PHYSICAL REVIEW A **72**, 042715 (2005)

Collision-induced rototranslational absorption in compressed methane gas

Michael Buser* and Lothar Frommhold†
Physics Department, University of Texas, Austin, Texas 78712, USA

(Received 14 July 2005; published 27 October 2005)

The collision-induced, rototranslational absorption spectrum of compressed methane gas is computed, based purely on the reliably known, leading multipole-induced dipole components of CH_4 molecular pairs. In contrast to previous work of the kind no *ad hoc* empirical corrections of unknown exchange force-induced dipole components are attempted. Not surprisingly, the calculated spectra show a sizeable absorption defect at virtually all frequencies, when compared to existing laboratory measurements. The defect suggests the presence of dipole-induction mechanisms in addition to those due to the leading multipole-induced dipole terms. The excess absorption, the differences between measured and calculated spectra, resembles in certain ways the excess absorption spectra seen at the same frequencies in methane-X gas mixtures, where X stands for helium, hydrogen, or nitrogen, respectively [Buser and Frommhold, J. Chem. Phys. **122**, 024301 (2005)]. To a large extent, the excess absorption seems to be related to collisional distortions of the tetrahedral frame of the unperturbed CH_4 molecule.

DOI: 10.1103/PhysRevA.72.042715 PACS number(s): 34.10.+x, 33.20.Ea, 33.70.−w

I. INTRODUCTION

Intermolecular interactions cause minute shifts of the electronic charge distributions that typically induce temporary electric dipole moments and thus absorption in the infrared, even if the individual, unperturbed molecules are infrared inactive [1,2]. When diatomic molecules collide with atoms or other diatomics, three well-known mechanisms induce such dipole moments, namely the electron exchange and dispersion processes, and polarization of the collisional partner in the molecular electric multipole fields. These are the same mechanisms that are familiar from the studies of intermolecular forces [3,4].

The same three induction mechanisms are effective in virtually all molecular interactions at thermal energies, but more complex polyatomic molecules are believed to possess additional induction mechanisms. For example, a linear molecule such as CO_2 possesses two strong internal dipole moments which in the linear molecule cancel. However, collisional frame distortion may temporarily induce a nonzero dipole moment which interacts with radiation [5]. Similarly, molecules such as CH_4 possess four relatively strong internal dipole moments that in the undistorted frame add up to zero, but collisional frame distortions temporarily cause a nonzero dipole moment and collision-induced absorption. Previous estimates of such frame distortion-induced dipole moments have suggested that these dipoles may well be of a strength comparable to the universal mechanisms mentioned above [5,6]. Reasonably detailed modeling of such frame distortion-induced dipoles has apparently not been attempted yet so that the spectroscopic effects of collisional frame distortion are not known very well. It is therefore of interest to collect for further studies what might be considered the spectroscopic evidence of such frame distortion-induced dipoles.

The absorption spectra of the collisional pairs CH_4-He, CH_4-H_2 [7], and CH_4-N_2 [8], were previously computed and compared with existing measurements at various temperatures. Since quantum chemical computations of induced dipole surfaces of CH_4-X complexes, with X=He, H_2, or N_2, do not exist, line-shape calculations were based mainly on the well-known, leading classical multipole-induction mechanisms, the effects of molecular field inhomogeneities, and dispersion force-induced dipoles; no attempts were made to model the unknown exchange force-induced and frame distortion-induced dipole components in these computations of the spectra [7]. The comparison with measurements shows a substantial absorption defect of theory, evidence that some substantial dipole components are missing from such calculations. Since known exchange force-induced dipoles are typically small corrections of the associated multipole-induced dipole components, we argued that the modeling of exchange force-induced dipoles alone cannot account for the observed substantial absorption defects so that frame distortion-induced dipole components are likely significant in CH_4-X complexes [7]. The present paper extends these studies [7,8] to the case of unmixed methane gas.

II. INDUCED DIPOLE COMPONENTS

For the present purpose, we accept the well-known, purely long-range parts of the spherical tensor dipole components of Ref. [9], but do not include here the *ad hoc*, exponential short-range terms of Ref. [9] that are supposed to mimic the unknown exchange force-induced dipole components. Specifically, we consider the dipole components that are induced by the electric multipole moments Q_ℓ of order ℓ, given by

$$B_{\ell,0,\ell,\ell+1}(R) = |B_{0,\ell,\ell,\ell+1}(R)| = (-1)^\ell \sqrt{\ell+1}\frac{\alpha Q_\ell}{R^{\ell+2}}. \qquad (1)$$

Here, α is the isotropic polarizability of CH_4, and R is the center-to-center distance of the two CH_4 molecules. We ac-

---

*Present address: Physics Department, University of Ulm, Germany.

