He–C₂H₂ is applied in Chapter 10 in the calculation of state-to-state rate constants and pressure broadening coefficients for rotational transitions in C₂H₂ interacting with helium. The state-to-state rate constants are computed with the CC method, while for the pressure broadening coefficients the more approximate coupled-states (CS) approach is used. Theoretical pressure broadening coefficients for transitions with Δj = 1 are in good agreement with the experimental results. Calculated state-to-state rate constants, however, show large deviations from the measured values. This discrepancy appears to be caused by experimental inaccuracies.

As a final conclusion, it can be stated that ab initio SAPT potentials yield observable properties that are in good agreement with the corresponding measured values, at least for the atom–molecule complexes considered in the present work.
Samenvatting


De intermoleculaire wisselwerkingen worden berekend met symmetrie-angepaste storingsrekening (SAPT). In de SAPT-benadering worden de verschillende bijdragen aan de interactie-energie, te weten de elektrostatische, inductie-, dispersie- en exchangecomponenten afzonderlijk en met grote nauwkeurigheid berekend. Effecten als gevolg van intramoleculaire elektronische correlatie worden meegenomen door uit te gaan van een formalisme waarin deze correlatie als tweede storing — naast de intermoleculaire wisselwerking — wordt opgevat. Voor grote intermoleculaire afstanden kunnen multipoolexpansies worden gebruikt om de elektrostatische, inductie- en dispersiecomponenten te berekenen uit de multipoolmomenten en polariserbaarheden van de vrije monomeren.

De eerste drie hoofdstukken van dit proefschrift zijn gewijd aan studies van eigenschappen van botsingscomplexen. In Hoofdstuk 1 worden door wisselwerking geïnduceerde dipoolmomenten en polariseerbaarheden verkregen uit finite-fieldberekeningen gebaseerd op de SAPT-methode. Asymptotische uitdrukkingen (voor grote intermoleculaire afstanden) worden afgeleid door het formalisme van de multipoolexpansie uit te breiden naar botsingsgeïnduceerde eigenschappen. De nauwkeurigheid van de SAPT-benadering wordt getest door numerieke resultaten voor het dipoolmoment van He-\(\text{H}_2\) en de polariserbaarheid van \(\text{He}_2\) te vergelijken met resultaten van volledige configuratieinteractieberekeningen. Verder wordt er gekeken naar de rol van kortedracht-effecten als gevolg van ladingoverlap. De convergentie van de SAPT-expansie voor botsingsgeïnduceerde eigenschappen blijkt voldoende te zijn, in ieder geval voor de vier-elektronensystemen beschouwd in Hoofdstuk 1.

Door wisselwerking geïnduceerde polariseerbaarheden voor het helium-dimeer, verkregen uit SAPT-berekeningen, worden in Hoofdstuk 2 toegepast in quantumdynamische studies van binaire botsingsgeïnduceerde Raman spectra. Het theoretische gedeplearpolariseerde spectrum is in goede overeenstemming met het experiment. De experimentele fout in het gepolariseerde spectrum is
daarentegen te groot voor een zinvolle vergelijking tussen theorie en experiment. *Ab initio* berekende diëlektrische viriaalcôefficiënten, met eerste- en tweede-orde quantumcorrecties, blijken in goede overeenstemming met experimentele resultaten uit indirecte metingen.

Een volledig quantumstatistische uitdrukking voor de tweede diëlektrische viriaalcôefficiënt wordt afgeleid in Hoofdstuk 3. Het belang van quantumeffecten en de convergentie van de semi-klassieke expansie uit Hoofdstuk 2 worden besproken. Vergelijking met het experiment laat kwantitatieve overeenstemming zien voor temperaturen boven 50 K. Bij lagere temperaturen begint de semi-klassieke expansie te divergeren en wijken de theoretische resultaten substantieel af van de experimentele waarden uit directe metingen. Echter, het afwijken van de volledig quantumstatistische resultaten lijkt hoofdzakelijk te worden veroorzaakt door experimentele onnauwkeurigheden.

Een *ab initio* potentiëleoppervlak voor He–CO, met afhankelijkheid van de vibrationele coördinaat, wordt beschreven in Hoofdstuk 4. De potentiaal wordt toegepast in de berekening van niveaus van gebonden toestanden en infraroodspectra voor $^3$He–CO en $^4$He–CO die de fundamentele overgang in CO begeleiden. Alle berekende lijnoposities verschillen 0.1 cm$^{-1}$ of minder met resultaten van hoge-resolutiemetingen.

