Interaction-induced light scattering by gaseous methane: The bound dimer contribution (CH$_4$)$_2$

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The two-body depolarized, collision-induced light-scattering spectrum of gaseous methane has been measured and analyzed at five temperatures from 295 to 130 K. This spectrum consists of a low-frequency component, which is due to bound dimers (CH$_4$)$_2$, and an intermediate-frequency, purely translational contribution which is due to collisionally interacting CH$_4$ pairs. (The high-frequency part, the rotational induced spectrum, was analyzed elsewhere and is of no great concern here.) The experimental spectra are compared with line-shape calculations based on a refined, empirical pair polarizability model and the spherical average of the Righini-Maki-Klein potential [Chem. Phys. Lett. **80**, 301 (1981)]. At all temperatures agreement of measured and computed profiles is observed on an absolute intensity scale.

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I. INTRODUCTION

Interaction-induced light scattering, alternatively referred to as collision-induced light scattering (CILS), arises from fluctuations of the polarizability during intermolecular interactions ("collisions"). The polarizability of two (or more) interacting molecules differs from the simple sum of polarizabilities of the unperturbed (i.e., noninteracting) molecules, mainly because the local field differs from the externally applied field if another molecule happens to be nearby. In not too dense gases, this effect may be closely modeled with the help of classical electrodynamics. On the other hand, quantum effects arising from exchange and dispersion forces also contribute to a certain extent. The fluctuations of the invariants of the polarizability tensor, in turn give rise to CILS, the translational and rotovibrational Raman spectra of fluids which are observable even at frequencies where the (noninteracting) molecules are Raman-inactive. The intensities of these CILS spectra vary as the gas density squared (or cubed, etc.), just as one would expect of pairs (or triplets, etc.) of interacting molecules. In the roughly twenty five years since the discovery of CILS [1,2], more than eight hundred original papers have appeared [3,4], which elucidate many of the intriguing aspects of this supermolecular Raman process.

In this work, we are concerned with CILS spectra that are predominantly of a binary nature. Such spectra may be obtained near the "zero-density limit," i.e., at gas densities low enough to render ternary (and higher-order) contributions insignificant. In that case, the basic process of CILS may be written as

$$A + B + h\nu \to A^{(*)} + B^{(*)} + h\nu' + \Delta T, \tag{1}$$

where A and B represent the molecular pair, the asterisks (if present) indicate a change of the rotovibrational state during interaction, $h\nu$ and $h\nu'$ designate incident and scattered photons, and ΔT represents the change of the translational state of relative motion, e.g., the change of the kinetic energy (ΔK) and angular momentum ($\Delta \ell$). Bohr's frequency condition relates the energies of incident and scattered photons, according to

$$h\nu = h\nu' + h\Delta\nu_A + h\Delta\nu_B + \Delta K, \tag{2}$$

where $\Delta\nu_A$ and $\Delta\nu_B$ are the rotovibrational transition frequencies of molecules A and B; these are zero if no rotovibrational transitions take place. In other words, besides the purely translational bands ($\Delta\nu_A = \Delta\nu_B = 0$) which are centered at zero frequency shift, rotovibrational induced bands are expected if at least one of the $\Delta\nu_A$, $\Delta\nu_B$ differs from zero. These are centered at the various rotovibrational transitions frequencies (even of transitions that are Raman inactive in the noninteracting molecules).

Specifically, we will focus on the role of bound pairs in CILS, a topic that was often neglected in such work. In samples of the common gases at not too low temperatures, at any instant most pairs of molecules will be free, that is either not interacting with other molecules, or else in collisional interaction with another molecule — but not bound to another molecule. In other words, the bulk of intensity of interaction-induced Raman spectra commonly arises from free-to-free transitions of pairs. However, for practically all common gases (with the pos-

