**Ab initio** potential-energy surface and rotationally inelastic integral cross sections of the Ar–CH$_4$ complex

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Symmetry-adapted perturbation theory has been applied to compute the intermolecular potential-energy surface of the Ar–CH$_4$ 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 $\varepsilon_m = -144.30$ cm$^{-1}$ at $R_m = 7.00$ bohr, for structures in which the argon atom approaches the face of the CH$_4$ tetrahedron. 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 CH$_4$ 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. © 1997 American Institute of Physics. [S0021-9606(97)01726-1]

I. INTRODUCTION

Methane is an active constituent of the atmospheres of the earth, outer planets of the solar system, and Saturn’s satellite Titan. 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, viscosities, diffusion coefficients, and thermal diffusion factors. 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. Early experiments were mainly concerned with the studies of the rotational relaxation processes and integral and differential cross sections. The rotational relaxation experiments were interpreted using a classical rough-sphere model, while the molecular beam data 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 sections and (state-unresolved) integral cross sections for rotational excitation of methane in collisions with argon. Using spectroscopic techniques to monitor the populations of the CH$_4$ rotational states after collision, the authors of Ref. 29 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. 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. McKellar, Miller et al., and Nesbitt et al. recorded the infrared spectrum of the complex corresponding to the simultaneous excitation of the $v_3$ 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.

Surprisingly, *ab initio* calculations for the Ar–CH$_4$ complex are scarce. Fowler et al. reported the long-range dispersion coefficients for Ar–CH$_4$ computed from RPA polarizabilities. More recently, Szczesniak et al. 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 ab initio calculation of the full potential-energy surface for Ar–CH₄ overestimated by 0.5 bohr. So an

In the present paper we report symmetry-adapted perturbation theory (SAPT) calculations of the potential-energy surface for Ar–CH₄, and dynamical calculations of the state-to-state integral cross sections for rotational excitation of methane in collisions with argon. The plan of this paper is as follows. In Sec. II the SAPT calculations are briefly described. In Sec. III we present analytical fits to the computed potential-energy surface. The formalism used in dynamical calculations is outlined in Sec. V. The calculated cross sections are compared with the experiment in Sec. VI. 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 our previous papers (see also Ref. 48 for a review). The SAPT interaction energy is represented as sum of the first- and second-order polarization and exchange contributions,

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

where $E^{(1)}_{\text{pol}}$ is the classical electrostatic energy calculated with full account of charge-overlap (penetration) effects, $E^{(2)}_{\text{pol}}$ is the sum of the induction and dispersion energies, $E^{(2)}_{\text{exch}} = E^{(2)}_{\text{ind}} + E^{(2)}_{\text{disp}}$, rigorously damped by charge-overlap effects, and $E^{(n)}_{\text{exch}}$, $n=1,2$, 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, $E^{(2)}_{\text{exch}} = E^{(2)}_{\text{exch-ind}} + E^{(2)}_{\text{exch-disp}}$. The exchange–induction $E^{(2)}_{\text{exch-ind}}$ and the exchange–dispersion energies $E^{(2)}_{\text{exch-disp}}$ 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 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

$$E^{(n)} = \sum_{l=0}^{\infty} E_{\text{pol}}^{(n,l)} + E_{\text{exch}}^{(n,l)},$$

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 Eq. (2) must be truncated. In the present study we consider first- and second-order contributions to $E_{\text{int}}$ were approximated as follows:

$$E^{(1)}_{\text{pol}} = E_{\text{pol}}^{(1)} + E_{\text{pol}}^{(2)} + E_{\text{pol}}^{(13)},$$

$$E^{(1)}_{\text{exch}} = E_{\text{exch}}^{(1)} + E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)} + \Delta_{\text{exch}}^{(1)} (\text{CCSD}),$$

$$E^{(2)}_{\text{pol}} = E_{\text{pol}}^{(2)},$$

$$E^{(2)}_{\text{exch}} = E_{\text{exch}}^{(2)} + E_{\text{exch}}^{(22)} + \Delta_{\text{exch}}^{(2)} (\text{CCSD}),$$

