Reorientational Correlation Functions Obtained from Raman Line Shapes

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Abstract: The analysis of Raman vibrational line shapes in terms of time-correlation functions is discussed. Earlier work in this area is extended to include nonorientation-dependent contributions to the Raman line shape. For polarized Raman lines, reorientational time-correlation functions may be deconvoluted from other broadening agencies with the use of Fourier-transform techniques. Experimental results are reported and discussed for d-chloroform and methyl iodide. Extensions of this analysis and its use with nmr relaxation times to determine nuclear-quadrupole coupling constants are examined.

In recent years, there have been several attempts to obtain information about molecular motion in liquids from infrared or Raman vibrational line shapes.[2-15] Much of this interest was stimulated by the work of Gordon, who cast the familiar "Golden Rule" expressions of spectroscopy in the Heisenberg representation.[2] Since, in this representation, time dependence is expressed in terms of operator motion, we are led quite naturally to the inclusion of molecular motion in the description of the operator motion and hence the description of the spectral band shape. As the result of this work, Gordon found an equivalent expression for the "Golden Rule" in terms of a Fourier transform of a time correlation function for the spectral operators involved. As a result, the frequency dependent infrared absorption spectrum, $I_{ir}(\omega - \omega_0)$, may be expressed as the Fourier transform of an equilibrium time-correlation function for the transition dipole moment M

$$I_{ir}(\omega - \omega_0) \propto \int_{-\infty}^{\infty} \langle M(0)M(\tau)\rangle e^{i(\omega - \omega_0)\tau}\, d\tau \qquad (1)$$

where the brackets represent an equilibrium statistical average of the enclosed operators and τ is the time interval for which the correlation is expressed. In the case of the Raman spectrum, $I_R(\omega - \omega_0)$, we may write

$$I_R(\omega - \omega_0) \propto \int_{-\infty}^{\infty} \langle \beta(0)\beta(\tau)\rangle e^{i(\omega - \omega_0)\tau}\, d\tau \qquad (2)$$

where β is the Raman polarizability derivative tensor

$$\beta = \left(\frac{\partial\alpha}{\partial Q}\right)_0 Q(t) \qquad (3)$$

where α is the molecular polarizability and Q is the vibrational normal mode.

Time-correlation functions arise quite often in the description of random time processes and are used to describe the persistence of correlation in a sequence of time-ordered events.[16] As an example of a random time process, we can examine the Brownian motion of a particle. This is a random process as the particles motion is influenced by many collisions with the molecules of its surrounding medium. Since we are unable to describe all of these processes in causal terms, we must resort to a statistical description of the motion. In this way, the motion of the Brownian particle must be considered as a random process. It may also be considered a stationary random process, as it is not tied to a specific origin in time.

If we choose an arbitrary origin and consider the displacement of the particle from the point, we would expect the displacement to vary in a random fashion. However, if we examine the displacement at one instant in time, pause a moment, and examine the displacement again, we would expect the position of the particle to be very close to the original position. Thus, the particle's position or displacement will be very highly correlated for short-time intervals between observation. However, as our pause becomes longer, it becomes increasingly probable that we might find the particle at any point in space. After a long time interval, the particle's position is no longer correlated with its original position, and the system will have become randomized. Thus, the correlation function, $G(\tau)$

$$G(\tau) = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} x(\tau) \times (t + \tau)\, dt \qquad (4)$$

where x is the displacement of the particle from an arbitrary origin, and t is time, describes the approach of the system to randomization.

The persistence of correlation in the position of the particle betrays the existence of order and distinguishes the Brownian motion from a completely disordered process. Our information about the Brownian motion

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process is tied to the existence of this correlation, and as the correlation decays, our information about the system will also decay.

Gordon's equations [eq 2 and 3] are an example of the Weiner–Khinchin relations[17] which state that the power spectrum of a random process $s(\omega)$ (which for the purposes would be the infrared or Raman spectrum in the frequency domain) and the correlation function $G(\tau)$ form a Fourier transform pair.

$$s(\omega) = \int_{-\infty}^{\infty} G(\tau)e^{i\omega\tau}\, d\tau \tag{5}$$

These relations bear a strong analogy to the uncertainty relations. For, if the correlation function decays very slowly, our information about the system will persist for a long time, and the frequency spectrum will be very narrow. However, if our information about the system decays very quickly, the frequency spectrum will be very broad.

Since the operators involved are vectors or tensors, their time dependence will involve both changes in the direction and the magnitude of the operator. As the operator is fixed in the molecular axis system, changes in the projection of operator direction viewed in the laboratory axis system will result from the orientational motion of the molecule. Assuming for the purpose of discussion that the magnitude of the operator remains constant over times for which the orientation is randomized, we may rewrite expressions 2 and 3 as

$$I_{\mathrm{ir}}(\omega - \omega_0) \propto |M(0)|^2 \int_{-\infty}^{\infty} \langle \mathbf{u}(0)\mathbf{u}(\tau)\rangle e^{i(\omega-\omega_0)\tau}\, d\tau$$

$$I_{\mathrm{R}}(\omega - \omega_0) \propto |\beta(0)|^2 \int_{-\infty}^{\infty} \langle u(0)u(\tau)\rangle e^{i(\omega-\omega_0)\tau}\, d\tau \tag{6}$$

