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Raman line shapes in liquid CH_3I and CD_3I *

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The six fundamental bands of CH_3I and CD_3I , both as pure liquids and in solution with CS_2 , have been studied in order to obtain information about the molecular rotational and vibrational dynamics. Emphasis was placed on the features of the spectra that can be interpreted independent of a particular model. An examination for Boltzmann asymmetry in the A_1 and E bands indicates that the former, being symmetric, are amenable to classical description, while the latter, being asymmetric, definitely require quantum mechanical interpretations. With respect to the validity of the assumption that rotation-vibration coupling can be ignored, we give evidence of substantial coupling effects in a nondegenerate A_1 mode (ν_1) as well as in the doubly degenerate E modes. We emphasize that, in attempting to obtain dynamical information, several bands of any given liquid must be studied and compared in order to decide which can be used with confidence in a detailed analysis. The consistency of the rotational diffusion model for describing the tumbling motion of the methyl iodide molecules has been confirmed.

I. INTRODUCTION

The analysis of the Raman bands of a liquid can, in principle, provide much information on both the vibrational and the rotational motions of the molecules in the liquid. Theoretical effort has generally been directed more toward the study of rotational rather than vibrational phenomena. Most recently Bratoz *et al.*¹ have put forth a theory for the vibration of a diatomic molecule in an inert solution, however, even for this "simple" case, their theory yields a line whose shape depends, in quite a complex manner, on various correlations of the intermolecular potential. From spectra observed in various substances and solutions, several workers²⁻⁴ have been able to draw some qualitative conclusions about the relative importance of different intra- and intermolecular interactions that affect the vibrational lineshapes and widths. The most commonly used rotational theory is the "rotation diffusion" model, which, from a microscopic point of view, is the angular analog of the translational Brownian motion or random walk problem. Variations of this theory have appeared that allow for large "steps" in the diffusion process⁵ or for quasifree rotation.⁶ Numerous experimentalists have analyzed their data on the basis of these models and have obtained values for the important model parameters such as the rotation diffusion constants.

One of the key problems to be faced in the analysis of the Raman (and infrared) bands is whether or not the separation of the rotational and the vibrational effects is possible and how to effect this separation when it is. On the whole, experimentalists have tended to skirt this issue by considering one or the other effect to be negligible. Only recently has it been emphasized that in fact the simultaneous presence of both effects cannot be so readily ignored and procedures for effecting the separation of the vibrational line from the rotational line have been proposed.^{7,8} Unfortunately, both the procedures and the theories that have been suggested to date are only valid under the condition that

the vibrations and the rotations are independent of one another. While it has long been recognized that rotation-vibration coupling can play a significant part in determining the line shapes of bands in low density gases,⁹ little attention has been given to coupling effects in liquids.

In this paper we have focused our attention on the bands of CH_3I and CD_3I . We show that by analyzing as many bands as possible in a given liquid, more information can be reliably gleaned than is available from the commonly employed experimental procedure of studying only one or two bands. We emphasize that a number of important conclusions about the molecular dynamics can be drawn without having to resort to any one model of the vibrations or rotations. In particular, we suggest that rotation-vibration coupling may be more of a factor in the bands of liquids than has been considered the case in the past.

II. THEORETICAL

Methyl iodide has been studied by a number of techniques, e.g., infrared and microwave absorption,^{10,11} nuclear spin relaxation,¹² and, to a small extent, Raman scattering.^{13,14} It has many features that make it an interesting subject for investigation. It is a simple polyatomic "symmetric top" molecule, having a moderately high degree of symmetry. It is free of isotopic complications (other than the 1% natural abundance of ^{13}C), exists as a liquid at room temperature, and is clear and colorless. In addition, its vibration-rotation bands are reasonably well separated and have relatively large scattering cross sections. Further, the suggestion has been made¹⁵ that rotations of the molecule about its major (symmetry) axis (called "spinning") and the rotations about its minor axes ("tumbling") exhibit different dynamical behaviors. The point group symmetry⁹ of CH_3I is C_{3v} . There are nine vibrational modes, three totally symmetric (i.e., preserving the symmetry of the molecule) of symmetry species A_1 , and three non-totally symmetric, doubly degenerate modes of sym-

metry species E . All modes are both Raman and infrared active.

We briefly review the relevant Raman scattering theory as it applies to C_{3v} type molecules. Under the assumption that the vibrations on different molecules are uncorrelated, the quantity of interest in Raman scattering is the single molecule polarizability tensor α . Neglecting rotation-vibration coupling, the part of α that gives rise to the vibrational bands is given by $(\partial\alpha/\partial\mathbf{q})\mathbf{q}(t)$ to first order in \mathbf{q} , the normal vibrational coordinate, where the derivative is taken in the Born-Oppenheimer sense (i.e., the electrons follow the nuclei adiabatically). Then we may write by symmetry the Raman tensors of the i th A_1 mode and the j th pair of degenerate E modes in a rotating frame of reference frame fixed to the molecule (designated as MF) as follows¹⁶:

$$\alpha_{A_{1,i}}(\text{MF}) = \begin{pmatrix} a_i & 0 & 0 \\ 0 & a_i & 0 \\ 0 & 0 & b_i \end{pmatrix} \mathbf{q}_i(t), \quad (1)$$

$$\alpha_{E,j_1}(\text{MF}) = \begin{pmatrix} c_j & 0 & 0 \\ 0 & -c_j & d_j \\ 0 & d_j & 0 \end{pmatrix} \mathbf{q}_{j_1}(t)$$

$$\alpha_{E,j_2}(\text{MF}) = \begin{pmatrix} 0 & -c_j & -d_j \\ -c_j & 0 & 0 \\ -d_j & 0 & 0 \end{pmatrix} \mathbf{q}_{j_2}(t), \quad (2)$$

where z is the symmetry axis, and where $a_i = (\partial\alpha/\partial\mathbf{q}_i)_{zz}$, etc. It is convenient to separate α into an isotropic part, $\bar{\alpha} = \frac{1}{3} \text{Tr}\alpha$, and an anisotropic part $\beta = \alpha - \bar{\alpha}\mathbf{I}$, where \mathbf{I} is the identity matrix.

For the i th mode, the spectrum of Raman radiation scattering with polarization perpendicular to the incident light (i.e., the so-called depolarized or HV component) is given¹⁷ by the Fourier transform of

$$C_i^{HV,R}(t) = 1/10 \langle \text{Tr}[\beta_i(t)\beta_i(0)] \rangle. \quad (3)$$

The spectrum of light scattered with polarization parallel to that of the incident light (the so-called polarized or VV component) is given by the transform of

$$C_i^{VV,R}(t) = \langle \bar{\alpha}_i(t)\bar{\alpha}_i(0) \rangle + 4/3 C_i^{HV,R}(t). \quad (4)$$

The brackets indicate an equilibrium ensemble average.