sible exception of helium) small concentrations of bound pairs (van der Waals molecules) exist. In other words, a realistic treatment of CILS spectra must account for the spectroscopic transitions involving bound states, that is bound-to-bound transitions (or "ordinary" Raman bands of van der Waals molecules), free-to-bound and bound-to-free transitions (which are sometimes referred to as half-collisions), along with the free-to-free ones which, of course, generate the bulk of the observed spectral intensity in most cases. In the following, we will make use of the labels $b \to b, b \to f, f \to b, f \to f$, to distinguish among the various types of spectroscopic transitions when the need arises. Interaction-induced Raman intensities are given by the squares of transition matrix elements like $\langle I|\beta|F\rangle$ where $|I\rangle$, $|F\rangle$ designate the initial and final states of a pair (which may be bound or free) and β is the interaction-induced part of the polarizability invariant of the molecular pair, which is the same for free and bound pairs. Interaction-induced Raman spectra of bound and free pairs are closely related [5].

Much of the early work in CILS was concerned with monatomic gases at room temperature, i.e., at translational energies so small that the internal states of the interacting atoms cannot undergo changes [6–8]. The resulting spectra are purely translational. If molecular gases are considered, especially those whose (non-interacting) molecules are Raman inactive (e.g., CH_4 in the rotational band), the translational band is still clearly discernible. At higher frequency shifts, rotational bands are also discernible [9,10], which, however, will not concern us here very much. In other words, the asterisks seen above, in Eq. (1), may be dropped for most of what we will be concerned with below.

II. MEASUREMENT AND PREVIOUS ANALYSIS

In a desire to avoid as much as possible the complications of a theoretical treatment associated with the anisotropy of the interaction and yet focus on molecular gases, the methane molecule with its high degree of symmetry is an obvious choice. CH_4 is a tetrahedral molecule whose rotational transitions are Raman inactive (see, however, [11,12]). However, its depolarized induced spectrum contains all the features of the collision-induced spectra while the quantum characteristics of CH_4 pairs are still quite small, as far as the molecular dynamics is concerned. Finally, due to the small moment of inertia, the rotational spectral features, when present, are well separated in frequency and can be analyzed with little interference from the translational band.

In the low-frequency region (< 20 cm^{-1}) at room temperature, a sizeable contribution from bound dimers is discernible in the CILS spectrum [13,14]. This contribution increases with decreasing temperatures relative to the $f \to f$ component [15]. At intermediate frequencies ($20 - 100$ cm^{-1}), the spectrum is determined almost exclusively by the pure translational ($f \to f$) component, which is the analog of the CILS spectrum of a rare gas such as helium or argon [7,8]. At higher frequencies ($100 - 500$ cm^{-1}), a weak, collision-induced rotational wing

emerges. It is generated by the dipole-quadrupole- (A) and dipole-octopole- (E) induced polarizability which gives rise to a pair polarizability that is modulated by the rotational motion of the molecules [9,10].

The previous analysis [15] of our measurement of the binary methane spectra, which were recorded over a broad range of temperatures, compared the CILS spectra with a calculation based on classical trajectories and empirical models of both the induced pair polarizability anisotropy and the pair interaction potential. The calculation was performed in two steps. First, the purely translational spectrum was evaluated. Then the collision-induced rotational Raman scattering (CIRRS) [9] spectrum was computed by assuming values for the dipole-quadrupole- (A) and dipole-octopole- (E) induced polarizabilities which were consistent with previous independent determinations [15].

By inspection of the results, Figs. 1 – 5 of Ref. [15], the following conclusions were drawn: (i) The high-frequency portion up to frequencies of about 400 cm^{-1} of the spectra is well reproduced on the basis of the long-range model of the dipole-quadrupole and dipole-octopole polarizabilities. Beyond this limit this model is known to be inadequate and higher-order multipoles or, alternatively, effective short-range contributions, must be accounted for. (ii) In the intermediate frequency range agreement of theory and experiment was observed. However, (iii) at the lower frequencies (< 20 cm^{-1}), the bound dimer contributions increase enough so that the measured intensities exceed the classical calculation substantially (cf. Fig. 8 of Ref. [15]). In summary, experiment and calculations were found to be in fair agreement above 20 cm^{-1}. But below this limit, contributions arising from the bound dimers were discernible whose spectral shape was not reproduced by the classical theory.

