

ORIGINAL ARTICLE

Multiproperty empirical isotropic interatomic potentials for CH₄–inert gas mixtures



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Abstract An approximate empirical isotropic interatomic potentials for CH₄–inert gas mixtures are developed by simultaneously fitting the Exponential-Spline-Morse-Spline-van der Waals (ESMSV) potential form to viscosity, thermal conductivity, thermal diffusion factors, diffusion coefficient, interaction second pressure virial coefficient and scattering cross-section data. Quantum mechanical lineshapes of collision-induced absorption (CIA) at different temperatures for CH₄–He and at $T = 87$ K for CH₄–Ar are computed using theoretical values for overlap, octopole and hexadecapole mechanisms and interaction potential as input. Also, the quantum mechanical lineshapes of collision-induced light scattering (CILS) for the mixtures CH₄–Ar and CH₄–Xe at room temperature are calculated. The spectra of scattering consist essentially of an intense, purely translational component which includes scattering due to free pairs and bound dimers, and the other is due to the induced rotational scattering. These spectra have been interpreted by means of pair-polarizability terms, which arise from a long-range dipole-induced-dipole (DID) with small dispersion corrections and a short-range interaction mechanism involving higher-order dipole–quadrupole **A** and dipole–octopole **E** multipole polarizabilities. Good agreement between computed and experimental lineshapes of both absorption and scattering is obtained when the models of potential, interaction-induced dipole and polarizability components are used.

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Introduction

In a previous work, we compared measurements of collision-induced absorption (CIA) and of collision induced light scattering (CILS) spectra of hydrogen, inert gas mixtures and CF₄–He gas mixtures with theoretical profiles that were based on the empirical induced dipole for CIA, induced trace and anisotropy polarizabilities for CILS, and new advanced interaction potential [1–4]. Due to the observed agreements for both spectra of absorption and scattering for these gas mixtures, we use the same treatment of transport, thermophysical properties

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and scattering cross-sections data for CH₄-inert gas mixtures, to construct the parameters of the interaction potentials.

Collisional pairs of molecules in dense phase show an absorption band in the far infrared region of the spectrum [5,6]. This absorption is due to the induced dipole moment arising from the distortion of the electronic clouds during the collision of two molecules. As the induced dipole moment depends on the distance between the colliding pair, the translational state of the system can change due to the interaction of the induced dipole with the electromagnetic field, giving rise to a rototranslational absorption band. Measurements of collision-induced absorption (CIA) spectra give therefore information on interatomic interactions. Specifically, spectral lineshapes and intensities reflect certain details of the induced dipole as function of the interatomic separation and the collision dynamics (i.e. the interatomic potential).

On another level, the anisotropic collision-induced light scattered by a fluid and dense gases due to collisional interactions, has a power spectrum which is shaped by two functions of the interatomic separation r , the interatomic potential $V(r)$ and the anisotropy $\beta(r)$ of the induced polarizability [7,8]. Information on the molecular interactions may be obtained from this spectrum. For the lower-frequency part of collision-induced spectrum, the dipole-induced-dipole (DID) interaction and electron exchange contributions account for most of the observed scattering intensities, whereas, at high frequency range (the well region of the intermolecular potential), higher-order multipolar polarizabilities have to be taken into account and can thus be measured for molecular pair against the classical DID background [9]. For mixtures and molecular gases, the excess polarizability induced by interactions in a pair is a tensor that has anisotropy $\beta(r)$ related to the anisotropic collision-induced light scattering (CILS). Recently, we showed for a few characteristic systems that the spectral properties of anisotropic interaction-induced light scattering can be calculated for the gaseous state, on the basis of classical, empirical or *ab initio* models of the induced anisotropy and of the interaction potential [10–12].

As no adequate potentials are available for these mixtures, we calculate an approximate isotropic interatomic potential using mostly the methods outlined in a previous paper [4]. Since the details of the methods are given there and the references therein, we will only restate the equations when it is necessary for the sake of continuity. To reiterate, the basic strategy in this paper is to include collision-induced absorption and collision-induced light scattering data in addition to the data on second pressure virial coefficients, mixtures viscosity, diffusion, thermal conductivity coefficients and isotopic thermal factors to fit the simple functional form of the Exponential-Spline-Morse-Spline-van der Waals (ESMSV) interatomic potentials for CH₄-inert gas interactions.

