THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 4 15 AUGUST 1965

Molecular Motion in Infrared and Raman Spectra

R. G. GORDON

Society of Fellows and Department of Chemistry, Harvard University, Cambridge, Massachusetts

(Received 8 April 1965)

It is suggested that Fourier transformation of infrared and Raman band shapes reveals the meaning of the spectrum in terms of molecular rotation much more clearly than does the usual frequency shape. By looking at the time dependence directly, one may separately examine the molecular motion at short and long times The motion at short times may be analyzed directly in terms of the molecular dyanmics, by the use of a power series in the time, whereas the behavior at long times is best examined by statistical arguments. This kind of analysis is illustrated by several examples, including the spectra of liquid CO and CH_4.

I. INTRODUCTION

INFRARED and Raman spectra of molecular solids, liquids, and gases appear to contain considerable information about molecular rotation in these systems. We may distinguish two related goals for the interpretation of these spectra: The recovery of information from the spectra about (1) the intermolecular forces and torques which determine the molecular motion, and (2) the nature of the molecular motion itself. We have previously[1] given some attention to the first of these goals, and it was found that certain averages over the intermolecular interactions, such as the mean-squared torque on a molecule, may be deduced directly from the spectral band shapes. In this paper we turn to the second of these goals, that of understanding as precisely as possible, just what a spectral band shape tells us about molecular motion, and, in particular, about molecular rotation.

The interpretation of spectroscopic information is almost always based on the assignment of lines in a spectrum to transitions, induced by the measuring radiation, between the various quantum states of the system. We may call this conventional spectroscopic view the Schrödinger picture, since attention is focused on the energy levels of the system, rather than on its time development. However, several circumstances may make this method of interpretation difficult or impossible. (1) There may be so many transitions that an assignment is difficult, or the lines may blend together to form a continuous band, which is usually the case in dense gases, liquids, solutions, and many solids. Then the assignment of individual transitions is impossible. (2) The intensity distribution in such a spectrum is determined by off-diagonal matrix elements between all the many-molecule wavefunctions for the system. Such matrix elements and wavefunctions would be essentially impossible either to visualize or to calculate. Thus there is very little *interpretive* value to this conventional "Schrödinger picture" of the spectroscopy of complicated systems. (3) A third difficulty is that there is no classical analog of a single quantum state, so that even for systems which are described reasonably well by classical mechanics, the Schrödinger picture does not allow any classical correspondence to be exploited.

The point which we wish to emphasize in this paper is that the Heisenberg picture of quantum mechanics provides a powerful interpretive tool for spectra of complicated systems. By focusing attention on the time development of the system, rather than on its quantum states, one may avoid the three difficulties which we outlined above. (1) Interpretation is possible in the Heisenberg picture even if lines are not resolved. (2) The interpretation is easily visualized in terms of the molecular motion in the system. (3) A classical correspondence exists which may be exploited for systems which approach classical behavior.

The Heisenberg picture of spectroscopy leads naturally to the consideration of a spectrum as the Fourier transform of an appropriate time correlation function. From an interpretive point of view, the most important feature of this Fourier relationship is that it can be inverted to give the time correlation function as a Fourier integral over a complete experimental frequency spectrum.[2] In this way the short-time and long-time behavior of the correlation function are experimentally isolated and may then be discussed separately. It is appropriate to make such a separation since the short-time behavior of a correlation function may be discussed fairly rigorously in terms of the dynamics of the many-molecule system. However, at long times, the dynamics becomes too difficult; but then one may rely instead on statistical arguments to establish the form of the correlation functions at long times. By way of contrast, if one attempts to interpret the frequency spectrum directly, the intensity at any particular frequency includes contributions from the *entire* time development of a correlation function, including both the short- and long-time parts.

It is very often argued in statistical mechanics that correlation functions should decay exponentially at long times. However, it is seldom possible to verify this exponential form experimentally, since most macroscopic measurements are done at essentially zero frequency (on a molecular time scale). Thus, the usual

[1] R. G. Gordon, J. Chem. Phys. **39**, 2788 (1963); **40**, 1973 (1964); **41**, 1819 (1964).

