

CONTRIBUTION TO THE RAMAN LINE PROFILE IN LIQUIDS  
FROM MOLECULAR REORIENTATION\*

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The profiles of several Raman lines arising from nontotally symmetric molecular vibrations in liquid benzene and carbon tetrachloride were analyzed. That these lines have shown greater intensity in the wings than can be accounted for by a Raman process that involves molecular vibrations alone is interpreted as evidence for time-dependent reorientations of vibrationally excited molecules through small angles in the liquid phase. Data analysis on this basis indicates a weaker rotational coupling between molecules in the ground state than there is between vibrationally excited molecules and those in the ground state.

Recent increased interest in profile studies of scattered light spectra in liquids has been brought about by recognition of the information about molecular motion that is contained in the "wings" of the Rayleigh line.<sup>1-6</sup> The present Letter reports analyses of the profiles of several Raman lines in benzene and carbon tetrachloride which provide evidence for the existence of time-dependent reorientations of vibrationally excited molecules in the liquid. Quantitative measurements are given for the widths of spectra traceable to reorientation phenomena to show that the orientation kinetics of vibrationally excited molecules are in those cases investigated considerably differently from those of molecules in the ground vibrational state.

On the assumption that orientational fluctuations of molecules in unassociated liquids occur by a series of sudden reorientations through small angles (rotational Brownian motion), the spectral distribution of depolarized scattered light from a liquid consisting of symmetric top molecules is<sup>1</sup>

$$I(\Delta\omega)_{HV} = I_{HV} \beta / \pi(\beta^2 + \Delta\omega^2), \quad (1)$$

where  $\Delta\omega$  is the frequency measured from the center of the line,  $HV$  refers to horizontally polarized scattered light observed at  $90^\circ$  from a horizontal beam of vertically polarized incident light,  $\beta = 6kT/\xi_x$ , the half-width of the spectral line at half-maximum, with  $\xi_x$  the friction constant for rotation about an axis perpendicular to the top axis of the molecule, and  $I_{HV}$  is the total intensity of the depolarized scattered light (proportional to the square of the anisotropy in the

molecular polarizability). This broad Lorentzian line is centered at the frequency of the incident light and forms a part of what is sometimes called the "wings" of the Rayleigh line. For brevity we refer to this broad spectral line as an orientational spectrum,<sup>4</sup> although other names are also used.<sup>2</sup>

The intensity and depolarization characteristics of Raman-scattered light in distinction to that treated above involve the partial derivatives of the components of the polarizability tensor with respect to a normal coordinate,  $\partial\alpha_{ij}/\partial\xi_k = \alpha_{ij}'$ , rather than  $\alpha_{ij}$  itself, as in the case of Rayleigh scattering. But since  $\alpha_{ij}'$  can be divided into a spherical and nonspherical part, just as  $\alpha_{ij}$  itself, arguments analogous to those of Steele lead to the conclusion that certain Raman lines should contain a contribution from orientational scattering. A strong central feature due to  $\Delta J = 0$  transitions, which we shall refer to as the vibration line, is the predominant component of the Raman line. This is expected to appear superposed on the broad, weaker spectrum that is due to orientational scattering. Calculations of Valiev<sup>7</sup> indicate that the major broadening of  $\Delta J = 0$  (vibration) Raman lines in nonpolar liquids occurs from molecular exchange interactions, and he is thus led to expect a Lorentzian spectrum for this feature of the Raman line.

The total Raman profile is therefore expected to be a superposition of Lorentzian lines, the number of which depends on the symmetry of the rotational diffusion tensor.<sup>2</sup> For spherical symmetry the number of components is two: one each for vibrational and orientational scattering. Because of its tetrahedral symmetry, the polariz-

ability tensor of carbon tetrachloride is spherical. Orientation spectra of this molecule are therefore expected only at Raman lines that arise from nontotally symmetric vibrations. Assuming a spherical diffusion tensor, the orientation spectrum at these lines should then consist of a single broad Lorentzian line. Because of its lack of spherical symmetry benzene should show orientation spectra at Raman lines that arise from both totally symmetric and nontotally symmetric vibrations, and with the assumption of near-spherical symmetry for its diffusion tensor these orientation spectra should also consist of one Lorentzian line.