†Electronic address: frommhold@physics.utexas.edu

count for octopole ($\ell=3$) and hexadecapole ($\ell=4$) induction, but not for any higher-order multipoles. These multipole-induced dipole components occur twice: once for molecule 1 inducing a dipole in 2, and once more for molecule 2 inducing a dipole in 1.

We also need to account for the components that describe the dipole induced by the multipolar field gradient through the dipole-quadrupole polarizability $\boldsymbol{A}$. These components cause simultaneous rotational transitions in both molecules. For $\ell=3$, the dipole components with $\Lambda=4$ and 6 cancel and only the one labeled 3,3,5,5 survives [9],

$$B_{3,3,\_,5}(R) = \frac{16}{7}\frac{Q_3 A_3}{R^6}. \tag{2}$$

For $\ell \neq 3$, we may similarly summarize various components and get in this case two dipole components [9],

$$B_{(\ell,3,\_,\ell+1)}(R) = |B_{(3,\ell,\_,\ell+1)}(R)| = \sqrt{\frac{1}{45}(\ell+1)(\ell+2)(2\ell+3)}\frac{Q_\ell A_3}{R^{\ell+3}}. \tag{3}$$

Here, A_3 is an element of the $\boldsymbol{A}$ tensor mentioned above. For the present purpose we consider only the two dipole components of (3) with $\ell=4$, that is a total of seven components. Since the dipole components with subscripts $\lambda_1,\lambda_2,\Lambda,L=3$, 0, 3, 4 and 0,3,3,4 are identical (except for the sign), the 4,0,4,5 and 0,4,4,5 are identical, and the 4,3,_,6 and 3,4,_,6 are identical, the numerical calculations of the spectral profiles in the isotropic interaction approximation amount to no more than four different spectral profiles that must be computed.

We note that in these expressions (1)–(3), we have assumed that the molecular frame of CH_4 is rigid so that the multipole moments and tensor component A_3 do not depend on the rotational quantum numbers. The quantities that enter the calculation of the spectra are

$$Q_3^2 = \frac{12}{5}(2.6ea_0^3)^2 \quad \text{from Refs. [10,11]},$$

$$Q_4^2 = \frac{12}{7}(8.2ea_0^4)^2 \quad \text{from Refs. [10,11]},$$

$$A_3^2 = 6(12.8a_0^4)^2 \quad \text{from Ref. [12]},$$

$$\alpha = 17.22a_0^3 \quad \text{from Ref. [13]},$$

with electronic charge e and Bohr's radius a_0.

III. SPECTRAL PROFILES

From the induced dipole components $B_{\lambda_1,\lambda_2,\Lambda,L}$ the absorption spectra are calculated in the isotropic interaction approximation by numerical integration of the Schrödinger equation as described elsewhere [2,7,8]. For the numerical integration we input the recent isotropic intermolecular potential-energy surface by Capelletti [14], which is based on scattering data and is of the Morse–Spline–van der Waals (MSV) form. The integration gives the wave functions of free and bound pairs of CH_4, which we use to compute the "translational" spectral functions $g_{\lambda_1,\lambda_2,\Lambda,L}(\omega,T)$. These functions $g_{(c)}(\omega,T)$ do not depend on the quantum numbers of initial and final rotational states j_1,j_1',j_2,j_2' of molecules 1 and 2, according to our assumption of a rigid molecular frame. The spectral profile $G(\omega,T)$ is then computed by shifting the weighted g functions to the rotational transition frequencies of the supramolecule and summing over these and the seven $\lambda_1,\lambda_2,\Lambda,L$ subscripted spectral contributions as usual [2]. For the single transitions, the statistical weights of the g functions are given by [9]

$$a_{j,j'}^{\ell,0} = \frac{1}{2\ell+1}P_j^{(\ell)}(2j+1)(2j'+1). \tag{4}$$

For the simultaneous transitions the g functions are summed with weights [9,15],

$$a^{(\ell)}_{j_1 j_1' j_2 j_2'} = \frac{1}{(2\times 3+1)(2\times\ell+1)} \times P_{j1}^{(\ell)}P_{j_2}^{(3)}(2j_1+1)(2j_1'+1)(2j_2+1)(2j_2'+1). \tag{5}$$

These weights are set to 0 where the selection rules are not satisfied. The selection rules for the multipole-induced components are given by

$$\Delta j_1 = 0, \pm 1, \pm 2, \ldots \pm \lambda_1 \quad \text{and} \quad \Delta j_2 = 0, \tag{6}$$

and by an identical expression, with subscripts 1 and 2 interchanged. For the simultaneous transitions, we have

$$\Delta j_1 = 0, \pm 1, \pm 2, \ldots \pm \lambda_1, \tag{7}$$

$$\Delta j_2 = 0, \pm 1, \pm 2, \ldots \pm \lambda_2. \tag{8}$$

If $\ell=3$, that is if $\lambda_1=\lambda_2=3$, there is only one spectral contribution. For $\ell \neq 3$, λ_1 and λ_2 differ and, as a consequence, two (identical) spectral contributions result.

