Double Incoherent Raman Scattering Induced by Molecular Interactions in Gases

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(Received 23 January 2003; published 12 May 2003)

A new Raman band is observed in two gases, CF_4 and CH_4. It is attributable to a double incoherent Raman scattering that takes place in pairs of interacting molecules. Spectral scattering intensities are given on an absolute scale. Zero order spectral moments are measured and are found higher than their long-range interaction value.

DOI: 10.1103/PhysRevLett.90.193001 PACS numbers: 33.20.Fb, 34.90.+q, 82.37.Vb

Molecular interactions have long been known to induce light scattering in high density gases and more generally in dense fluids. Quantitative studies of interaction induced light scattering (IILS) were first reported in the vicinity of the Rayleigh line in gaseous argon [1,2] and then in several other gases and liquids [3]. IILS generally consists of a weak spectral band more or less broadened and partially polarized. Its spectral intensities may include two-body or higher order correlation contributions depending on the density of the sample and on the coherence of the scattered waves involved in the process [4,5]. IILS intensities have been measured in the wings of several bands of atomic or molecular gases [6,7]. However, they have never been given at the center of IILS bands of gases since, at this frequency, stray light and scattering from monomers may contribute to experimental intensities in the interaction induced bands of gases studied up to now.

In this work, we report a new kind of interaction induced scattering observed at a frequency shift equal to twice the Raman frequency of an allowed vibrational Raman mode. This scattering has been studied in two gases, CF_4 and CH_4. The spectral scattering intensities are given on an absolute scale and include the intensity at the center of the band, information that is missing in the IILS studies previously performed in gases. The density behavior of the integrated intensity of the new band is investigated up to several hundreds of amagat. The zero order spectral moment is measured and compared with the value calculated from a long-range interaction model.

When a laser beam is incident on a pair of two interacting molecules, the IILS from this pair may be approached using the double light scattering model [8]: the electric dipole induced by the incident field in one molecule of the pair creates a dipolar field which polarizes the nearby molecule that will in turn scatter light. Therefore a portion of the scattered signal at long range is due to IILS and has been scattered twice. Such IILS intensities have been observed in Rayleigh wings and in vibrational Raman bands for several gases and liquids [3,5]. For each of the interaction induced bands reported up to now in gases, one or two Rayleigh scattering were involved in the double scattering process. We now consider a pair of two identical molecules and the scattered light that results from two successive Raman scattering processes associated, for the first one, with the vibrational normal mode v of one of the molecules, and, for the second, with the same vibrational mode of the other molecule. We have a double Raman scattering (DRS) band centered at $2\nu_v$, where ν_v is the Raman frequency of the normal mode v. This Raman band is generated by an r dependent polarizability $\Delta\alpha(r)$ induced by the internal interactions of the molecular pair (r is the distance between the two molecules). As a first approximation, the intensity of this DRS band may be calculated from dipole induced dipole (DID) interactions [9] giving a good estimation of the long-range interaction contribution. Thus, within this model, the anisotropy $\beta(r)$ of the interaction induced polarizability tensor $\Delta\alpha(r)$ for a molecular pair is

$$\beta(r) = 6(\partial\alpha/\partial Q_v)^2 Q_v^2 r^{-3}, \tag{1}$$

where Q_v is the normal coordinate corresponding to the vibrational mode v of the two molecules and $\partial\alpha/\partial Q_v$ is the polarizability derivative associated with this mode. Then, from Eq. (1), we obtain the zero order spectral moment M_0 for the DRS band,

$$M_0 = A(\nu_v)(\partial\alpha/\partial Q_v)^4 \langle r^{-6} \rangle, \tag{2}$$

where $A(\nu_v)$ is a function of the Raman frequency ν_v [5] and $\langle\,\rangle$ an average over the molecular pairs of the sample. The DRS occurs at a frequency for which no Raman scattering from monomers is expected to take place in contradistinction to the previous studies of IILS bands in gases observed in the vicinity of the Rayleigh or the vibrational Raman lines [5]. This remarkable feature yields an opportunity to measure the intensity at the center of an IILS band of a gas. Concerning the magnitude of DRS intensities it should be observed that the Raman scattering cross section is generally much smaller than the Rayleigh one (about 1000 times smaller) and therefore the DRS that takes place after two Raman scattering processes is very weak. This may explain why until now such a scattering has never been reported in molecular gases.