In Eq. (3), the tensor β_i refers to the anisotropic part of the Raman tensor relative to a fixed laboratory frame and is obtained from $\beta_i(\text{MF})$ by writing

$$\beta_i = R^{-1}(\Omega)\beta_i(\text{MF})R(\Omega), \quad (5)$$

where \mathbf{R} is the appropriate rotational transformation tensor, and Ω represents the Eulerian angles describing

the instantaneous orientation of the molecule. The trace component $\bar{\alpha}$, being a scalar, is independent of the reference frame. On the basis of our assumptions, it is clear that the vibrational coordinate $\mathbf{q}_i(t)$ factors out of $\bar{\alpha}_i$ and β_i . Hence, the HV correlation function $C_i^{HV,R}(t)$ can be written as the product of a vibrational correlation function $C_i^{\text{vib}}(t) = \langle \mathbf{q}_i(0)\mathbf{q}_i(t) \rangle$ and a rotational correlation function $C_i^{\text{rot,R}}(t) = \langle g_i[\Omega(t)] \rangle$. Here g_i represents the angular dependence of $\text{Tr}[\beta(0)\beta(t)]$. The first term in Eq. (4) gives $C_i^{\text{vib}}(t)$ directly because, as noted above, $\bar{\alpha}_i$ is independent of the molecule's orientation.

For the A_1 modes, where $\bar{\alpha} \neq 0$, we can obtain, on the basis of the above considerations, $C_{A_1}^{\text{vib}}(t)$ and $C_{A_1}^{\text{rot,R}}(t)$ experimentally as follows. The transform of the result of subtracting 4/3 times the depolarized spectrum from the polarized spectrum yields $C_{A_1}^{\text{vib}}(t)$ directly. Since the transform of the depolarized spectrum yields the product $C_{A_1}^{\text{vib}}(t)C_{A_1}^{\text{rot,R}}(t)$, one may obtain $C_{A_1}^{\text{rot,R}}(t)$ by dividing out $C_{A_1}^{\text{vib}}(t)$. If $\bar{\alpha} = 0$, as is the case for the E modes, then according to Eq. (4) the polarized and depolarized spectra differ only by a constant factor and hence the rotational and vibrational correlation functions cannot in general be separated with the use of the Raman bands alone. In Appendix A we show, however, that with the aid of the infrared absorption bands this separation can be made (as long as there is no rotation-vibration coupling). The usual procedure followed is to compare these empirical correlation functions with functions obtained on the basis of some theoretical model in order to test the validity of the model. However, we would like to emphasize that certain features of the spectra are independent of the particular model used. First, if classical dynamics are assumed, then the lineshapes must be symmetrical.¹⁷ Hence any observed Boltzmann asymmetry implies that quantum mechanical corrections are important. Second, as shown in Appendix A, for molecules with C_{3v} symmetry, if there is no vibration-rotation coupling, then all Raman A_1 bands must have the same rotational correlation function, as must all the infrared A_1 bands [with, however, $C_{A_1}^{\text{rot,ir}}(t)$ not in general equal to $C_{A_1}^{\text{rot,R}}(t)$], as must the infrared E bands. Conversely, if differences do appear in the correlation functions for these bands of the same symmetry then rotation-vibration coupling is strongly suggested.

Finally we note that an examination of $\alpha_{A_{1,i}}$ in Eq. (1) shows that a rotation of the molecule about the symmetry axis does not change the polarizability tensor. Hence the A_1 modes do not provide information on the spinning motions of the molecule. Rotation about a perpendicular axis does however modulate the tensor and hence can be studied using the A_1 modes. On the other hand, the E mode tensors of Eq. (2) change for both kinds of rotations and so these contain information on both the spinning and tumbling motions. Unfortunately, as noted above, we cannot readily separate out the rotational correlation function from the vibra-

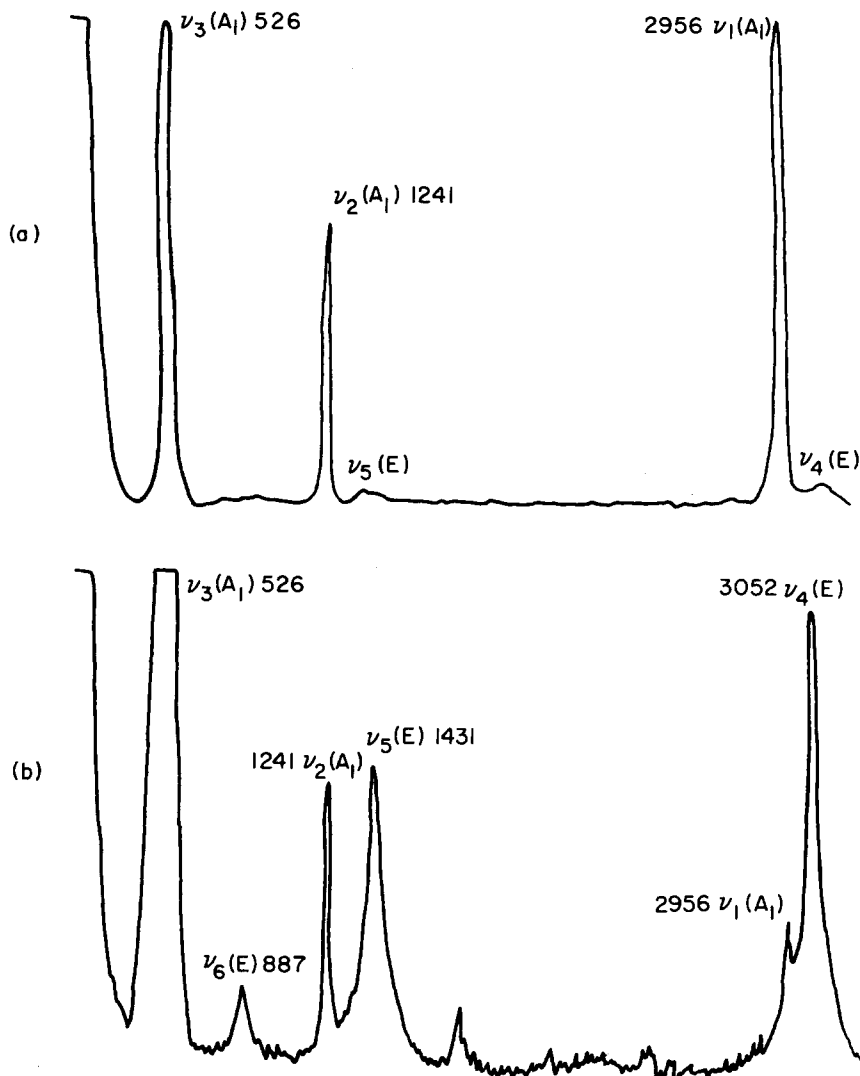


FIG. 1. Raman spectrum of pure liquid CH_3I (band positions in cm^{-1}). (a) Polarized, (b) depolarized.

tional correlation function for the E modes and hence it is relatively difficult to obtain information on the molecular spinning motion. We turn now to the experimental results for methyl and methyl- d_3 iodide.

III. ANALYSIS OF A_1 BANDS

Figure 1 shows the Raman spectrum of pure liquid CH_3I , between the laser line and about 3000 cm^{-1} , on the Stokes side of the line. The three A_1 bands dominate the polarized spectrum, while in the depolarized spectrum the E bands are clearly evident. Although the scales of the VV and HV spectra are different, they are related by the fact that the polarized perpendicular bands (being traceless) are $4/3$ times as intense as the corresponding depolarized bands.

In Fig. 2 we show the analysis of the ν_3 (C-I stretch) band of CH_3I to illustrate several important features. It is clear that there is a substantial asymmetry to the line shape. Doge¹³ and Bulanin¹⁵ have suggested that this asymmetry is due to the presence of hot bands.

