The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/16116

Please be advised that this information was generated on 2018-12-07 and may be subject to change.
**Ab initio** potential energy surface, infrared spectrum, and second virial coefficient of the He–CO complex

Robert Moszynski  
Institute of Theoretical Chemistry, Nijmegen-SON Research Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands and Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

Tatiana Korona  
Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

Paul E. S. Wormer and Ad van der Avoird  
Institute of Theoretical Chemistry, Nijmegen-SON Research Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

(Received 28 February 1995; accepted 29 March 1995)

Symmetry-adapted perturbation theory has been applied to compute the intermolecular potential energy surface of the He–CO complex. The interaction energy is found to be dominated by the first-order exchange contribution and the dispersion energy. The **ab initio** potential has a single minimum of \( e_m = -24.895 \) cm\(^{-1}\) for the linear CO–He geometry at \( R_m = 6.85 \) bohr. The computed potential energy surface has been analytically fitted and used in converged variational calculations to generate bound rovibrational states of the He–CO molecule and the infrared spectrum, which corresponds to the simultaneous excitation of vibration and internal rotation in the CO subunit within the complex. The predicted positions and intensities of lines in the infrared spectrum are in good agreement with the experimental spectrum [C.E. Chuaqui et al., J. Chem. Phys. 101, 39 (1994)]. The theoretical potential was also checked by comparison of computed excess second virial coefficients with the experimental data. The **ab initio** interaction virial coefficients, including quantum corrections, lie within the experimental error bars over a wide range of temperatures. © 1995 American Institute of Physics.

I. INTRODUCTION

The CO molecule plays a fundamental role in theoretical and experimental studies of the thermal balance in dense interstellar molecular clouds. Due to its small rotational constant, it can be rotationally excited in low temperature thermal collisions. Excitations of CO occur mostly via collisions with the most abundant species such as He or H\(_2\). This fact and the resemblance of the para–H\(_2\) molecule in its ground state to a rare gas atom are the reasons that van der Waals complexes of CO with H\(_2\) and noble gas atoms have attracted interest of both theoreticians and experimentalists.

Because of the relatively small number of electrons involved, the He–CO interaction has been a subject of many **ab initio** studies.\(^{1–7}\) Until recently, the most elaborate potential energy surface for the He–CO complex was the CI potential of Thomas et al.\(^2\) Later, this potential was extended\(^3\) to include the dependence on the bond length of the CO molecule. Very recently, Kukawska-Tarnawska et al.\(^6\) and Tao et al.\(^7\) reported interaction potentials for He–CO, both computed by the supermolecular approach at the MBPT4 level of theory. In addition, Hettema et al.\(^8\) reported correlated long-range induction and dispersion coefficients for this system.

The He–CO complex has also been studied using various experimental techniques. Collisional probabilities for rotational\(^9,10\) and vibrational\(^11,12\) relaxation of the excited CO molecule by collisions with He have been measured. Keil et al.\(^13\) and later Kohl\(^14\) reported total differential cross sections at different collision energies, while Faubel et al.\(^15\) measured state-to-state differential cross sections for selected deflection angles. The scattering data could be rather successfully reproduced\(^16\) using the **ab initio** potential of Thomas et al.\(^2\) with minor scalings. Also bulk properties of the He–CO mixtures (viscosity\(^17\) and diffusion\(^18\) coefficients) are well reproduced\(^19,20\) using the modification of the CI potential proposed in Ref. 16. Schramm and collaborators\(^21,22\) measured excess second virial coefficients for He–CO over a wide range of temperatures, but these data were not used to check the accuracy of the **ab initio** potentials.

Numerous experiments have been devoted to the study of pressure broadening of rotational and rotation-vibrational lines of CO by the He atom as a perturber at various temperatures\(^23–33\). Especially recent low temperature results\(^27–30\) are interesting, since they constitute a very sensitive probe of the interaction potential in the region of the van der Waals well. The measurements of the pressure broadening cross sections simulated several theoretical studies in this field\(^34–39\) (see also Refs. 40 and 41 for a review of the experimental and theoretical work in this field). The results of theoretical calculations of pressure broadening cross sections based on the CI potential\(^2\) have shown that this potential predicts very well all pressure broadening measurements, including the low temperature data of De Lucia et al.\(^27,29,30\) This, in turn, suggested that the CI potential is accurate, also in the region of the van der Waals minimum.

It thus came as a surprise that the **ab initio** potential of Thomas et al.\(^2\) could not reproduce the recent infrared spectrum\(^42\) recorded in a long path low temperature cell. Chuaqui et al.\(^42\) assigned the experimental spectrum by fitting a two-dimensional potential energy surface to reproduce line positions and intensities. This empirical potential failed,
however, to reproduce the low temperature pressure broadening data $^{27,29,30}$ Very recently Le Roy et al. $^{45}$ fitted a new potential to reproduce the experimental spectrum. The starting point for the new fit was the exchange Coulomb (XC) model potential, $^{46}$ partly based on ab initio information on the exchange-repulsion energy and long-range induction and dispersion coefficients. Also this potential did not reproduce $^{45}$ the low temperature pressure broadening data. $^{27,29,30}$ Recent ab initio potentials from MBPT4 calculations $^{6,7}$ were not checked against the experimental data. Tao et al. $^{7}$ computed the energy levels of the $^4$He–CO complex, but did not generate the complete infrared spectrum to be confronted with experiment. $^{42}$

