COLLISION-INDUCED LIGHT SCATTERING FROM LIQUID CCl_4 AND C_6H_{12}*

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Collision-induced light scattering was observed in pure CCl_4 and C_6H_{12} and in their mixtures. The intensity $I(\omega)$ in the high frequency wing was fitted to an expression, $I(\omega) \propto \omega^q \exp(-\omega/\omega_0)$ where q and ω_0 are variable parameters. It was found that the values of q and ω_0 are dependent upon the region of the profile over which the fit is made; possible interpretations are discussed.

1. Introduction

Collision-induced light scattering (CIS) is a newly-identified phenomenon which has increased the scope of the information obtainable about dense media by scattering methods [1—4]. While free, optically isotropic atoms or molecules do not depolarize light, an anisotropy can be induced in the total polarizability of a system of interacting atoms which produces a broad depolarized wing centred about the polarized Rayleigh line. Three models for the induction mechanism have been proposed based on studies of liquids and compressed gases.

(i) *Dipole-induced dipole (DID)* [1,2,5]. The anisotropy results from the interaction between electric dipoles induced in the atoms by the incident light. The total field acting on a given atom is the sum of this external light field and the internal field due to the induced dipoles in its neighbours. Orientational fluctuations in the net induced moment due to the atomic motion yield the depolarized scattering. This is a long-range interaction giving an effective pair polarizability which varies as r^{-3} where r is the distance between the atoms in a collision pair.

(ii) *Electron overlap (EO)* [3,4]. The distortion of the electron clouds during close encounters is responsible for the induced polarizability. Originally, the

form $r^2 \exp(-ar^2)$ was proposed but recently**, an r^{-9} dependence has been derived in the case of argon.

(iii) *Frame distortion* [6]. Bucaro and Litovitz [7,8] have made an extensive study of CIS in atomic and molecular liquids and concluded that frame distortion during close collisions which gives a pair polarizability varying as r^{-13} is the principal induction mechanism in liquids composed of isotropic and non-isotropic molecules.

With the use of several simplifying assumptions, principally binary collisions with zero impact parameter, Bucaro and Litovitz were able to derive an expression for the intensity I in the wings as a function of frequency ω,

$$I(\omega) \propto \omega^{2[(m-7)/7]} \exp(-\omega/\omega_0), \qquad (1)$$

where the induced incremental polarizability is given by

$$\Delta\alpha(r) \propto r^{-m}. \qquad (2)$$

The constant ω_0 is inversely proportional to a characteristic time associated with the duration of the interaction giving rise to $\Delta\alpha$.

In the analysis of their spectra, they assumed a value for m and determined the corresponding ω_0 from their data. As there is evidence from experiments on compressed gases [1,2] that the DID contribution diminishes at high densities, they assumed that, in the

** M.R. Vukcevich, private communication quoted in ref. [6].

case of atomic liquids, the electron overlap effect predominates. They found that $m = 9$ in the case of argon and xenon and $m = 13$ in the case of molecular liquids gave values of ω_0 in agreement with their calculations. This work is an excellent attempt to categorize CIS in liquids while providing insight into the interaction mechanisms responsible for the scattering. Primarily, it shows that binary interactions remain important even in the liquid phase.

Gersten [9,10] has pointed out that in the spectra of compressed rare gases, different parts of the profile are affected by different details of the interaction.

Encouraged by the success of Bucaro and Litovitz but mindful that the complications envisaged by Gersten should apply to liquids as well as gases, we have repeated observations of the CIS spectra in pure CCl_4 and C_6H_{12}, as well as in mixtures, with the goal of further investigating the form of the spectral profile.

2. Experimental method

The experimental set-up is typical of laser Raman scattering studies. Light from an argon-ion laser (CRL 52) operating at about 3/4 watt at 4880 Å is passed through a half-wave plate and prism polarizer before being focussed in the sample cell. The light scattered at $90°$ is collected by an f/2 system and brought to a double scanning monochromator (Jarrell–Ash 25-100) having a spectral slit width of $1\ cm^{-1}$. The detector is a cooled EMI 6256B photomultiplier tube used in the photon-counting mode. With the discriminator levels set for an optimum signal-to-noise ratio at low light intensities, the dark count is 1/3 cpsec. The output is stored in a multichannel analyzer (Victoreen ST400M) whose channel advance is controlled by the stepping drive for the monochromator gratings. The geometry used is such that if the incident light is considered to travel in the x direction, polarized in the z direction, then observations are made in the z direction. All experiments are performed at $295°K$.

3. Analysis of results

If a frame distortion origin for the induced polarizability is assumed, eq. (1) leads to a linear relationship between $\ln[I(\omega)/\omega^{12/7}]$ and ω with a slope $(-1/\omega_0)$. When this test is applied to the data, it is found that $\omega_0 = 12.1\ cm^{-1}$ for CCl_4 and $14.7\ cm^{-1}$ for C_6H_{12} in excellent agreement with Bucaro and Litovitz (11.9 and 14.8 cm^{-1} respectively). The frequency range over which this linear relation holds is 30 to 80 cm^{-1} for CCl_4 and 30 to 120 cm^{-1} for C_6H_{12} (fig. 1).