In the present investigation, we used a typical 90° scattering setup [10] with an argon ion laser source (514.5 or 488 nm) operating at 2 W and a double monochromator associated with a multichannel charge-coupled device photodetector. The gaseous sample was contained in a four-window high-pressure cell stabilized at 294.5 ± 1 K. Purified gases were used with residual impurities less than 50 ppm for CF_4 and less than 5 ppm for CH_4. Two kinds of scattering intensities $I_\perp$ and $I_\parallel$ were measured. They correspond to a polarization of the incident beam perpendicular ($I_\perp$) or parallel ($I_\parallel$) to the scattering plane [11], respectively. The dependence of the spectral sensitivity of our apparatus on the wavelength of the light was taken into account.

Gaseous CF_4.—The Raman spectral intensities $I_\perp(\nu)$ and $I_\parallel(\nu)$ scattered by gas CF_4 have been recorded from 1760 to 1880 cm^{-1}. Several densities have been studied up to about 300 amagat. In Fig. 1, the depolarized spectrum $I_\parallel(\nu)$ obtained at 269 amagat and room temperature, between 1800 and 1833 cm^{-1} is presented. It shows an almost symmetric Raman band which has not been previously reported. The Raman shift at the maximum intensity of this band, deduced from several spectra obtained at about 269 amagat, is $\Delta\nu_m = 1816.3 \pm 1.5\ \mathrm{cm}^{-1}$. Taking into account the experimental uncertainty, this value is twice the frequency shift of the ν_1 vibrational Raman line which is $\Delta\nu_1 = 908.1 \pm 1\ \mathrm{cm}^{-1}$ at the same density. This result is in agreement with the aforementioned double scattering model ($\Delta\nu_m = 2\Delta\nu_1$). A small increase of the frequency shifts, $\Delta\nu_m$ and $\Delta\nu_1$, is observed when the gas density decreases.

We have studied the density dependence of the scattering intensities of this new Raman band. The integrated parallel intensity $I_\parallel$ of the band centered at 1816.3 cm^{-1} divided by the integrated parallel intensity of the ν_2 vibrational Raman band at about 440 cm^{-1} is plotted in Fig. 2 as a function of the CF_4 density up to 270 amagat. Taking into account the dependence of the ν_2 Raman band intensity on the density, it results from our data that the integrated intensity of the band centered at 1816.3 cm^{-1} varies as the square of the gas density showing that this DRS band is generated by molecular pairs. Thus, in our experimental conditions, no significant contribution from three-body or four-body correlations is observed. To understand this behavior it is worth noting that for this DRS band centered at 1816.3 cm^{-1} two vibrational Raman scattering processes are involved for each molecular pair, one for each molecule. These are two incoherent scattering processes and therefore interference effects between several molecular pairs do not take place. On the contrary, for IILS bands of CF_4 previously reported in the vicinity of the Rayleigh line and the ν_1 Raman line [5,12], coherent Rayleigh scattering is involved and consequently four- and/or three-body