According to Placzek¹⁸ the intensity of Raman scattering for a transition between the n and $(n+1)$ quantum level of a vibrational mode ν is proportional to $(n+1) \exp[-(n+\frac{1}{2})h\nu/kT]$. Hence, at room temperature, the ratio of the intensity of the $n=1$ hot band to the fundamental ($n=0$) is approximately 0.15. (The corresponding ratio for the $n=2$ hot band is about 0.02.)

To separate out the fundamental spectrum from the hot band, we assume that the lineshape due to the hot band is the same (but at this stage still unspecified) as that of the fundamental and so we numerically fit the observed spectrum $S^{\text{obs}}(\omega)$ by a calculated spectrum $S^{\text{calc}}(\omega)$ given by $S^{\text{calc}}(\omega) = S(\omega) + fS(\omega - \Delta\omega)$, where $S(\omega)$ is assumed to be symmetric about the band origin and $\Delta\omega$ and f are adjustable parameters. [As a first approximation to $S(\omega)$ we used the structure-free side of $S^{\text{obs}}(\omega)$ and then we followed an iterative procedure.]

The corrected polarized spectrum $S_{\text{pol}}(\omega)$ and the corresponding $S_{\text{pol}}^{\text{calc}}(\omega)$ are shown in Fig. 2(a), where

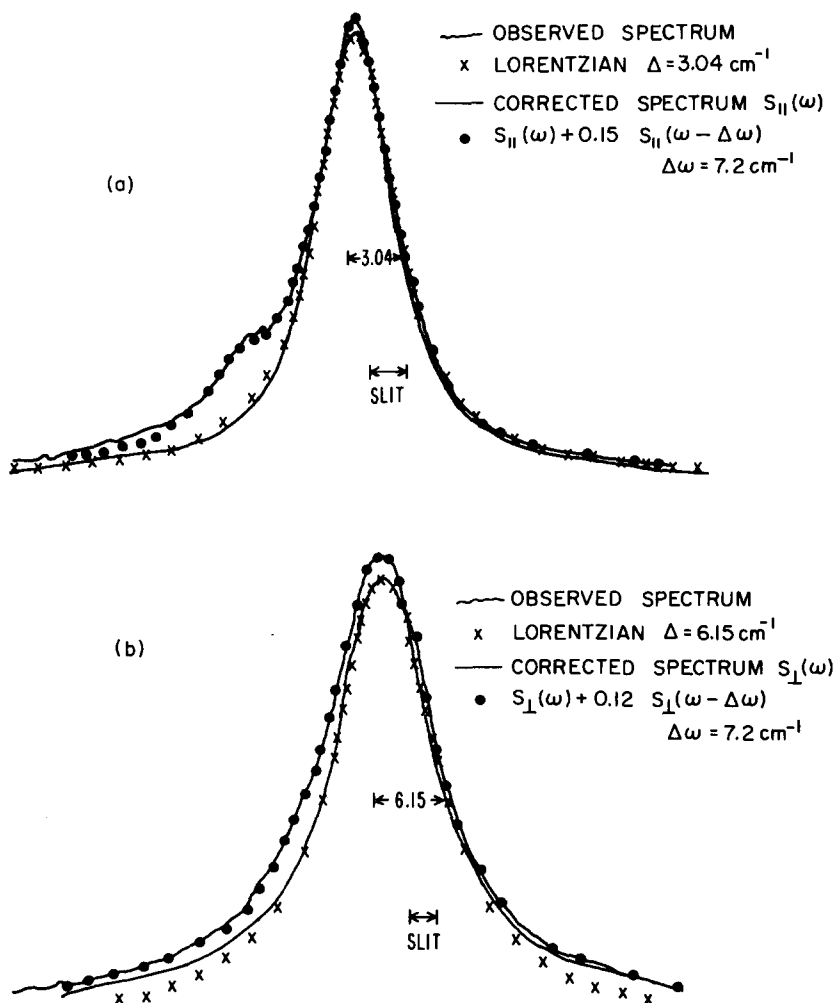


FIG. 2. Analysis of C-I stretch ($\nu_3 - \nu_1$) in CH₃I. (a) Polarized, (b) depolarized.

$\Delta\omega$ and f were found to be 7.2 cm^{-1} and 0.15 , respectively. The value of f and the quite reasonable fit to the observed spectrum are consistent with the hot band hypothesis. Indeed, the position and amount of the deviation of $S_{\text{pol}}^{\text{calc}}(\omega)$ from $S_{\text{pol}}^{\text{obs}}(\omega)$ in the wing appears to correspond well to an $n=2$ hot band (for which $\Delta\omega$ is expected to be about 14 cm^{-1}). The same method was used to extract $S_{\text{dep}}(\omega)$ and the results are shown in Fig. 2(b). (The best value of f in this case was found to be 0.12 . The reason for the different f value is unclear, but is not believed to be significant.)

In both cases a Lorentzian with half-width equal to that of $S(\omega)$ is plotted for comparison only, since, as will be seen below, there is no necessity for these line-shapes to be Lorentzian at this point.

A. Vibrational Effects

In order to obtain the pure vibrational or trace scattering, the anisotropic part must be removed according to Eq. (4). Note that this step is especially important in the case of ν_3 because of the large anisotropic component. The result of this subtraction is shown in Fig. 3. A Voigt function fit to this trace

scattering is shown. (The Voigt function is the convolution of a Gaussian and a Lorentzian.) Because our slit function was well described by a Gaussian whose width corresponded to the "Gaussian fraction"¹⁹ of the width of the Voigt function, we conclude that the trace line-shape is in fact Lorentzian.

This procedure was followed for the three parallel bands for pure CH₃I and CD₃I as well as for 1% CH₃I and 1% CD₃I in CS₂. All of the vibrational lines appeared to be reasonably well described by Lorentzians. We list the half-widths at half-maxima (HWHM) in Table I. The error in the half-widths of the vibrational lines of the pure liquids was principally the result of the nonlinearity in the spectrometer grating drive at the low speeds necessary to provide adequate resolution and of the uncertainty involved in making the hot band corrections. The experimental error for these widths was believed to be about $\pm 0.3 \text{ cm}^{-1}$ (or about $\pm 15\%$). In the case of the bands corresponding to the dilute solutions, statistical uncertainties due to the smaller signal to noise ratios added to the above uncertainties to give an estimated experimental error of approximately $\pm 0.4 \text{ cm}^{-1}$. The widths for the ν_2 and

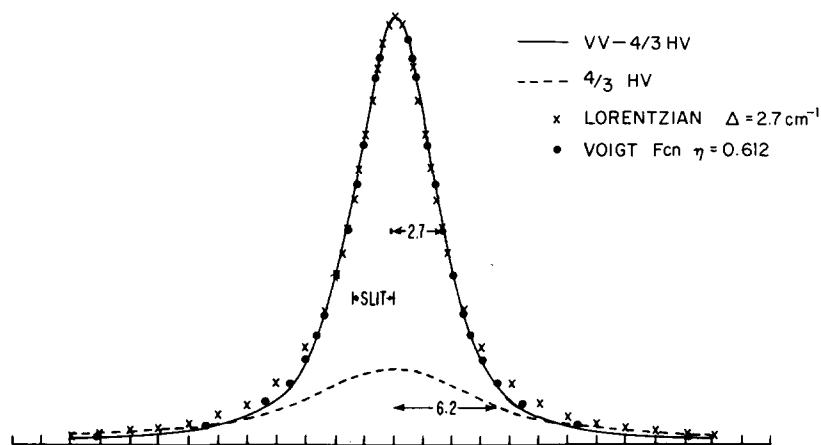


FIG. 3. Trace scattering of C-I stretch in CH_3I computed by subtracting corrected depolarized line from corrected polarized line with appropriate relative intensity.