where $\mathbf{u}(\tau)$ is a unit vector along $M(\tau)$ and $u(\tau)$ is a unit dyadic associated with $\beta(\tau)$. Taking the inverse transforms of eq 6, we obtain eq 7 for the correlation

$$G(\tau) = \langle \mathbf{u}(0)\mathbf{u}(\tau)\rangle \propto \int_{-\infty}^{\infty} I_{\mathrm{ir}}(\omega -$$

$$\omega_0)e^{-i(\omega-\omega_0)\tau}\, d(\omega - \omega_0)$$

$$\tag{7}$$

$$G(\tau) = \langle u(0)u(\tau)\rangle \propto \int_{-\infty}^{\infty} I_{\mathrm{R}}(\omega -$$

$$\omega_0)e^{-i(\omega-\omega_0)\tau}\, d(\omega - \omega_0)$$

functions which can be conveniently normalized with the band intensity. Thus, the normalized Fourier transform of the spectral band shapes will be the time-correlation function reflecting the orientational motion of the molecules.[2] The rate and form of the decay of the reorientational-correlation functions will depend upon the details of the molecule's reorientational motion and thus it provides a probe of molecular dynamics in liquids.

In order to obtain reorientational correlation functions from infrared and Raman line shapes by Fourier transformation, the magnitude of the operator must remain constant on the time scale of the decay in correlation of the reorientational correlation function. This approximation may be appropriate for a dilute solution of the absorbing vibrator in a medium which does not perturb the vibrational energy levels of the

system.[2] Several observations[7-9,12-15,18-21] make the assumption that the magnitude of the operator remains correlated rather questionable.

If we assume that the thermal average may be performed over the magnitude and direction separately, eq 2 and 3 may be written

$$I_{\mathrm{ir}}(\omega - \omega_0) \propto \int_{-\infty}^{\infty} \langle M(0)M(\tau)\rangle\langle\mathbf{u}(0)\mathbf{u}(\tau)\rangle e^{i(\omega-\omega_0)\tau}\, d\tau \tag{8}$$

and

$$I_{\mathrm{R}}(\omega - \omega_0) \propto \int_{-\infty}^{\infty} \langle \beta(0)\beta(\tau)\rangle\langle u(0)u(\tau)\rangle e^{i(\omega-\omega_0)\tau}\, d\tau \tag{9}$$

This assumption requires that the operator's magnitude and direction be uncorrelated.

By inversion, we may write eq 10 for eq 8, where the

$$\langle M(0)M(\tau)\rangle\langle\mathbf{u}(0)\mathbf{u}(\tau)\rangle =$$

$$\frac{\int_{-\infty}^{\infty} I_{\mathrm{ir}}(\omega - \omega_0)e^{-i(\omega-\omega_0)\tau}\, d(\omega - \omega_0)}{\int_{-\infty}^{\infty} I_{\mathrm{ir}}(\omega - \omega_0)\, d(\omega - \omega_0)} \tag{10}$$

denominator provides for normalization of the correlation function. As can be seen, the Fourier transform of the infrared absorption spectrum will be the product of two correlation functions. Without further a priori assumptions, the contribution of the reorientational motion to the infrared band shape cannot be determined in the presence of the correlation function for the magnitude of the operator.

As we shall subsequently show, there is an orientation-independent contribution to the line shape which must be independently evaluated before information about reorientational correlation functions can be obtained from infrared line shapes.

The correlation function for the magnitude of the transition dipole moment operator may be written

$$\langle M(0)M(\tau)\rangle = \left|\left(\frac{\partial\mathbf{u}}{\partial Q}\right)_0\right|^2 \langle Q(0)Q(\tau)\rangle \tag{11}$$

where Q is the vibrational normal coordinate and μ is the electric dipole moment. Thus, in the Heisenberg representation, a contribution to the spectral line shape will arise due to the time dependence of changes in the normal coordinate associated with the transition. The normal coordinate will become uncorrelated due to the interactions of the vibrator with neighboring molecules as well as with other groups in the same molecule. The more quickly this loss of correlation occurs, the less certain we will be about the vibrator's interaction with its environment, and the corresponding power spectrum will be broader, reflecting our greater uncertainty concerning the accessible states of the vibrational system in the liquid.

We can show that in the case of the Raman line shape, it is possible in some cases to separate the reorientational correlation function from orientation-dependent contributions.[12-15] In particular, this may be done for experimental line shapes by the use of numerical Fourier transformation techniques. The only new assumption required is the statistical inde-

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pendence of the magnitude and direction of the Raman polarizability-derivative tensor. Thus, we can obtain reorientational correlation functions without reference to a specific model for the liquid state. A comparison of our results to those obtained using assumed functional forms for rotation correlation function should allow us to comment on the validity of those models and their use in interpreting spectral line shapes.

The possibility of determining the reorientational correlation function in the presence of nonorientation-dependent contributions to the Raman line shape is possible if one employs polarized Raman lines. For these bands, the intensity of light scattered with the same polarization as the incident radiation is increased due to a component arising from isotropic scattering. Since the isotropic component has no orientational dependence, the line shape associated with this component of the polarized or parallel spectrum will depend on nonorientational processes. By measuring the polarized and depolarized Raman line shapes, it is possible to separate the orientational and nonorientational contributions to the line shape.