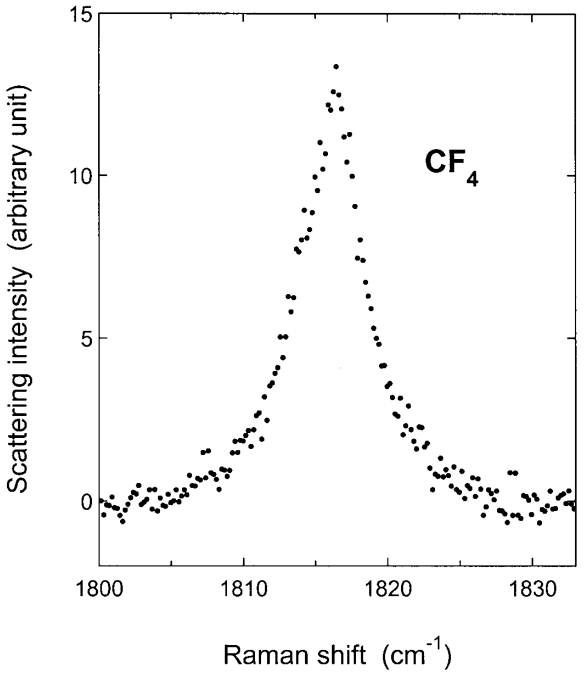

FIG. 1. Parallel Raman pair intensities ($I_\parallel$) versus Raman shift in cm^{-1}, measured for gaseous CF_4 at 269 amagat and room temperature. The scattering intensities were recorded using an argon laser ($\lambda = 514.5$ nm) and an apparatus function of 0.5 cm^{-1}.

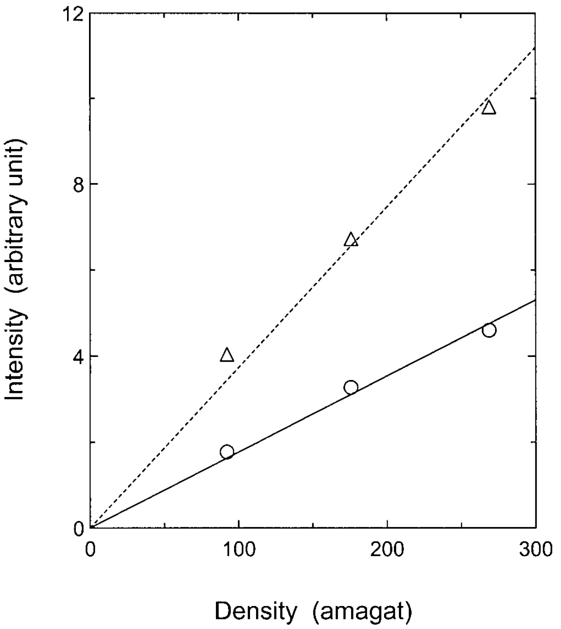

FIG. 2. Integrated parallel intensity of the Raman band of CF_4 centered at about 1816 cm^{-1} divided by the integrated parallel intensity of the ν_2 Raman band measured in gas CF_4 versus density in amagat. Spectra were recorded using an argon laser ($\lambda = 514.5$ nm). Triangles (△) correspond to the integrated intensity of the whole band at 1816 cm^{-1} and circles (○) correspond to the integrated intensity of the Stokes side of this band.

interactions modify significantly the IILS intensities in the same density range.

Interaction induced intensities were calibrated on an absolute scale (cm^6) on the basis of the comparison with the intensity of the $S_0(1)$ rotational line of hydrogen used as an external reference. Then the experimental zero order spectral moment of the parallel component of the DRS band was deduced from the relation:

$$M_0 = 15/2(\lambda_s/2\pi)^4(V\partial\sigma/\partial\Omega)_p, \qquad (3)$$

where $(V\partial\sigma/\partial\Omega)_p$ is the experimental depolarized pair scattering cross section and λ_s the wavelength of the scattered light. Thus, by integrating parallel intensities from 1800 to 1833 cm^{-1} and subtracting the baseline contribution we measured

$$M_0 = (23.1 \pm 4)10^{-6}\ \text{Å}^9.$$

The theoretical parallel scattering zero order moment in the DID approximation was calculated from Eqs. (1) and (2). Using a Lennard-Jones potential [13] and the polarizability derivative given in Ref. [14] we obtained the theoretical moment $M_0 = 31 \times 10^{-6}$ Å^9, which is slightly higher than the experimental value. However the DID anisotropy considered in Eq. (1) does not take into account short-range interactions (overlap, frame distortion, etc.) which may influence the theoretical moment value.