ν_3 modes in pure CH_3I agree, within experimental uncertainties, with other available Raman data as shown in the table. The following generalizations can be made:

- (i) the widths in the solution are narrower than the corresponding widths in the pure liquids,
- (ii) the widths of CD_3I are narrower than the corresponding widths of CH_3I ,
- (iii) the line shapes are Lorentzian.

The first is consistent with the expectation that in a dilute solution with an inert solvent, the CH_3I (or CD_3I) vibrations should have longer lifetimes than they do in a pure liquid. This is so because in the solution, dipole-dipole interactions are absent and hydrogen bonding effects are eliminated as well as the likelihood of any "resonant" coupling of a vibration on a given CH_3I molecule to that on a neighboring CH_3I molecule because of their equal vibrational frequencies. Further evidence that there is less intermolecular interaction in solution than in the pure liquid is provided by Doge¹³ who lists the locations of the vibrational frequencies of the ν_3 mode of CH_3I for the gas state and for mixtures of (x) $\text{CH}_3\text{I}/(1-x)\text{CS}_2$ (x being the fraction by volume). He shows that the ν_3 frequency shifts toward that observed in the gas phase (where there are small interactions between molecules) with greater dilution (i.e., smaller x).

In regard to (ii) we note that Zubova *et al.*² have observed the same phenomenon in the pair of molecules CHCl_3 and CDCl_3 . As they point out, since one assumes

that apart from the small mass difference the molecules are identical, the sizable difference in the linewidths is difficult to explain.

As far as (iii) is concerned, we simply point out that Lorentzian line shapes have been found for the intrinsic vibrational line shape in many systems by a number of authors.

B. Rotational Effects

As was discussed earlier, in order to obtain the rotational correlation function (or line shape) we must remove the vibrational line from the depolarized line. According to the remarks following Eq. (5), this may be done by dividing $C_{A_1}^{HV,R}(t)$ by $C_{A_1}^{vib}(t)$. As an example, consider again the ν_3 mode. In Fig. 3, we have the vibrational line while in Fig. 2(b) we have the corrected depolarized line shape. Note that both these spectra contain the instrumental line shape or, in terms of their transforms (e.g., correlation functions), are the product of an "intrinsic" correlation function and the transform of the instrumental line shape. However, one may divide the transforms of the two spectra directly without worrying about the instrumental correction because, as a factor common to both spectra, it divides out. Thus, this method of obtaining $C_{A_1}^{rot,R}(t)$ has the advantage of taking exact account of the instrument without explicitly considering it. The results of this procedure are shown in Fig. 4.

We observe from Fig. 4 that after about 0.3 psec the rotational correlation function is well described by an exponential. [The small oscillation apparent in

TABLE I. Vibrational half-widths (HWHM) of A_1 bands (cm^{-1}).

	CH_3I			CD_3I	1% CH_3I in CS_2	1% CD_3I in CS_2
	Present	Ref. 11	Ref. 8			
ν_1	2.4	1.2	2.0	0.9
ν_2	2.3	...	2.6	1.9	1.5	0.8
ν_3	2.2	2.1	2.6	1.8	1.5	1.2

TABLE II. Rotational half-widths (HWHM) of A_1 bands (cm⁻¹).

	CH ₃ I			CD ₃ I	1% CH ₃ I in CS ₂	1% CD ₃ I in CS ₂
	Present	Ref. 11	Ref. 14			
ν_1	7.0	4.4
ν_2	4.8	...	3.8	3.2	...	7.5
ν_3	3.8	3.0	3.5	3.5	5.6	6.5

$C_{A_1}^{\text{rot,R}}(t)$ is mainly due to truncation errors in the numerical analysis.] The deviation from the exponential at short times is essentially equivalent to the deviation of the shape of the depolarized spectrum in Fig. 2(b) from a Lorentzian in the wings.

Because, as we have seen, both the vibrational and rotational line shapes are Lorentzian, we may in this situation obtain the rotational line width without having to go through the above procedure, basically merely by subtracting the vibrational width from the width of the depolarized spectrum. (With this method we must,

however, take into account the instrumental line shape, which is nearly Gaussian, by an analysis such as described in Ref. 19.) In Table II, we list the rotational line widths for the A_1 modes of CH₃I, CD₃I, and their dilute solutions in CS₂.

The error in the ν_2 and ν_3 rotational widths of the pure liquids was the result of the uncertainty in the vibrational widths as discussed previously, the approximations in the numerical analysis involved in separating the rotational and vibrational widths and the hot band corrections. This error was estimated to be about ± 0.5 cm⁻¹. In the case of the dilute solutions, the rotational widths are listed only for those bands for which the signal to noise ratio permitted a reasonably accurate (to within about $\pm 25\%$) measurement to be made.

Because of the importance to our conclusions of the ν_1 widths, we took pains to obtain values as reliable as possible. As discussed earlier, the intensity of the hot bands goes down exponentially with the frequency of the band. Hence, the ν_1 bands should have relatively small hot band corrections. The principal difficulty in measuring the widths of these bands arises from the fact that they each lie in the wings of their respective ν_4 band. The procedure followed was to take careful measurements of the Stokes and anti-Stokes sides of the ν_4 bands and to subtract the Stokes sides multiplied by the Boltzmann factor from the anti-Stokes side to give the ν_1 band (see Fig. 5).

One possible source of error was leakage of the very strong polarized component of the ν_1 bands through the polarizer used in the measurement of the depolarized bands. While this leakage was experimentally kept to a minimum (the measured relative peak intensity of VV to HV was about 170 to 1), any polarized component appearing in the depolarized band would make the observed half-width smaller than the true width and hence would not affect the conclusions drawn below. The estimated uncertainty of the two ν_1 bands was about $\pm 15\%$ (the smaller absolute error in the CD₃I band being the result of the larger ν_1 to ν_4 spacing than in the CH₃I band).

As discussed earlier, we may draw certain conclusions without reference to any particular model. First, we note that the A_1 bands (after correcting for hot band asymmetry) are symmetrical. Thus we expect that a classical model should provide an adequate description of the tumbling motion of the molecules. (Recall that

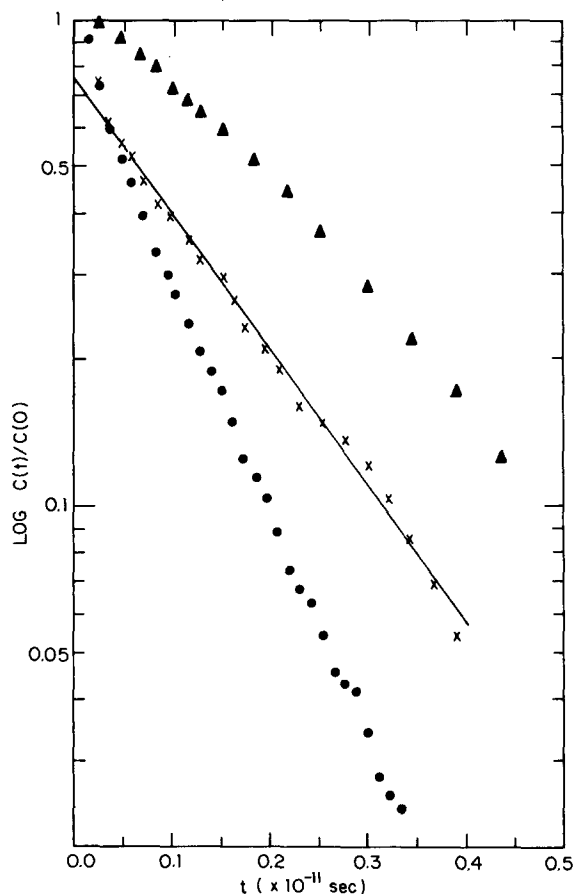


FIG. 4. Numerical calculation of rotational correlation function for pure liquid CH₃I. ● Transform of the depolarized spectrum. ▲ Transform of the trace spectrum. × Rotational transform (ratio of the above transforms). — Fit to rotational transform.