This can be seen more clearly by considering eq 3 rewritten in spherical tensor form. Equation 3 may be rewritten in this form for the two $90°$ scattering geometries with the linearly polarized incident radiation employed in this study as follows

$$I_{\parallel}(\omega_0\omega_0) \propto \int_{-\infty}^{\infty} \left\{ \langle \beta_{00}(0)\beta_{00}(\tau) \rangle + \right.$$

$$\left. \frac{4}{9} \sum_{m=-2}^{2} \langle \beta_{2m}(0)\beta_{2m}(\tau) \rangle \right\} e^{i(\omega-\omega_0)\tau} \, d\tau \quad (12a)$$

$$I_{\perp}(\omega - \omega_0) \propto$$

$$\int_{-\infty}^{\infty} \left\{ \frac{1}{3} \sum_{m=-2}^{2} \langle \beta_{2m}(0)\beta_{2m}(\tau) \rangle \right\} e^{i(\omega-\omega_0)\tau} \, d\tau \quad (12b)$$

where $I_{\parallel}$ refers to the spectral band shape obtained with the polarization analyzer admitting radiation of the same polarization as the incident radiation and $I_{\perp}$ refers to the spectrum obtained with the polarization analyzer rotated $90°$. The subscript m runs over the components of the second order ($l = 2$) spherical tensor. The subscript 00 refers to the isotropic component of the Raman polarizability tensor.

With the assumption of statistical independence of magnitude and direction, eq 12 may be rewritten as eq 13a and 13b where the directional properties of the

$$I_{\parallel}(\omega - \omega_0) \propto \int_{-\infty}^{\infty} \left\{ \langle \beta_{00}(0)\beta_{00}(\tau) \rangle + \right.$$

$$\frac{4}{9} \sum_{m=-2}^{2} \langle |\beta_{2m}(0)||\beta_{2m}(0)| \rangle \langle Y^{*}_{2m}(0)Y_{2m}(\tau) \rangle \right\} e^{i(\omega-\omega_0)\tau} \, d\tau$$

$$(13a)$$

$$I_{\perp}(\omega - \omega_0) \propto \int_{-\infty}^{\infty} \frac{1}{3} \left\{ \sum_{m=-2}^{2} \langle |\beta_{2m}(0)||\beta_{2m}(\tau)| \rangle \times \right.$$

$$\langle Y_{2m}^{*}(0)Y_{2m}(\tau) \rangle \right\} e^{i(\omega-\omega_0)\tau} \, d\tau \quad (13b)$$

spherical components of the Raman polarizability-derivative tensor are expressed by the normalized spherical harmonics. In most cases, molecular symmetry and the symmetry of the normal mode associated

with the vibration will limit the number of components of the polarizability-derivative tensor which are non-zero. For those vibrations for which β_{00} or the isotropic scattering vanishes, the ratios of intensity for the parallel to perpendicular spectra will be: $I_{\parallel}/I_{\perp} = 4/3$. However, this ratio is increased for bands associated with totally symmetric vibrational modes for which the isotropic scattering term can be nonzero. Isotropic scattering occurs only for the parallel spectrum of the symmetric vibrational mode as required by symmetry. For this case, we can obtain the orientational correlation functions by Fourier inversion of eq 3 and simultaneous solution of the resulting pair of equations. In this case, we obtain eq 14

$$\sum_{m=-2}^{2} \left| \frac{\partial \beta'_{2m}}{\partial Q} \right|^{2} \overline{\langle Y^{*}_{2m}(0)Y_{2m}(\tau) \rangle} =$$

$$N \frac{F[I_{\perp}]}{F[I_{\parallel}] - {}^{4}/_{3}F[I_{\perp}]} \quad (14)$$

where $F[f]$ denotes the Fourier transform of the bracketed function, f, and the substitution

$$\beta_{2m} = (\partial\beta'_{2m}/\partial Q)_0 Q(t) \quad (15)$$

has been made where β'_{2m} is the spherical tensor component of the molecular polarizability. In this manner, we can obtain the orientational correlation function without contributions from the correlation function

$$V(\tau) \equiv \langle Q(0)Q(\tau) \rangle \quad (16)$$

which can make a substantial contribution to the Raman line shape.

Although in principle the Fourier transform of the line shape does not convey additional information about the molecular processes involved, there are advantages in their use. As regards this study, the relationship between the dynamic processes which determine the line shape are simplified. In the theory outlined above, the Fourier transforms of the line shapes were related to products of correlation functions. This simple product relation allows us to separate the two time-correlation functions using simple algebraic techniques. In the frequency domain, the two processes would be convoluted and the separation would be rather difficult. The simplification we observe is the result of the deconvolution theorem of Fourier transform theory. Simply stated, it says the Fourier transform of the convolution of two functions is equal to the product of the Fourier transforms of the individual functions, or

$$F[g(\omega)^{*}h(\omega)] = F[g(\omega)]F[h(\omega)] \quad (17)$$

where

$$g(\omega)^{*}h(\omega) = \int_{-\infty}^{\infty} g(\omega')h(\omega - \omega') \, d\omega' \quad (18)$$

expresses the convolution.[21] The second advantage results from the more direct relation between the time correlation function and the dynamics of the processes which determine the line shape. As a result, the dynamics may be more easily "visualized," an advantage often taken too lightly.