The transport, thermophysical properties and scattering cross-section data used in the fitting are complementary ones for that purpose. For these mixtures, the viscosity, thermal conductivity, isotopic thermal factor and diffusion data are most sensitive to the wall of the potential from r_m inward to a point, where the potential is repulsive [13]. The second pressure virial coefficients reflect the size of r_m and the volume of the attractive well [14], while the integral scattering cross-section contains detailed information on the potential well features and long-range attraction [15].

Our paper is organized as follows. The adopted intermolecular potential model with the calculations of different

properties are presented in Section 2. The analysis of collision-induced absorption (CIA) and light scattering (CILS) spectral moments to determine the parameters of the induced dipole and the anisotropy models is given in Section 3, with the results are presented and discussed in detailed and the concluding remarks are given in conclusion section.

The intermolecular potential models and multiproperty analysis

In order to calculate the line profiles of absorption and scattering and their associated moments, the intermolecular potential is needed. Results with different potentials can be compared with experiment to assess the quality of the potential.

The intermolecular potential we provide here is obtained through the analysis of a set of gaseous transport properties [16–19], the second pressure virial coefficients [19–24] and integral scattering cross-section [25].

For the analysis of all these experimental data we consider the Exponential-Spline-Morse-Spline-van der Waals (ESMSV) model [26].

$$V(r) = \varepsilon A_0 (\exp(-B_0(r/r_m - 1)) \quad 0 \leq r \leq r_1 \quad (1)$$

$$= \varepsilon \exp(a_1 + (r/r_m - r_1/r_m)\{a_2 + (r/r_m - r_2/r_m)[a_3 + (r/r_m - r_1/r_m)a_4\}) \quad r_1 \leq r \leq r_2 \quad (2)$$

$$= \varepsilon \{\exp[-2\xi(r - r_m)] - 2\exp[\xi(r - r_m)]\} \quad r_2 \leq r \leq r_3 \quad (3)$$

$$= \varepsilon (B_1 + (r/r_m - r_3/r_m)\{B_2 + (r/r_m - r_4/r_m)[B_3 + (r/r_m - r_3/r_m)B_4]\}) \quad r_3 \leq r \leq r_4 \quad (4)$$

$$= \varepsilon \left(-\frac{C_6}{(r/r_m)^6} - \frac{C_8}{(r/r_m)^8} \right) \quad r \geq r_4 \quad (5)$$

where ε is the potential depth, r_m is the distance at the minimum potential and C_6 and C_8 are fitting parameters.

The parameters of the spline parts of the potential (a_1 , a_2 , a_3 , a_4 , b_1 , b_2 , b_3 and b_4) are completely determined by the continuity on the value and slope of the potential at r_1 , r_2 , r_3 and r_4 .

Even at the present (ESMSV) level, there are eleven free parameters (ε , A_0 , B_0 , r_m , ξ , r_1 , r_2 , r_3 , r_4 , C_6 and C_8) which are far too many to determine from the present data. Accordingly we proceeded as follows: the long-range dispersion coefficients C_6 and C_8 were fixed at the values given by Fowler et al. [27] for CH₄-He, -Ne, -Ar and at the values given by Dunlop and Bignell [17] for CH₄-Kr, -Xe, leaving only nine parameters ε , A_0 , B_0 , r_m , ξ , r_1 , r_2 , r_3 and r_4 that were varied to fit the viscosity, diffusion data, isotopic thermal factors and thermal conductivity. This fitting is further supported by calculating the interaction second pressure virial coefficients and scattering cross-section data. Calculations were speeded by determining rough values of these parameters and then final convergence was obtained by iteration with the full isotropic potential. This decision leads to potential parameters of Table 1 as our best estimate of the CH₄-inert gas mixtures intermolecular potentials.

Analysis of traditional transport properties

The first check on the proposed potentials is to compare the transport properties i.e. viscosity (η), thermal conductivity (λ), self diffusion coefficient (D) and isotopic thermal factor (Iso) at different temperatures for CH₄-inert gas which are deduced using the formulas of Monchick et al. [28] and compared with the accurate experimental results of Kestin and

Table 1 Parameters of the trial potentials and the associated values of δ^a .