In the previous analysis, the dimer contribution to the line shape was qualitatively approximated by the sum of a Lorentzian and a Gaussian function such that the total intensity was conserved. However, while the final picture of this investigation turned out in reasonable agreement of the experimental and the calculated spectral shapes, the empirical character of the approximation is not satisfactory. It is well known that for CH_4 at low temperature a purely classical picture of the dynamics of pairs does not allow a satisfactory description of the dimers. In this work, we compute the spectrum from a quantum formalism for a more meaningful comparison of theory and experiment.

III. LINE-SHAPE COMPUTATION

For binary systems an exact line-shape theory has been formulated, based on isotropic interaction. For molecules of spherical symmetry this approximation should be quite reasonable. In that case, the translational profile is given by an expression of the form [7,13]

$$\frac{\partial^2 \sigma_\parallel(\nu;T)}{\partial\Omega\,\partial\nu} = \frac{1}{15}\,k_0\,k^3\lambda_0^3\,hc\sum_{\ell,\ell'}(2\ell+1)\,C(\ell 2\ell';000)^2$$

$$\times\left\{\int_0^\infty |\langle\ell,E_t|\beta(r)|\ell',E_t+hc\nu\rangle|^2\,\exp\left(-E_t/kT\right)\,dE_t\right.$$

$$+\sum_{v,v'}\exp\left(-E_{v\ell}/kT\right)|\langle\ell,E_{v\ell}|\beta(r)|\ell',E_{v'\ell'}\rangle|^2\,\delta((E_{v'\ell'}-E_{v\ell})/hc-\nu)$$

$$+\sum_{v}\exp\left(-E_{v\ell}/kT\right)|\langle\ell,E_{v\ell}|\beta(r)|\ell',E_{v\ell}+hc\nu\rangle|^2$$

$$\left.+\sum_{v'}\exp\left(-(E_{v'\ell'}-hc\nu)/kT\right)|\langle\ell,E_{v'\ell'}-hc\nu|\beta(r)|\ell',E_{v'\ell'}\rangle|^2\right\}. \tag{3}$$

In this expression, the various symbols have the following meaning: $\partial^2\sigma_\parallel/\partial\Omega\,\partial\nu$ is the differential light-scattering cross section of pairs per unit frequency, it is a function of frequency ν (expressed in cm^{-1} units) and temperature T, $k_0 = 2\pi\nu_0$ and $k = 2\pi\nu$ are the wave vectors of incident and scattered photons, λ_0 is the thermal de Broglie wavelength of the molecular pair, given by $\lambda_0^2 = 2\pi\hbar^2/mkT$; the $C(\ell_1\ell_2\ell_3;m_1m_2m_3)$ are Clebsch-Gordan coefficients which determine the selection rules $\Delta\ell = 0,\pm2$, the $\langle\ell E|\beta|\ell'E'\rangle$ are the radial matrix elements which are computed by numerical integration of the Schrödinger equation of the pair, a prime indicates final state of the pair, and v and ℓ are the vibrational and rotational quantum numbers of the bound dimer (ℓ is also the angular momentum of the partial wave). The spectral profile is seen to be a sum of four terms. Specifically, these are the $f\to f, b\to b, b\to f$ and $f\to b$ transitions. Further details may be found elsewhere [7,13].

Since we consider the high-frequency region of the depolarized induced spectrum of methane satisfactorily described by the CIRRS model [15], the quantum mechanical calculations were limited to the translational spectra and the bound dimer contributions. This means that the comparison between the present calculation and the experimental data will be limited to frequencies of less than $80\ cm^{-1}$, where CIRRS is thought to be not significant.

The calculations were carried out using again the empirical polarizability model [16],

$$\beta(r) = 6\alpha_0^2\,r^{-3} + A\,r^{-6} - B\exp(-r/r_0), \tag{4}$$

where α_0 is the isotropic molecular polarizability, r is the separation of the pair, and A, B, and r_0 are parameters that have been determined by a moment analysis of the CILS spectra of methane at room temperature: $\alpha_0 = 2.642\times10^3\ nm^3$, $A = 1.3563\times10^{-7}\ nm^9$, $B = 1.8\ nm^3$, and $r_0{=}0.03952\ nm$ [16], assumed to be independent of temperature.