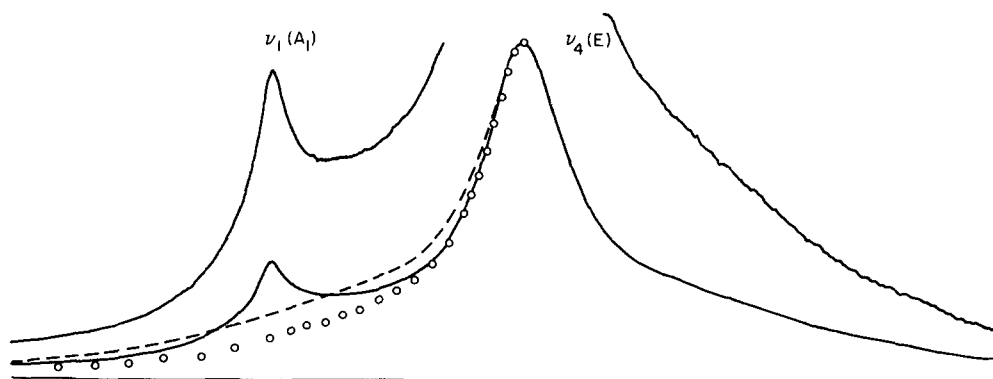


FIG. 5. Depolarized Raman spectrum of $\nu_4(E)$ and $\nu_1(A_1)$ bands of CH_3I . -- Stokes (right side) of ν_4 band. \circ Stokes side multiplied by the Boltzmann factor.

the A_1 bands are insensitive to the spinning reorientations.) Second, we observe that the rotational line shapes are all nearly Lorentzian. Recall that the assumption of no vibration-rotation coupling required that all the A_1 rotational line shapes be identical (for the same liquid). Hence not only must all the lines be Lorentzian but also the line widths in each vertical column in Table II should be equal. If we ignore the widths for the ν_1 modes then, within experimental uncertainty, the ν_2 and ν_3 widths appear to agree reasonably well for each system where sufficient data are available. The two values of ν_1 given, on the other hand, do seem to be consistently larger than their respective ν_2 and ν_3 widths. A glance at Fig. 1 shows that the ν_1 mode is the most difficult to measure because of its very small depolarized component and because of its location on the wing of the band and so one is tempted to consider the discrepancy to be spurious. Bulanin and Tonkov¹⁵ have, however, measured the ν_1 and ν_2 infrared bands of CH_3I in CCl_4 and have found that the former band is about 15% broader than the latter. (As discussed in Appendix A, the A_1 infrared bands are analogous to the depolarized A_1 Raman bands.)

We suggest that in fact the higher values of the ν_1 widths are significant and imply that rotational-

vibrational interaction is present. This conclusion is somewhat surprising for the following reason. It has long been known that the Coriolis force can introduce strong rotation-vibration coupling effects into the E -type modes because these vibrations are doubly degenerate. On the other hand, one expects that for the A_1 modes, being nondegenerate, the Coriolis perturbation should appear as a small higher order correction to the band shape. This is in fact the case, except in the particular situation where a weak A_1 band is near a strong E band. In this instance, a very strong perturbation in the band shape can occur via a Coriolis coupling of the A_1 mode to the E mode.²⁰⁻²² (diLauro and Mills²⁰ show a particularly dramatic example of the opposite situation in CH_3F , where a weak E band is greatly modified by a neighboring strong A_1 band.)

As Fig. 1 clearly indicates, the ν_1 bands of CH_3I and CD_3I , with their small depolarized components and proximity to the relatively intense ν_4 band, fulfill the conditions for a significant A_1 - E type Coriolis coupling. The ν_2 and ν_3 bands, on the other hand, do not satisfy the conditions and so we do not expect this type of rotational-vibrational coupling to be present.

Previous studies^{15,23,24} of CH_3I and similar molecules have indicated that the simple rotational diffusion

TABLE III. Values of D_1 for CH_3I ($\times 10^{11} \text{ sec}^{-1}$).

	Present	Ref. 11	Ref. 14	Ref. 10	Ref. 12	Theory ²⁵
ν_0	...	1.0 ^b	1.6 ^c	...	1.2-3.5 ^e	1.2
ν_1	2.2	1.2
ν_2	1.5	1.2 ^a	1.2
ν_3	1.2	1.1 ^a	1.0 ^a	1.4 ^d	...	1.2

^a Raman.

^b Rayleigh.

^c Far ir.

^d Near ir.

^e Dipolar relaxation.

model is the appropriate one for the description of the axial tumbling motion. As noted in Appendix I, the model predicts that the Raman rotational line is Lorentzian with an HWHM given by $6D_{\perp}$, where D_{\perp} is the rotation diffusion constant for the tumbling re-orientation. On the basis of the theory one can also calculate values of D_{\perp} from infrared, nuclear relaxation, and microwave data, etc. For example, in Appendix A, the rotational line width of an infrared A_1 absorption band is given by $2D_{\perp}$. In Table III, we list a number of values of D_{\perp} for pure methyl iodide obtained from various experiments, where $D(\text{sec}^{-1}) = 2\pi cD(\text{cm}^{-1})$. In the table, ν_0 refers to pure rotation as opposed to the vibration-rotation bands. One measures ν_0 in experiments such as Rayleigh scattering, microwave and far infrared absorption, and nuclear magnetic relaxation. The theoretical value given in the last column is based on a modified Debye-Stokes hydrodynamical model and was computed from the formula given in Ref. 25. The range of values given for the dipolar relaxation measurement is necessitated both by the fact that it is difficult to properly separate out the various contributions to the relaxation in this kind of experiment²⁶ and also because the formula relating the rotational diffusion constant to the relaxation time involves a knowledge of the spinning motion as well as the tumbling motion.¹²

The general consistency of these various values of D_{\perp} appears to substantiate both the use of the rotational diffusion model and the fact that for the ν_2 and ν_3 modes, rotation-vibration coupling is negligible. Further, the deviation of D_{\perp} for the ν_1 mode again suggests that rotation-vibration coupling is significant in this case.

IV. ANALYSIS OF E BANDS

Figure 5 shows the ν_4 band of CH₃I (along with the depolarized component of ν_1). Plotted also are points representing a symmetric line, each side of which equals the Stokes (right hand) side of the ν_4 band multiplied by the Boltzmann factor $\exp[-\hbar(\omega - \omega_0)/kT]$ where ω_0 is the band center. It is seen clearly that the ν_4 band is asymmetric and that the asymmetry (ignoring the ν_1 band) can be accounted for by the Boltzmann factor.