Potential parameters	CH ₄ -He	CH ₄ -Ne	CH ₄ -Ar	CH ₄ -Kr	CH ₄ -Xe
ε (K)/ k_B	25.0	64.0	170.0	197.0	227.5
σ (nm)	0.333963	0.337244	0.344628	0.362329	0.38046
r_m (nm)	0.374	0.3775	0.385	0.404	0.424
ζ	6.475	6.50	6.61	6.72	6.75
A_0	0.00315	0.0035	0.0041	0.0045	0.011
B_0	20.6822	21.5175	19.15375	18.18	20.99648
r_1 (nm)	0.1575214	0.16	0.14	0.135	0.15
r_2 (nm)	0.230	0.2405	0.2359	0.25	0.3
r_3 (nm)	0.4441412	0.4077	0.440825	0.418342	0.4402
r_4 (nm)	0.6545	0.5983375	0.59675	0.56964	0.65
δ_η	0.45	0.61	0.39	0.54	0.68
δ_D	0.43	0.68	0.78	0.83	0.88
δ_{Iso}	0.9	0.99	0.85	0.81	0.92
δ_λ	–	–	0.67	–	–
δ_B	0.1	0.09	0.53	0.6	0.73
δ_{SC}	–	0.72	0.63	0.99	0.75
δ_t	0.55	0.71	0.66	0.77	0.8

δ^a is defined by $\delta^a = \sqrt{(1/N) \sum_{j=1}^N (1/n_j \sum_{i=1}^{n_j} A_{ji}^{-2} (P_{ji} - p_{ji})^2)}$, where P_{ji} and p_{ji} are, respectively, the calculated and experimental values of property j at point i and A_{ji} is the experimental uncertainty of property j at point i . The subscripts η , D , Iso , λ , B , SC and t refer, respectively, to the viscosity, diffusion, isotopic thermal factor, thermal conductivity, pressure virial coefficient, integral scattering cross-section and total.

Ro [16], Dunlop and Bignell [17], Trengove et al. [18] and Zarkova et al. [19]. The agreement is excellent in the whole temperature range.

Analysis of the pressure second virial coefficient

The pressure second virial coefficient B at temperature T was calculated classically from [29]:

$$B(T) = 2\pi N_o \int_0^\infty [1 - \exp(-V(r)/k_B T)] r^2 dr \quad (6)$$

where N_o is the Avogadro number. The calculated $B(T)$ with the first three quantum corrections using the present ESMSV and other potentials [17,30,31] were compared with the experimental results [19–24] for CH₄-inert gas mixtures. The comparison is as shown in Fig. 1 for CH₄-Ar.

Analysis of integral scattering cross-sections

In the atom-atom interaction it is well known that the glory pattern contains detailed information on the potential well

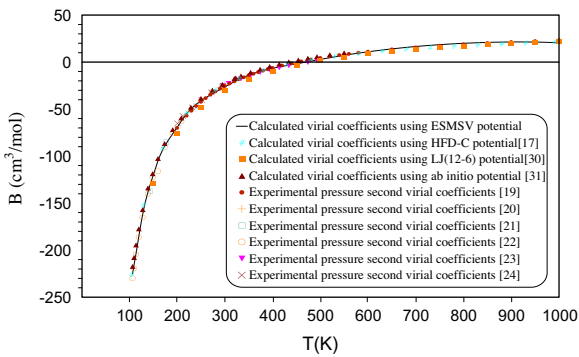


Fig. 1 CH₄-Ar second pressure virial coefficients in cm³/mole vs. temperature in K using ESMSV potential with the parameters given in Table 1 and different literature potentials.

features, while the absolute value of the cross-section contains information about the long-range attraction. The experimental cross-sections [25] are compared with the results from calculations performed with the ESMSV of Table 1 in case of CH₄-Xe. From this comparison it can be seen that this potential yields good agreement with the experiment and better fitting to the glory extrema velocity locations.