We used the same temperature-dependent, isotropic potential employed in the previous analysis [17,18], which is written in the Hartree-Fock-dispersion form,

$$U_{\rm eff}(r) = \epsilon\,\{Cx^y\exp(-ax)$$

$$- f(x)[C_6x^{-6} + C_8x^{-8} + C_{10}x^{-10}]\}\ . \tag{5}$$

The damping function $f(x)$ is given by

$$f(x) = \begin{cases} \exp-[(D/x)-1]^2 & \text{for } x \le D \\ 1 & \text{for } x > D, \end{cases} \tag{6}$$

with $x = r/r_m$ and r_m representing the position of the minimum of the potential. The temperature dependence of the interaction function comes from the rotational averaging of the modified anisotropic Righini-Maki-Klein [18] potential for a pair of methane molecules and is accounted for by the temperature-dependent parameters of the effective potential which are listed in Table II of Ref. [15].

IV. RESULTS

Figures 1–5 compare the experimental data (dots) with the quantum calculations. Two main contributions are shown: the translational, continuous portion of the spectrum $(f\to f, f\to b, b\to f$, dashed) and the total,
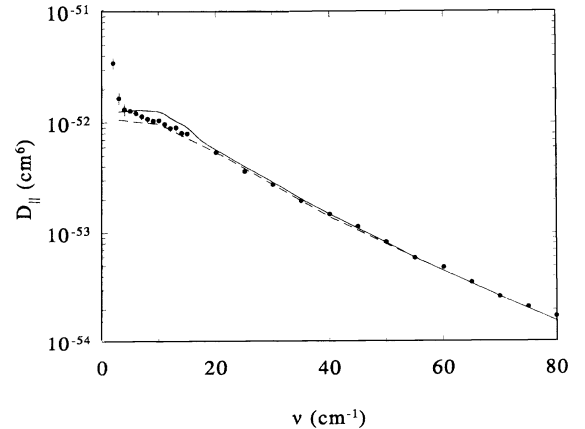

FIG. 1. Comparison of the measurement (dots, from Ref. [15]) of the pair spectrum of methane at 295 K with the theory: the dashed line presents the calculation of the free-to-free, free-to-bound, and bound-to-free contributions and the solid line is the total, computed intensity (which includes the bound-to-bound contributions as well). Where the experimental errors exceed the dot size, error bars are drawn to provide an estimate of the experimental uncertainties.
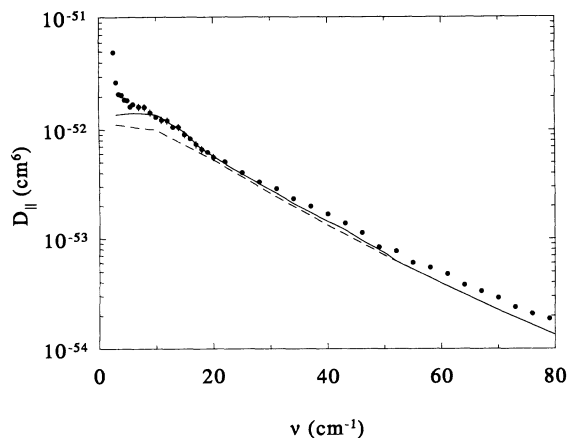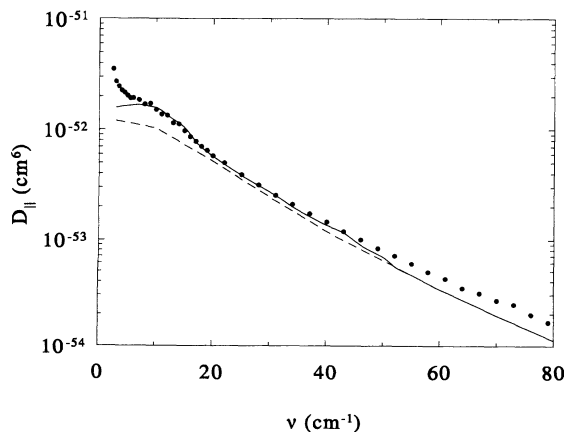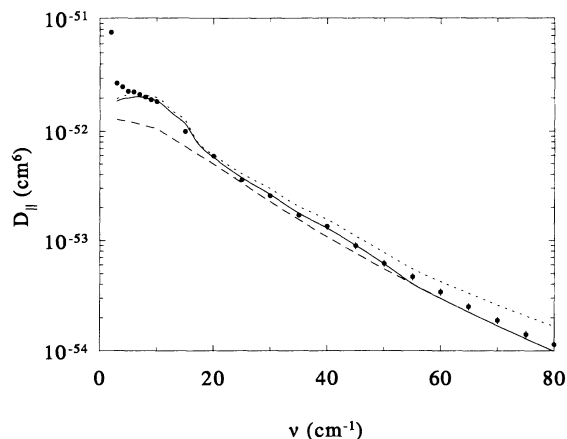
FIG. 2. Same as Fig. 1, at 250 K.