The recorded trace of the  $606\text{-cm}^{-1}$  Raman line in benzene, polarized in the plane of scattering HV, is shown in Fig. 1. Scattered light in the double monochromator was found to be negligible, which allowed accurate placement of the base line. This and the other Raman lines recorded were analyzed assuming each to be a superposition of two Lorentzian lines of different widths and amplitudes, each convoluted with the instrument function. The instrument function was determined by scattering the laser line from frosted glass, and was found to be adequately represented by a Gaussian function. The best fit of two superposed Voigt functions to the observed line profiles was found from values of the imaginary part of the plasma-dispersion function tabulated by Fried and Conte,<sup>8</sup> to which the Voigt function is equivalent.<sup>9</sup>

Points in Fig. 1 are calculated from a single Voigt function and illustrate the additional intensity in the wings of the line accounted for by molecular reorientation. The solid curve in the figure was calculated from the two Voigt func-

tions into which the  $606\text{-cm}^{-1}$  line in benzene was analyzed. This line has two desirable features that allow analysis with a high degree of certainty. It is sufficiently intense to give a good signal-to-noise ratio, and it is free of the complicating structure that arises from isotopes, overtones, or combinations in some lines. Only the side free of structure was analyzed in the cases where structure was present.

The results of the analyses of six Raman lines are presented in Table I. The third and fourth columns give the half-width at half-maximum of the vibration line and the orientation line, respectively, with estimated errors, and the fifth column gives the mean reorientation time  $\tau_r$  calculated from the half-width of the orientation line.

The sixth and seventh columns give the measured depolarization ratio of the lines from the integrated intensities. The same depolarization ratio is predicted for both the vibration and the orientation lines for nontotally symmetric vibrations. Values of  $\rho = 0.748$  and  $0.749$ , respectively, for these components of the  $606\text{-cm}^{-1}$  line in benzene agree well with the theoretical value of  $0.750$ , and verify independently that the superposed lines of each polarization have been analyzed properly into their components. The depolarization ratios for the  $849_{VV}$  and  $1178\text{-cm}^{-1}$  lines were measured from the intensities at the line centers.

The mean reorientation times of  $\sim 10^{-13}$  sec obtained in the present experiments are short compared with the periods of rotation of the unperturbed benzene and carbon tetrachloride molecules,  $\sim 10^{-10}$  sec, and provide justification for the assumption of rotational Brownian motion.

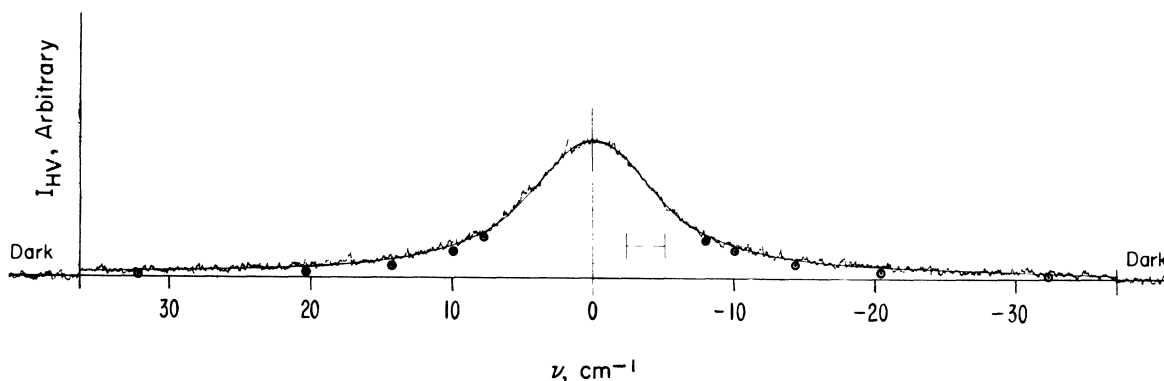


FIG. 1. The  $606\text{-cm}^{-1}$  Raman line in liquid benzene; horizontally polarized scattered light viewed at  $90^\circ$  from a horizontal beam of vertically polarized incident light. The solid curve through the recorded trace was calculated from the two Voigt functions into which the trace was analyzed. The inset marker shows the half-width of the instrumental line. The circled points are calculated from a single Voigt function.