Theory of lineshapes

In this section the quantum mechanical calculations for collision-induced absorption (CIA) and for collision-induced light scattering (CILS) are described. The atomic wavefunctions, which enter the computation of the matrix elements, are obtained by numerical integration of the radial Schrödinger equation [10] using the energy density normalization.

Collision-induced absorption

Collision-induced absorption spectra (CIA) can be computed from quantum mechanical theory if the interaction potential is known along with a suitable model of the collision-induced dipole moment [8,32]. The absorption coefficient $\alpha(\omega, T)$ is related to the product of volume V and the so-called spectral function, $G(\omega, T)$, according to [10]

$$\alpha(\omega; T) = \frac{4\pi^2}{3\hbar c} n_1 n_2 \omega (1 - \exp(-\hbar\omega/k_B T)) G(\omega; T) \quad (7)$$

Here, ω designates angular frequency; \hbar is Planck's constant; c is the speed of light in vacuum and n_1, n_2 is the number densities of the gases.

The spectral density $G(\omega, T)$ is defined in terms of the matrix elements of the isotropic overlap induction $A = 0$, induced electric octopole $A = 3$ and hexadecapole $A = 4$ as

$$G(\omega; T) = \sum_{A=0,3,4} \sum_{j,j'} \rho_{jj'}^{(A)} \frac{(2j+1)(2j'+1)}{(2A+1)} g_{LA}(\omega - \omega_{jj'}), \quad (8)$$

with the different coefficients which are defined in detailed in [32].

The spectral density $g_{LA}(\omega, T)$ is defined in terms of the matrix elements of the induced electric dipole moment $B_A(L; r)$ and Clebsch–Gordan coefficients $C(\lambda_1 \lambda_2 A; M_1 M_2 M_A)$ as

$$g_{LA}(\omega; T) = \lambda_o^3 \hbar \sum_{l, l'} (2l+1) C(l l'; 000)^2 \omega (l' j_1 j_2 j_2')^2 \times \left(\int_0^\infty \exp(-E_l/k_B T) dE_l |\langle l, E_l | B_A(L; r) | l', E_l + \hbar\omega \rangle|^2 + \sum_{v, v'} \exp(-E_{v'l}/k_B T) |\langle l, E_{v'l} | B_A(L; r) | l', E_{v'l} \rangle|^2 \delta(E_{v'l} - E_{v'l} - \hbar\omega) + \sum_v \exp(-E_{v'l}/k_B T) |\langle l, E_{v'l} | B_A(L; r) | l', E_{v'l} + \hbar\omega \rangle|^2 + \sum_{v'} \exp(-(E_{v'l} - \hbar\omega)/k_B T) |\langle l, E_{v'l} - \hbar\omega | B_A(L; r) | l', E_{v'l} \rangle|^2 \right) \quad (9)$$

where the first term in the right-hand side of Eq. (9), the integral, represents the free-free transitions of the collisional pair and is usually the dominant term in this expression. The second term, a sum, gives the bound-bound transitions of the van der Waals dimers with the vibrational and rotational quantum numbers n and l respectively. The last two terms account for bound-free and free-bound transitions of the molecular pair with the positive free-state energies, i.e. $E_l + \hbar\omega > 0$ and $E_{l'} - \hbar\omega$.

Spectral moments are defined as

$$M_n(T; \lambda_1 \lambda_2 LA) = \int_{-\infty}^{\infty} \omega^n G(\omega; T) d\omega \quad (10)$$

for $n = 0, 1, 2, \dots$. These moments can be compared to values calculated directly from the sum rules [33].

It is often inconvenient to use tabular data in spectral moments and line shape computations. We have therefore, obtained an analytical models for the overlap ($L = 1, A = 0$), the octopole ($L = 4, A = 3$) and hexadecapole ($L = 5, A = 4$) contributions in the range of interest (near 5.98 Bohr) by a least mean squares fit. The different forms of these contributions are

$$B_0(L; r) = \mu_o \exp(-(r - \sigma)/r_o) \quad (11)$$

$$B_A(L; r) = \sqrt{(A+1)} \alpha Q_A / r^{L+1} \quad (12)$$

Here, $\alpha = 1.384$ a.u. [34] and $\alpha = 11.3304633$ a.u. [35] are the dipole polarizability of helium and argon respectively. $Q_3 = 3.96439$ a.u. [36] and $Q_4 = 10.723$ a.u. [36] are the octopole and hexadecapole moments of methane.