The thermal population factors $P_j^{(\ell)}$ are given by [15]

$$P_j^{(\ell)} = \frac{\exp - \beta chBj(j+1)}{\sum_{j=0}^{\infty}(2j+1)^2 \exp - \beta chBj(j+1)} \times \left(1 + \frac{12Y_\ell(j,j')-1}{4}\right), \tag{9}$$

where $\beta=1/kT$ is related to temperature as usual. The $Y_\ell(j,j')$ reflect proton spin statistics of rotational transitions in the CH_4 molecule [16]. The B coefficient is the rotational constant of CH_4.

Finally, the absorption coefficient α is obtained from

$$\alpha(\omega,T) = \frac{4\pi^2}{3\hbar c}\frac{\rho^2}{2}\omega\left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right]G(\omega,T) \tag{10}$$

with ρ representing the number density of the gas.

Line shapes are computed for various temperatures. Figure 1 compares calculated spectral profiles at temperatures of

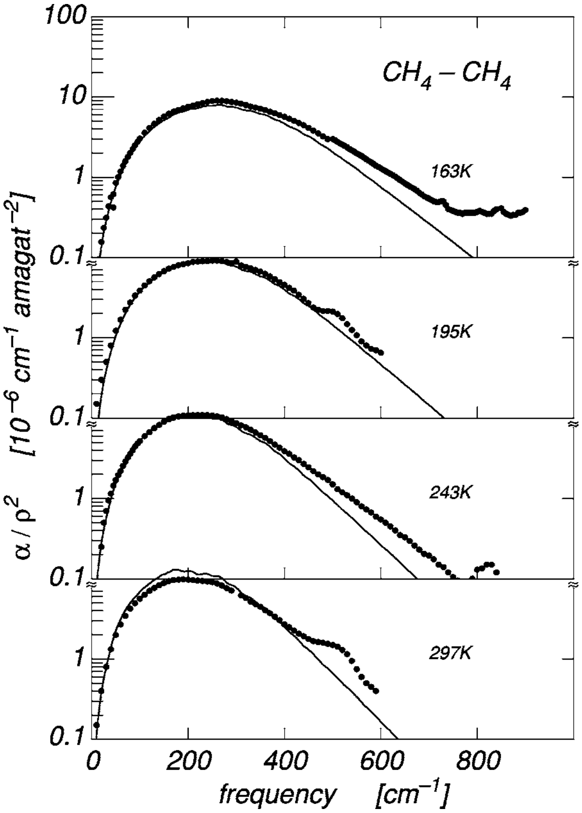

FIG. 1. Existing measurements [17] at temperatures of 163, 195, 243, and 297 K (dots) are compared to calculated absorption spectra (solid line) in methane.

163, 195, 243, and 297 K with existing measurements [17]. Since the resolution of the measurements is low so that the small structures of the calculated line shapes due to bound and predissociating van der Waals molecules are not discernible, we convolute the calculated profiles with a triangular slit function of 8.75 cm^{-1} half width that flattens these "ripples" but hardly affects anything else. The comparison shows generally fairly good agreement at the lower frequencies, up to about 300 cm^{-1} or so, but at the higher frequencies the calculations fall off faster than the measured absorption. There is an absorption defect of theory, much like what was seen in mixtures of methane with helium, hydrogen, or nitrogen [7], which is especially clearly seen at the temperatures of 163 and 243 K.

At the two temperatures of 195 and 297 K the measurements shown in Fig. 1 exhibit a hump at roughly 500 cm^{-1} which, however, is not seen in the recordings at the other two temperatures. We think that this feature is an artifact and choose to ignore it for our present purposes. Other smaller peaks near 800 cm^{-1} seen in the recordings at 243 and 163 K will likewise be ignored here. These features are not much stronger than the noise and other uncertainties of the measurement.

