

Contributions of multipolar polarizabilities to the isotropic and anisotropic light scattering induced by molecular interactions in gaseous methane

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The binary isotropic and anisotropic collision-induced light scattering spectra of gaseous methane at room temperature are analyzed in terms of a recent *ab initio* intermolecular potential and interaction-induced pair polarizability trace and anisotropy models, using quantum line-shapes computations. The translational spectra at relatively low frequencies are determined largely by the effects of bound and free transitions. At intermediate frequencies the spectra are sensitive to both the attractive part of the potential and the short-range part of the polarizability trace and anisotropy. The high frequency wings are discussed in terms of the collision-induced rotational Raman effect and estimates for the dipole-quadrupole polarizability **A** and the dipole-octopole polarizability **E** are obtained and checked with recent *ab initio* theoretical values. © 2009 American Institute of Physics. [DOI: 10.1063/1.3180823]

I. INTRODUCTION

Interaction-induced Raman spectra permit detailed studies of certain interatomic properties. The spectra are shaped by two quantities: the interaction potential and the interaction-induced polarizability (i.e., the excess polarizability of two interacting atoms over the sum of polarizabilities of the noninteracting atoms). In the past, mostly the spectra of dense gases have thus been studied.¹⁻³

For most rare-gas pairs, highly refined interatomic potential models exist, so that such measurements permit a determination of the induced polarizabilities of atom pairs. Here we are concerned with the collision-induced (CILS), isotropic and anisotropic Raman spectra of dense methane gas. The main features of the Raman spectra of this molecule have been reported in the past.⁴⁻⁶ Recent measurements from a few cm^{-1} up to 900 cm^{-1} with a higher resolution have been added for studying more closely the low-frequency part of the spectra (below 10 cm^{-1} , where discernible bound dimer features appear superimposed with the Raman transitions of the free pairs).⁷ Such a spectrum, recorded at a temperature of 294.5 K, will be analyzed here with the goal of developing refined models of the relevant interaction-induced properties, which permit an accurate reproduction of the observed spectrum from line-shapes calculations.

CH_4 is an ideal molecule for such an investigation as its spectra contain features that highlight several aspects of induced scattering. The spectra consist essentially of an intense, purely translational component and a weaker induced rotational wing. Effects due to scattering by bound dimers⁸⁻¹⁰ and to the quantum nature of the collision dynamics¹¹ are expected to become increasingly important to

the translational component for light molecules. Induced rotational Raman scattering was first identified in the CH_4 spectrum.¹² It is a particularly propitious example in that the rotational wing clearly extends beyond the translational component over a broad frequency range; for this reason the two contributions may then be studied independently.

The leading term in the pair polarizability, which gives rise to the translational scattering by spherical molecules, is due to the first-order dipole-induced dipole interaction. Small intermediate- and short-range overlap contributions also play a role.³ Induced rotational scattering has been interpreted by means of pair-polarizability terms, which arise from a long-range interaction mechanism involving higher-order multipole polarizabilities, such as the dipole-quadrupole polarizability **A** and the dipole-octopole polarizability **E**.¹² This paper assesses the validity of these models and the concomitant choice of parameter values in the description of the experimental spectra.

For all computations of intensities and profiles, the intermolecular potential plays an important role. The recent *ab initio* potential energy surface of Hellmann *et al.*¹³ is the most accurate available. It is based on supermolecular coupled-cluster calculations for 17 different angular orientations with 16 center-of-mass separations for each orientation. The methane monomers were assumed to form rigid regular tetrahedrons corresponding to the zero-point vibrationally averaged geometry. An analytical site-site potential function with nine sites per monomer was fitted to the calculated interaction energies. The potential function also includes a semiempirical correction for zero-point vibrational effects. This potential was utilized to calculate the second pressure virial coefficient,¹³ as well as transport and relaxation properties of dilute methane gas.^{14,15} For most of the calculated

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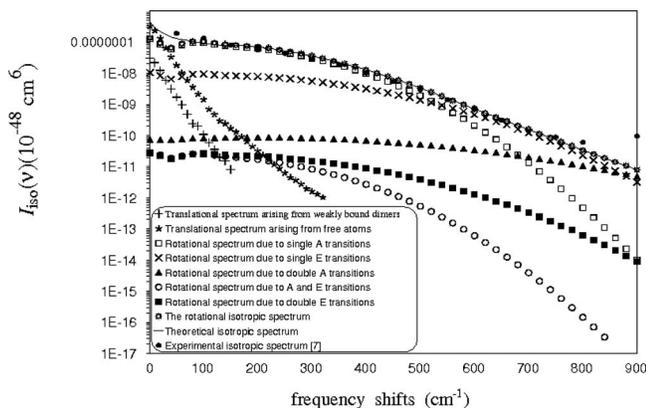


FIG. 1. Intensity of the two-body isotropic light scattering spectrum at $T=294.5$ K of CH_4 gas plotted as a function of frequency shifts. Calculations were performed with the recent *ab initio* intermolecular potential given in Ref. 13. Theoretical curves are provided for several contributions using $\alpha_o=2.642 \text{ \AA}^3$, $A=0.68 \text{ \AA}^4$, and $E=0.9 \text{ \AA}^5$.

properties, very good agreement with the best experimental data was found.