This asymmetry alone immediately implies that quantum effects cannot be ignored in the study of the E bands. Because, as we have seen from the discussion of the A_1 bands, the tumbling motion can be represented classically and because the E bands reflect both tumbling and spinning, we must conclude that it is the spinning motion that exhibits these quantum effects. It follows, of course, that the rotational diffusion model cannot give a complete description of this latter motion. Physically, this is quite reasonable. The moment of inertia about the symmetry axis is about 20 times smaller than that about the perpendicular axis²⁷ and hence the free rotational velocity (which is inversely proportional to $I^{1/2}$) for spinning is nearly 5 times that for tumbling. For a given collisional frequency, then,

it is clear that a molecule will rotate about the symmetry axis through a much larger angle before interruption than it will about a perpendicular axis and hence the former motion will look more like that of a free rotor than will the latter. We have observed that there is little difference in the E bands of the pure liquid when compared to those in the solutions. This is consistent with a relatively unhindered rotation independent of the environment. Other authors (mainly from infrared measurements) have also reached the conclusion that "inertial" (i.e., angular momentum) effects are significant. What we suggest here is that one does not have to go through much analysis to reach this conclusion. A simple examination for the presence or absence of Boltzmann symmetry is sufficient. Note, however, that the asymmetry is more immediately obvious in the Raman band for these modes than in the infrared band because of the greater width of the former.

In addition to the fact that E bands depend on the more complicated spinning motion, they also suffer from a susceptibility to rotation-vibration coupling because they are degenerate. Edgell and Moynihan²⁸ have computed the dependence of an infrared E band on the Coriolis coupling constant ζ for a freely rotating oblate symmetric top with $I_B/I_A = 0.7$ (e.g., cyclopropane C₃H₆). Their results are shown in Fig. 6. No similar Raman calculation has been done but analogous results are expected. The point here is that the Coriolis force can substantially alter the perpendicular bands and if present can clearly not be ignored. As we discuss in Appendix A, one consequence of the absence of rotation-vibration coupling is that the rotational correlation functions of all infrared E bands are identical to each other. Hence, differences in the observed bands imply either that the vibrational lines have different widths (or shapes) or that coupling is present. Bulanin and Tonkov¹⁵ have measured the infrared E bands of CH₃I and CD₃I in solutions with CS₂ and CCl₄ and have found that the half-widths differ considerably. Further, the differences are on the order of 10–20 cm⁻¹, which are too large to be reasonably attributed to vibrational effects. Thus we see that by comparing the bands of the same symmetry, we can quickly obtain information on whether or not rotation-vibration coupling need be considered. Because the spinning motion is relatively unhindered, it follows that we should be able to get an estimate of the magnitude of the Coriolis effect by looking at the size of ζ obtained for gaseous CH₃I. Jones and Thompson²⁹ find +0.059, -0.240, and +0.206 for the coupling constants of the ν_4 , ν_5 , and ν_6 bands, respectively. (In Ref. 30 corresponding values for other methyl and methyl-*d*₃ halides are given.) The ν_4 band then is likely to be the most amenable to quantitative study of the rotational dynamics since its small value of ζ indicates that at least in a first approximation, we can ignore the coupling.

It is interesting to note that Bulanin and Tonkov¹⁵ conclude that the infrared ν_6 band is best for studying

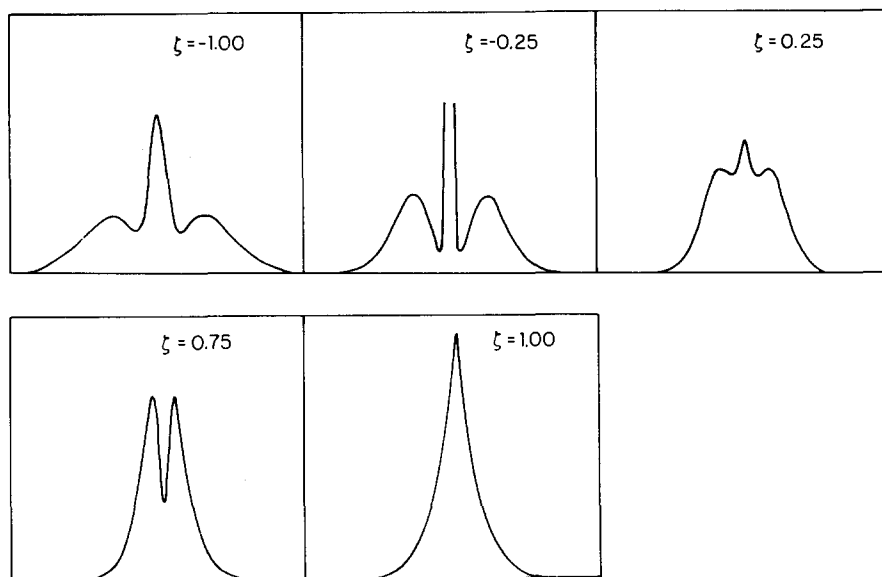


FIG. 6. Infrared bandshape as a function of the Coriolis coupling constant ζ for an oblate symmetric top molecule. [W. F. Edgell and R. E. Moynihan, *J. Chem. Phys.* **45**, 1205 (1966)].

the coupling effects themselves (or more generally the factors that lift the degeneracy of the E bands). On the basis of the above values of ζ alone, it is clear that both ν_5 and ν_6 should exhibit Coriolis perturbations. Bulanin and Tonkov singled out ν_6 because they felt that, being the most isolated band, it would be the least susceptible to further perturbations from its neighboring bands. As evidence of this they point out that the ν_6 band has the smallest half-width of the E bands. We would like to point out that while it may indeed be true that ν_6 is the least effected by other bands, the fact that it is the narrowest is not conclusive. Herzberg⁹ gives the expression $2[A(1-\zeta)-B]$ for the separation of the "Q branches" for this type of band, where A and B are positive molecular constants. Very crudely we may use this separation as a measure of the band-width. For CH_3I , $A \sim 5 \text{ cm}^{-1}$ and $B \sim 0.3 \text{ cm}^{-1}$. Thus it follows that when ζ is positive, the separation is smaller than when ζ is negative. Hence we suggest that the smaller width of ν_6 may be due not to less interaction with neighboring bands but rather to the smaller Coriolis splitting of the two degenerate components of the ν_6 itself.

In order to give a qualitative feel for the shape of the E bands, we show in Fig. 7 the ν_4 (and ν_1) band of CD_3I and superimposed on it a Lorentzian whose half-width was chosen to be the same as the half-width of the band itself. From Eqs. (A4) and (A8) of Appendix A we know that if the rotational diffusion model were applicable, the rotational correlation function of a Raman E band would be the sum of two exponentials of different exponents, and hence the band would be the sum of two Lorentzians convoluted, of course, with the vibrational component and the instrumental line shape. (We note parenthetically that the half-width of the observed Raman E band is not a very meaningful quantity even in the simple diffusion case.) Taking the

vibrational line shape to be Lorentzian, one can empirically attempt to fit this theoretical band to the observed band. One finds that while such a theoretical line shape can be made to generally approximate the actual band, it must be concluded that a good fit cannot be obtained. This conclusion is consistent with our previous observations that the rotational diffusion model is inadequate to describe the E bands.

Finally, we mention the fact that the depolarization ratio ρ of an E band may contain some useful information on interactions. Ideally, $\rho = \frac{3}{4}$. Deviation from this value indicates that some disturbance of the symmetry has occurred, for example, by coupling to an A_1 mode, or by a physical distortion of the molecule in the liquid itself. Early measurements³¹ of ρ for the three E bands of CH_3I indicated that ρ was indeed close to its theoretical value. We have found that $\rho = 0.72 \pm 0.01$. Hence there is evidence for some small symmetry perturbations. We note that Priestley³² has measured the depolarization ratio of the 606 cm^{-1} line in benzene and has found that it changes from 0.75 in the vapor to about 0.70 in the liquid.