In order to investigate the applicability of the theory outlined above, we have investigated polarized Raman line shapes attributed to totally symmetric vibrations of
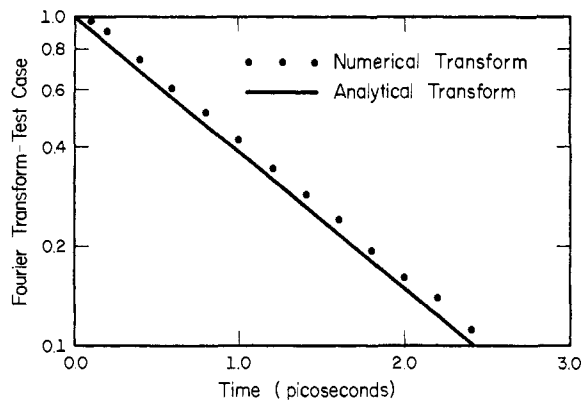
Figure 1. Program test case. Deconvolution of a Lorentzian from a Gaussian and triangular line shape.

Figure 2. Typical spectrum observed for $DCCl_3$ at 294°K. The parallel spectrum is an order of magnitude more intense.

$CDCl_3$ and CH_3I. The results of these experiments suggest that we can successfully extract information about molecular motion from suitable Raman line shapes using the Fourier analysis we have outlined.[22] A similar study has been completed on hydrochloric and hydrobromic acids and their deuterated analogs and suggests this hypothesis.[21]

Experimental Section

Reagents. $DCCl_3$ was obtained from Aldrich Chemical Co. and was analyzed grade with 99.8% purity. The methyl iodide was obtained from Eastman Kodak. Both reagents were used without further purification. Raman bands that might be indicative of impurities were not observed in the spectrum.

Instrumentation. Raman line shapes were recorded with a Spex Model 1401 Raman spectrometer. The 4880-Å line from a coherent Radiation Model 52 MG laser was used as a light source. An ITT Model FW-130 photomultiplier tube with an extended S20 response was employed. The photomultiplier tube was cooled to −20° with a thermoelectric housing. Photon counting rates were recorded with a strip chart recorder and digitized using an Oscar Model F electronic digitizer.

The sample was contained in a tube whose axis was perpendicular to the scattering plane. The tube was mounted in a Harney–Miller cryostat supplied by Spex and thermostated with a flow of nitrogen gas. Temperatures were measured with a copper–constantan thermocouple placed in the sample tube near the light beam.

Computational Procedure. The Fourier transforms calculated in this study were evaluated by direct numerical integration of the transform integral for each time point. The deconvolution was then accomplished by division of two numerical transforms at each time point. The frequency origin was chosen so that the calculated first moment of the polarized spectrum became negligibly small.[23]

Fujiyama and Crawford[10] have discussed some of the errors which may arise in the computation of the Fourier transform. These errors arise because we are viewing a finite portion of the frequency spectrum and are sampling the spectrum only at certain points. The truncation of the Fourier integral to the region of the spectral band will produce a nonnegligible distortion of the transform if the range of integration is not large compared with the width of the spectral band. In this case, diffraction effects occur and the Fourier transform will be the convolution of the Fourier transforms of the line shape and a rectangular function of unit height and length equal to the range of integration. The sampling interval will limit the times for which we can accurately calculate the Fourier integral. At longer times, the integrand in the Fourier integral will begin to oscillate more strongly and the sampling interval must be smaller in order to accurately evaluate the integral by numerical quadrature. We did not observe any aliasing[24] on the test case which might also arise from choosing too large a sampling interval. This seems to be

an advantage of direct evaluation of the Fourier transform over techniques based on periodic functions (Fast Fourier Transform techniques).

Fujiyama and Crawford concluded that the range of integration should be taken as ten times the half-width for a Lorentzian band shape. We have exceeded this criterion in all cases. The Fourier transforms we calculate are considered unreliable after ca. 3.0 psec for the 1-cm^{-1} sampling interval. This is in rough agreement with Shannon's[24,25] sampling theorem based on periodic function techniques. In addition to these sources of error an other inherent in the method, the division of one transform by another will increase the error in the reorientational correlation function we obtain. In order to judge our ability to deconvolute a desired function with our program, we constructed a test case.

For our test case, we chose to deconvolute the Fourier transform of a Lorentzian spectrum which had been convoluted with a Gaussian spectrum and a triangular function chosen to represent a hypothetical slit function. The result of this deconvolution and the theoretical result are shown in Figure 1. With the exception of some initial round off, our result closely parallels the true curve. The correlation time calculated from the slope of our result is $\tau_{20} = 1.09$ psec. The true value is 1.06 psec. In addition, the calculated transform appears to be accurate at times much longer than expected from the Shannon criterion.

Nonlinear least-squares functional fits of the reorientational correlation functions were performed using the digital computer. A program was written based on the description of this method by Hamilton.[26] Matrix inversions were performed in double precision using library subroutines at the University of Illinois Digital Computer Laboratory. The program was tested by fitting known exponential and Gaussian curves.