II. LIGHT SCATTERING SPECTRA

The measurements and calculations of the $\text{CH}_4\text{-CH}_4$ light scattering spectra have recently been fully reported.⁷ For purposes of completeness, some details are repeated here. Collision-induced light scattering refers to scattering from clusters, here pairs, of interacting isotropic molecules. The spectral feature of interest is a broad depolarized band about the Rayleigh line. The experimental setup is that typical of laser Raman spectroscopy. Excitation radiation was from an argon-ion laser operating on 514.5 nm at 1 W. The absolute calibration of each measured spectrum was performed by means of three intense consecutive rotational lines of hydrogen.¹⁶ In order to increase the statistical accuracy an increasing spectral slit width was used, at increasing frequency shift, for the weak tails of the nearly exponential CILS spectra. The polarizations of the laser beam are perpendicular and parallel to the scattering plane, that is the plane defined by the incident and the scattered beams. The intensities of the scattered light are then referred to as $I_{\perp}(\nu)$ and $I_{\parallel}(\nu)$ and constitute the polarized (which is related to the isotropic spectrum) and depolarized (anisotropic) spectrum, respectively.

The intensity of the collision-induced light scattering $I(\nu)$ at each frequency ν for densities less than 2 mol/l may be expressed by a virial expansion in the density ρ ,

$$I(\nu) = I^{(2)}(\nu)\rho^2 + I^{(3)}(\nu)\rho^3 + \dots, \quad (1)$$

where $I^{(2)}$ and $I^{(3)}$ relate to the two- and three-body correlation spectra, respectively. The two-body isotropic and anisotropic spectra of CH_4 gas at $T=294.5$ K are shown in Figs. 1 and 2.⁷

III. THE SPECTRAL LINESHAPE AND ITS MOMENTS

In this section the calculations of the experimental quantities are described. The Monchick–Mason approximation,¹⁷ which neglects the effects of inelastic transitions on the rela-

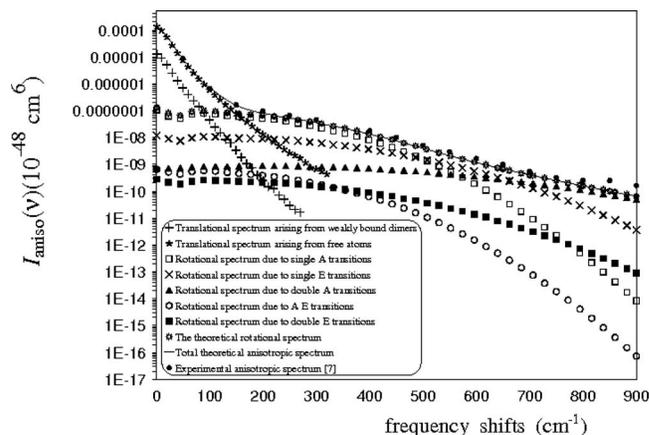


FIG. 2. Intensity of the two-body anisotropic light scattering spectrum at $T=294.5$ K of CH_4 gas plotted as a function of frequency shifts. Calculations were performed with the recent *ab initio* intermolecular potential given in Ref. 13. Theoretical curves are provided for several contributions using $\alpha_o=2.642 \text{ \AA}^3$, $A=0.7 \text{ \AA}^4$, and $E=1.25 \text{ \AA}^5$.