V. CONCLUSIONS

We have tried to show that much information about the molecular dynamics in liquid methyl iodide can be obtained by a study of the Raman bands. After removing extraneous effects, such as hot bands, we first examined the fundamentals in order to determine whether or not they were symmetric. We found that the A_1 bands were in fact symmetric implying that classical mechanics was appropriate for describing the tumbling reorientations. The E bands, on the other hand, exhibited a Boltzmann asymmetry indicating the importance of quantum effects in the spinning motion.

We proceeded to separate out the vibrational and

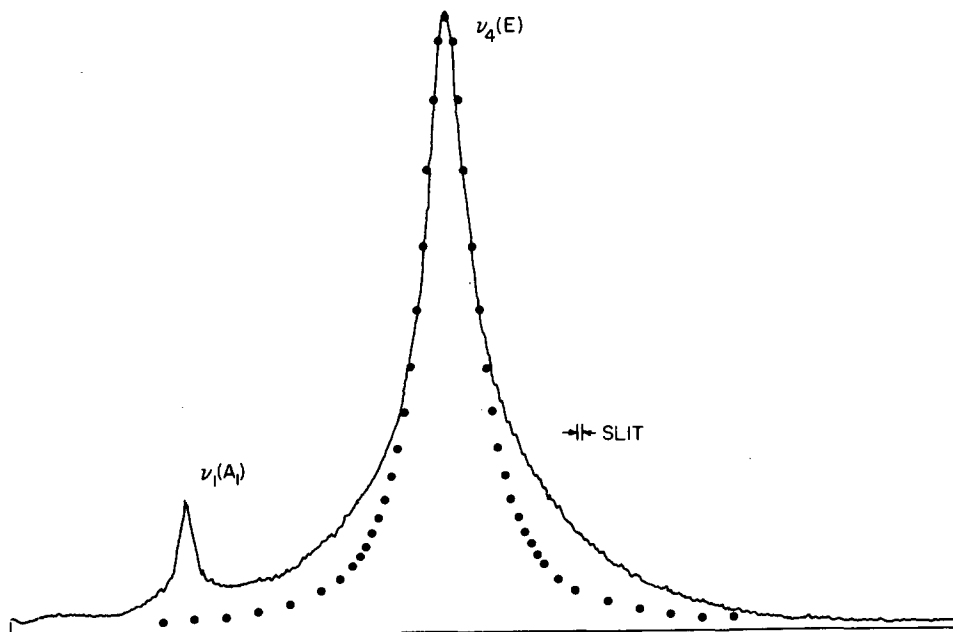


Fig. 7. Depolarized Raman spectrum of $\nu_4(E)$ and $\nu_1(A_1)$ bands of CD_3I . \cdots Lorentzian with width equal to that of ν_4 band.

rotational parts of the A_1 bands. We were able to make several qualitative statements about vibrational phenomena from the linewidths of the vibration lines in the pure liquids and solutions. A comparison of the linewidths of the A_1 rotational spectra indicated that, generally, rotation-vibration coupling effects were absent except for the ν_1 band. This latter mode, we concluded, exhibited a Coriolis coupling with its neighboring mode. By comparing values of the rotational diffusion constant D_{\perp} obtained from the present work to those obtained from other experimental techniques, we have confirmed that the simple rotational diffusion model appears to be consistent in explaining the molecular tumbling.

Various considerations led to conclude that rotation-vibration coupling was a significant factor in the E bands. By examining the Coriolis constant for a free rotor we suggest that the ν_4 band was the least susceptible to the coupling effects and hence that it should be the best for detailed study. An infrared absorption measurement of this band in the pure liquid would be of value to compare with the Raman data. In general, then, one of the major implications of this work is that because of rotation-vibration coupling, not all bands of a given substance are equally amenable to simple analysis and that only by a study of as many of the bands of the material in question as possible can a reasonable selection be made.

APPENDIX A

In this Appendix, we briefly review the general forms of the Raman and infrared rotational correlation func-

tions for molecules with C_{3v} symmetry. We show how different bands depend on different terms in an expansion of the probability distribution that describes the rotational dynamics and discuss the extent to which these terms may be obtained from experimental data. Finally we use the rotation diffusion model as an example to illustrate the discussion.

From a theoretical standpoint, to obtain $C_i^{\text{rot,R}}(t)$ we must, according to the discussion following Eq. (5) evaluate an equilibrium ensemble average. To do this we require the distribution function $P(\Omega, t)$, which gives the probability that the orientation of a molecule after a time t is related to its initial orientation by a rotation through the Eulerian angles Ω . It is this function that in fact provides the link between the experimental observations and the theoretical model. For symmetric top molecules, using the notation of Bartoli and Litovitz,¹⁴ $P(\Omega, t)$ can be expanded in terms of the diagonal elements of the rotation matrices $D_{mm'}^j(\Omega)$ as follows:

$$P(\Omega, t) = \sum_{jk} D_{kk}^j(\Omega) f_k^j(t), \quad (A1)$$

where $f_k^j(t)$ are functions of time determined by the statistics of the problem. The expression for β , given in Eq. (5), and hence the functions $g_i(\Omega)$ may also be rewritten in terms of the $D_{mm'}^j$. To obtain $C_i^{\text{rot,R}}(t)$ we simply multiply $P(\Omega, t)$ times $g_i(\Omega)$ and integrate over angles giving¹⁴

$$C_i^{\text{rot,R}}(t) \propto \sum_{k=-2}^2 |\beta_i^k(\text{MF})| f_k^{(2)}(t), \quad (A2)$$

where $\beta_i^k(\text{MF})$ are related to the Cartesian components

$\beta_i^{jk}(\text{MF})$ by³³

$$\begin{aligned}\beta_i^0(\text{MF}) &= (6^{1/2}/2)\beta_i^{zz}(\text{MF}), \\ \beta_i^{\pm 1}(\text{MF}) &= \mp \beta_i^{xz}(\text{MF}) - i\beta_i^{yz}(\text{MF}), \\ \beta_i^{\pm 2}(\text{MF}) &= \frac{1}{2}[\beta_i^{xx}(\text{MF}) - \beta_i^{yy}(\text{MF})] \pm i\beta_i^{xy}(\text{MF}).\end{aligned}\quad (\text{A3})$$

Using the form of the tensors given in Eqs. (1) and (2) and the definition of β_i , it follows from Eqs. (A2) and (A3) that

$$\begin{aligned}C_{A_1, i}^{\text{rot}, \text{R}}(t) &\propto |a_i - b_i|^2 f_0^{(2)}(t), \\ C_{E, i}^{\text{rot}, \text{R}}(t) &\propto |d_j|^2 f_1^{(2)}(t) + |c_j|^2 f_2^{(2)}(t).\end{aligned}\quad (\text{A4})$$

One very important conclusion that follows from Eq. (A4) is that under the assumptions discussed in Sec. II, the time dependence of the rotational correlation functions of all A_1 bands must be the same. However, this need not be the case for the E bands because the relative size of c and d may differ for each band.