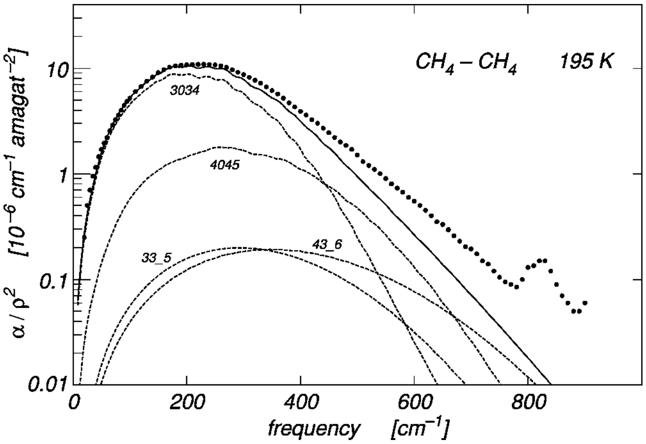

FIG. 2. Collision-induced rototranslational absorption of methane at 195 K (solid line) as sum of their individual dipole components (dotted lines), labeled with $\lambda_1\lambda_2\Lambda L$. The dots represent the measured enhancement spectrum in the far infrared.

It is interesting to look briefly at some intermediary results. Figure 2 shows that the combined octopole-induced λ_1, λ_2, Λ, L=3,0,3,4 and 0,3,3,4 (labeled 3034) spectral components are by far the strongest contributors to the absorption, except at the highest frequencies. Next are the hexadecapole-induced contributions 4,0,4,5 and 0,4,4,5 (labeled 4045), whose spectral contributions exceed the former only at the highest frequencies. Simultaneous transitions 3,3,_,5 (labeled 33_5) and the combined 4,3,_,6 and 3,4,_,6 contribute relatively little, except at the highest frequencies. For comparison, the measurement and the sum of the calculated contributions are also shown, as in Fig. 1.

IV. DISCUSSION

Our focus is on the absorption defect of theory at frequencies above of roughly 200 cm^{-1}, which is seen in the spectra presented. Figure 3 shows the excess, the difference of measured and calculated absorption, at the four temperatures. At the three lowest temperatures the excess absorption is very small at low frequencies <200 cm^{-1} relative to measurement, Fig. 1, and is comparable to measurement noise so that the data, Fig. 3, are quite uncertain at the lowest frequencies. (At the highest temperature, at these low frequencies, theory

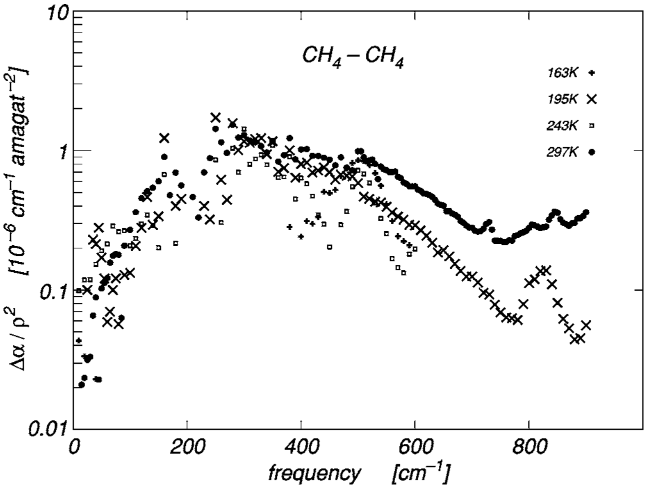

FIG. 3. Excess absorption—the difference of measured and calculated absorption, from Fig. 1.

is actually slightly above measurement, again by fairly small amounts which we ignore here.) However, at frequencies above roughly 200 cm^{-1}, the data displayed in the figure are significant, up to almost 800 cm^{-1}, except for the artifacts of the measurement mentioned above.

The intensities of the excess absorption by CH_4 pairs amount roughly to 1×10^{-6} cm^{-1} amagat^{-2} near their broad maxima, that is at frequencies from roughly 200 to 500 cm^{-1}. At these frequencies, the profiles of the excess spectra look much like those obtained previously in gas mixtures of methane and helium, hydrogen, or nitrogen (Figs. 4–6 of Ref. [7]), except that the latter are roughly twice as intense when compared with the CH_4-CH_4 data, Fig. 3.