tive kinetic energy is applied as a check in the computation of the CILS profiles. At moderate densities, the CILS spectra are determined by binary interactions. They consist of purely translational scattering, which includes scattering due to free pairs and bound dimers, and of the induced rotational scattering. The pair polarizability trace and anisotropy giving rise to the translational scattering contributions of the isotropic and anisotropic light spectra in the case of inert gases and spherical top molecules are given by¹⁸

$$\alpha(r) = \frac{A_6}{r^6} + \frac{20\alpha_o^2 C}{r^8} - t_o \exp\left(-\frac{r-\sigma}{r_t}\right), \quad (2)$$

$$\beta(r) = \frac{6\alpha_o^2}{r^3} + \frac{A}{r^6} + \frac{24\alpha_o^2 C}{r^8} - g_o \exp\left(-\frac{r-\sigma}{r_o}\right), \quad (3)$$

with^{4,19-23}

$$A_6 = \left(4\alpha_o^3 + \frac{5}{9}\gamma C_6/\alpha_o\right), \quad (4)$$

and

$$A = (6\alpha_o^3 + \gamma C_6/3\alpha_o). \quad (5)$$

Here, α_o and γ designate atomic polarizability and hyperpolarizability, respectively, C_6 is the dispersion force coefficient, C is the quadrupole polarizability, and σ is the separation distance at which $V(r)=0$. The values of the parameters used here are as follows:^{13,24,25}

$$\alpha_o = 17.828 \text{ a.u.}, \quad \gamma = 3079.2 \text{ a.u.}, \quad C = 60.45 \text{ a.u.},$$

$$C_6 = 129.6 \text{ a.u.}, \quad \text{and} \quad \sigma = 6.93341 \text{ a.u.}$$

The other parameters have been determined by fitting to the total integrated intensities as $t_o=0.0278$ a.u. and $r_t=0.671$ a.u. for the trace and $g_o=0.091$ a.u. and $r_o=0.735$ a.u. for the anisotropy.

A purely long-range interaction mechanism, involving the participation of higher-order polarizabilities, has been invoked to account for induced rotational scattering.¹² Contributions from the dipole-quadrupole polarizability A and the dipole-octopole polarizability E for methane symmetry give

the intensity of the observed rotational spectra with the predictions of the mean square polarizability models in the case of the isotropic and anisotropic spectra as

$$\begin{aligned} \langle \alpha_{zz}^2 \rangle &= (\alpha_1 + \alpha_2)^2 + \frac{16}{5}(\alpha_1\alpha_2)^2 r^{-6} + \frac{592}{105}((\alpha_1\mathbf{A}_2)^2 \\ &+ (\alpha_2\mathbf{A}_1)^2) r^{-8} + \frac{52}{9}((\alpha_1\mathbf{E}_2)^2 + (\alpha_2\mathbf{E}_1)^2) r^{-10} \\ &+ \frac{95\,616}{4725}(\mathbf{A}_1\mathbf{A}_2)^2 r^{-10} + \frac{344}{21}((\mathbf{A}_1\mathbf{E}_2)^2 + (\mathbf{A}_2\mathbf{E}_1)^2) r^{-12} \\ &+ \frac{8591}{105}((\mathbf{E}_1\mathbf{E}_2)^2) r^{-14} + \dots, \end{aligned} \quad (6)$$

$$\begin{aligned} \langle \alpha_{xz}^2 \rangle &= \frac{12}{5}(\alpha_1\alpha_2)^2 r^{-6} + \frac{48}{35}((\alpha_1\mathbf{A}_2)^2 + (\alpha_2\mathbf{A}_1)^2) r^{-8} \\ &+ \frac{11}{9}((\alpha_1\mathbf{E}_2)^2 + (\alpha_2\mathbf{E}_1)^2) r^{-10} + \frac{62\,912}{4725}((\mathbf{A}_1\mathbf{A}_2)^2) r^{-10} \\ &+ \frac{232}{21}((\mathbf{A}_1\mathbf{E}_2)^2 + (\mathbf{A}_2\mathbf{E}_1)^2) r^{-12} + \frac{5863}{105}((\mathbf{E}_1\mathbf{E}_2)^2) r^{-14} \\ &+ \dots. \end{aligned} \quad (7)$$

The angular brackets $\langle \dots \rangle$ denote an average over all orientations of the intermolecular and molecular axes.

The various terms in Eqs. (6) and (7) give rise to the following selection rules on the total angular momentum quantum number J :

$$\alpha_i\mathbf{A}_j, \quad \Delta J_i = 0, \quad \Delta J_j = 0, \pm 1, \pm 2, \pm 3, \quad J_j + J'_j \geq 3,$$

$$\alpha_i\mathbf{E}_j, \quad \Delta J_i = 0, \quad \Delta J_j = 0, \pm 1, \pm 2, \pm 3, \pm 4$$

$$J_j + J'_j \geq 4,$$

$$\mathbf{A}_i\mathbf{A}_j, \quad \Delta J_i = 0, \pm 1, \pm 2, \pm 3,$$

$$\Delta J_j = 0, \pm 1, \pm 2, \pm 3, \quad J_i + J'_i \geq 3, \\ J_j + J'_j \geq 3,$$

$$\mathbf{A}_i\mathbf{E}_j, \quad \Delta J_i = 0, \pm 1, \pm 2, \pm 3,$$

$$\Delta J_j = 0, \pm 1, \pm 2, \pm 3, \pm 4 \quad J_i + J'_i \geq 3, \\ J_j + J'_j \geq 4,$$

$$\mathbf{E}_i\mathbf{E}_j, \quad \Delta J_i = 0, \pm 1, \pm 2, \pm 3, \pm 4$$

$$\Delta J_j = 0, \pm 1, \pm 2, \pm 3, \pm 4 \quad J_i + J'_i \geq 4, \\ J_j + J'_j \geq 4.$$