In the present paper we report calculations of the potential energy surface for He–CO, and nuclear motion calculations of the positions and intensities of lines in the infrared spectrum of the complex in the region of the fundamental band of CO. We also check the ab initio potential by computation of the second virial coefficient and comparison with the experimental data $^{21,22}$ over a wide range of temperatures. Our calculations of the potential energy surface use the recently developed many-body formulation $^{6,58-53}$ of the symmetry-adapted perturbation theory of intermolecular forces. $^{54-57}$ In this approach, referred to as the many-body symmetry-adapted perturbation theory (SAPT), 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 intramonomer 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, $^{58,59}$ 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. $^{60-62}$ This method has been applied to determine interaction potentials for the He–K$^+$, $^{63}$ He–Na$^+$, $^{64}$ Ar–H$_2$, $^{65}$ He–HF, $^{66}$ and He–C$_2$H$_2$ $^{67}$ systems (see Ref. 68 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 far- and near-infrared spectra of Ar–H$_2$, $^{69}$ and the near-infrared spectra of He–HF $^{70}$ and He–C$_2$H$_2$. $^{67}$ In general, the resulting line positions were in very good agreement with the experimental data (see Ref. 71 for a review of dynamical calculations). Also state-to-state integral cross sections and total differential cross sections for He–HF agree rather well with the available experimental data, suggesting that SAPT maintains good accuracy both at short and large distances. The plan of this paper is as follows. In Sec. II the SAPT calculations are briefly described, and the analytical fits to the computed points are presented. In Sec. III we describe the features of the computed potential energy surface. The formalism used in dynamical calculations is outlined in Sec. IV. The results of bound state calculations are discussed in Sec. V. In Sec. VI we report ab initio calculations of the second virial coefficient for He–CO. Finally, in Sec. VII we present conclusions.

II. OUTLINE OF SAPT CALCULATIONS

A. Method and definitions

In the present paper we follow the approach introduced and tested in previous papers. $^{63-67}$ The SAPT interaction energy is represented as a sum of components corresponding to the Hartree–Fock ($E_{\text{HF}}$) and correlated ($E_{\text{corr}}$) levels of the theory, $E_{\text{int}} = E_{\text{HF}} + E_{\text{int}}$. The Hartree–Fock interaction energy can be decomposed as $^{72-75}$

$$E_{\text{HF}} = E_{\text{pol}} + E_{\text{exch}} + E_{\text{disp}} + E_{\text{exch-disp}} + \delta E_{\text{int}},$$

where $E_{\text{pol}}$ and $E_{\text{exch}}$ are the electrostatic and exchange contributions, respectively, with complete neglect of the intramolecular correlation effects. $^{76}$ $E_{\text{ind}}$ and $E_{\text{exch-ind}}$ are the Hartree–Fock induction and exchange-induction energies, respectively, accounting for the coupled-Hartree–Fock-type response. $^{73,75}$ and $\delta E_{\text{int}}$ collects higher-order induction and exchange contributions. For the He–CO interaction at large intermonomer distances $R$ the latter term is dominated by the third-order induction energy and vanishes as $R^{-10}$. At the correlated level, the SAPT interaction energy is represented by

$$E_{\text{int}} = E_{\text{pol}} + E_{\text{exch}} + E_{\text{disp}} + E_{\text{exch-disp}},$$

where $E_{\text{disp}}$ is the dispersion energy, and $E_{\text{pol}}$ and $E_{\text{exch}}$ are the electron correlation contributions to the exact electrostatic ($E_{\text{pol}}^{\text{el}}$) and exchange ($E_{\text{exch}}^{\text{el}}$) energies, respectively, i.e., $E_{\text{pol}}^{\text{el}} = E_{\text{pol}}^{\text{el}} - E_{\text{pol}}^{\text{H-F}}$ and $E_{\text{exch}}^{\text{el}} = E_{\text{exch}} - E_{\text{exch}}^{\text{H-F}}$. Each term on the right hand side of Eq. (2) can be evaluated using many-body perturbation expansions with respect to the intermolecular electronic correlation $E_{\text{el}}(R) = \Sigma_{\text{el}} E_{\text{el}}(R)$ and $E_{\text{exch}} = \Sigma_{\text{exch}} E_{\text{exch}}(R)$, where $E_{\text{el}}(R)$ and $E_{\text{exch}}(R)$ are the polarization and exchange corrections of $k$th order in the intermolecular interaction and $n$th order in the intramolecular correlation. In the present study the contributions to $E_{\text{int}}$ were approximated as follows:

$$E_{\text{pol}}^{\text{el}} = E_{\text{pol}}^{\text{el}} + E_{\text{pol}}^{\text{exch}},$$

$$E_{\text{exch}}^{\text{el}} = E_{\text{exch}}^{\text{el}} + E_{\text{exch}}^{\text{exch}},$$

$$E_{\text{disp}} = E_{\text{disp}} + E_{\text{disp}} + E_{\text{disp}} + \Sigma_{\text{disp}} E_{\text{disp}}(R),$$

$$E_{\text{exch-disp}} = E_{\text{exch-disp}}.$$
\( \theta \) is the angle between the vector pointing from the center of mass of CO to He and the vector pointing from the carbon to the oxygen atom. Calculations have been performed for five intermolecular distances \( R \) ranging from \( R = 5 \) bohr to \( R = 10 \) bohr, and seven equi distant angles \( \theta \) from \( \theta = 0^\circ \) to \( \theta = 180^\circ \). In addition, \( \theta = 75^\circ \) and \( 115^\circ \) potential energy curves have been computed. In total, we calculated 45 points on the surface. In all calculations the geometrical parameters of the CO subunit were fixed at their experimental values, i.e., \( r_{(CO)} = 2.132 \) bohr. For the helium atom we used a \([5s3p2d] \) basis. The \( s \) orbitals were represented by the \([6111] \) contraction of Van Duijneveldt’s 10s set, and the exponents of the polarization functions were taken from Ref. 78. For the CO monomer we used the \([8s6p3d1f8s8p3d1f] \) basis set of Diercksen and Sadlej optimized for dipole and quadrupole properties of this molecule. 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 done using the full dimer basis set.