We note that it is certainly no surprise that calculations of absorption spectra, which are based solely on the long-range induction mechanisms (as are our calculations shown above), exhibit an absorption defect relative to measurements. That is a fact familiar from virtually every analysis of collision-induced rototranslational spectra [2]. For simple systems, such as atom-diatom and diatom-diatom complexes, additions of relatively small *ad hoc* exchange force-induced, short-range dipole components have always satisfactorily reproduced the measurements, often over a wide range of temperatures so that these absorption defects appeared to be quite believable. Moreover, for systems with small numbers of electrons, these exchange force-induced dipole components are well known from quantum chemical calculations [2]; the known quantal corrections of the individual classical multipole-induced dipoles were always relatively small. However, for systems such as CH_4-X, where X may be almost any atom or molecule, such *ad hoc* short-range corrections that were introduced to simulate exchange force-induced contributions were commonly found to be quite large, namely comparable to, or even larger than the multipole-induced components of the same symmetry. Furthermore, several free parameters that were introduced for least mean squares fits of measurements at various temperatures often showed unexpected temperature variations and other strange behavior that looked suspicious, see previous analyses of the CH_4-CH_4 system [9,15,18,19]; for CH_4-X systems similar observations were reported [7,8,20–24].

In the present work and in Refs. [7,8], we purposely refrained from introducing empirical exponential short-range terms, because such attempts did not work very well in earlier analyses of the CH_4-X systems studied. Whereas some of the excess absorption seen in Fig. 1 may certainly be due to the suppressed exchange force-induced dipole components, it seems clear that the inclusion of such a short-range exponential alone will not solve the problem of the absorption defect of CH_4-X systems. Rather, an additional induced dipole mechanism seems to be necessary for a satisfactory explanation of the excess absorption of CH_4-X systems, most likely a collisional frame distortion-induced dipole component, perhaps combined with some other dipole components that are somehow caused by, or related to the high flexibility of the frame of the CH_4 molecule [7].

A. Historical sketch

Bar-Ziv and Weiss have pointed out that, because of the low polarizability of He, only a few percent of the observed rototranslational spectral intensities of CH_4-He is due to multipolar induction [25]. Afanasev *et al.* also measured the CH_4-He spectra and concluded that multipolar induction amounts to not more than 3% of the total intensity [26]. The remaining ≈97% of the observed intensity then should be due to exchange force-induced dipoles (interchangeably also called overlap-induced dipoles) of the *anisotropic* variety. Such an anisotropy of the induced dipole surface could generate the observed rotational band envelopes [26].

A different analysis based on quantum line shape calculations supports this conclusion [24]. However, the spectral contributions of the anisotropic exchange force-induced dipoles of octopolar and hexadecapolar symmetry would have to be an order of magnitude stronger than those of the corresponding multipole-induced dipole contributions, which seems unacceptably large. Moreover, such models feature strange temperature dependencies. We suggest that such *ad hoc* models of overlap-induced dipoles by themselves are unlikely to explain the observed excess absorption in terms of basic collisional processes.

Birnbaum *et al.* showed different measurements of the rototranslational absorption of compressed methane gas and analyzed the data with the help of quantum-mechanical line profile calculations [18]. The octopole and hexadecapole moments were entered as adjustable parameters and satisfactory fits of the spectra could thus be obtained. However, these *ad hoc* multipole moments, although of reasonable magnitude, showed a striking temperature dependence, which of course is inconsistent with the assumption of a rigid CH_4 frame. Furthermore, it was stated that the "… discrepancy between experimental and computed absorption in the high frequency wing is not understood and requires further study." It was suggested that the absorption defect at high frequencies may at least in part be due to the neglected 2^6 multipole, an assumption which, however, now is out of question [23].

A theoretical line-shape analysis finds "excellent agreement" between measured spectral absorption profiles of methane [18], based on octopolar and hexadecapolar induction [27]. Still, at frequencies above 300 cm^{-1}, an absorption defect of theory is clearly discernible, which the authors attribute to quantum effects that were neglected in their classical treatments, "… or possibly to the operation of another, shorter-range, induction mechanism in addition to those postulated." A similar analysis of measurements concludes that "… theory underestimates the measured absorption at higher frequencies by an amount greater than the experimental uncertainties" [19]. The possible reasons given for the absorption defect of theory include missing induction mechanisms and possibly the lack of more realistic intermolecular potentials.

Further analyses of the collision-induced rototranslational absorption band of compressed methane account for the dipoles induced by octopolar and hexadecapolar induction, exchange force-induced induction of hexadecapolar symmetry, and the gradient induction (simultaneous transitions) by the octopolar fields [15,28], using quantum calculations of the spectral profiles which accounts for both, free and bound molecular pairs. Remarkably, at the lower temperatures, agreement of the *ad hoc* octopole and hexacedapole moments with the *ab initio* values is observed. With increasing temperature, these empirical multipole moments increase in a monotonic way which might suggest a centrifugal distortion of the rotating methane molecules; not much further support was offered to really establish such a mechanism. A number of other possible reasons for the problems of fitting the measurements by a meaningful theoretical model were listed, e.g., various further, previously unaccounted for rotation-induced properties related to the quite flexible tetrahedral frame of CH_4; such processes were known to exist and were thought to be possibly important for explaining the observed excess absorption. But useful quantitative models of such induction models were not proposed.