Een vergelijkbare studie wordt in Hoofdstuk 5 gepresenteerd voor de Ne–C$_2$H$_2$ en Ne–C$_2$HD complexen. Een *ab initio* potentiaal wordt gegenereerd en toegepast in de berekening van gebonden niveaus en infraroodfrequenties en -intensiteiten voor de overgangen die de fundamentele $\nu_3$ overgang in (gedeutererd) acetylen begeleiden. De theoretische lijnoposities en intensiteiten zijn in kwalitatieve overeenstemming met het experiment maar de potentiaal voor het vibrationeel aangeslagen dimeer moet enigszins worden geschaald om kwantitatieve overeenstemming te verkrijgen en om quantumgetallen te kunnen toekennen aan de overgangen.

In Hoofdstuk 6 wordt de *ab initio* berekening van een Ar–CH$_4$ potentiële beschreven. In de analytische representatie van de potentiaal worden tetraëdrisch-invariante functies gebruikt. State-to-state integrale botsingsdoorsneden worden gegenereerd uit de SAPT-potentiaal door middel van geconvergeerde gekoppelde-kanalen (close-coupling — CC) berekeningen. Deze botsingsdoorsneden worden vergeleken met experimentele resultaten. De grotere botsingsdoorsneden stemmen goed overeen met het experiment maar bij de kleinere botsingsdoorsneden waarbij quasi-ontaarde toestanden zijn betrokken blijken er afwijkingen te zijn. Gedeeltelijk kunnen deze worden verklaard door het plaatsvinden van sequentiële botsingen, zoals een analyse gebaseerd op een mastervergelijking laat zien.

De SAPT-potentiaal voor Ar–CH$_4$ wordt verder getest in Hoofdstuk 7 waar
Samenvatting

De state-to-state en totale differentiële botsingsdoorsneden worden verkregen uit CC-berekeningen. Om vergelijking met het experiment mogelijk te maken worden de botsingsdoorsneden getransformeerd van het massacentrum- naar het laboratoriummassenstelsel. Verder wordt er gecorrigeerd voor de experimentele condities. De goede overeenstemming met de experimentele waarden laat zien dat de diepte van de potentiaalput en de aanvangspositie van het repulsieve gedeelte realistisch zijn. Kleine afwijkingen in de helling van de theoretische curve suggereren echter dat er een kleine onnauwkeurigheid zit in de anisotropie van de potentiaal rond het buigpunt.


In Hoofdstuk 9 worden differentiële botsingsdoorsneden en vluchttijdspectra berekend voor de verstrooing van helium aan acetylen. Hiertoe wordt een SAPT-potentiaal toegepast en wordt gebruikgemaakt van de CC-methode. Middelingsprocedures worden uitgevoerd om vergelijking tussen berekende en experimentele waarden mogelijk te maken. Theorie en experiment blijken in uitstekende overeenstemming te zijn. Dit geeft aan dat met name het laagenergetische repulsieve gedeelte van de potentiaal zeer nauwkeurig is.

De SAPT-potentiaal voor He–C₂H₂ wordt in Hoofdstuk 10 toegepast in berekeningen van state-to-state snelheidsconstanten voor rotationele overgangen en van lijnverbredingscoëfficiënten voor dergelijke overgangen in C₂H₂ wisselwerkend met helium. De overgangsconstanten worden berekend met de CC-methode, voor de lijnverbredingscoëfficiënten wordt de meer benaderde coupled-states (CS) methodiek toegepast. Theoretische lijnverbredingscoëfficiënten voor overgangen met Δj = 1 zijn in goede overeenstemming met experimentele resultaten. Berekende state-to-state overgangsconstanten vertonen echter grote afwijkingen met de meetwaarden. Experimentele onnauwkeurigheden lijken de oorzaak te zijn voor deze discrepancie.

Als slotconclusie kan worden gesteld dat ab initio SAPT-potentiaal aan het experiment toetsbare eigenschappen leveren die in goede overeenstemming zijn met de betreffende meetwaarden. Dit geldt in ieder geval voor de atoommolecuulcomplexen die in dit proefschrift worden beschouwd.