Frame distortion may not however be the only interaction mechanism contributing to the scattering. It was noted that much of the high frequency tail of the CCl_4 could not be accounted for by the above method. When $m = 9$ was tried, a value consistent with an electron overlap interaction (at least for rare gas atoms), eq. (1) held over an increased frequency range, 20 cm^{-1} to 100 cm^{-1}. Moreover the quality of the fit was much improved over that with $m = 13$. This result led us to perform the analysis based on the following considerations.

All authors who have proposed mechanisms for collision-induced scattering conclude that the high frequency profile is described by an expression:

$$I(\omega) = f(\omega)\exp(-\omega/\omega_0)\,. \tag{3}$$

In the original model of Levine and Birnbaum, $f(\omega)$ is approximated by $\omega^{1/2}$; the more general function $\omega^{2[(m-7)/7]}$ shows clearly that the power of ω is a function of the induction process. Gersten [10] has emphasized that the exponential factor in (3) is model independent (although the value of ω_0 is not). The accurate determination of $f(\omega)$ should lead to meaningful information not available through the exponential. Because of the presence of this strong exponential factor, the exact form of $f(\omega)$ is difficult to extract from the experimental data.

In an effort to acquire some estimate of $f(\omega)$ directly from the observed spectra, we have assumed that the high frequency profile can be represented by:

$$I(\omega) \propto \omega^q \exp(-\omega/\omega_0)\,, \tag{4}$$

where both q and ω_0 are taken as variable parameters and made a least squares fit to the spectra by applying the technique of multiple regression. The results given in table 1 are averages over several spectra. The errors quoted represent one standard deviation. For C_6H_{12}, the fits in the range 25 cm^{-1} and 40 cm^{-1} to 100 cm^{-1} are the more significant as they are over a region sufficiently removed from the laser line to be
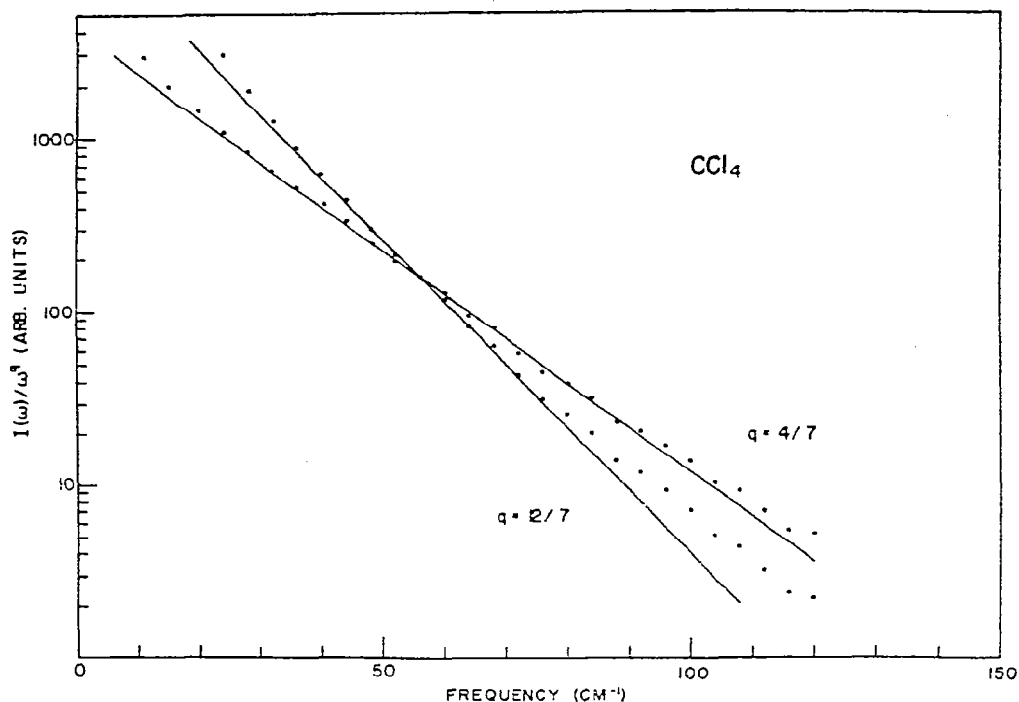
Fig. 1. $I(\omega)/\omega^q$ for the observed spectrum of CCl_4 at $293°K$ where q is $12/7$ and $4/7$ corresponding to $\Delta\alpha(r)$ varying as r^{-13} and r^{-9} respectively. Data points are shown only every $4\ cm^{-1}$.