An expert panel formulated the most complete induced dipole model to date of CH_4 pairs. It includes a rigorous treatment of the long-range induction by the octopole and hexadecapole moments, together with the components associated with the gradient of both the octopolar and hexadecapolar electric fields of CH_4 molecules assumed to possess a *rigid frame* [9]. The comparison with measurements of the rototranslational absorption spectra clearly indicated a need for additional, substantial dipole induction mechanisms, and empirical octopolar and hexadecapolar short-range exchange force-induced components were introduced to improve the fits of the measured spectra. Further improvements of these fits were still desirable [9] and it was suggested that additional empirical short-range terms should be used with dipole components that are responsible for the simultaneous transitions which, however, was not actually attempted in the work [9]. In short, the excess absorption problem at high frequencies persists, even when three or more free empirical parameters are introduced.

Summarizing previous work in gaseous methane and its mixtures, one may say that in every one of these studies no plausible explanation of the consistently observed excess absorption problem was offered. This is in striking contrast to similar analyses of collision-induced spectra of diatomic gases and mixtures, where generally a remarkable and unproblematic consistency of theory and measured spectra was observed. In all previous analyses a rigid molecular frame of CH_4 was implied. We note that it is now well known that the molecular frame of a CH_4 molecule is extremely soft; evidence for the high degree of flexibility is briefly summarized near the end of the Sec. IV B below. One would think that the problem of the excess absorption would find at least a partial solution if the spectroscopic effects of the high flexibility of the molecular frame of CH_4 were somehow taken into account.

In recent work [7], and again in the present paper, we have shown that the fairly strong excess absorption spectra of CH_4-He, CH_4-H_2, CH_4-N_2, and CH_4-CH_4 systems in the CH_4 rotational bands are all very much the same. They all consist of a broad maximum from roughly 200 to 400 cm^{-1}, with peak intensities of roughly 2×10^{-6} cm^{-1} amagat^{-2} for the dissimilar pairs, and roughly half as much for the like pair. These spectra are apparently CH_4 specific, but do not seem to be affected very much by the collisional partner, except for the like pair. Naively, for CH_4 pairs one might have expected *twice* the intensities seen for dissimilar pairs if these excess absorption spectra were indeed due to collisional frame distortion-induced dipoles, but Fig. 3 shows only about *half* as much. Apparently, in a collision of two CH_4 molecules some destructive interference occurs so that spectral intensities are reduced. We think that destructive interference seems to be quite plausible in such a symmetric system, especially if the dipole component in question were a collisional frame distortion-induced dipole.

B. Frame-distortion-induced dipoles and spectra

As discussed previously [7], absorption measurements in the far infrared in liquid carbon tetrachloride, another molecule of cubic symmetry like CH_4, demonstrated several bands of excess absorption that were believed to arise from distortions of the cubic frame of the CCl_4 molecule [29,30]. The associated collision-induced dipole moments were estimated to be in the order of 0.1–0.2 D, or about 0.25–0.5 atomic units—a very strong dipole moment if compared to other well-known induced dipoles [2]. Such a dipole corresponds to a bending of the C-Cl bond of about 10° [29,31]. The observed absorption spectrum of the liquid resembled the unresolved rotational band of CCl_4 at frequencies from about 5 to 35 cm^{-1} in the far infrared [29].

Weiss considered the case of a CO_2-X collision, when the impact occurs at the C atom of CO_2 [5]. Here, X designates a helium atom or anything else. The resulting bending of the molecule causes a net dipole to briefly appear. He views this mechanism to be an intensity borrowing coupling between the far-infrared band of the CO_2-X supramolecule and the allowed, intense CO_2 bending vibration. Weiss concludes that frame distortion-induced dipoles are comparable in strength to the exchange force-induced dipoles of known systems; the associated absorption contributions probably were seen in absorption measurements of gas mixtures of carbon dioxide and helium [25]. Weiss later extended his studies to tetrahedral molecules, including CH_4, again with a suggestion of the likely spectroscopic significance of transient collisional distortion of the molecular frame [6]. The CH_4 molecule has even lower bending force constants than CO_2 and was suspected to actually have stronger frame distortion-induced dipoles under otherwise comparable conditions (e.g., temperature controlling the impact). The estimates of the CH_4-He frame distortion-induced dipole indicate a dipole strength in the range of 0.003–0.03 D, which is of the order of magnitude of many other well-known collision-induced dipoles. Such frame distortion-induced dipoles should give rise to various absorption bands or significant parts thereof, probably including the ones seen above and in Ref. [7].