Error Analysis. Estimates of error in computed correlation times were obtained from several sources. One estimate was obtained from error analysis on repeated runs at a single temperature analyzed for several temperatures. This was in agreement with deviations of the correlation times from a hypothetical Arrhenius temperature dependence. Based on these considerations, a rough error estimate of 5% was obtained. This error is consistent with the results of the program test case and of the nuclear quadrupole coupling-constant determination. A more conservative estimate would place the error somewhat higher. These errors are comparable to those for nmr spin-lattice relaxation times.

Results and Discussion

Spectra obtained for the totally symmetric stretching mode of d-chloroform which occurs at ca. 2250 cm^{-1} is shown in Figure 2. These spectra were obtained at room temperature. The intensity of the polarized spectrum is approximately an order of magnitude greater than the intensity of the depolarized spectrum. Since the contribution of depolarized scattering to

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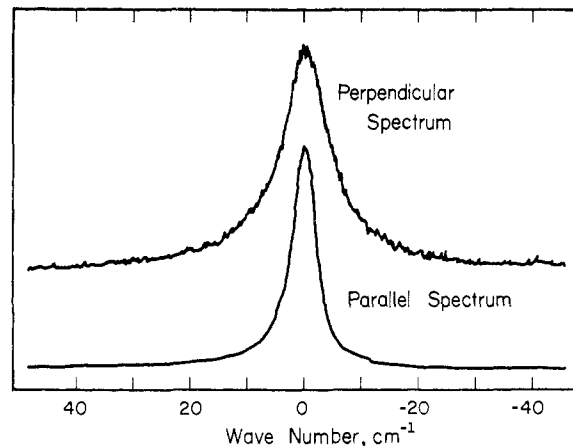(24) R. G. Gordon, J. Chem. Phys., 38, 1724 (1963).

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the polarized spectrum is small, the polarized spectrum largely reflects the spectrum arising from nonorientation-dependent processes convoluted with the instrument distortion function. The depolarized spectrum reflects the convolution of the parallel spectrum with the Fourier transform of the reorientational correlation function.

Figure 3 displays the Fourier transforms of the two spectra as well as the reorientational correlation function obtained from the two transforms by the deconvolution theorem as discussed in the introduction. For a C_{3v} molecule such as d-chloroform, the totally symmetric mode and the α_{00} and α_{20} components of the Raman polarizability derivative tensor exclusively transform alike under the group operations. Thus, the normalized orientational correlation function $R_{20}(\tau)$ obtained from this treatment is simply

$$R_{20}(\tau) = \langle Y^*{}_{20}(\Omega,0)Y_{20}(\Omega,\tau)\rangle \tag{19}$$

where other components have been eliminated by the symmetry of the normal mode and of the molecule.

The reorientational correlation function appears to be an exponential decay although, at short times, the curve appears to deviate more from this simple form. An exponential decay is expected from a diffusional model for the reorientational motion. The expected result for anisotropic diffusional motion for a symmetric top molecule such as d-chloroform has been shown by Huntress[27] to be

$$R_{20}(\tau) = \exp(-6D_\perp\tau) \tag{20}$$

where $D_\perp$ is the diffusion constant characterizing the reorientational motion of the molecule about an axis perpendicular to the principal symmetry axis of the molecule.

A description of the reorientational motion by a diffusion process should be accurate only in the limit that the molecule reorients in small, random angular steps. However, at very short times on the time scale of intermolecular interactions, the molecule's angular motion may more closely approximate the motion of a free rotor. In this case, the correlation function should depend on the inertial parameters of the molecule. Such a correlation function has been derived by Steele[28] for this limiting situation. This correlation function is a Gaussian of the form

$$R_{20}{}^{FR}(\tau) = \exp\left(-3\,\frac{kT}{I_\perp}\,\tau^2\right) \tag{21}$$

where k is Boltzmann's constant, T is the absolute temperature, and $I_\perp$ is the component of the moment of inertia tensor describing motion about an axis perpendicular to the principal symmetry axis in d-chloroform. The roughly Gaussian character of the observed correlation functions at short times suggests that the correlation functions may approach this limiting case at short times.

In order to ascertain how closely experimentally determined correlation functions conformed to these two limiting cases, we attempted to fit the experimental curves with two parameterized functions by the method of nonlinear least squares.

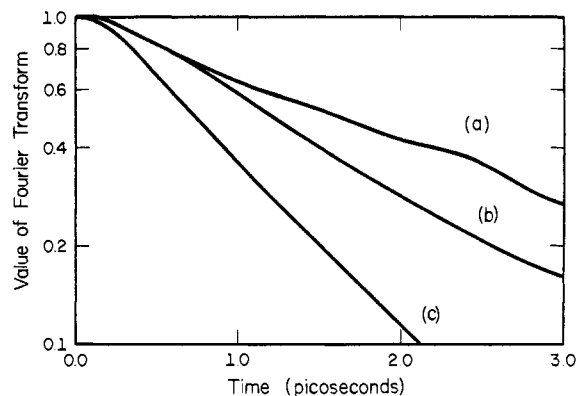The first parameterized function, F_1, was chosen as a

Figure 3. Reorientational correlation function for methyl iodide at 270 °K: (a) $R_{20}(\tau)$, (b) Fourier transform of parallel spectrum, (c) Fourier transform of perpendicular spectrum.

simple exponential to correspond to the result expected if the motion were accurately described as a diffusion process.

$$F_1 = A\,\exp(-at) \tag{22}$$

Here A and a are the parameters to be estimated in the least-squares sense. The parameter a should then be related to the rotational diffusion constant.