All calculations have been performed with the SAPT system of codes.\(^{5,61}\) In addition, long-range induction and dispersion coefficients corresponding to the multipole-expanded induction\(^8\) and dispersion energies\(^{86}\) have been computed at the same level of theory and the same basis sets using the Polcor package.\(^{61}\) These coefficients have been subsequently used in the analytical fits of the induction and dispersion energies. We used the Boys-Bernardi counterpoise correction to eliminate the basis set superposition error from the supermolecular Hartree-Fock calculations.\(^{81}\)

C. Analytical potential fits

In SAPT calculations different contributions to the interaction energy exhibit different radial dependence, and each component of the interaction energy can be fitted separately. The fitting procedure adopted in the present work was the same as in Ref. 67. Below, we give only a short summary.

We performed separate fits of the sum of short-range contributions \( E_{\text{short}} \),

\[
E_{\text{short}} = E_{\text{pol}}^{(1)} + E_{\text{exch}} + E_{\text{exch-ind}} + E_{\text{exch-disp}} + \delta E_{\text{int}}^{\text{HF}},
\]

of the induction energy \( E_{\text{ind}}^{(2)} \), and of the dispersion energy \( E_{\text{disp}}^{(2)} \). Note, that the last term on the right hand side of Eq. (7), \( \delta E_{\text{int}}^{\text{HF}} \), is the sum of higher-order induction and exchange contributions and its dominant term decays as \( R^{-10} \). Since at He–CO distances considered in this work higher-order induction energies are dominated by the short-range charge-overlap effects, we decided to include this term into the \( E_{\text{short}} \) component. It is known that the short-range term \( E_{\text{short}}(R, \theta) \) depends exponentially on \( R \). However, a precise analytical expression has been derived thus far only for the hydrogen atom–proton interaction.\(^8\) Therefore, we decided to represent the short-range contribution by the function

\[
E_{\text{short}}(R, \theta) = C_1 \exp(-\alpha(\theta) [R - R_0(\theta)]) + C_2 R \exp(-\alpha(\theta) [R - R_1(\theta)]),
\]

where \( C_1 = 1 \) hartree and \( C_2 = 1 \) hartree/bohr. The parameters \( \alpha(\theta) \), \( R_0(\theta) \), and \( R_1(\theta) \) were determined for fixed \( \theta \), using the weighted least-square method with weights exponential in \( R \). Subsequently, each set of parameters \( \{\alpha(\theta)\}_{i=1}^9, \{R_0(\theta)\}_{i=1}^9, \{R_1(\theta)\}_{i=1}^9 \) was interpolated using cubic splines with derivatives at \( \theta = 0^\circ \) and \( \theta = 180^\circ \) fixed at zero. The parameters \( \alpha_i \), \( R_{0i} \), and \( R_{1i} \) in the Legendre expansions,

\[
\alpha(\theta) = \sum_{i=0}^{8} \alpha_i P_i(\cos \theta),
\]

\[
R_0(\theta) = \sum_{i=0}^{8} R_{0i} P_i(\cos \theta),
\]

\[
R_1(\theta) = \sum_{i=0}^{8} R_{1i} P_i(\cos \theta),
\]

were obtained by numerical integration of the spline functions using Gauss–Legendre quadrature.

The induction component \( E_{\text{ind}}^{(2)}(R, \theta) \) 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\(^{83-85}\)),

\[
E_{\text{ind}}^{(2)}(R, \theta) = C_1 \exp(-\beta(\theta) [R - R_0(\theta)]) - \sum_{n=6}^{12} f_n(R; \beta(\theta)) C_{n,\text{ind}}(\theta) R^{-n},
\]

where \( C_1 = 1 \) hartree. The induction constants for a given \( \theta \) are defined by

\[
C_{n,\text{ind}}(\theta) = \sum_{i=0}^{n-4} C_{n,\text{ind}}^{i} P_i(\cos \theta),
\]

where \( C_{n,\text{ind}}^{i} \) are standard long-range induction coefficients as defined in Ref. 8. The coefficients \( C_{n,\text{ind}} \) were not fitted but computed \( \textit{ab initio} \) in the same basis set and at the level of theory corresponding to the fitted function \( E_{\text{ind}}^{(2)}(R, \theta) \). We assumed the damping function \( f_n(R; b) \) in the Tang-Toennies form\(^8\)

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

The damping parameter \( \beta(\theta) \) was not determined from the fit of the short-range energy [i.e., not put equal to the parameter \( \alpha(\theta) \) of Eq. (8)], but fitted independently. Similarly as in the case of the \( E_{\text{short}} \) component, the fits were made for fixed values of the angle \( \theta \) using the weighted least-square method with \( R^0 \) weights. The fitted parameters \( \beta(\theta) \), \( R_0(\theta) \), and \( \beta'(\theta) \) were interpolated with cubic splines and expanded as series in Legendre polynomials.
The potential of Ref. 42 predicts a minimum of 

\[ \epsilon_m = -20.32 \text{ cm}^{-1}, \]

while the empirical potential of Ref. 42 is better. These differences are not so surprising, since both empirical potentials fitted to reproduce the spectrum \(^{42,43}\) predict different positions for the minima, and shows that the spectroscopic data are not sensitive enough to locate the minimum. This, in turn, suggests that the He atom in the complex will be strongly delocalized.