The electrostatic terms $E^{(1)}_{\text{pol}}$ and $E^{(1)}_{\text{exch}}$ are defined in Ref. 51. The first-order exchange components $E^{(1)}_{\text{exch}}$ are defined as in Refs. 52 and 53. The quantity $\Delta_{\text{exch}}^{(2)} (\text{CCSD})$, obtained from coupled cluster singles and doubles calculations, gives first-order exchange contributions which are higher than second order in the nonmonomer correlation. The dispersion components $E^{(2)}_{\text{disp}}$ are derived in Ref. 54. The uncorrelated induction and exchange–induction energies, $E^{(2)}_{\text{ind}}$ and $E^{(2)}_{\text{exch-ind}}$, are defined as in Refs. 55 and 56, respectively. The induction–correlation term $E^{(2)}_{\text{ind}}$ represents the true correlation contribution to the nonrelaxed $E^{(2)}_{\text{exch}}$ term, as defined in Ref. 57. Finally, $E^{(2)}_{\text{exch-disp}}$ is the so-called “Hartree–Fock” exchange–dispersion energy.

The uncorrelated induction energy $E^{(2)}_{\text{ind}}$ is significantly quenched by its exchange counterpart $E^{(2)}_{\text{exch-ind}}$ and the same must be true in the case of $E^{(2)}_{\text{exch-disp}}$. 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 $E^{(2)}_{\text{exch-disp}}/E^{(2)}_{\text{exch-ind}}$.

$$E^{(2)}_{\text{exch-disp}} = E^{(2)}_{\text{exch-disp}} E^{(2)}_{\text{exch-ind}}.$$

In our previous investigations of the atom–molecule interactions using SAPT we found that the inclusion of the third- and higher-order Hartree–Fock induction and exchange effects is necessary to obtain accurate potential-energy surfaces. In the present paper we follow Refs. 44–47, and include these higher-order contributions from the equation

$$\delta E_{\text{int}}^{\text{HF}} = E_{\text{int}}^{\text{HF}} - (E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{exch-ind}}^{(1)} + E_{\text{exch-disp}}^{(1)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-disp}}^{(2)}).$$

where $E_{\text{int}}^{\text{HF}}$ is the supermolecule Hartree–Fock interaction energy.

B. Computational details

In the literature several systems of axes have been reported to describe the Ar–CH₄ complex. We adopted a
frame fixed to CH$_4$ 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, 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. Calculations were performed for five intermolecular distances $R$ ranging from $R = 5-10$ 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 $T_d$ 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 $15^\circ$. 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. We employed the $[7s4p3d2f1g]$ basis set from Ref. 44 for the argon atom and the $[6s4p3d1f4s2p1d]$ basis from Maroulis for the methane molecule. The Boys–Bernardi counterpoise correction 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, 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, 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. 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 $E_{\text{disp}}^{(2)}$ and the induction energy $E_{\text{ind}}^{(2)}$ [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. 71 and the multipole moments and polarizabilities of the methane molecule were calculated using the [9s7p3d2f] and [5s4p2d] basis sets from Ref. 70 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 $ab$ 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. 45.

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

$$V(R, \Theta, \Phi) \approx \sum_{n=6}^{\infty} C_n(\Theta, \Phi) R^{-n},$$

(11)

where the coefficients $C_n$ are uniquely defined by $V$. Using the multipole expansion of the intermolecular interaction operator, 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 $T_i^j$,

$$C_n(\Theta, \Phi) = \sum C_n^j T_j^i(\Theta, \Phi),$$

(12)