As a first step, we used the induced dipole, Eqs. (11) and (12) with the parameters given in Taylor and Borysow [32]. The crossed line in Fig. 2 gives the calculated line shape for comparison with the measurement at $T = 150$ K [32] for CH₄–He. The agreement is less than perfect. The calculated absorption is too weak and the high frequency wing is not well represented at all, in spite of the fact that the lowest three spectral moments of the measurements agree very closely with those of the computed line shape. Therefore, we add an overlap parts to the dispersion for octopole and hexadecapole contributions,

$$B_A(L; r) = \sqrt{(A+1)} \alpha Q_A / r^{L+1} + \mu_A \exp(-(r - \sigma)/r_A) \quad (13)$$

where μ_A are the dipole strengths at the root σ of the potential, $V(r) = 0$ at $r = \sigma$ and r_A are the ranges of the induced dipole. Ranges and strengths are the parameters determined by the analysis, with the results are given in Table 2.

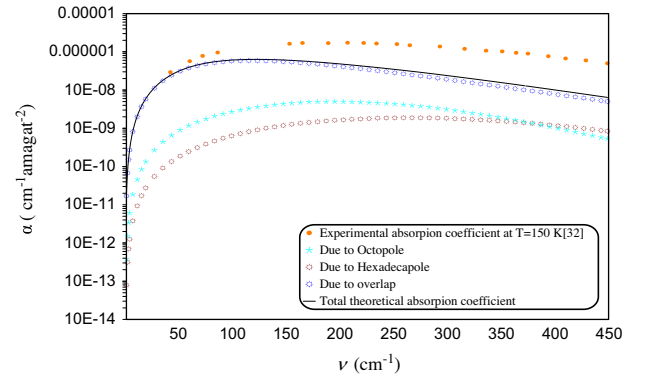


Fig. 2 Comparison between the calculated rototranslational collision-induced absorption spectrum of CH₄–He at $T = 150$ K using the present ESMSV potential given in Table 1 and induced dipole moment Eqs. (11) and (12) with the experimental one.

Table 2 Parameters of the dipole moment expansion coefficients defined in Eqs.(11) and (13).

Term LA	μ_A (a.u.)		r_A (a.u.)	
	CH ₄ –He	CH ₄ –Ar	CH ₄ –He	CH ₄ –Ar
10	0.00323	0.00375	0.70392	0.70865
43	0.00255	0.0105	0.6992	0.2551
54	0.00116	0.0035	0.62361	0.6142

Since an accurate determination of these spectral integrals requires knowledge of the absorption coefficient $\alpha(\omega, T)$ at low and high frequencies, which are not available, it is best to approximate the spectral function $G(\omega, T)$ by a three-parameter analytical model profile, the so-called BC model [37]. This model was chosen to provide a remarkably close representation of virtually all line shapes arising from exchange and dispersion force induction. These parameters have been determined by fitting the experimental spectrum, using a least mean squares procedure. The parameters of the fit are collected in Table 2 and the three lowest spectral moments of the measurements at different temperatures for CH₄–He [32] and at $T = 87$ K for CH₄–Ar [38] for each contribution are readily obtained. They are given in Table 3, and the absorption spectra are shown in Figs. 3 and 4.

The spectral lineshapes of scattering

At moderate densities, the CILS spectra are determined by binary interactions. It consists of purely translational scattering which includes scattering due to free pairs and bound dimers, and the other is due to the induced rotational scattering. The pair polarizability anisotropy giving rise to the translational scattering of the anisotropic light spectrum in the case of inert gases and spherical top molecules mixtures is given by the following formula [39].

$$\beta(r) = \frac{6\alpha_1\alpha_2}{r^3} + \frac{(3\alpha_1^2\alpha_2 + 3\alpha_2^2\alpha_1 + C_6(\frac{\gamma_1}{3\alpha_1} + \frac{\gamma_2}{3\alpha_2}))}{r^6} + \frac{12(\alpha_1^2C_2 + \alpha_2^2C_1)}{r^8} - g_o \exp\left(-\frac{r-\sigma}{r_o}\right) \quad (14)$$

Table 3 Translational spectral moments of absorption from different contributions of CH₄-He and CH₄-Ar using our empirical ESMSV potential.