For $\text{CH}_4\text{-CH}_4$ interactions $\alpha_1 = \alpha_2 = \alpha_0$, $\mathbf{A}_1 = \mathbf{A}_2 = \mathbf{A}$, and $\mathbf{E}_1 = \mathbf{E}_2 = \mathbf{E}$.

The quantum theory is applied for the accurate computation of the CILS absolute translational intensities of the methane pairs. Numerically, this is done by means of the propagative two-point Fox–Goodwin integrator,^{26,27} where the ratio of the wave function, defined at adjacent points on a spatial grid, is built step by step.

Concerning our problem, binary isotropic and anisotropic spectra are computed quantum mechanically as a function of frequency shifts ν at temperature T by using the expressions^{28–31}

$$I_{\text{iso}}(\nu) = hc\lambda^3 k_S^4 \sum_{J=0, J \text{ even}}^{J_{\text{max}}} (2J+1) \int_0^{E_{\text{max}}} |\langle \psi_{E', J'} | \alpha | \psi_{E, J} \rangle|^2 \times \exp\left(-\frac{E}{k_B T}\right) dE, \quad (8)$$

$$I_{\text{aniso}}(\nu) = \frac{2}{15} hc\lambda^3 k_S^4 \sum_{J=0, J \text{ even}}^{J_{\text{max}}} g_j b_j^{J'} (2J+1) \times \int_0^{E_{\text{max}}} |\langle \psi_{E', J'} | \beta | \psi_{E, J} \rangle|^2 \exp\left(\frac{-E}{k_B T}\right) dE. \quad (9)$$

The symbol k_S stands for the Stokes wave number of the scattered light, h is Planck's constant, and c is the speed of the light. The constant λ accounts for the thermal de Broglie wavelength, $\lambda = h/\sqrt{2\pi\mu k_B T}$, with μ as the reduced mass of $(\text{CH}_4)_2$ and k_B as Boltzmann's constant. The symbol $\psi_{E, J}$ designates the scattering wave function and E_{max} the maximum value of the energy that is required to obtain convergence of the integrals. In these expressions, $\alpha = \alpha(r)$ and $\beta = \beta(r)$ denote the trace and anisotropy of the quasimolecule, g_j the nuclear statistical weight, and $b_j^{J'}$ are intensity factors involving the rotational quantum numbers J and J' of the initial and final states, respectively.

With the spectral intensities $I_{\text{iso}}(\nu)$ and $I_{\text{aniso}}(\nu)$ in cm^6 as input and through the following analytical expressions, we are able to deduce the isotropic moments,^{32,33}

$$M_0^{\text{iso}} = \int_V \alpha^2(r) \exp(-U(r)/k_B T) 4\pi r^2 dr, \quad (10)$$

$$M_2^{\text{iso}} = \left(\frac{2k_B T}{\mu}\right) \int_V \left(\frac{d\alpha(r)}{dr}\right)^2 \exp(-U(r)/k_B T) 4\pi r^2 dr, \quad (11)$$

$$M_4^{\text{iso}} = \left(\frac{k_B T}{\mu}\right)^2 \int_V 4\pi \exp(-U(r)/k_B T) \times \left(\frac{d^2\alpha(r)}{dr^2} r \left(3\frac{d^2\alpha(r)}{dr^2} r + \frac{d\alpha(r)}{dr} \left(2 - \frac{rdU(r)/dr}{k_B T}\right)\right) + \frac{d\alpha(r)}{dr} \left(\frac{d^2\alpha(r)}{dr^2} r \left(2 - \frac{rdU(r)/dr}{k_B T}\right) + \frac{d\alpha(r)}{dr} \times \left(8 - \frac{rdU(r)/dr}{k_B T} + \left(\frac{rdU(r)/dr}{k_B T}\right)^2\right)\right)\right) dr, \quad (12)$$

and anisotropic moments,³

$$M_0^{\text{aniso}} = \int_V \beta^2 \exp(-U(r)/k_B T) 4\pi r^2 dr, \quad (13)$$

$$M_2^{\text{aniso}} = \left(\frac{4k_B T}{15\mu}\right) \int_V \left(\left(\frac{d\beta(r)}{dr}\right)^2 + 6\left(\frac{\beta(r)}{r}\right)^2\right) \times \exp(-U(r)/k_B T) 4\pi r^2 dr, \quad (14)$$