Table I. Analysis of several Raman line profiles in liquid benzene and carbon tetrachloride.

Liquid	*Raman line, cm <sup>-1</sup>	Vibration line half width, cm <sup>-1</sup>	Orientation line half width, cm <sup>-1</sup>	Mean reorientation time, $\tau_r, 10^{-13}$	Depolarization ratio of Raman line	Depolarization ratio of orientation line	$\rho$ theory
C <sub>6</sub> H <sub>6</sub>	992 <sub>VV</sub>	1.2 ± 0.1					
C <sub>6</sub> H <sub>6</sub>	992 <sub>HV</sub>		3.9 ± 0.5	13.7			
C <sub>6</sub> H <sub>6</sub>	606 <sub>HV</sub>	3.29 ± 0.2	24.3 ± 5.0	2.18			
C <sub>6</sub> H <sub>6</sub>	606 <sub>VV</sub>	3.24 ± 0.2	20.0 ± 5.0	2.65			
C <sub>6</sub> H <sub>6</sub>	606	3.29 ± 0.2	24.3 ± 5.0	2.18	0.748	0.749	0.750
C <sub>6</sub> H <sub>6</sub>	849 <sub>VV</sub>	6.82 ± 0.4	28.5 ± 5.0	1.86	0.763**		0.750
C <sub>6</sub> H <sub>6</sub>	1178	6.56 ± 0.4	>29	<1.83	0.756**		0.750
CCl <sub>4</sub>	218 <sub>VV</sub>	4.12 ± 0.4	>35.5	<1.49	~0.71		0.750
CCl <sub>4</sub>	314 <sub>HV</sub>	3.85 ± 0.4	30.9 ± 5.0	1.72	~0.79		0.750

\*HV and VV designate horizontally and vertically polarized scattered light, respectively, for vertically polarized incident light. Lines not so marked were analyzed for best fit to both VV and HV polarizations.

\*\*Measured from amplitude at line center.

The mean reorientation time for benzene in the ground vibrational state (measured from the orientation spectrum at the Rayleigh line)  $\tau_0$ , is approximately  $2.6 \times 10^{-12}$  sec. Letting  $\tau_v$  be the lifetime of the vibration in the liquid,

$$(\tau_r)^{-1} > (\tau_0)^{-1} + (\tau_v)^{-1}$$

for all the Raman lines measured. This indicates weaker rotational coupling between molecules in the ground vibrational state than between vibrationally excited molecules and those in the ground state. This might be expected from the lower symmetry of the molecular wave function for the vibrationally excited state and suggests that collisions effective in causing reorientations are predominantly exchange rather than Van der Waals interactions. It is expected that a change in symmetry with only a small change in the magnitude of  $\alpha$  affects the latter interaction considerably less than the former. This conclusion is compatible with the orientation spectrum observed for the 992-cm<sup>-1</sup> Raman line in benzene. The  $\nu_2$  vibration, a totally symmetric vibration, gives rise to this line. Here the symmetry of the molecular wave function is unchanged from that of the ground state, and the measured mean reorientation time is only about one-half of the ground state. Even this amount is largely accounted for by the lifetime of the vi-

brational state, since  $(\tau_v)^{-1} = 1.2 \text{ cm}^{-1}$ . Therefore, the rotational coupling of the  $\nu_2$  vibrationally excited molecule to its surroundings is not much greater than that of the ground-state molecule.

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