A completely analogous derivation holds for infrared absorption, where the dipole moment μ_i replaces the polarizability tensor. Because μ_i is a vector rather than a tensor, the D matrices with $j=1$ appear, and one may show easily that the infrared rotational correlation functions are given by

$$\begin{aligned}C_{A_1, i}^{\text{rot}, \text{ir}}(t) &\propto |M_i^0|^2 f_0^{(1)}(t) \\ C_{E, j}^{\text{rot}, \text{ir}}(t) &\propto |M_j^1|^2 f_1^{(1)}(t),\end{aligned}\quad (\text{A5})$$

where $M_i^0 = M_i^z$, $M_i^{\pm 1} = 1/\sqrt{2}(M_i^x \pm iM_i^y)$, and $\mathbf{M}_i = \partial\mu/\partial\mathbf{q}_i$.

Note that the vibrational correlation function remains the same as for the Raman spectra. The observed absorption spectrum is given basically by the transform of

$$C_i^{\text{ir}}(t) = C_i^{\text{vib}}(t)C_i^{\text{rot}, \text{ir}}(t).\quad (\text{A6})$$

As with the Raman bands, the infrared A_1 bands depend only upon the tumbling motion of the molecules, while the E bands depend upon both the tumbling and spinning motions.

According to the discussion in Sec. II, from a Raman A_1 band we can in principle (subject to the assumptions used) obtain both $C_{A_1}^{\text{vib}}(t)$ and $C_{A_1}^{\text{rot}, \text{R}}(t)$, i.e. $f_0^{(2)}(t)$. Using the vibrational correlation function thus obtained, we may get from the corresponding infrared band $C_{A_1}^{\text{rot}, \text{ir}}(t)$, i.e., $f_0^{(1)}(t)$ [see Eq. (A6)]. Hence we may learn a substantial amount about that part of the probability distribution that describes the tumbling reorientations of the molecules (in addition to the information contained in the vibrational correlation function).

While we have seen that the Raman E bands alone are insufficient to separate the rotation from the vibration, this can be done with the use of the corresponding infrared E band. From Eqs. (A5) and (A4), and

$$C_E^{\text{HV}, \text{R}}(t)/C_E^{\text{ir}}(t) = [|d|^2 f_1^{(2)}(t) + |c|^2 f_2^{(2)}(t)]/f_1^{(1)}(t).\quad (\text{A7})$$

Although this technique does not give the individual f 's, it does nevertheless provide some information on these functions (and hence on the spinning motion) without having to assume anything about the vibration (other than the fact that the vibration is uncoupled from the rotation). If the ratio of $|c|^2$ to $|d|^2$ is known, then one can get the ratios $f_1^{(2)}(t)/f_1^{(1)}(t)$ and $f_2^{(2)}(t)/f_1^{(1)}(t)$. For example, if one can resolve the rotational structure in the rotation-vibration band of the molecular substance in question as a low density gas, then $|c|^2/|d|^2$ is precisely the relative intensity of the $\Delta\kappa = \pm 2$ subband to the $\Delta\kappa = \pm 1$ subband.⁹

Of course, if one specializes to a particular model for which the f 's are not all independent, and if the relationships between them are known, then $f_1^{(1)}$, $f_1^{(2)}$, and $f_2^{(2)}$ may be determined with the help of the above procedure.

As an example of this latter situation, we cite the rotational diffusion model. In this model, the rotational diffusion constants D_{\parallel} and D_{\perp} describe the spinning and tumbling motions, respectively. The f 's are given by¹⁴

$$f_k^{(j)}(t) = \exp\{-t/[D_{\perp}j(j+1) + (D_{\parallel} - D_{\perp})k^2]\}.\quad (\text{A8})$$

A Raman A_1 band that gives us $f_0^{(2)}(t)$ will yield D_{\perp} . Substituting Eq. (A8) into Eq. (A7), we get

$$\begin{aligned}C_E^{\text{HV}, \text{R}}(t)/C_E^{\text{ir}}(t) &= \exp(-D_{\perp}t) \\ &\times [|d|^2 \exp(-3D_{\perp}t) + |c|^2 \exp(-3D_{\parallel}t)]\end{aligned}\quad (\text{A9})$$

and hence D_{\parallel} may be found. Thus all the f 's are completely determined.

APPENDIX B

In this Appendix, we make several general observations about a technique postulated by Berne *et al.*³⁴ for computing the Raman rotational correlation for a symmetric band function when only the corresponding infrared rotational correlation function is known. Recently this method has been applied to some experimental data and mixed success has been reported.^{11,35}

Basically the theory hypothesizes that the actual probability distribution $P(l, t)$ has maximum "information entropy" given by $-\int P(\Omega, t) \ln P(\Omega, t) d\Omega$.³⁶ A Lagrange multiplier technique is used to maximize this entropy using the constraint that P is nonnegative, integrates to unity, and yields the correct infrared correlation function. (Note that according to Appendix A the last constraint fixes only the $f_0^{(1)}(t)$ term in the expansion of P .) The result found is that the Raman correlation function is given by

$$C^{\text{rot}, \text{R}}(t) = 1 - [3/\beta(t)]L[\beta(t)],\quad (\text{B1a})$$

where

$$L(\beta) = -1/\beta + \coth\beta\quad (\text{B1b})$$

and

$$C^{\text{rot}, \text{ir}}(t) \equiv L[\beta(t)].\quad (\text{B1c})$$

From Eqs. (B1a) and (B1c) it follows immediately

that if $C^{\text{rot,R}}(t)$ as well as $C^{\text{rot,ir}}(t)$ is known, then $\beta(t)$ is completely defined:

$$\beta(t) = 3C^{\text{rot,ir}}(t)/[1 - C^{\text{rot,R}}(t)]. \quad (\text{B2})$$

Because the correlation functions are defined so that $C(0) = 1$, it follows from Eq. (B2) that at short times, β is very large. Using the definition of $L(\beta)$, one can show that for large β

$$C^{\text{rot,ir}}(t) \equiv L(\beta) \simeq 1 - 1/\beta + O(1/\beta^2) \quad (\text{B3a})$$

or

$$\beta(t) = [1 - C^{\text{rot,ir}}(t)]^{-1}. \quad (\text{B3b})$$

Then, from Eq. (B1a)

$$C^{\text{rot,R}}(t) \simeq 1 - 3/\beta + O(1/\beta^2). \quad (\text{B4})$$

It easily follows that as $t \rightarrow 0$

$$C^{\text{rot,R}}(t) \simeq 3C^{\text{rot,ir}}(t) - 2. \quad (\text{B5})$$

Thus the Berne theory defines the short time relationship between the correlation functions. Note that Eq. (B5) is consistent with what Gordon¹⁷ shows to be the general short time expansion of these correlation functions.

As $t \rightarrow \infty$, the correlation functions go to zero and so also, from Eq. (B2), must $\beta(t)$. At long times then, we may write from Eqs. (B1c) and (B1b)

$$C^{\text{rot,ir}}(t) \simeq \beta(t)/3 - [\beta(t)]^3/45 + \dots \quad (\text{B6})$$

Hence, to lowest order

$$\beta(t) \sim 3C^{\text{rot,ir}}(t). \quad (\text{B7})$$

Substituting Eq. (B6) into Eq. (B1a) we have

$$C^{\text{rot,R}}(t) \sim (3/5)[C^{\text{rot,ir}}(t)]^2. \quad (\text{B8})$$

Because of this asymptotic relationship of the correlation functions, it is clear that the theory will only be applicable to a restricted number of cases.

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