where the constants $C_n^j$ are the long-range coefficients. The authors of Ref. 41 derived a few of the lowest functions.
TABLE I. Functions $T^l$ carrying the $A_1$ representation of the group $T_d$. The functions $S^m_0$ are defined as $(C^l_m + C^{l}_{-m})/(1 + \delta_{m0})$, where $C^l_m$ 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>$T^l(\Theta,\Phi)$</th>
<th>$S^0_0(\Theta,\Phi) = 1$</th>
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</thead>
<tbody>
<tr>
<td>$T^1(\Theta,\Phi)$</td>
<td>$S^1_0(\Theta,\Phi) - \sqrt{\frac{3}{14}} S^1_1(\Theta,\Phi)$</td>
</tr>
<tr>
<td>$T^2(\Theta,\Phi)$</td>
<td>$S^2_0(\Theta,\Phi) + \sqrt{\frac{5}{14}} S^2_1(\Theta,\Phi)$</td>
</tr>
<tr>
<td>$T^3(\Theta,\Phi)$</td>
<td>$S^3_0(\Theta,\Phi) - \sqrt{\frac{11}{14}} S^3_1(\Theta,\Phi)$ + $\sqrt{\frac{6}{13}} S^3_2(\Theta,\Phi)$</td>
</tr>
<tr>
<td>$T^4(\Theta,\Phi)$</td>
<td>$S^4_0(\Theta,\Phi) + \sqrt{\frac{19}{14}} S^4_1(\Theta,\Phi)$</td>
</tr>
<tr>
<td>$T^5(\Theta,\Phi)$</td>
<td>$S^5_0(\Theta,\Phi) - \sqrt{\frac{21}{14}} S^5_1(\Theta,\Phi)$ + $\sqrt{\frac{8}{13}} S^5_2(\Theta,\Phi)$</td>
</tr>
<tr>
<td>$T^6(\Theta,\Phi)$</td>
<td>$S^6_0(\Theta,\Phi) + \sqrt{\frac{25}{14}} S^6_1(\Theta,\Phi)$</td>
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</table>

By definition $W^{l}_i$ is invariant under any simultaneous rotation of methane and the position vector of argon. Under inversion it obtains the parity factor $(-1)^{l_A + l_A + l}$. On physical grounds we expect the quantity $W^{l}_i$ 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

$$W^l_{\text{ind}} = \sum_{m = -l}^{l} (-1)^m [Q^l_A \otimes Q^l_A]_{-m} g C^l_m(\Theta,\Phi)$$

for all $g \in T_d$. (14)

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

$$T^l_m = \frac{1}{24} \sum_{g \in T_d} g C^l_m.$$

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 $l = 0, 2, 6$, and unity for all other cases with $l < 12$ and two for $l = 12$. The first threefold multiplicity occurs for $l = 24$. See Ref. 76 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

$$T^l = \left\{ \begin{array}{ll}
N_l \sum_{g} g C^l_0 & \text{for } l = 0, 4, 6, 8, 10 \\
N_l \sum_{g} g C^l_2 & \text{for } l = 3, 7, 9.
\end{array} \right.$$

The other $A_1$ functions are simply proportional to these

$$T^l_m = \gamma_m T^l.$$ (17)

In Table I we see that

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

where the $\tau^l_m$ are simple coefficients. We choose $N_l$ such that $\tau^l_m = 1$ for the lowest $m$-value with nonvanishing coefficient.

Returning to Eq. (14) and using Eqs. (15) and (17) we find that

$$W^l_{\text{ind}} = \left[ \sum_{m = -l}^{l} (-1)^m [Q^l_A \otimes Q^l_A]_{-m} \gamma_m \right] T^l = \beta_l T^l.$$ (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 $C^l_0$ in $W^l_{\text{ind}}$ and $\beta_l T^l$ and find

$$\beta_l = [Q^l_A \otimes Q^l_A]_{10},$$

since, due to our normalization condition, $\tau^l_0$ is unity. Likewise we find by equating the coefficients of $C^l_2$ in the case of $l = 3, 7, 9$ that

$$\beta_l = [Q^l_A \otimes Q^l_A]_2.$$ (21)