In Fig. 3, the spectral intensities measured for the Stokes side of the DRS band of $\mathrm{CF_4}$ at 269 amagat are shown. The perpendicular spectrum $[I_\perp(\nu)]$ and the parallel $[I_\parallel(\nu)]$ including the spectral intensities at the center of the band are given on an absolute scale. The spectral shapes of both spectra, $I_\perp(\nu)$ and $I_\parallel(\nu)$, are similar and almost exponential. From these spectra, we have checked that the spectral depolarization ratio $\eta(\nu)$ is roughly constant in the frequency domain displayed. Thus we found

$$\eta(\nu) = I_\parallel(\nu)/I_\perp(\nu) \approx 0.85.$$

This result is typical of a depolarized scattering. Besides, since the maximum intensity of the band is measured, the spectral width at half of the maximum intensity (SWHMI) may be also measured. The parallel Stokes spectrum displayed in Fig. 3, recorded with an instrumental function of 0.5 cm^{-1}, has a half SWHMI equal to 2.1 cm^{-1}. If the whole band is considered, the SWHMI is 5.0 cm^{-1}. It is larger than twice the Stokes value due to a weak monomer Raman line that slightly broadens the DRS band on the anti-Stokes side. This weak line is polarized and centered at about 2 cm^{-1} from the maximum of the DRS band. When several densities are considered we observe that the width of the DRS line decreases when the gas density increases as shown in Table I. This change in the spectral width is too large to be explained by a motional narrowing effect [15] in the Q branch of the ν_1 Raman line of $\mathrm{CF_4}$. On the other hand, correlations between two or more collisions of the same particle, known as the intercollisional interference effect [16], could influence the width of the DRS band. Indeed, on account of this effect predicted previously by Lewis and Van Kranendonk [16] an increase of the scattering intensity and a modification of the spectral shape are expected to occur at very low frequency shift when the gas density goes up.

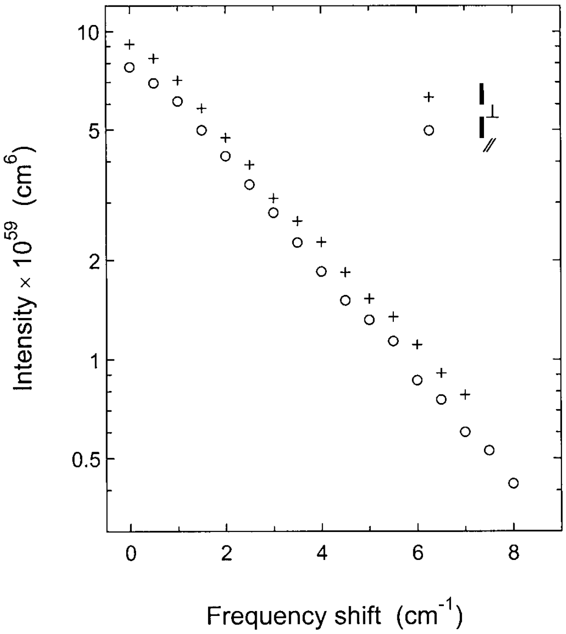

FIG. 3. Spectral Stokes intensities of the Raman band centered at 1816.3 cm^{-1} measured in cm^6, for gaseous $\mathrm{CF_4}$ at 269 amagat and room temperature. Frequency shifts, in cm^{-1}, are measured relatively to the center of the band. Two kinds of data are displayed, the parallel ($I_\parallel$) and the perpendicular ($I_\perp$) Stokes intensities. Spectra were recorded using an argon laser ($\lambda = 514.5$ nm) and an apparatus function of 0.5 cm^{-1}.

Gaseous $\mathrm{CH_4}$.—The spectral intensities $I_\perp(\nu)$ and $I_\parallel(\nu)$ scattered by gas $\mathrm{CH_4}$ have been recorded from 5790 to 5860 cm^{-1}, a frequency domain centered at twice the Raman frequency of the vibrational mode ν_1 of $\mathrm{CH_4}$. Several densities were studied up to 320 amagat. Parallel scattering intensities $I_\parallel(\nu)$ obtained at 320 amagat are displayed in Fig. 4 on an absolute scale. They show a Raman band centered at the Raman frequency $\Delta\nu_m = 5824.8 \pm 2\ \mathrm{cm}^{-1}$. At the density considered, the Raman

TABLE I. Spectral width at half of the maximum intensity ($\Delta\nu_{1/2}$) for depolarized Raman bands recorded for gaseous $\mathrm{CF_4}$ (269, 176, 92 amagat) and $\mathrm{CH_4}$ (320 amagat) at about 1816 and 5825 cm^{-1}, respectively. The Raman spectra have been obtained using an argon laser ($\lambda = 514.5$ nm for $\mathrm{CF_4}$ and $\lambda = 488$ nm for $\mathrm{CH_4}$) and an apparatus function of 0.5 cm^{-1}.