Rotation-induced dipole moments arising from rotational and rotovibrational frame distortion of CH_4 have been spectroscopically discovered in gaseous methane at room temperature [32–36]. Methane (and all group-IV hydrates) show stronger rotation-vibration coupling than other common molecules [37]. The first-order Coriolis constant of CH_4 is 5 cm^{-1}, which is one to two orders of magnitude stronger than other common values. The second-order constant is 0.8 cm^{-1}, which is larger than most molecules' first-order Coriolis constants. The result is the distortion of the CH_4 frame at standard temperature and pressure to a D_{2d} or C_{3V}

system, thus allowing dipole moments of several tens of μD strength to form at room temperature [35,36,38]. These dipole moments typically increase strongly with increasing rotational quantum numbers. Specifically, weak purely rotational transitions are known to exist at frequencies from about 42 to 208 cm^{-1}, the so-called ground-state to ground-state transitions. Transitions within the polyad system ν_2/ν_4 exist at frequencies from about 14 to 500 cm^{-1} at room temperature [36]. These are dipole-allowed, weak transitions which are likely to occur also as collision-induced bands.

Temperature variations of the polarizability of CH_4 have been reported [39–41] which are related to rotation-induced frame distortion. A strong dependence of the rotation-induced corrections on the rotational state is again noted. Spectral contributions to the observed collision-induced Raman spectra, which were thought to be due to molecular frame distortions, were seen in highly pressurized gaseous methane [42] and in liquid carbon tetrachloride [30].

V. CONCLUSION

In the collision-induced spectroscopies, the CH_4 molecule with its soft tetrahedral frame and its strong internal dipoles has long been believed to act in ways that are different, compared to simpler molecules, such as H_2, N_2, or the helium atom. More or less compelling evidence has been reported over the past forty years or so, suggesting that various forms of frame distortions manifest themselves in discernible spectroscopic signatures. We think that virtually all CH_4-X systems, with an arbitray X, show signatures, some of which are CH_4 specific (e.g., rotational and polyad CH_4 bands). Others spectroscopic signatures are X and CH_4-X specific, e.g., "forbidden" X bands and bands at sums or differences of the rotational transition frequencies of CH_4 and X, arising from simultaneous transitions. We have considered four different collisional systems involving a methane molecule. Common features are seen in the 200–500-cm^{-1} region and may involve CH_4 combination bands whose dipole-allowed transitions were recently studied extensively [36]. Collision-induced absorption intensities may be "borrowed" from such infrared active combination bands at higher frequencies.

Other dipole induction mechanisms that are enabled by the high degree of flexibility of the molecular frame of CH_4 could conceivably also contribute to the observed excess absorption bands, e.g., dipoles and higher-order multipoles induced by collisional and/or rotational frame distortions. Since frame distortion will also modify the polarizability of CH_4, some unexpected temperature dependencies may well result, even in the familiar multipole-induced absorption bands.

ACKNOWLEDGMENT

It is a pleasure to acknowledge valuable communications with Dr. M. Moraldi.

[1] H. L. Welsh, in *MTP International Review of Science—Physical Chemistry, Series One, Vol. III: Spectroscopy*, edited by A. D. Buckingham and D. A. Ramsay (Butterworths, London, 1972), Chap. 3, pp. 33–71.

[2] L. Frommhold, *Collision-induced Absorption in Gases* (Cambridge University Press, Cambridge, England, and New York, 1993 and 2005).

[3] A. D. Buckingham, in *Propriétés Optiques et Acoustiques des Fluides Comprimés et Actions Intermoléculaires* (Centre National de la Recherche Scientifique, Paris, 1959), p. 57, Colloques Internationaux du C.N.R.S., Vol. 77.

[4] J. van Kranendonk, in *Propriétés Optiques et Acoustiques des Fluides Comprimés et Actions Intermoléculaires* (Centre National de la Recherche Scientifique, Paris, 1959), pp. 53–56, Colloques Internationaux du C.N.R.S., Vol. 77.

[5] S. Weiss, J. Phys. Chem. **86**, 429 (1982).

[6] S. Weiss, Chem. Phys. Lett. **114**, 536 (1985).

[7] M. Buser and L. Frommhold, J. Chem. Phys. **122**, 024301 (2005).