Using this expression for $W^l_{\text{ind}}$, we finally find from the general expression of Refs. 73–75 the coefficients with $l \leq 10$ in the expansion of Eq. (12)
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 \( \alpha_M^{(ll, l)}(\omega) \) 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.\(^{77}\)

### 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 \( E_{\text{short}} \).

\[
E_{\text{short}} = E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-disp}}^{(2)} + \delta E_{\text{HF}}^{(1)},
\]

of the induction energy \( E_{\text{ind}}^{(2)} \) and of the dispersion energy \( E_{\text{disp}}^{(2)} \).

The fitting procedure adopted in the present work was similar to that of our previous papers.\(^{46,47}\) 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

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

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,

\[
A_{\text{short}}(\Theta, \Phi) = \sum_{l=0, 3, 6, 7} A_l^{\text{short}} T_l(\Theta, \Phi),
\]

and analogous expressions for \( B_{\text{short}}(\Theta, \Phi) \) and \( \alpha_{\text{short}}(\Theta, \Phi) \).

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\(^ {78-80}\)).

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

The induction constant for a given set of angles \((\Theta, \Phi)\) is defined by Eqs. (12) and (22). The coefficients \( C_{10, \text{ind}} \) 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 \( C_{10, \text{ind}} \) 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\(^ {81}\)

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

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 to 6 inclusive. The damping parameter \( \beta_{\text{ind}} \) 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

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

The fitted parameters \( A_{\text{disp}}(\Theta, \Phi), \beta_{\text{disp}}(\Theta, \Phi), \) and \( \beta_{\text{disp}}(\Theta, \Phi) \) were expanded in tetrahedral harmonics with \( l \leq 7 \) as in Eq. (26). The long-range dispersion coefficients \( C_{n, \text{disp}} \) 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 \( C_{n, \text{disp}} \) were replaced after the fitting by...
FIG. 2. Cut through the ab initio Ar–CH₄ potential-energy surface at \( \Phi = 0^\circ \) (in cm⁻¹).

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 ab initio results on which the fit was based, as well as with the additional 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–CH₄ potential can be requested by E-mail from avda@theochem.kun.nl.

IV. FEATURES OF THE POTENTIAL ENERGY SURFACE

In the remainder of this paper, 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 configurations, where the argon atom is above the midpoint of any of the four triangular faces of the CH₄ molecule. The first minimum corresponds to the geometry \( (\Theta_m, \Phi_m) = (125.26^\circ, 0^\circ) \) 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 \( (\Phi = 0^\circ) \). An inspection of Fig. 2 shows that the minimum of the potential is well defined. Note that the local minimum at \( \Theta = 0^\circ \) 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 \( (\Theta_s, \Phi_s) = (0^\circ, 0^\circ) \) 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.⁴³ The authors of Ref. 43 computed three cuts through the potential-energy surface of Ar–CH₄ using the supermolecule Möller–Plesset perturbation theory truncated at the second-order (MP2) and small basis sets. Their calculation correctly predicts an equilibrium structure for the facial configuration 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.⁴³ 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 II 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