FIG. 4. Same as Fig. 1, at 163 K. The dotted line shows for comparison the results of a line-shape calculation based on the DID approximation.

including the bound dimer contribution ($b \rightarrow b$, solid line). The $b \rightarrow b$ contribution consists of hundreds of (here unresolved) rotovibrational dimer lines (delta functions) which have been broadened according to the pressure-broadening formulas of Frenkel and McTague [19]. A Lorentzian shape is assumed and the half-widths amounted to 1.7–3.1 cm^{-1} for pressures from 7.8–11.2 amagats, at the temperatures of the measurements; when the dimer bands were simply convoluted with an instrumental profile of 1 cm^{-1} half-width and pressure broadening was neglected, a slightly poorer agreement of theory and measurement than what is shown in the figures was obtained. It appears that the bound dimer contribution tends to fill in the slight discrepancy that was previously [15] observed in the region from 30 to 80 cm^{-1} for the two intermediate temperatures. In particular, a small difference of the order of 20% persists near 50 and 60 cm^{-1}. At the higher frequencies (above 60–80 cm^{-1}), the measured spectra are slightly more intense than the calculations suggest. This is the region where the CIRRS starts to emerge. This is understandable, because we have not accounted for CIRRS in the present calculation.

For the room-temperature spectrum, Fig. 1, the overall agreement is good, perhaps with the exception of the region from 5 to 15 cm^{-1} where some inconsistencies re-

main. This agreement might be considered a consequence of fitting the intermolecular polarizability anisotropy directly from the room-temperature CILS spectral moments [16]. In particular, the use of integral quantities for the determination of the polarizability function, thought to be effective, may be susceptible to improvements—for example by taking advantage of the large temperature range of the present measurements. However, we point out that the two room-temperature spectra (the present one and that used in Ref. [16]) are experiments done in different laboratories, which in fact testifies to the remarkable consistency of the measurements on an absolute scale.

As the temperature decreases, we note a slight excess intensity in the experiment between 50 and 80 cm^{-1}, both at 250 and 203 K (Figs. 2 and 3). However, this excess intensity is recovered at the two lower temperatures of 163 and 130 K (Figs. 4 and 5). The origin of this slight discrepancy may be twofold. On the one hand, there is the possibility that the spectral separation between CILS and CIRRS, which was used in order to determine the collision-induced polarizability model, could be improved with respect to the previous analysis. On the other hand, we remind the reader that CIRRS was
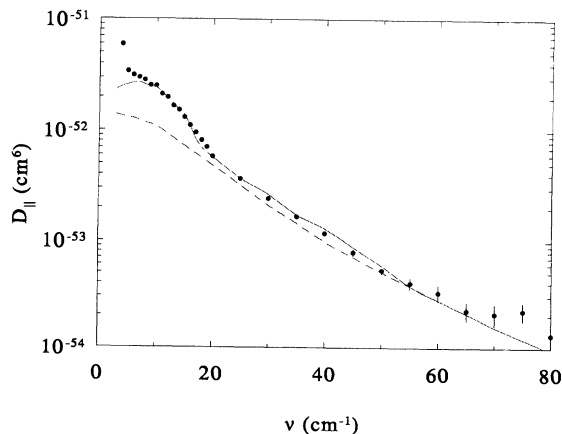