The second function was chosen in an attempt to account for inertial motion at short times and diffusive motion at long times. This function, which was modeled after a function suggested by Ornstein for translational diffusion,[29] is given in eq 23 where A and a

$$F_2 = A\,\exp\left[\frac{-6kTI_\perp}{a^2}\left(\frac{at}{I_\perp} - 1 + e^{-at/I_\perp}\right)\right] \tag{23}$$

are again the parameters to be estimated. In this case, a may be identified with the friction coefficient which appears in the Stokes–Einstein relation

$$D = (kT)/(8\pi\eta r^3) = (kT)/a \tag{24}$$

where η is the viscosity, r is the hydrodynamic radius, and a is called the friction coefficient.[30] Although this function varies continuously between the limiting cases for the molecular motion in the liquid, there is no theoretical reason to suspect that it will accurately reflect the form of the correlation function between the two limiting cases. Rather, we are using it in the hope that it may represent empirical results well when the correlation function contains inertial contributions.

In Figure 4, an orientational correlation function for d-chloroform is displayed along with the functional fit. We have fit the orientational correlation functions obtained for d-chloroform at several temperatures. In addition, we also determined orientational correlation functions for CH_3I at several temperatures and fit the parameterized functions to them. The Raman band studied for methyl iodide occurs at ca. 580 cm^{-1} and is polarized. A crystallographic "R factor"[26] was chosen as a goodness of fit criterion. According to this criterion, the function incorporating the inertial terms provided a substantially better fit of the results for d-chloroform than the simple exponential. However, little improvement of the fit using the second function was noted for methyl iodide. This suggests that inertial

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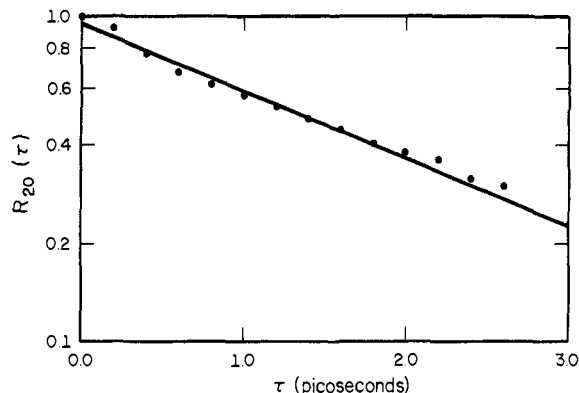(30) A. Einstein, Ann. Phys. (Leipzig), **17**, 549 (1905).

Figure 4. Least-squares functional fit of the reorientational-correlation function for d-chloroform at 276°K with eq 23. The solid line represents the best fit and the points represent experimental results.

Figure 5. Temperature dependences of correlation times for methyl iodide and d-chloroform: (a) methyl iodide ($\triangle$), (b) d-chloroform (O).

motion may be more important in the statistical description of reorientational motion for liquid chloroform than for methyl iodide.

Another reason for obtaining a functional fit of the reorientational correlation functions was to obtain reorientational correlation times. Reorientation correlation times, τ_{lm}, are defined as the zero frequency Fourier transform of the reorientational correlation function.

$$\tau_{lm} \equiv \int_{-\infty}^{\infty} R_{lm}(\tau)\, d\tau \qquad (25)$$

Correlation times could be obtained by directed numerical evaluation of the integral above. However, we cannot determine the correlation function accurately at sufficiently long times to evaluate this integral. The parameterized functional fits allow us to extrapolate the correlation functions to longer times and evaluate the integral.

Correlation times appear in the theoretical description of experimentally observable phenomena which depend upon molecular motion in the liquid but which involve much lower frequencies, e.g., nmr relaxation times, dielectric relaxation times, and viscosity measurements. With a knowledge of the results of these experiments and the correlation times obtained from the Raman experiment, we are provided with an experimental comparison on which we can judge the correctness of this analysis of Raman line shapes.

Using the two parameterized functions described earlier, we were able to obtain correlation times from the functional fits. In the case of the simple exponential or diffusion limit, the correlation time could be estimated from the time constant for the exponential decay from the least-squares estimation, or

$$\tau_{20} = {}^1/_6 D_\perp = 1/a \qquad (26)$$

However, in the case of the second parameterized function, the function was used to extrapolate the experimental results to longer times, and the correlation time, eq 25, was evaluated by numerical integration.