<table>
<thead>
<tr>
<th></th>
<th>Facial</th>
<th>Edge</th>
<th>Vertex</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^{(1)}_{\text{ind}} )</td>
<td>-56.91</td>
<td>-45.18</td>
<td>-48.83</td>
</tr>
<tr>
<td>( E^{(1)}_{\text{pol}} )</td>
<td>190.83</td>
<td>158.60</td>
<td>196.40</td>
</tr>
<tr>
<td>( E^{(2)}_{\text{exch}} )</td>
<td>-51.64 (-50.90)</td>
<td>-43.92 (-45.64)</td>
<td>-54.07 (-52.63)</td>
</tr>
<tr>
<td>( E^{(2)}_{\text{disp}} )</td>
<td>50.21</td>
<td>42.82</td>
<td>50.15</td>
</tr>
<tr>
<td>( E^{(2)}_{\text{exch-disp}} )</td>
<td>-277.54 (-287.92)</td>
<td>-231.00 (-235.83)</td>
<td>-206.75 (-210.84)</td>
</tr>
<tr>
<td>( E^{(2)}_{\text{disp}} )</td>
<td>16.81</td>
<td>13.79</td>
<td>14.45</td>
</tr>
<tr>
<td>( \delta^{\text{H}}_{\text{HF}} )</td>
<td>-6.90</td>
<td>-5.46</td>
<td>-8.39</td>
</tr>
<tr>
<td>( E_{\mu} )</td>
<td>-135.15 (-144.25)</td>
<td>-110.33 (-116.07)</td>
<td>-85.00 (-84.48)</td>
</tr>
</tbody>
</table>

TABLE II. 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.
FIG. 3. Dependence of the different contributions to the Ar–CH$_4$ interaction energy on the angle $\Theta$ at $R=1.5$ bohr. $\phi=0^\circ$. 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.

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 II 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 nonnegligible 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% to 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 II it is seen that the anisotropy of the potential is dominated by the first-order exchange and dispersion energy, in particular the first-order exchange energy, and 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

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

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 quadrature. 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, $[(l+1)/(2l+1)]^{1/2}$. Around the minimum $R=7.00$ bohr the interaction potential is dominated by the isotropic term and 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

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

where $\mu$ is the reduced mass of the complex, $\hat{l}^2$ 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 $\hat{l}^2$, the total angular momentum $\hat{J}^2$, and of the monomer Hamiltonian $H_{\text{mon}}$.

$$\Psi_E^{JM} = R^{-1} \sum_{l, \Gamma} \chi_{l\Gamma}^J(R) [\Psi^I(\alpha_R, \beta_R) \otimes \Phi^{I/2}(\alpha_R, \beta_R)],$$

where $\Psi^I(\alpha_R, \beta_R)$ is the wave function of the $I$th monomer state, $\Phi^{I/2}(\alpha_R, \beta_R)$ is the wave function of the $I/2$th monomer state, and $\chi_{l\Gamma}^J(R)$ are the reduced states of the collisional complex.
where \( \Phi_{m_j}^{ij} \) is the rotational wave function of the monomer with angular momentum \( j \), depending on the Euler angles \((\alpha, \beta, \gamma)\) of the monomer in the space-fixed coordinate system; \((\alpha_R, \beta_R)\) denote the spherical polar angles of the intermolecular vector \( \mathbf{R} \) in the space-fixed frame. The index \( \tau \) contains additional information about the symmetry of the monomer state \((A, E, \text{and } F \text{ symmetry})^{76,82}\).

The rovibrational levels of \( \text{CH}_4 \) can be classified under the molecular symmetry group \( T_d(M) \). If the centrifugal distortion terms are neglected, the rovibrational levels of \( \text{CH}_4 \) are given by \( b_j(j+1) \), 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.\(^{76} \)

Note that the same symmetry may occur more than once for a given \( j \); in accordance with Ref. 76 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 \( \Phi_{m_j}^{ij} \) are linear combinations of the normalized rotation matrices \( D_{m_j}^{ij} \). 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

\[
\langle jk | H_{\text{mon}} | jk \rangle = b_j(j+1) - d_j j^2 (j+1)^2 + \frac{3}{2} d_j^2 (-3j(j-1)(j+1)(j+2) + 5k^2(6j^2 + 6j - 5) - 35k^4),
\]

\[
\langle jk | H_{\text{mon}} | jk \pm 4 \rangle = \frac{3}{2} d_j (j(j+1) - k(k \pm 1))(j(j+1) - k(k \mp 1)) \times (j(j+1) - k(k \pm 3)(k \mp 3)) \right)^{1/2},
\]

where \( b_j, d_j, \) and \( d_4 \) denote the rotational constant, centrifugal distortion constant, and the tetrahedral centrifugal distortion term, respectively. In this paper we have adopted the following values for these constants: \( b = 5.244035 \times 10^{-3} \text{ cm}^{-1} \), \( d_j = 1.10864 \times 10^{-4} \text{ cm}^{-1} \), and \( d_4 = 4.425 \times 10^{-6} \text{ cm}^{-1}. \)\(^{84} \)