Also shown in Fig. 1 is the angular dependence of the empirical potentials \(^{42,43}\) fitted to reproduce the spectrum. The agreement with the present potential is fairly good. It deteriorates somewhat at large angles, but in this region the interaction energy is repulsive, and the spectroscopic data are probably less sensitive to the shape of the repulsive wall.

The anisotropy of the potential in the repulsive region is much more pronounced. In Fig. 2 we report the angular scan of the potential energy surface at \(R=5\) bohr. There, the potential shows a very strong angular dependence: the interaction energy changes from 821.1 cm\(^{-1}\) at \(\vartheta=0°\) to 205.1 cm\(^{-1}\) at \(\vartheta=90°\), and to 4239.9 cm\(^{-1}\) at \(\vartheta=180°\), i.e., roughly by factors of 4 from 0° to 90°, and 20 from 90° to 180°. Again, the agreement with the empirical potentials \(^{42,43}\) is fairly satisfactory. Around the linear He–CO configuration our potential agrees well with the XC fit of Ref. 43 while in the vicinity of the linear He–OC configuration the agreement with the empirical potential of Ref. 42 is better. These differences are not so surprising, since both empirical potentials were fitted to the spectroscopic data, which is not sensitive to the anisotropy in the repulsive region.

To investigate the importance of the anisotropic contri-
FIG. 2. Angular dependence of the \textit{ab initio} (solid line) and empirical (dashed lines) He–CO interaction potentials in the repulsive region ($R=5.0$ bohr). Solid line represents the \textit{ab initio} potential, while lines with small and larger dashes show the empirical potentials from Refs. 43 and 42, respectively.

Contributions to the potential in various regions of the configuration space it is useful to expand it as a series in Legendre polynomials:

$$V(R, \theta) = \sum_{l=0}^{\infty} V_l(R) P_l(\cos \theta), \quad \text{(15)}$$

where $V$ is the sum of contributions in Eqs. (8) and (10), and the dispersion equivalent of (10). The expansion coefficients $V_l(R)$ can be written as

$$V_l(R) = \frac{2 l + 1}{2} \int_{0}^{\pi} V(R, \theta) P_l(\cos \theta) \sin \theta \, d \theta, \quad \text{(16)}$$

and can be easily evaluated numerically by the use of the Gauss–Legendre quadrature. The advantage of the expansion (15) 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. 3 the radial dependence of the $V_l(R)$ coefficients for $l=4$. Around the van der Waals minimum ($R=6.85$ bohr) all terms up to $l=4$ contribute significantly to the potential, and a closer analysis shows that higher anisotropic terms are also important. To obtain converged results for $\theta$ varying from $0^\circ$ to $180^\circ$, one has to sum up all terms up to and including $l=8$.

The total interaction energy $E_{\text{int}}$ and its dominant components ($E_{\text{short}}$, $E_{\text{disp}}^{(2)}$, and $E_{\text{ind}}^{(2)}$) for $R=7$ bohr and varying $\theta$ are shown in Fig. 4. A more detailed analysis of the interaction energy in terms of various contributions as defined by Eqs. (1) and (2) is presented in Table I. An inspection of Fig. 4 shows that the short-range energy and the dispersion energy are two major contributions to the interaction potential determining its anisotropy. The induction energy is much less important and is very flat as function of $\theta$. Obviously, the dispersion component favors the linear He–CO minimum in the potential energy surface. However, the short-range energy (dominated by the exchange energy, cf. Table I) behaves, to a good approximation, in a reversed manner to $E_{\text{disp}}^{(2)}$, and shows a stronger anisotropy. Consequently, the position of the minimum is determined by the anisotropy of the exchange-repulsion term (see also Ref. 6 for a detailed discussion of the nature of the interaction in He–CO).

Since the exchange-repulsion term governs the anisotropy of the interaction, the second-order (in the intramonomer correlation) approximation of Eq. (3) may not be accurate enough. To investigate this point we performed calculations of the exchange energy in the coupled-cluster singles and doubles approximation (CCSD). In Table I we report the correction to $e_{\text{exch}}^{(1)}$ of Eq. (3) due to CCSD-type correlation (i.e., beyond the second-order approximation), denoted by $\Delta_{\text{exch}}^{(1)}(\text{CCSD})$. An inspection of Table I shows that although this term contributes a few percent to the overall interaction potential, it is strongly anisotropic. We also note that $\Delta_{\text{exch}}^{(1)}(\text{CCSD})$ mainly increases the potential at both

FIG. 3. Expansion coefficients $V_l(R)$ [cf. Eq. (15)] of the \textit{ab initio} He–CO interaction potential.