		$\mathrm{CF_4}$		$\mathrm{CH_4}$
Density (amagat)	269	176	92	320
$\Delta\nu_{1/2}$ (cm^{-1})	5	6.4	7.8	17

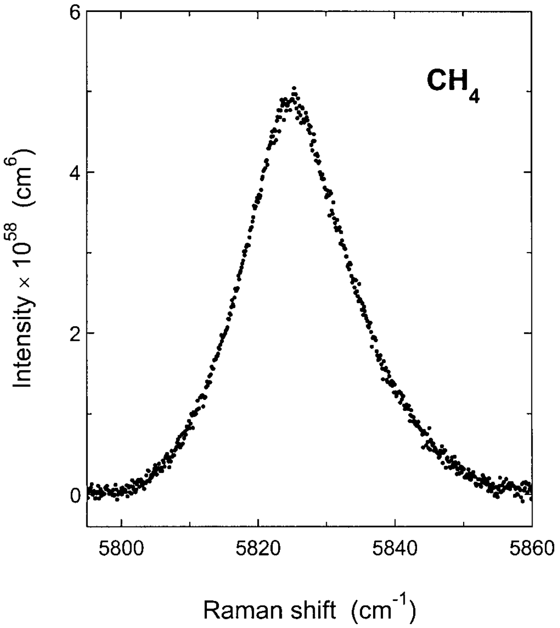

FIG. 4. Parallel Raman pair intensities in cm^6 ($I_{||}$) versus Raman shift in cm^{-1}, measured for gaseous CH$_4$ at 320 amagat and room temperature. These intensities were recorded using an argon laser ($\lambda = 488$ nm) and an apparatus function of 0.5 cm^{-1}.

shift for the maximum intensity of the ν_1 vibrational band of CH$_4$ is $\Delta\nu_1 = 2912.0 \pm 1.5$ cm^{-1}. Thus, the new Raman band observed in CH$_4$ is centered at twice the ν_1 Raman frequency, similar to the CF$_4$ case. The spectral shape is roughly symmetric and its SWHMI is 17 cm^{-1}. By studying several gas densities, we have found that the integrated intensity of the band centered at about 5824.9 cm^{-1} varies as the square of the density. We have also deduced the experimental zero order spectral moment M_0 for the parallel component of this new CH$_4$ band. From the measured intensities $I_{||}(\nu)$, we have

$$M_0 = (10.6 \pm 4)10^{-4}\ \text{Å}^9.$$

Using the DID model with the intermolecular potential of Palmer *et al.* [17] and the polarizability derivative of Ref. [14], we calculated, according to Eq. (2),

$$M_0 = 26.7 \times 10^{-4}\ \text{Å}^9.$$

Thus, the DID moment is comparable but greater than its experimental value. This result is qualitatively similar to the one found for CF$_4$. A more general theoretical study of the DRS intensities should take into account all intermolecular-force effects and, in particular, the contribution of high order polarizabilities as proposed previously by Samson *et al.* [18].

In conclusion, in spite of an extremely weak scattering cross section of the DRS we have investigated this new kind of IILS occurring in the frequency region centered at twice a vibrational Raman frequency in two gases. Pair scattering spectral intensities, including those at the center of the band, have been measured on an absolute scale. The measured zero order spectral moment for the DRS band is of the same order of magnitude as its DID value although the DID moment is clearly higher than the experimental one, in particular, for CH$_4$. The integrated intensity of DRS bands varies as the square of the density up to several hundreds of amagat without any contribution from three- or four-body correlations. Thus, it is suggested that the study of these DRS spectral intensities would be useful when investigating the dependence on the density of the radial pair distribution function for gases and liquids. Moreover, the DRS effect could give the opportunity to study IILS from anisotropic molecules without any significant contribution from rotational Raman lines of monomers at low frequency shifts as it occurs in the Rayleigh winds [19].

We thank Dr. V. Sergiescu for a critical reading of the manuscript.

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