TABLE I. Different contributions from bound, free and rotational isotropic, and anisotropic zeroth-order M_0 , second-order M_2 and fourth-order M_4 moments of CH_4 gas at $T=294.5$ K deduced from experiment and theory using different intermolecular potential models. Also, the comparison between the calculated and experimental values of the second dielectric constant B_ϵ and the second Kerr coefficient B_K are shown.

Moments	Potential								Experimental	
	LJ (12-6) ^a		RMK ^b		PA ^c		<i>ab initio</i> ^d			
	Iso.	Aniso.	Iso.	Aniso.	Iso.	Aniso.	Iso.	Aniso.	Iso.	Aniso.
$M_{0B}(\text{\AA}^9)$	0.021	37.96	0.0193	32.13	0.0224	33.023	0.0174	27.1		
$M_{0F}(\text{\AA}^9)$	0.1093	181.44	0.1014	181.0	0.1143	185.3	0.1063	180.7		
$M_{0R}(\text{\AA}^9)$	1.474	1.513	0.562	1.67	1.8823	1.126	1.219	1.33		
$M_0(\text{\AA}^9)$	1.604	220.913	0.683	214.8	2.019	219.45	1.343	209.1	...	192.24 ± 10^e
$M_{2B}(\text{\AA}^9/s^2)$	1.463	273.62	1.34	148.34	1.594	166.16	1.217	59.5		
$M_{2F}(\text{\AA}^9/s^2)$	7.681	3879.48	7.03	3870	8.204	3983.04	7.479	3674.9		
$M_{2R}(\text{\AA}^9/s^2)$	1573.4	1902.7	451.6	2109.5	2105.4	1267.5	1508.7	1551.4		
$M_2(\text{\AA}^9/s^2)$	1582.5	6055.8	459.97	6127.84	2115.2	5416.7	1517.4	5285.8	...	5310.07 ± 65^e
$M_{4B}(\text{\AA}^9/s^4)/10^5$	0.035	0.825	0.0294	0.39	0.031	0.405	0.075	2.0		
$M_{4F}(\text{\AA}^9/s^4)/10^5$	0.142	6.875	0.176	6.71	0.178	6.785	0.209	5.94		
$M_{4R}(\text{\AA}^9/s^4)/10^5$	10.3	79.6	10.3	83.3	5.8	47.03	8.5	60.6		
$M_4(\text{\AA}^9/s^4)/10^5$	10.48	87.3	10.51	90.4	6.0	54.22	8.78	68.54	...	68.61 ± 5.92^e
$B_\epsilon(\text{cm}^6/\text{mol}^2)$	7.24	...	7.043	...	7.043	...	7.03	...	7.29 ± 0.32^f	...
	7.03	...	6.85	...	6.86	...	6.77	...	6.75 ± 0.29^g	...
$B_K(\text{C}^2 \text{ m}^8 \text{ J}^{-2}) \times 10^{33}$...	33.8	...	32.9	...	33.6	...	32.0	...	39 ± 5^h

^aReference 37.

^bReference 39.

^cReference 38.

^dReference 13.

^eReferences 5 and 7.

^fAt $T=322.5$ K.

^gAt $T=373.4$ K. Reference 40.

^hAt $T=292$ K. Reference 41.

$$\begin{aligned}
 M_4^{\text{aniso}} = & \int_0^\infty \left(4\pi \left(\frac{k_B T}{\mu} \right)^2 \left(3 \left(\frac{d^2 \beta}{dr^2} \right)^2 + 4 \left(\frac{d\beta}{dr} \right) \left(\frac{d^2 \beta}{dr^2} \right) \right. \right. \\
 & - 12 \frac{\beta}{r^2} \left(\frac{d^2 \beta}{dr^2} \right) + \frac{32}{r^2} \left(\frac{d\beta}{dr} \right)^2 - 96 \frac{\beta}{r^3} \left(\frac{d\beta}{dr} \right) \\
 & + 120 \frac{\beta^2}{r^4} \left. - 4\pi \frac{2k_B T}{\mu} \left(\frac{1}{\mu} \left(\frac{dU}{dr} \right) \left(\frac{d^2 \beta}{dr^2} \right) \left(\left(\frac{d^2 \beta}{dr^2} \right) \right. \right. \right. \\
 & + \left. \left. \frac{2}{r} \left(\frac{d\beta}{dr} \right) - 6 \frac{\beta}{r^2} \right) \right) + 4\pi \frac{1}{\mu^2} \left(\left(\frac{dU}{dr} \right) \right. \right. \\
 & \left. \left. \times \left(\frac{d\beta}{dr} \right) \right)^2 \right) \exp(-U(r)/k_B T) r^2 dr, \quad (15)
 \end{aligned}$$