The radial functions \( \chi_{J,R}(R) \) are solutions of the system of close-coupling equations. In our calculations these equations were solved using the log-derivative propagator as modified by Alexander and Manolopoulos.\(^{86} \) The log-derivative algorithm of Mrugala and Secrest\(^{85} \) was used to propagate from \( R_{\text{min}} = 5 \) bohr to \( R_{\text{end}} = 15.0 \) 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 \( R_{\text{max}} = 100 \) 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 Å\(^2\). The highest value of \( J \) was \( J_{\text{max}} = 87, 99, \) and 78 for the \( A, F, \) 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 quadrature. The integration parameters \( (R_{\text{min}}, R_{\text{end}}, \) 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 \( \text{Ar-CH}_4 \) was 11.441 478 a.m.u.\(^{87} \) All calculations were performed with the MOLSCAT system of codes.\(^{88} \)

VI. ROTATIONALLY INELASTIC CROSS SECTIONS FOR \( \text{Ar-CH}_4 \): CONFRONTATION WITH EXPERIMENT

In Table III we compare the computed state-to-state integral cross sections for \( \text{Ar-CH}_4 \) with the experimental data.\(^{32} \) Initially, the \( \text{CH}_4 \) molecules are in the lowest permissible rotational state for each of the symmetry types: \( j'' = 0, 1, \) and 2 for \( A, F, \) and \( E \) symmetries, respectively. An inspection of Table III 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 \( \text{Ar-CH}_4 \) collisions, although some deficiencies are also evident. First we note that the cross sections larger than 3 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 \( F_1(1), F_2, \) and \( F_1(2) \) symmetries, respectively. An inspection of Table III shows the ordering of the cross sections predicted by the theory \((F_1(1) > F_1(2) > F_2)\) is different from the ordering observed in the experiments \((F_1(1) > F_1(2) > F_2)\).

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 than those computed from the empirical potential of Buck et al. 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 III, 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 $0.1 \, \text{Å}^2$. 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 III, namely $11.546 \, \text{Å}^2$. 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 III 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. 29 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 $j'' \rightarrow j'' \rightarrow j'$. This mechanism will be especially important when the cross section $\sigma_{j'' \rightarrow j'}$ 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. 32. 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

$$
\frac{dP_j}{dt} = \sum_{i \neq j} \sigma_{i \rightarrow j} P_i - \sum_{i \neq j} \sigma_{j \rightarrow i} P_j,
$$

where $P_j$ denotes the population of the $j$th rotational state of CH$_4$ of a given symmetry. The initial populations are obviously $P_j(t=0) = \delta_{j',0}$, 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 III. 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 $\sigma_{j'' \rightarrow j'}/\sigma_{\text{tot}}^{(j'' \rightarrow j')}$.