$B_A(L; r)T(K)$	$M_0 \times 10^{62} (\text{erg cm}^6)$	$M_1 \times 10^{50} (\text{erg cm}^6/\text{s})$	$M_2 \times 10^{36} (\text{erg cm}^6/\text{s}^2)$	
	Calculated	Calculated	Calculated	
CH₄-He				
150	B_{10}	1.1334	8.35	4.391
	B_{43}	1.095	8.92	4.78
	B_{54}	0.0954	1.418	0.832
293	B_{10}	2.08	15.37	13.88
	B_{43}	1.9	16.34	14.96
	B_{54}	0.2125	3.102	3.01
353	B_{10}	2.51	18.55	19.7
	B_{43}	2.263	19.7	21.2
	B_{54}	0.27	3.93	4.404
CH₄-Ar				
87	B_{10}	1.201	2.422	0.678
	B_{43}	14.28	86.68	25.42
	B_{54}	0.1584	0.564	0.179

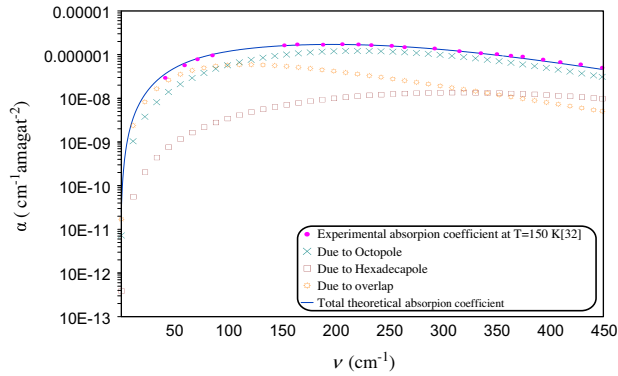


Fig. 3 Comparison between the calculated rototranslational collision-induced absorption spectrum of CH₄-He at $T = 150$ K using the present ESMSV potential given in Table 1 and induced dipole moment Eqs. (11) and (13) with the experimental one.

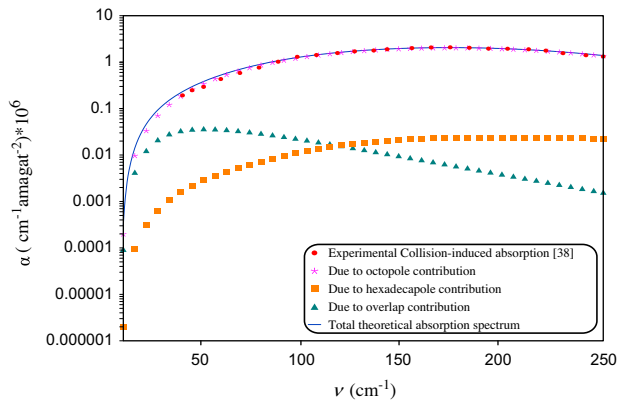


Fig. 4 Comparison between the calculated rototranslational collision-induced absorption spectrum of CH₄-Ar at $T = 87$ K using the present ESMSV potential given in Table 1 and induced dipole moment Eqs. (11) and (13) with the experimental one.

where α , γ and C are the dipole, hyperpolarizability and quadrupole polarizability with the label 1 refers to CH₄ and 2 refers to Ar or Xe. Values of the polarizabilities used in Eq. (14) are given in Table 4.