Figure 5 displays the correlation times obtained using this analysis. As can be seen from the figure, the correlation times obtained for both liquids display a temperature dependence characteristic of a thermally activated rate process. This characteristic temperature
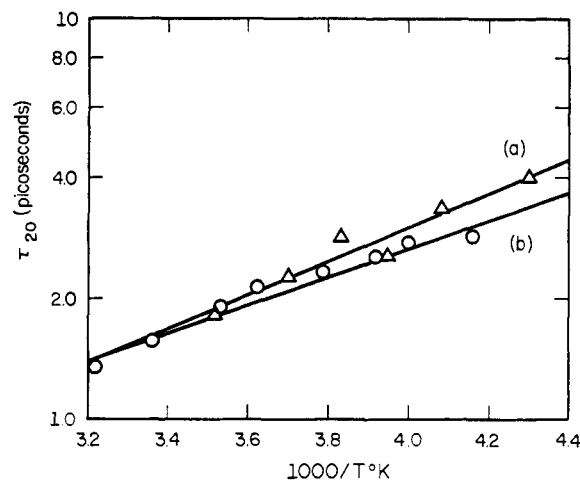
dependence has been found in the other experiments noted above and has the form

$$\tau = \tau_0 \exp(-E_a/RT) \qquad (27)$$

where R is the gas constant, T is the absolute temperature, and E_a is analogous to the Arrhenius activation energy. A comparison of the E_a obtained from the correlation times found in this work with those obtained from other experiments provides another means of identifying the results of our analysis with reorientational correlation functions.

In Table I, we compare the values of E_a obtained in

Table I. Comparison of Experimental Results

Experiment	E_a, kcal/mol	D, sec^{-1} at 20°
d-Chloroform		
Raman	1.61	1.05×10^{11}
Nmr relaxation[a]	1.6 ± 0.1	
Dielectric relaxation[b]	1.75	0.68×10^{11}
Methyl Iodide		
Raman	1.88	1.1×10^{11}
Microviscosity[c]	1.9	1.07×10^{11}
Dielectric relaxation[c]		1.17×10^{11}

[a] W. T. Huntress, *J. Phys. Chem.*, **73**, 103 (1969). [b] S. Mallikarjun and N. E. Hill, *Trans. Faraday Soc.*, **61**, 1389 (1965). [c] Reference 32.

this work with those *found in other studies*. Of the three types of experimental results offered for comparison, those determined from nmr relaxation times provide the closest check. For the spin-lattice relaxation time, T_1, of the deuteron in d-chloroform, we may write the following relation

$$(T_1)^{-1} = {}^3/_8 (2\pi)^2 (eqQ/h)^2 \tau_{20} \qquad (28)$$

where $(eqQ/h)^2$ is the nuclear quadrupole coupling constant and τ_{20} is the reorientational correlation time determined in the Raman experiment.[31] Thus, the temperature dependence of the spin-lattice relaxation time will reflect the temperature dependence of the correlation time determined in the Raman experiment.

Relations have been developed between the correla-

(31) A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.

tion times observed in the Raman and nmr experiments and those determined by dielectric relaxation and viscosity measurements. However, the latter measurements are related to the bulk properties of the liquid and less easily interpretable in terms of individual molecular properties.

The dielectric relaxation experiment is related to the destruction of an induced electrical polarization of the liquid by the thermal motion of the constituent molecular dipoles. Since molecular dipoles are involved, we are dealing with dipolar correlation times.[32] However, in the diffusion limit, the following relation holds

$$\tau_{\text{dipole}} = 3\tau_{20} \qquad (29)$$

and the temperature dependence of the dielectric relaxation time should be the same as that observed in the nmr and Raman experiments. Since the electric dipole moment of the molecule is aligned with the principal symmetry axis, the components of the diffusive motion seen in the three experiments should be identical.

The viscosity is related to the diffusion constant by the Stokes–Einstein equation, eq 26. Since the diffusion constant is related to the correlation time

$$\tau_{20} = (6D_\perp)^{-1} \qquad (30)$$

the temperature dependence should be similar, although we obtain an isotropic diffusion constant from the viscosity measurements. Serious criticism has been leveled at the use of the Stokes–Einstein equation to describe microscopic situations. It is thought, however, that the comparison of temperature dependences over limited ranges is possible, when corrections are made for the microscopic nature of the process (microviscosity theory).[33]

The values of E_a appearing in Table I compare quite favorably and suggest that the correlation functions obtained from this treatment of Raman band shapes are reorientational correlation functions for the molecule. Additional corroboration is supplied in Table I where we also provide a comparison of diffusion constants obtained for methyl iodide using our method and others.

Conclusion

In this paper, we have extended Gordon's[2] reorientational time-correlation function analysis of Raman and infrared vibrational line shapes to include nonorientation dependent line broadening. When this additional contribution to the vibrational line shape is statistically independent of molecular orientation, the Fourier transform of the vibrational line shape may be factored into the product of two time-correlation functions. One time-correlation function will provide a statistical description of the molecule's reorientational motion, as proposed earlier by Gordon, and the other will describe the nonrotational changes in the molecular vibration. Such changes in the molecular vibration may arise from a variety of interactions in the liquid state, e.g., electrical interactions with neighboring molecules, vibrational energy transfer to other modes of vibration, etc.

With the assumption of statistical separability of

orientational from nonorientational line broadening, we have obtained experimental reorientational time correlation functions for liquid d-chloroform and methyl iodide at a variety of temperatures using numerical Fourier transform techniques. As can be seen from the polarized spectrum in Figure 2, the contribution to the line shape arising from nonorientation-dependent phenomena is substantial and must be separated from the line shape arising from the orientational motion of the vibrator, if Raman line shapes are to be used to investigate the dynamics of the liquid state. This also suggests that the results of previous experiments which have not assessed the extent of nonorientational broadening should be reexamined to ascertain this contribution to published correlation functions.