FIG. 4. Angular dependence of the He–CO interaction energy components in the region of the van der Waals minimum ($R=7.0$ bohr).
linear geometries, while its contribution to $E_{\text{int}}$ at the $T$ geometry is smaller. Thus, the CCSD correction is important in those regions where the electron density of the CO molecule shows a depletion or excess of electronic charge. This is not surprising since the exchange energy can be written in terms of the density matrices of the isolated monomers, and the electron densities of molecules with triple bonds are known to be sensitive to electronic correlation beyond the MBPT2 level of theory. This also suggests that the CCSD correction would mainly affect even terms in the Legendre expansion of the potential.

**TABLE I. Components of the interaction energy near the van der Waals minimum ($R = 7$ bohr). Energies are in cm$^{-1}$**

<table>
<thead>
<tr>
<th>Component</th>
<th>$\vartheta=0^\circ$</th>
<th>$\vartheta=90^\circ$</th>
<th>$\vartheta=180^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{disp}}$</td>
<td>3.24</td>
<td>-1.91</td>
<td>-30.02</td>
</tr>
<tr>
<td>$E_{\text{exch}}$</td>
<td>15.31</td>
<td>9.72</td>
<td>162.24</td>
</tr>
<tr>
<td>$E_{\text{exch-indexp}}$</td>
<td>-0.87</td>
<td>0.54</td>
<td>9.55</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>0.04</td>
<td>0.42</td>
<td>9.31</td>
</tr>
<tr>
<td>$E_{\text{ind-rcsp}}$</td>
<td>11.32</td>
<td>7.04</td>
<td>118.28</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>-0.61</td>
<td>0.24</td>
<td>-1.81</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>2.59</td>
<td>1.01</td>
<td>6.51</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>1.03</td>
<td>0.42</td>
<td>2.28</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>-38.81</td>
<td>-27.04</td>
<td>-94.48</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>0.86</td>
<td>0.44</td>
<td>5.70</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>-24.64</td>
<td>-18.79</td>
<td>34.20</td>
</tr>
<tr>
<td>$E_{\text{pol}}$</td>
<td>-23.61</td>
<td>-18.37</td>
<td>36.48</td>
</tr>
</tbody>
</table>

$\Delta^{(1)}_{\text{exch}}$(CCSD) neglected.

$\Delta^{(1)}_{\text{exch}}$(CCSD) included.

### IV. OUTLINE OF DYNAMICAL CALCULATIONS

It is well known that nuclear motions in weakly bound van der Waals complexes can be described in a set of coordinates related to a space-fixed or body-fixed frame. Although the anisotropy of the He–CO potential in the region of the van der Waals minimum is not particularly weak, in this work we follow Chuaqui et al. and assume that the space-fixed description is appropriate. If this is the case, the energy levels and infrared transitions in He–CO can be approximately classified by the use of the case $a$ coupling of Bratoz and Martin (see Refs. 71 and 89 for a review). We also assume that the intramolecular vibration, can to a good approximation, be decoupled from the intramolecular modes due to its high frequency (2143.2712 cm$^{-1}$, Ref. 90), and vibrationally averaged rotational constants $b_a$ of CO can be used instead. Thus, we have the following Hamiltonian describing the nuclear motion:

$$H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial \theta^2} R + \frac{\hbar^2}{2\mu R^2} b_a \frac{\partial^2}{\partial \phi^2} + V(R, \theta),$$

where $\mu$ is the reduced mass of the dimer, $J$ is the angular momentum of CO, and $I$ denotes the angular momentum associated with the end-over-end rotation of the complex.

In the limit of vanishing anisotropy the following are good quantum numbers: $j$, which corresponds to the rotation of CO in the dimer, and $l$, which corresponds to the end-over-end rotation of the vector $R$. The total angular momentum $J = j + l$ is always conserved, due to the isotropy of space, but $j$ and $l$ are broken by the anisotropy in the potential. A degenerate ($j, l$) level splits into sublevels $J = |j - l|, \ldots, j + l$ under the influence of the anisotropy. If these splittings are small, like in the He–C$_2$H$_2$ or Ar–H$_2$ cases, the states can still be labeled to a good approximation by $j$ and $l$.

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

$$[ Y^j(\hat{R}) \otimes Y^l(\hat{\phi}) ]_m = \sum_{m,j,m_j} \langle jm_j; lm_j; JM \rangle Y^j_m(\hat{R}) Y^l_m(\hat{\phi}),$$

where $Y^j_m$ denotes normalized spherical harmonics, $\langle jm_j; lm_j; JM \rangle$ is a Clebsch–Gordan coefficient, $\mathbf{R}$ stands for the spherical polar angles of the intermolecular vector $\mathbf{R}$ with respect to a space-fixed frame and an analogous definition holds for the CO bond vector $\mathbf{\mathbf{R}}$. The angular basis functions have a well defined parity $p = (-1)^{j+l}$, so the full Hamiltonian, Eq. (17), is blocked in both $p$ and $l$. Within each block various $j$ and $l$ are mixed through the potential.

The radial basis consisted of Morse type oscillator functions 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 $J=0$ state. This gave $R_e = 11.618$ bohr, $D_e = 14.3758$ cm$^{-1}$, and $\omega_e = 9.8764$ cm$^{-1}$, and $R_e = 12.950$ bohr, $D_e = 14.3758$ cm$^{-1}$, and $\omega_e = 9.8764$ cm$^{-1}$ for $^4$He–CO and $^3$He–CO, respectively. The final basis was restricted to the space with $j \leq 10$ and $n \leq 23$. The rotational constants of the CO molecule were fixed at 1.922 5165 and 1.905 0135 cm$^{-1}$ for ground and excited vibrational states, respectively. In the calculations we used the following masses, $^3$He–3.01603 amu, $^4$He–4.00260 amu, $^{12}$C–12.0 amu, and $^{16}$O–15.99491 amu. All the calculations were performed by the AITLARS program.