A purely long-range interaction mechanism, involving the participation of high order polarizabilities, has been invoked to account for induced rotational scattering [8,44]. Contributions from the dipole-quadrupole (**A**) and dipole-octopole (**E**) polarizabilities for CH₄ 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

$$\langle \alpha_{xz}^2 \rangle = \frac{12}{5} (\alpha_1 \alpha_2)^2 r^{-6} + \frac{48}{35} ((\alpha_2 \mathbf{A}_1)^2) r^{-8} + \frac{11}{9} ((\alpha_2 \mathbf{E}_1)^2) r^{-10} + \dots \quad (15)$$

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

The various terms in Eq. (15) give rise to the following selection rules on J the total angular momentum quantum number:

$$\begin{aligned} \alpha_i \mathbf{A}_j, \quad \Delta J_i = 0, \quad \Delta J_j = 0, \pm 1, \pm 2, \pm 3, \quad J_j + J'_j \geq 3 \\ \alpha_i \mathbf{E}_j, \quad \Delta J_i = 0, \quad \Delta J_j = 0, \pm 1, \pm 2, \pm 3, \pm 4, \quad J_j + J'_j \geq 4, \\ \mathbf{A}_i \mathbf{A}_j, \quad \Delta J_i = 0, \pm 1, \pm 2, \pm 3, \quad \Delta J_j = 0, \pm 1, \pm 2, \pm 3, \\ J_i + J'_i \geq 3, \quad J_j + J'_j \geq 3 \\ \mathbf{A}_i \mathbf{E}_j, \quad \Delta J_i = 0, \pm 1, \pm 2, \pm 3, \quad \Delta J_j = 0, \pm 1, \pm 2, \pm 3, \pm 4, \\ J_i + J'_i \geq 3, \quad J_j + J'_j \geq 4, \\ \mathbf{E}_i \mathbf{E}_j, \quad \Delta J_i = 0, \pm 1, \pm 2, \pm 3, \pm 4, \quad \Delta J_j = 0, \pm 1, \pm 2, \pm 3, \pm 4, \\ J_i + J'_i \geq 4, \quad J_j + J'_j \geq 4, \end{aligned}$$

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 [45,46], where the ratio of the wavefunction, defined at adjacent points on a spatial grid, is built step-by-step.

As regards our problem, binary anisotropic light scattering spectrum is computed quantum-mechanically, as a function of frequency shifts ν , at temperature T by using the expressions [47-49]:

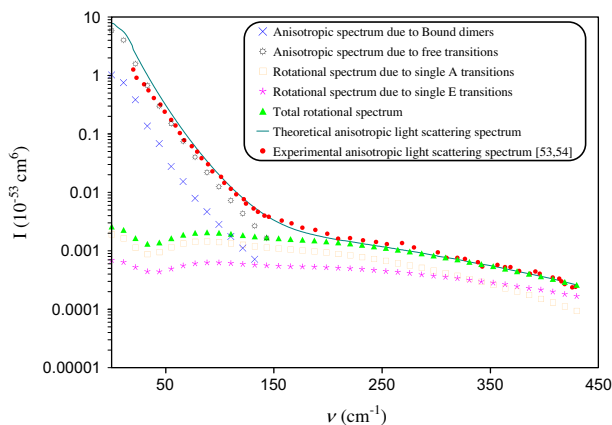
$$I_{\text{aniso}}(\nu) = \frac{2}{15} hc \lambda^3 k_s^4 \sum_{J=0, J \text{ even}}^{J_{\text{max}}} g_J b_J' (2J+1) \times \int_0^{E_{\text{max}}} |\langle \psi_{E', J'} | \beta | \psi_{E, J} \rangle|^2 \exp\left(\frac{-E}{k_B T}\right) dE \quad (16)$$

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. Constant λ account for the thermal de Broglie wavelength, $\lambda = h/\sqrt{2\pi\mu k_B T}$, with μ the reduced mass of methane and argon or xenon and k_B Boltzmann's constant. 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 this expressions, $\beta = \beta(r)$ denote the anisotropy of the quasimolecule, g_J the nuclear statistical weight and b_J' are intensity factors involving the rotational quantum numbers J and J' of the initial and final states, respectively.

Table 4 Parameters of Eq. (14) used in calculations.

	CH ₄	Ar	Xe	CH ₄ -Ar	CH ₄ -Xe
α (a.u.)	17.828 [40]	11.3304633 [35]	27.0514 [43]	—	—
γ (a.u.)	3079.2 [41]	1170.735 [42]	7889.9375 [43]	—	—
C (a.u.)	60.45 [41]	50.21 [35]	211.053 [43]	—	—
g_o (a.u.)	—	—	—	1.01225	1.2147
r_o (a.u.)	—	—	—	0.85605	0.94486

**Fig. 5** Total anisotropic collision-induced light scattering spectrum of CH₄-Ar at $T = 295$ K using the isotropic ESMSV potential given in Table 1.