In addition to assumptions required in Gordon's[2] original work, the analysis outlined in this paper rests on the assumption that the contribution of reorientational motion to Raman line shapes is statistically independent of other contributions. Secondly, this method relies upon an accurate numerical evaluation of the Fourier integral transforms involved. Direct evaluation of the Fourier transforms of the line shapes frees us from restrictive assumptions required in fitting spectra with hypothetical line shapes[12,15] or in using only line widths.[6-8] In addition, line-width studies ignore the wealth of experimental data present in the complete spectral band shape, and the line-shape analysis is employed in a previous study[15] had to be restricted to a narrower frequency range. The latter situation suggests that the model on which the line shape is based cannot account for short-time phenomena which will be expressed over a wide frequency range and which will be most apparent in the wings of the spectrum. The success of our first assumption as a working hypothesis and of the numerical Fourier transformation are demonstrated by the comparison of reorientational correlation times and their temperature dependences presented earlier.

When nonorientation-dependent broadening makes a significant contribution to the Raman or infrared vibrational line shape, the number of experimental situations from which information about molecular motion may be gleened is restricted. In addition to requiring a Raman or infrared vibrational spectral band free from interfering extraneous absorption or scattering lines, the spectral band must contain a component arising from an isotropic scattering or absorption term. This latter restriction precludes the use of depolarized Raman lines and infrared absorption bands unless additional information is available about the nonorientation-dependent line shape. This restricts the present analysis to polarized Raman bands, and as a consequence of molecular symmetry will restrict the number of components of the anisotropic reorientational motion we can study. However, in some cases, it may be possible to study depolarized lines and infrared absorption.

The isotropic Raman line shapes observed in this study did not display a significant temperature dependence. This suggests that by observing depolarized Raman bands and infrared absorption bands at low temperatures or for frozen liquids where reorientational correlation times are very long and the contribution of reorientational motion to the line shape is negligible, a separation is effected. If this situation prevails, the

(32) P. Debye, "Polar Molecules," Dover Publications, New York, N. Y., 1929.
(33) K. T. Gillen and J. H. Noggle, J. Chem. Phys., 53, 801 (1970); K. T. Gillen, M. Schwartz, and J. H. Noggle, Mol. Phys., 20, 899 (1971).

line shapes under these conditions will be the line shape due to nonorientation-dependent broadening and may be used to deconvolute reorientational correlation functions from spectral bands observed under different conditions. The results of line-shape[15,20] and line-width[7] studies suggest that this may be possible. By using this technique, information about additional components of the anisotropic reorientational motion in the liquid phase would be available.

In addition to providing an excellent tool for the study of the liquid state, the method we have described can also be of use to chemists with more diverse interests. As Gordon[34] has pointed out, reorientational correlation times obtained from Raman line shapes can be used with nmr relaxation times to determine molecular properties. As can be seen in eq 28, a knowledge of the nmr spin-lattice relaxation time T_1

and the reorientational correlation time τ_{20} allows us to determine the nuclear quadrupole coupling constant for deuterium in d-chloroform. The value, we determine, for the nuclear quadrupole coupling constant is $(eqQ/h) = 0.174$ MHz, which compares quite favorably with a value of $(eqQ/h) = 0.168$ MHz determined from nqr measurements on solid d-chloroform.[35] This result is encouraging and suggests the wider importance of this method.

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A Semicontinuum Model for Trapped Electrons in Polar Liquids and Solids. Trends with Matrix Polarity

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Abstract: A semicontinuum model is extended to trapped electrons in 2-methyltetrahydrofuran glass and in three amine glasses at 77°K. It is shown to account for recent experimental results quite well. The semicontinuum model has also been modified for trapped electrons in aqueous glasses like 10 M NaOH by neglecting long-range polarization interactions. This modification successfully predicts no bound excited state in agreement with experiment. Revised calculations are given for electrons in water and ice and configuration coordinate diagrams are presented for the above matrices and for electrons in liquid and glassy methanol and ethanol. The effects of the various physical constants of the matrices on the trapped electron energy level structure is discussed from the viewpoint of matrix polarity.

One of the surprising and generally significant findings of radiation chemical studies in the last decade has been the discovery of solvated and trapped electrons as distinct chemical entities in a variety of liquids and glassy solids.[2,3] These species have typical lifetimes of microseconds in room temperature liquids and seem indefinitely stable in many glassy solids at 77°K. All of these electrons are characterized by a strong absorption spectrum in the visible or infrared regions. Early theoretical studies were oriented toward accounting for the absorption spectrum of solvated electrons in water and liquid ammonia.[4-8] The electron cavity radius was used as a parameter to fit the energy of the absorption maximum to the calculated

energy difference between the ground and first excited states. In more recent theoretical work a semicontinuum model has been developed by which the configurational stability of the ground state of the electrons has been determined in water and ice,[9] and in methanol and ethanol.[10,11] The configurational stability of electrons in liquid ammonia has also been established by a slightly different method of calculation.[12] In the semicontinuum model the cavity radius is no longer a parameter, but the energy of the electron in the quasi-free electron state or conduction state, V_0, does remain as a limited (between -1 and 1 eV) parameter. However, V_0 seems amenable to experimental measurement.[13]

Recent experimental work on electrons in several glassy matrices[14-16] and in crystalline ice[16,17] at 77°K

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