In the calculation of the intensities of the intermolecular transitions, accompanied by the monomer transition $u''=0 \rightarrow v''=1$ we calculated a Boltzmann average over the $v = 0$ van der Waals states (with a temperature of $T = 50$ K). The contribution to the infrared absorption coefficient

$$\mathcal{J}(0_i, J'' \rightarrow 0_v, i', J')$$

from the transition $0_i, J'' \rightarrow 0_v, i', J'$ is proportional to

$$\exp \left( \frac{-E_{\text{int}}(kT)}{Z(T)} \right) \frac{(E_{i',v} - E_{i,v})^n}{S(0_i, i', J'' \rightarrow 0_v, i', J')},$$

where $E_{i,v}$ denotes the energy of the state labeled by $(v, i, J)$, $k$ is the Boltzmann constant, and $Z(T)$ is the partition function, i.e., the sum over Boltzmann factors (weighted by $2J + 1$). Assuming that the He atom does not affect the monomer transition dipole, the line strength is given by

$$S(0_i, i', J'' \rightarrow 0_v, i', J') = \sum_{M', M''} |\langle i' J'M' \mid (v' \mid \mu_m \mid 0) \mid i'' J'M'' \rangle|^2.$$
TABLE II. Energy levels (in cm\(^{-1}\)) of the \(^4\)He–CO\((v = 0)\) complex.

<table>
<thead>
<tr>
<th>(j = 0)</th>
<th>(j = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(l)</td>
<td>(J = l)</td>
</tr>
<tr>
<td>0</td>
<td>-6.962 (91.61%)</td>
</tr>
<tr>
<td>1</td>
<td>-6.389 (92.26%)</td>
</tr>
<tr>
<td>2</td>
<td>-5.255 (90.62%)</td>
</tr>
<tr>
<td>3</td>
<td>-3.584 (89.83%)</td>
</tr>
<tr>
<td>4</td>
<td>-1.420 (89.45%)</td>
</tr>
</tbody>
</table>

where \(\mu_m^{0v} = \langle 0 | \mu_m | v \rangle\) is the transition dipole corresponding to \(v = 0 \rightarrow v = 1\) transition in the free CO. Since we are only interested in relative intensities, we omitted in Eq. (19) all natural constants, and divided by the absolute intensity of the monomer vibrational transition. Thus, in actual calculations of the infrared intensities we can use the simple dipole model

\[
\mu_m^{0v} = \mu_m C_1^1(\hat{r}),
\]

where \(C_1^1(\hat{r})\) are the spherical harmonics in the Racah normalization.\(^{91}\) The explicit formula for the matrix element of the transition dipole, Eq. (21), can be found in Ref. 67. The infrared transitions in He–CO accompanying the fundamental band of CO will obey the following selection rules: \(|\Delta J| = 1\), and \(|\Delta l| = 1\) or 0. Additionally, if the energy levels can be labeled with the quantum numbers \(j\) and \(l\), the selection rules \(\Delta l = 0\) and \(|\Delta J| = 1\) should hold approximately.

V. THE INFRARED SPECTRUM OF HE–CO

In Table II we summarize the results of bound state calculations. Our potential energy surface supports 13 bound states. [Note that the states of positive energy with parity \(p = (-1)^{J+1}\) that lie below the \(j = 1\) state of CO are truly bound, because they cannot mix with the \(j = 0\) continuum due to the parity constraint.] As expected, He–CO is a very weakly bound complex. The ground state of \(^4\)He–CO is bound only by 6.962 cm\(^{-1}\). All other states correspond to angularly excited energy levels of the complex. No states excited in the van der Waals stretch are supported by the \textit{ab initio} potential. As discussed in Sec. III, the anisotropy of the He–CO potential in the region of the van der Waals minimum is relatively strong, so it is interesting to see if the energy levels of He–CO can still be approximately labeled with \(j\) and \(l\) quantum numbers. The labeling of the states with these approximate quantum numbers is listed in Table II. Also shown in this table are contributions of the dominant \((j,l)\) angular function to the wave function of the \(i\)th state for a given \(J\), defined as

\[
|/\rangle(j,l) = 100 \sum_n |C_{i,j,l,n}^j|^2,
\]

where \(C_{i,j,l,n}^j\) is the coefficient in the eigenvector of the \(i\)th state with \(J, l, p, v\) fixed, multiplying the basis function \(x_i(R)[Y_l^j(\hat{r}) \otimes Y_l^j(\hat{R})]_M\). For most of the eigenstates, the dominant \((j,l)\) contribution to the wave function is of the order of 90%. This result suggests that the CO molecule in the dimer behaves like a slightly hindered rotor. The anisotropy of the present \textit{ab initio} potential is quite similar to that of the empirical potentials\(^{42,43}\) fitted to reproduce the infrared spectrum, so the pattern of the levels is qualitatively the same.