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 $\epsilon_m = -144.30 \, \text{cm}^{-1}$ at $R_m = 7.00 \, \text{bohr}$, 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 ...
TABLE III. 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>( \sigma_{j'' \rightarrow j'} )</th>
<th>( P_{j'} )</th>
<th>( \sigma_{j'' \rightarrow j'} )</th>
<th>( P_{j'} )</th>
<th>( \sigma_{j'' \rightarrow j'} )</th>
<th>( P_{j'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3A_2 )</td>
<td>26.685</td>
<td>29(7)</td>
<td>22.9</td>
<td>54.598</td>
<td>52.806</td>
<td>53(7)</td>
</tr>
<tr>
<td>( 4A_1 )</td>
<td>20.661</td>
<td>20(5)</td>
<td>19.3</td>
<td>42.274</td>
<td>42.098</td>
<td>38(5)</td>
</tr>
<tr>
<td>( 6A_2 )</td>
<td>0.428</td>
<td>1.4(2)</td>
<td>0.376</td>
<td>0.876</td>
<td>1.788</td>
<td>2.3(5)</td>
</tr>
<tr>
<td>( 6A_1 )</td>
<td>0.737</td>
<td>2.0(3)</td>
<td>1.70</td>
<td>1.507</td>
<td>2.475</td>
<td>4.6(7)</td>
</tr>
<tr>
<td>( 7A_2 )</td>
<td>0.364</td>
<td>0.3(2)</td>
<td>0.819</td>
<td>0.745</td>
<td>0.834</td>
<td>0.8(6)</td>
</tr>
<tr>
<td>Total</td>
<td>48.875</td>
<td>52(9)</td>
<td>44.9</td>
<td>53.48</td>
<td>52.806</td>
<td>53(7)</td>
</tr>
</tbody>
</table>

- **A states**
- **F states**
- **E states**

- From 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.
- Experimental data, Ref. 29.
- Computed from close-coupling calculations on the empirical potential of Buck et al. (Ref. 25). The reported values represent a weighted average around the mean collision energy \( E_{CM} = 300 \) cm⁻¹.
- Defined as the ratio of the state-to-state cross section to the total inelastic cross section, \( \sigma_{j'' \rightarrow j'}/\sigma_{CM} \). A definition for \( \sigma_{CM} \) is given in Eq. (15).
- Computed from the master equation at 20% depletion of the initial state.
- Total inelastic cross section for a given initial state \( j'' \), \( \sigma_{CM} \), defined in Eq. (15).

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APPENDIX: THE CONSTRUCTION OF TETRAHEDRAL \( A_1 \) FUNCTIONs

Our goal is to find angular functions \( T_m^j \) 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 \( D_{2d} \), because functions that are invariant under \( D_{2d} \) are easily written down. Indeed, these functions are the tesseral (real) harmonics of the cosine type

\[
S_m^j = \left[ (1 - i)^m C_m^j + C_m^{-j} \right] (1 + \delta_m)^j, \quad m \geq 0, \tag{A1}
\]
that satisfy the condition that \( l + m/2 \) is an even integer. This has the consequence that for odd values of \( l \) functions \( S^l_m \) 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

\[
T^\kappa (1 + C_3 + C_3^2) S^l_m, \tag{A2}
\]

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 \( g \in T_d \subseteq \text{SO}(3) \), so that

\[
g S^l_m = \sum_k C^l_{m'} [D^l_{m'}(g) + D^l_{m'}(-g)]/(1 + \delta_{k0}), \tag{A3}
\]

where \( D^l_{m'} \) is an element of the Wigner rotation matrix.\(^77\)

The Euler angles associated with the rotation \( C_3 \) are given by

\[
(\alpha, \beta, \gamma) = \left( \frac{7\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4} \right), \tag{A4}
\]

and those describing \( C_3^2 \) are

\[
(\alpha, \beta, \gamma) = \left( \frac{\pi}{4}, \frac{5\pi}{2}, \frac{3\pi}{4} \right). \tag{A5}
\]

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

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

\[
d^l_{m'}(\pi/2) = \frac{(-1)^{m - m'}}{2^l} \sqrt{(l + m')!(l - m')!}
\]

\[
\times \sum_k (-1)^k \left( \begin{array}{c} j + m' \\ k \\ \end{array} \right) \left( \begin{array}{c} j - m \\ k + m' - m \\ \end{array} \right),
\]

where \( d^l_{m'} \) are Wigner’s functions.\(^77,89\)

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 \( A_3(A_1) \) 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. 90.