The total theoretical intensities of the anisotropic light scattering spectrum are the sum of the translational spectra due to the transitions of bound-bound, bound-free and free-free states and rotational spectrum.

With the spectral intensities $I_{\text{aniso}}(\nu)$ in cm^6 as input and through the following analytical expression we are able to deduce the experimental anisotropic moments [50]

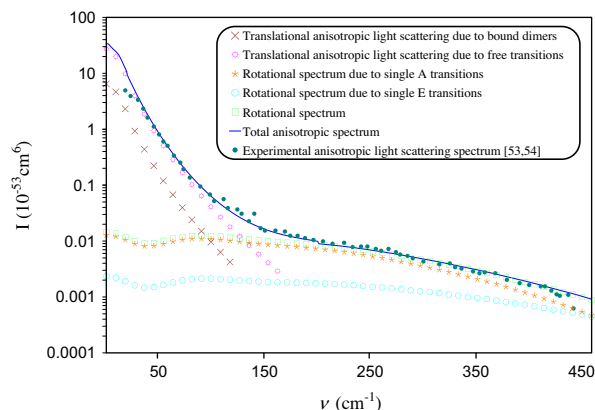
$$M_{2n}^{\text{aniso}} = \frac{15}{2} \left(\frac{\lambda_o}{2\pi} \right)^4 \int_{-\infty}^{\infty} (2\pi c\nu)^{2n} I_{\text{aniso}}(\nu) d\nu \quad (17)$$

These moments can be compared to values calculated directly from the sum rules with the quantum corrections [51].

In order to calculate the line profiles and the associated moments, the intermolecular potential and the anisotropy models are needed. Results with dipole-induced-dipole (DID) [52] and corrected dipole-induced-dipole (C.DID) [53] polarizability models can be compared with experiment [53,54] to assess the quality of our empirical potential and anisotropy models.

Comparisons between the calculations and experiments [53,54] are shown in Figs. 5 and 6 for the intensities of the anisotropic light scattering spectra at room temperatures for methane mixtures with argon and xenon.

Concerning the multipolar contributions of single **A** and single **E** transitions, different values of the dynamic independent tensor components **A** and **E** may be used to fit the experimental anisotropic intensities in the frequency ranges (75–450) cm^{-1} for CH₄-inert gas mixtures. Figs. 5 and 6 suggest that there are a choices of **A** and **E** for which the theoretical and experimental anisotropic spectra [53,54] fit the best $|\mathbf{A}| = 0.74 \text{ \AA}^4$ and $|\mathbf{E}| = 2.47 \text{ \AA}^5$ for CH₄-CH₄ using our empirical ESMSV intermolecular potential. These coefficients

**Fig. 6** Total anisotropic collision-induced light scattering spectrum of CH₄-Xe at $T = 295$ K using the isotropic ESMSV potential given in Table 1.

of multipolar polarizabilities are in good agreement with the experimental values of Shelton and Tabisz [55].

Conclusion

We have adopted a models for the dipole moment $\mu(r)$ and pair polarizability $\beta(r)$ with adjustable parameters for each, which we determined by fitting to the spectral profiles for absorption and scattering using quantum mechanics and to the first three moments of the measured absorption spectrum and anisotropic light scattering spectra using methods of classical mechanics with quantum corrections [33].

The present study further demonstrates that the empirical ESMSV potential models, with the parameters fitted to the different transport and thermophysical properties beside to the integral scattering cross-sections are a very good representation of the intermolecular potential of gaseous CH₄-inert gas mixtures. The profiles of the two-body anisotropic collision-induced light scattering spectra at room temperature 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 a 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 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 measured by Shelton and Tabisz [55]. Also for these mixtures, the

lineshape calculations for both induced pure translational and rotational scattering worked well at room temperature like CF_4 -inert gases [44] with the well known electric properties of CF_4 , but the spectra of CH_4 -inert gases are spreading over larger frequency shifts.

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