Since the rovibrational states of He–CO reveal a hindered rotor behavior, it may be interesting to see the contour plots of the corresponding wave functions. In Fig. 5(a) we depict the contour plot of the anisotropic potential, while in Figs. 5(b) and 5(c) we report the \(J = 0\) state wave functions for \(j = 0\) and 1, respectively. The wave function for the \(j = 0\) state shows a single maximum, rather close to the position of the minimum in potential, but shifted to larger \(R\), cf., Fig. 5(a). The state is highly delocalized, both in \(R\) and \(\theta\). Note, that in the limit of case a coupling the contour plots for this state should have spherical symmetry. Figure 5(b) shows, however, that the mixing of states with \(j \neq 0\) induced by the anisotropy strongly affects the shape of the wave function. The contour plot of the wave function for the \(j = 1\) state reveals a maximum for the linear CO–He geometry, and a minimum for the linear He–CO configuration. Also this state shows a substantial delocalization both in \(R\) and \(\theta\), while the presence of a horizontal nodal plane suggests that it can be considered as an almost pure bending excited state.

The highly delocalized character of the He–CO van der Waals states suggests that the average position of He may be very different from the minimum-energy geometry. Indeed, the expectation values of the van der Waals stretch coordinate \((R)\), the values of \(R_0 = \langle R^2 \rangle^{-1/2}\), and the values of the angle \(\theta_0 = \text{arccos}[(2(P_x \cdot \cos \theta)+1)/3]^{1/2}\) are 7.87 bohr, 7.64 bohr, and 53.82°, and 8.59 bohr, 8.25 bohr, and 42.08° for the \((j = 0, J = 0)\) and \((j = 1, J = 0)\) states, respectively. Both \((\langle R \rangle, \theta_0)\) and \((R_0, \theta_0)\) are rather different from the position corresponding to the minimum of the interaction potential \((R_m = 6.85\) bohr, \(\theta = 0°)\).

The infrared transition frequencies and intensities for the \(^4\)He–CO complex are reported in Table III (see also Fig. 6 for a graphical illustration). Since we assumed that the CO vibration is decoupled from the intermolecular modes, the transition frequencies were computed from the formula

\[
\Delta E(J'' \rightarrow J') = E_{v',0}^{J'} - E_{v''}^{J''} + Q_1(0),
\]

where \(Q_1(0) = 2143.2712\) cm\(^{-1}\) (Ref. 90) is the frequency of the CO stretching fundamental. First we note that unlike in the He–C\(_2\)H\(_2\) case\(^{57}\) most transitions do not obey selection rules corresponding to the case (a) coupling of Bratoz and Martin,\(^{88}\) although the most intense lines do correspond to the free internal rotor limit. This again confirms that CO behaves in the complex like a slightly hindered rotor. An
FIG. 5. (a) Cut through the ab initio He–CO potential (in cm$^{-1}$). (b) Cut through the $J=0, I=0$ rovibrational wave function of He–CO($v=0$). Amplitudes of the wave functions are in $10^{-3}$ (bohr)$^{-3/2}$. (c) Cut through the $J=0, I=1$ rovibrational wave function of He–CO($v=0$). Amplitudes of the wave functions are in $10^{-3}$ (bohr)$^{-3/2}$.

FIG. 6. Comparison of theoretical and experimental infrared spectra of the $^4$He–CO complex accompanying the fundamental band of CO. The temperature is 50 K.

inspection of Table III shows that the agreement of theoretical transition frequencies and intensities with the results of high-resolution measurements$^{42}$ is satisfactory. Most of the line positions agree within 0.1–0.2 cm$^{-1}$ or better. The intensities are also accurately predicted by the ab initio potential. However, four transition frequencies are in error by $\sim 0.5$ cm$^{-1}$, suggesting that the anisotropy of the ab initio potential is not entirely correct. These transitions involve angularly excited states (bending states) with $(j, l) = (1, 1)$. Perturbation theory analysis reported by Chuaqui et al.$^{42}$ shows that the energies of these states are mainly sensitive to even terms in the Legendre expansion of the potential. Our SAPT calculation neglected the CCSD contribution to the exchange-repulsion energy which affects especially the even anisotropy in the potential (cf. Sec. III). It is not surprising, then, that the agreement with experiment is somewhat less satisfactory. We repeated bound state calculations using a potential in which the contribution of the short-range energy to the $V_2(R)$ component was increased by 4.5%. This scaling is approximately consistent with the increase of the short-range energy by the CCSD contribution (at $R = 7$ bohr the ab initio short-range energy including the CCSD correction is equal to 16.06 and 140.51 cm$^{-1}$ for $\theta = 0^\circ$ and $180^\circ$, respectively; the fitted values without CCSD correction are 15.12 and 138.71 cm$^{-1}$, respectively). The resulting spectrum is shown in Fig. 7, while the errors of the transition frequencies are reported in Table III in parentheses. In general, the agreement with the measured line positions is much
better (~0.1 cm⁻¹), although some lines are reproduced with a somewhat lower accuracy. It should be stressed, however, that we did not attempt to fit the potential to the spectrum, but simply checked if by including approximately \textit{ab initio} information from more advanced CCSD calculations we can obtain better agreement with experiment.

Finally, in Table IV and Fig. 8 we report the transition frequencies and intensities for the $^4$He-CO complex (generated from the \textit{ab initio} potential). Here, the agreement is even better: all line positions are reproduced within 0.2 cm⁻¹ or better. Also the infrared intensities are correctly predicted. This confirms that the error in the anisotropy of the present potential is not very large.