[8] M. Buser, L. Frommhold, M. Gustafsson, M. Moraldi, M. H. Champagne, and K. L. C. Hunt, J. Chem. Phys. **121**, 2617 (2004).

[9] P. Dore, M. Moraldi, J. D. Poll, and G. Birnbaum, Mol. Phys. **66**, 355 (1989).

[10] R. D. Amos, Mol. Phys. **38**, 33 (1979).

[11] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids, Vol. 1: Fundamentals* (Clarendon Press, Oxford, 1984).

[12] D. P. Shelton and G. C. Tabisz, Mol. Phys. **40**, 299 (1980).

[13] H.-J. Werner and W. Meyer, Mol. Phys. **31**, 855 (1976).

[14] V. Aquilanti and D. Cappelletti, J. Chem. Phys. (to be published).

[15] A. Borysow and L. Frommhold, J. Mol. Spectrosc. **123**, 293 (1987).

[16] A. Rosenberg and J. Susskind, Can. J. Phys. **57**, 1081 (1979).

[17] P. Codastefano, P. Dore, and L. Nencini, J. Quant. Spectrosc. Radiat. Transf. **35**, 255 (1986).

[18] G. Birnbaum, L. Frommhold, L. Nencini, and H. Sutter, Chem. Phys. Lett. **100**, 292 (1983).

[19] I. R. Dagg, A. Anderson, S. Yan, W. Smith, C. G. Joslin, and L. A. A. Read, Can. J. Phys. **64**, 1467 (1986).

[20] G. Birnbaum, A. Borysow, and H. G. Sutter, J. Quant. Spectrosc. Radiat. Transf. **38**, 189 (1987).

[21] A. Borysow and L. Frommhold, Astrophys. J. **304**, 849 (1986).

[22] A. Borysow, L. Frommhold, and P. Dore, J. Chem. Phys. **85**, 4750 (1986).

[23] G. Birnbaum, A. Borysow, and A. Buechele, J. Chem. Phys. **99**, 3234 (1993).

[24] R. H. Taylor, A. Borysow, and L. Frommhold, J. Mol. Spectrosc. **129**, 45 (1988).

[25] E. Bar-Ziv and S. Weiss, J. Chem. Phys. **57**, 34 (1972).

[26] A. D. Afanasev, M. O. Bulanin, and M. V. Tonkov, Pis'ma Zh. Tekh. Fiz. **6**, 1667 (1980) [Sov. Tech. Phys. Lett. **6**, 1444 (1980)].

[27] C. G. Joslin, C. G. Gray, and S. Singh, Mol. Phys. **54**, 1469 (1985).

[28] A. Borysow and L. Frommhold, Astrophys. J. **318**, 940 (1987).

[29] H. S. Gabelnick and H. L. Strauss, J. Chem. Phys. **46**, 396 (1966).

[30] J. A. Bucaro and T. A. Litovitz, J. Chem. Phys. **55**, 3585 (1971).

[31] D. H. Whiffen, Trans. Faraday Soc. **46**, 124 (1950).

[32] A. Rosenberg, I. Ozier, and A. Kudian, J. Chem. Phys. **57**, 568 (1972).

[33] A. Rosenberg and I. Ozier, J. Mol. Spectrosc. **56**, 124 (1975).

[34] L. R. Brown, J. S. Margolis, J. P. Champion, J. C. Hilico, J. M. Jouvard, M. Loete, C. Chackerian, Jr., G. Tarrage, and D. C. Benner, J. Quant. Spectrosc. Radiat. Transf. **48**, 617 (1992).

[35] C. Wenger and J. P. Champion, J. Quant. Spectrosc. Radiat. Transf. **59**, 471 (1998).

[36] L. S. Rothman *et al.*, J. Quant. Spectrosc. Radiat. Transf. **96**, 139 (2005).

[37] F. Baglin, in *Collision- and Interaction-Induced Spectroscopy*, edited by G. Tabisz and M. Neuman, NATO Advanced Studies Institute, Series C: Mathematical and Physical Sciences (Kluwer, Dordrecht, 1995), Vol. 452, pp. 119–127.

[38] I. Ozier, Phys. Rev. Lett. **27**, 1329 (1971).

[39] K. Kerl and H. Häusler, Ber. Bunsenges. Phys. Chem. **88**, 992 (1984).

[40] U. Hohm and K. Kerl, Mol. Phys. **58**, 541 (1986).

[41] U. Hohm and K. Kerl, Ber. Bunsenges. Phys. Chem. **95**, 36 (1991).

[42] F. D. Medina and W. B. Daniels, Phys. Rev. A **17**, 1474 (1978).