where λ denotes the laser wavelength and $U(r)$ is the interatomic potential. These results were compared with the experimental moments obtained from the isotropic and anisotropic intensities of the light scattering spectra,^{3,32}

$$M_{2n} = \int_{-\infty}^{\infty} (2\pi c \nu)^{2n} I_{\text{iso}}(\nu) d\nu, \quad (16)$$

$$M_{2n} = \int_{-\infty}^{\infty} (2\pi c \nu)^{2n} I_{\text{aniso}}(\nu) d\nu. \quad (17)$$

An effective means for checking the validity of the induced trace and anisotropy models is to compare the computed second dielectric virial coefficient B_ϵ and second Kerr virial coefficient B_K with the experimental ones. This is done by using the following formulae:^{34,35}

$$B_\epsilon = \frac{8\pi^2}{3} N_A^2 \int_V \alpha(r) \exp(-U(r)/k_B T) r^2 dr, \quad (18)$$

$$B_K = \frac{8\pi^2}{405 k_B T} N_A^2 \int_V \beta(0, r) \beta(\omega, r) \exp(-U(r)/k_B T) r^2 dr, \quad (19)$$

where $\beta(0, r)$ and $\beta(\omega, r)$ are the anisotropies of CH_4 for static dipole polarizability $\alpha(\omega=0)=\alpha_o=2.642 \text{ \AA}^3$ and dipole polarizability at $(\omega>0)=\alpha=2.6064 \text{ \AA}^3$.³⁶

The total theoretical intensities of the isotropic and anisotropic light scattering spectra are the sum of the translational spectra due to the transitions of bound-bound, bound-free, and free-free states and rotational spectra. In order to calculate the line profiles and the associated moments, the intermolecular potential is needed. Results with different potentials can be compared with experiment to assess the quality of the potentials. In this paper we consider the different empirical and more recent *ab initio* potentials.^{13,37-39}

Comparisons between the calculations and experiments are shown in Figs. 1 and 2 for the intensities of the isotropic and anisotropic light scattering spectra of CH_4 and Table I for the first few even moments of these profiles. Also, the comparisons of the calculated and experimental values of the second dielectric constants and second Kerr coefficients are shown in Table I.

Concerning the multipolar contributions of single **A**, double **A**, single **E**, **A** and **E**, and double **E** transitions, different values of the dynamic independent tensor components **A** and **E** may be used to fit the experimental isotropic and anisotropic intensities in the frequency ranges

TABLE II. Values of the independent components **A** and **E** of the dipole-quadrupole and dipole-ctopole polarizability tensors, respectively, for the CH₄ molecule.

Present work	Method	A (Å ⁴)	E (Å ⁵)
Theory			
Buckingham and Tabisz ^a	Bond polarizability model	1.0	-1.0
Amos ^b	<i>Ab initio</i> (CI)	0.74	0.76
Diercksen and Sadlej ^c	<i>Ab initio</i> (SCF)	0.76	0.81
Fowler <i>et al.</i> ^d	<i>Ab initio</i> (RPA)	0.81	0.84
Maroulis ^e	<i>Ab initio</i> [CCSD(T)]	0.71	0.78
Experiment			
Shelton and Tabisz ^f		1.0	2.5
Penner <i>et al.</i> ^g		0.88 ± .05	...
Isnard <i>et al.</i> ^h	Virial coefficient	2.35	...
Rajan and Lalita ⁱ	NMR	2.71	...
Buck <i>et al.</i> ^j	Proton spin relaxation	0.89	
Barocchi <i>et al.</i> ^k	Anisotropic CILS spectrum	0.88	2.5
Meinander <i>et al.</i> ^l	Anisotropic CILS spectrum	0.75	2.7
Bancewicz <i>et al.</i> ^m	Isotropic CILS spectrum	0.7 ^{+0.1} _{-0.2}	0.6 ± 0.6
This work	CH ₄ isotropic spectrum using <i>ab initio</i> potential ⁿ	0.68 ± 0.5	0.9 ± 0.3
	CH ₄ anisotropic spectrum using <i>ab initio</i> potential ⁿ	0.7 ± 0.08	1.25 ± 0.5

^aReference 12.^bReference 42.^cReference 43.^dReference 44.^eReference 45.^fReference 46.^gReference 47.^hReference 48.ⁱReference 49.^jReference 50.^kReference 5.^lReference 6.^mReference 7.ⁿReference 13.