## VI. EXCESS SECOND VIRIAL COEFFICIENTS FOR $^4$He-CO

Using our \textit{ab initio} potential we have calculated the second virial coefficient $B(T)$ over the temperature range in which it has been measured \cite{21,22} (77 K ≤ T ≤ 300 K). We used directly the formulas for atom-molecule derived by Pack.\cite{35} Specifically, we have computed the classical term, $B^{(0)}(T)$, and included first quantum corrections due to relative translational motions, $B^{(1)}_R(T)$, the molecular rotations, $B^{(1)}_A(T)$, and the Coriolis term, $B^{(1)}_C(T)$:

$$B(T) = B^{(0)}(T) + B^{(1)}_R(T) + B^{(1)}_A(T) + B^{(1)}_C(T). \quad (24)$$

The angular integration has been done by using 17 points Gauss-Legendre quadrature, while for the radial integration we have used the extended Simpson rule. The integration over $R$ has been done in the range from $R = 2$ bohr to $R = 100$ bohr. In the inner region ($R < 2$ bohr) the function $\exp(-\nu_0/T)$ is effectively zero, while in the outer region, $R > 100$ bohr, all contributions are negligibly small. The number of radial abscissas was $N = 2^{n-1} + 1$. We increased $n$ by 1 in each iteration and stopped when the relative error was smaller than $10^{-6}$. We have checked that our results are stable against changes in the boundaries and/or integration parameters.

The results of our calculations, presented in Table V and in Fig. 9, agree well with the experimental data of Schramm and collaborators.\cite{21,22} Only at the two lowest temperatures this good agreement deteriorates somewhat, and the present results are outside the error bars of the new measurements.\cite{22}
but within the (larger) error bars of the previous experimental data. However, at low temperatures the quantum corrections become rather significant, so higher corrections may be important. Especially, the second \( (\mathcal{O}(\hbar^4)) \) radial correction may be non-negligible. Also presented in Fig. 9 is the second virial coefficient computed using the scaled \textit{ab initio} potential (cf. previous section). This scaling has a negligible effect on the computed second virial coefficients. Finally, it is worth noting that the effect of the anisotropy in the potential is relatively important (see Fig. 9). Except for the high temperature region, the neglect of the anisotropic terms in the potential would lead to second virial coefficients outside the experimental error bars.

VII. SUMMARY AND CONCLUSIONS

The interaction potential energy surface of the \( \text{He–CO} \) molecule has been calculated for a broad range of configurations using the symmetry-adapted perturbation theory. Our calculation provides separate values for the fundamental components of the interaction energy. As expected, the \( \text{He–CO} \) complex was found to be bound mainly by disper-

---

**TABLE IV. Frequencies (in cm\(^{-1}\)) and intensities (in arbitrary units) of the transitions in the infrared spectrum of \(^4\text{He–CO}\) accompanying the fundamental band of CO.**

<table>
<thead>
<tr>
<th>( j^* )</th>
<th>( j^0 )</th>
<th>( l^* )</th>
<th>( J^* )</th>
<th>( j^0 )</th>
<th>( l^0 )</th>
<th>Computed</th>
<th>Observed, Ref. 42</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E(J^*\rightarrow J^0) )</td>
<td>( \mathcal{F}(J^*\rightarrow J^0) )</td>
<td>( \Delta E(J^0\rightarrow J^0) )</td>
<td>( \mathcal{F}(J^0\rightarrow J^0) )</td>
<td>( \Delta^2 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2143.9658</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2139.0195</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2147.3260</td>
<td>100</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2144.6409</td>
<td>12.1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>2145.2621</td>
<td>16.8</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2147.4885</td>
<td>17.0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2142.5711</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2141.8957</td>
<td>11.5</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2139.1788</td>
<td>88.6</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2144.4189</td>
<td>5.8</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>2141.2740</td>
<td>15.5</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2142.0524</td>
<td>5.7</td>
</tr>
</tbody>
</table>

*Absolute error of the transition frequency computed from the \textit{ab initio} potential.*

---

**FIG. 7.** Comparison of theoretical and experimental infrared spectra of the \(^4\text{He–CO}\) complex accompanying the fundamental band of CO. The theoretical spectrum was generated from the scaled \textit{ab initio} potential. The temperature is 50 K.

**FIG. 8.** Comparison of theoretical and experimental infrared spectra of the \(^3\text{He–CO}\) complex accompanying the fundamental band of CO. The temperature is 50 K.
sian angularly excited states of the complex. The predicted JHe-CO with a dissociation energy of 6.96 cm$^{-1}$ experiment could be achieved by adjusting the anisotropy of the interaction result from a subtle balance of those components.

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 $^1$He–CO with a dissociation energy of 6.96 cm$^{-1}$ and several angularly excited states of the complex. The predicted positions and intensities of lines in the infrared spectrum are in good agreement with the experimental spectrum. Still a minor improvement in the agreement between theory and experiment could be achieved by adjusting the anisotropy of the exchange-repulsion energy based on the results of more advanced CCSD calculations.

Also the computed second virial coefficients for He–CO agree very well with the available experimental data, suggesting that the present potential is rather accurate, and may be very useful for the computation of other observable quantities like scattering cross sections or pressure broadening data. Work in this direction is in progress.

**ACKNOWLEDGMENTS**

We would like to thank Professor R.J. Le Roy for sending us FORTRAN routines to generate the empirical potentials for He–CO, and Professor B. Schramm for providing us with his unpublished second virial coefficients. We also thank Professor B. Jeziorski for reading and commenting on the manuscript. This work was supported by the Netherlands Foundation of Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and Polish Scientific Research Council Grant No. KBN 3 T09A 037 08.

**References**

\[ \text{References} \]