Table 1
Parameters obtained from the least squares fit

	Range (cm^{-1})	q	Effective m	$\omega_0\ (cm^{-1})$	Standard error of estimate
CCl_4	$16 \to 85$	0.49 ± 0.04	8.7 ± 0.13	17.0 ± 0.25	0.05
	$16 \to 105$	0.22 ± 0.03	7.8 ± 0.12	19.1 ± 0.25	0.06
	$16 \to 125$	0.15 ± 0.04	7.5 ± 0.13	19.6 ± 0.24	0.11
	$40 \to 100$	-0.72 ± 0.19	4.5 ± 0.67	25.3 ± 1.9	0.09
C_6H_{12}	$15 \to 115$	0.78 ± 0.05	9.7 ± 0.17	19.2 ± 0.32	0.11
	$25 \to 115$	1.36 ± 0.07	11.7 ± 0.23	16.7 ± 0.28	0.10
	$40 \to 115$	2.04 ± 0.13	14.1 ± 0.46	14.5 ± 0.33	0.10

free of contributions due to the permanent anisotropy of the molecule. The 'effective m' is determined by setting

$$q = (2/7)(m - 7).\qquad(5)$$

The standard error of estimate is calculated only over the range of the fit.

4. Discussion

The most striking result in table 1 is the fact that for both liquids, the values of q and ω_0 depend on the frequency region over which the fit is made. For C_6H_{12} the result in the range 40 to 115 cm^{-1} agrees with that of Bucaro and Litovitz. On the other hand,

for CCl_4, as more of the tail is included in the fit, the effective m decreases and ω_0 increases, nowhere approximating $m = 13$ or $\omega_0 = 11.9$ cm^{-1}.

The failure of eq. (1) to hold over the entire tail with one set of values for q and ω_0 indicates that more than one type of interaction is operative in the scattering. For C_6H_{12}, short-range effects seem to be important with frame distortion especially dominant beyond 40 cm^{-1}. The theory of Bucaro and Litovitz holds well in this case: basically a single short-range interaction. For CCl_4, both short- and long-range interactions contribute. Here the theory of Bucaro and Litovitz is not entirely applicable as their calculations of ω_0 are valid only near the turning point. Judging from the effective m values, the short-range part includes both electron overlap and frame distortion. The long-range interaction could be of the dipole-induced dipole type.

It should be recalled that because of symmetry effects, the intensity of the scattering through DID at liquid densities is much less than that predicted from an extrapolation of the gas results using a quadratic dependence on density; however it should not necessarily vanish. In liquids the DID interaction would be effective through rapid local fluctuations in the positions of molecules, not describable by the trajectory dynamics used to derive eq. (1). Thus the spectral profile due to DID would broaden as the density increases and it would be expected to contribute to the far wings of spectrum.

The ω_0 found for $40 < \omega < 100$ corresponds to a time of 2.1×10^{-13} sec which is of the order of magnitude of the time between collisions in a cell model for liquid CCl_4 [11]; the time between collisions would be the time characterizing these fluctuations in positions.

The values of ω_0 obtained from the spectra of mixtures in the range 40 to 100 cm^{-1} are plotted in fig. 2 as a function of CCl_4 concentration. A least squares fit to a polynomial in concentration shows that the variation of ω_0 with concentration can be well represented by a quadratic and a cubic term, the higher order and linear terms being negligible. Since ω_0 characterizes the spectral profile, this means that changes in the line shape occur roughly in the same way with concentration. The cell model used by Thibeau [1,2] to explain the results in gaseous argon at high pressures predicts a density dependence of the
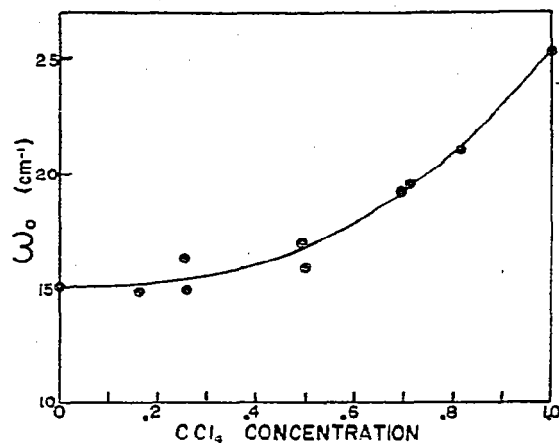

Fig. 2. The variation of ω_0 with the concentration of CCl_4 in the frequency range 40 to 100 cm^{-1}.

total intensity involving several terms of the form $(\rho/\rho_s)^x$ where x is between 2 and 3.3; ρ_s is the maximum density taken to be that of the solid. Therefore as one goes from pure C_6H_{12} which is of frame distortion origin to pure CCl_4, the concentration dependence of ω_0 is similar to the density dependence of the intensity for DID scattering in dense media. A thorough treatment of scattering from mixtures is complex and difficult to apply [12]; nevertheless this result appears to support the conclusion that the tail of the CCl_4 spectrum contains a contribution from DID scattering. In any event, the low power of the concentration dependence reaffirms that the scattering is due to interactions between a few molecules even in the liquid phase.

5. Summary

Based on the statistical accuracy of the data further speculation on the physical meaning of results in table 1 is uncertain. It is clear however that the values of q and ω_0 giving the best fit to the observed spectra change over the profile. This variation is attributable to the total induced polarizability being due to more than one type of interaction. For CCl_4, it appears that both short- and long-range forces are effective in the interaction; electron overlap, DID and frame distortion could all be contributing. On the other hand for C_6H_{12}, only the short-range interactions seem to be important.

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