180–900 cm⁻¹ and 230–900 cm⁻¹, respectively. Figures 1 and 2 suggest that there are choices of **A** and **E** for which the theoretical and experimental isotropic and anisotropic spectra fit the best: **A**=0.68 Å⁴, **E**=0.9 Å⁵ and **A**=0.7 Å⁴, **E**=1.25 Å⁵ respectively using the *ab initio* potential.¹³ Also in Table II we reported the theoretical and experimental values of these coefficients from the bond polarizability model, virial coefficient, NMR and molecular beam scattering,^{12,42–44,46–50} and those recently calculated *ab initio* by Maroulis [i.e., his “best or recommended” CCSD(T) values taking into account electron correlation corrections].⁴⁵ It is immediately apparent from the comparisons in Figs. 1 and 2 and Tables I and II that the *ab initio* potential¹³ is superior to the LJ,³⁷ PA,³⁸ and RMK (Ref. 39) potentials.

IV. CONCLUSION

The present study further demonstrates that the *ab initio* potential by Hellmann *et al.*¹³ is a very good representation of the intermolecular potential of methane gas. The profiles of the two-body isotropic and anisotropic collision-induced light scattering spectra at $T=294.5$ K can be accounted for by a calculation employing a classical trajectory to simulate the collision. The significant contributions to the spectra by bound dimers are found to be essentially the same as that arrived at by full quantum mechanical calculations. At high frequencies we show that most of the intensities may be attributed to multipolar contributions involving the dipole-quadrupole **A** and dipole-octopole **E** polarizability tensors. Moreover, the very broad frequency range probed by

Bancewicz *et al.* provides enough information to deduce values for the independent components of **A** and **E**. This is confirmed by the good agreement between our fitted values from spectra and the one computed *ab initio* by Maroulis.⁴⁵ In conclusion, this work shows that when high frequency intensities are observed CILS is a suitable technique for studying multipolar contributions in tetrahedral molecules.

¹G. C. Tabisz, in *Specialist Periodical Report-Molecular Spectroscopy VI*, edited by R. F. Barrow, D. A. Long, and J. Sheridan (Chemical Society, London, 1979), Vol. 136.

²L. Frommhold, *Adv. Chem. Phys.* **46**, 1 (1981).

³F. Barocchi and M. Zoppi, in *Phenomena Induced by Intermolecular Interactions*, edited by G. Birnbaum (Plenum, New York, 1985), Vol. 311.

⁴N. Meinander, G. C. Tabisz, and M. Zoppi, *J. Chem. Phys.* **84**, 3005 (1986).

⁵F. Barocchi, A. Guasti, M. Zoppi, S. M. El-Sheikh, G. C. Tabisz, and N. Meinander, *Phys. Rev. A* **39**, 4537 (1989).

⁶N. Meinander, G. C. Tabisz, F. Barocchi, and M. Zoppi, *Mol. Phys.* **89**, 521 (1996).

⁷T. Bancewicz, K. Nowicka, J.-L. Godet, and Y. Le Duff, *Phys. Rev. A* **69**, 062704 (2004).

⁸A. T. Prengel and W. S. Gornall, *Phys. Rev. A* **13**, 253 (1976).

⁹D. H. Godfried and I. F. Silvera, *Phys. Rev. Lett.* **48**, 1337 (1982); *Phys. Rev. A* **27**, 3008 (1982).

¹⁰Y. Le Duff, R. Ouillon, V. Chandrasekharan, and B. Silvi, *Mol. Phys.* **62**, 1065 (1987).

¹¹F. Barocchi, M. Moraldi, M. Zoppi, and J. D. Poll, *Mol. Phys.* **43**, 1193 (1981).

¹²A. D. Buckingham and G. C. Tabisz, *Opt. Lett.* **1**, 220 (1977); *Mol. Phys.* **36**, 583 (1978).

¹³R. Hellmann, E. Bich, and E. Vogel, *J. Chem. Phys.* **128**, 214303 (2008).

¹⁴R. Hellmann, E. Bich, E. Vogel, A. S. Dickinson, and V. Vesovic, *J. Chem. Phys.* **129**, 064302 (2008).