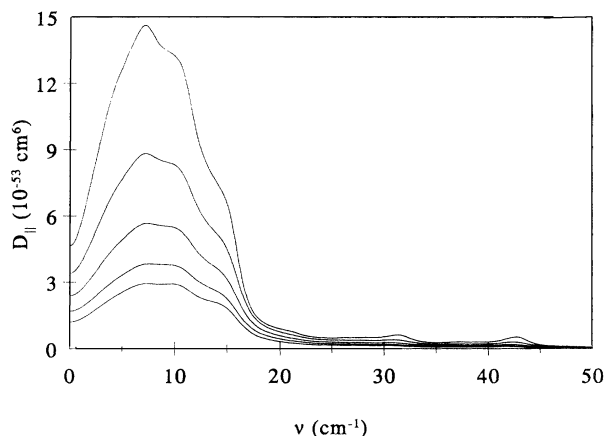FIG. 3. Same as Fig. 1, at 203 K.

FIG. 5. Same as Fig. 1, at 130 K.

1 IG. 6. The computed dimer spectrum $(b \to b)$ at the temperatures (from top to bottom) of 130, 163, 203, 250, and 295 K. Computed dimer lines were convoluted with a Lorentzian shape to simulate the effect of pressure broadening, as explained in the text.

accounted for by means of its long-range model, which assumes an anisotropic dipole-quadrupole (A) and dipole-octopole (E) polarizability only. The effects of higher-order polarizability terms, as well as of short-range effects upon this spectral feature are at present unknown. Besides, looking at Fig. 4, one may develop some idea of the size of these short-range effects. Here, together with the other spectra, we have reported the CILS spectrum that was computed on the basis of the long-range approximation [dipole–induced dipole (DID)] of the polarizability. This is the first term in Eq. (4). We see that the inclusion of the short-range corrections allows a much closer agreement of theory and experiment, especially at the higher frequencies.

The effect of the bound dimers upon the CILS spectrum is most striking over the first 20 cm^{-1} of the profile. It becomes more evident, as is expected, at the lower temperatures. As we observe especially from Fig. 5, the accounting for the bound-state contributions brings the calculation in almost perfect agreement with the measurement. Of course, at very low frequencies, below 5 or 6 cm^{-1}, the measurement is more intense than the calcu-

lation, but this is attributed to the effect of some residual stray light (which is always present at those frequencies). It is also possible that the pressure broadened wings of the elastic component $(\Delta J = 0)$ of the rotational dimer spectrum, which was included in the present calculation like all the other molecular lines, contributes to the excess intensity at low frequency. That effect should, however, be small (of 2nd order) as it is limited to the inadequacies of the Lorentzian profile, or to our estimate of the pressure broadening itself.

Finally, it is interesting to compare the computed $b \to b$ dimer spectra at the various temperatures, Fig. 6. As the temperature is increased, the shape of the spectrum does not change much while we observe an overall decrease of the intensity. Thus the bound dimer contribution decreases with increasing temperature, reflecting the decrease of the dimer population (which is normalized by density squared).

V. DISCUSSION

The present calculations of the low-frequency dimer spectrum and the translational band of the depolarized CILS spectral profile of methane pairs are based on quantum mechanics. As a result, the overall agreement with the experiment is significantly improved relative to the previous comparison. The agreement shown in Figs. 1 through 5 is remarkable, considering the fact that no fitting parameters have been used anywhere, and in view of the wide temperature range that was explored by the experiment. The small differences at 250 and 203 K in the intermediate frequency region (50–80 cm^{-1}) still persist and are unexplained at this point. We note that a similar difference was emerging from a previous comparison with the purely classical calculation. Beyond 80 cm^{-1}, the apparent small differences are obviously due to the effect of CIRRS, which was not included in the calculation. We feel that a fine tuning of the polarizability function might further improve the agreement of measurement and such calculations.

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