- ¹⁵R. Hellmann, E. Bich, E. Vogel, A. S. Dickinson, and V. Vesovic, *J. Chem. Phys.* **130**, 124309 (2009).
- ¹⁶F. Chapeau-Blondeau, V. Teboul, J. Berrue, and Y. Le Duff, *Phys. Lett. A* **173**, 153 (1993).
- ¹⁷L. Monchick, K. S. Yun, and E. A. Mason, *J. Chem. Phys.* **39**, 654 (1963).
- ¹⁸S. M. El-Sheikh, G. C. Tabisz, and A. D. Buckingham, *Chem. Phys.* **247**, 407 (1999).
- ¹⁹A. D. Buckingham, *Trans. Faraday Soc.* **52**, 1035 (1956).
- ²⁰A. D. Buckingham and K. L. Clarke, *Chem. Phys. Lett.* **57**, 321 (1978).
- ²¹K. L. C. Hunt and J. E. Bohr, *J. Chem. Phys.* **84**, 6141 (1986).
- ²²K. L. C. Hunt, Y. Q. Liang, and S. Sethuraman, *J. Chem. Phys.* **89**, 7126 (1988).
- ²³M. Jaszuński, A. Rizzo, and P. Jørgensen, *Theor. Chem. Acc.* **106**, 251 (2001).
- ²⁴N. Meinander, A. R. Penner, U. Bafle, F. Barocchi, M. Zoppi, D. P. Shelton, and G. C. Tabisz, *Mol. Phys.* **54**, 493 (1985).
- ²⁵G. Maroulis, *Chem. Phys. Lett.* **226**, 420 (1994).
- ²⁶D. W. Norcross and M. J. Seaton, *J. Phys. B* **6**, 614 (1973).
- ²⁷M. Chrysos and R. Lefebvre, *J. Phys. B* **26**, 2627 (1993).
- ²⁸N. Meinander, in *Spectral Line Shapes*, edited by L. Frommhold and J. W. Keto (AIP, New York, 1990), Vol. 6, p. 515.
- ²⁹O. Gaye, M. Chrysos, V. Teboul, and Y. Le Duff, *Phys. Rev. A* **55**, 3484 (1997).
- ³⁰M. Chrysos, O. Gaye, and Y. Le Duff, *J. Phys. B* **29**, 583 (1996).
- ³¹M. Chrysos, O. Gaye, and Y. Le Duff, *J. Chem. Phys.* **105**, 31 (1996).
- ³²H. B. Levine and G. Birnbaum, *J. Chem. Phys.* **55**, 2914 (1971).
- ³³T. Bancewicz, *Chem. Phys. Lett.* **213**, 363 (1993).
- ³⁴T. K. Bose, in *Collision- and Interaction-Induced Spectroscopy*, edited by G. C. Tabisz and M. N. Neuman (Kluwer-Academic, the Netherlands, 1995), pp. 77–86.
- ³⁵A. D. Buckingham and D. A. Dunmur, *Trans. Faraday Soc.* **64**, 1776 (1968).
- ³⁶A. D. Buckingham and B. J. Orr, *Trans. Faraday Soc.* **65**, 673, (1969).
- ³⁷J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- ³⁸B. J. Palmer and J. L. Anchell, *J. Phys. Chem.* **99**, 12239 (1995).
- ³⁹N. Meinander and G. C. Tabisz, *J. Chem. Phys.* **79**, 416 (1983).
- ⁴⁰T. K. Bose, J. Sochanski, and R. H. Cole, *J. Chem. Phys.* **57**, 3592 (1972).
- ⁴¹D. A. Dunmur, D. C. Hunt, and N. E. Jessup, *Mol. Phys.* **37**, 713 (1979).
- ⁴²R. D. Amos, *Mol. Phys.* **38**, 33 (1979).
- ⁴³G. H. F. Diercksen and A. J. Sadlej, *Chem. Phys. Lett.* **114**, 187 (1985).
- ⁴⁴P. W. Fowler, P. Lazzeretti, and R. Zanasi, *Mol. Phys.* **68**, 853 (1989).
- ⁴⁵G. Maroulis, *J. Chem. Phys.* **105**, 8467 (1996).
- ⁴⁶D. P. Shelton and G. C. Tabisz, *Mol. Phys.* **40**, 299 (1980).
- ⁴⁷A. R. Penner, N. Meinander, and G. C. Tabisz, *Mol. Phys.* **54**, 479 (1985).
- ⁴⁸P. Isnard, D. Robert, and L. Galatry, *Mol. Phys.* **31**, 1789 (1976).
- ⁴⁹S. Rajan and K. Lalita, *J. Magn. Reson.* **16**, 115 (1974).
- ⁵⁰U. Buck, J. Schleusener, D. J. Malick, and D. Secretst, *J. Chem. Phys.* **74**, 1707 (1981).