[2] R. G. Gordon, J. Chem. Phys. **42**, 3658 (1965).

transport measurements[3] yield only the *area* under appropriate time correlation functions, rather than their detailed dependence on time. Spectroscopy provides a welcome supplement to this information by permitting more detailed study of the time dependence of rotational correlation functions. Not only is the exponential form of these correlation functions verified at long times, but the "transient" behavior at short times is also observed.

In the following sections we amplify these introductory remarks, and then consider some specific applications of these ideas to the interpretation of infrared and Raman spectra.

II. INFRARED BAND SHAPES

As a simple example of the Heisenberg picture of a spectrum, we consider an infrared absorption band. For simplicity we neglect any coupling of the internal vibrations of a molecule with other degrees of freedom of the system. Then, the usual expression for an absorption band shape, in terms of transitions between quantum states (Schrödinger picture) is

$$I(\omega)\equiv\frac{\hbar c\sigma(\omega+\omega_0)}{4\pi^2(\omega+\omega_0)\{1-\exp[-\hbar(\omega+\omega_0)/kT]\}}$$
$$=\sum_{ij}\rho_i\,|\,\langle i\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{m}^v\,|\,f\rangle\,|^2\delta[(E_j-E_i)/\hbar-\omega], \quad \text{(II.1)}$$

where σ is the absorption cross section per molecule, ω_0 is the vibrational band center, ω is the frequency displacement from ω_0, $|\,i\rangle$ and $|\,f\rangle$ are the initial and final quantum states for the (coupled) rotation-translation motion of the molecules, with energy eigenvalues E_i and E_f, respectively. ρ_i is the Boltzmann factor for the initial rotation-translation state $|\,i\rangle$, assuming that the sample is initially in thermal equilibrium. $\boldsymbol{\varepsilon}$ is a unit vector along the electric vector of the incident radiation. $\mathbf{m}^v$ is the transition dipole moment for the particular vibrational band v. The first step in transforming to the Heisenberg picture is to represent the δ function by its Fourier integral

$$\delta(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(i\omega t)\,dt.$$

Then,

$$I(\omega)=\frac{1}{2\pi}\sum_{ij}\rho_i\langle i\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{m}^v\,|\,f\rangle\langle f\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{m}^v\,|\,i\rangle$$
$$\times\int_{-\infty}^{\infty}\exp[i(E_j-E_i)t/\hbar]e^{-i\omega t}dt. \quad \text{(II.2)}$$

The energy eigenvalues E_j and E_i are now expressed in terms of the Hamiltonian operator H for the rotation-translation motion, giving

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}\sum_{ij}\rho_i\langle i\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{m}^v\,|\,f\rangle$$
$$\times\langle f\,|\,e^{iHt/\hbar}\boldsymbol{\varepsilon}\cdot\mathbf{m}^v e^{-iHt/\hbar}\,|\,i\rangle dt. \quad \text{(II.3)}$$

[3] R. Zwanzig, Ann. Rev. Phys. Chem. (to be published).

Now the sum over the complete set of final states $|\,f\rangle$ may be performed:

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}\sum_i\rho_i\langle i\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{m}^v(e^{iHt/\hbar}\boldsymbol{\varepsilon}\cdot\mathbf{m}^v e^{-iHt/\hbar})\,|\,i\rangle dt. \quad \text{(II.4)}$$

Since the operator $(e^{iHt/\hbar}\boldsymbol{\varepsilon}\cdot\mathbf{m}^v e^{-iHt/\hbar})$ is the Heisenberg operator for the direction of transition dipole moment at time t, Eq. (II.4) may be written more concisely as

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}\langle[\boldsymbol{\varepsilon}\cdot\mathbf{m}^v(0)][\boldsymbol{\varepsilon}\cdot\mathbf{m}^v(t)]\rangle dt, \quad \text{(II.5)}$$

where the brackets represent an equilibrium statistical average

$$\langle \mathrm{Op}\rangle=\sum_i\rho_i\langle i\,|\,\mathrm{Op}\,|\,i\rangle.$$

For an isotropic sample, the same result is obtained if we average over the polarization directions $\boldsymbol{\varepsilon}$ of the radiation, giving

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}\tfrac{1}{3}\langle\mathbf{m}^v(0)\cdot\mathbf{m}^v(t)\rangle dt. \quad \text{(II.6)}$$

Finally, we convert to a spectrum normalized to unit area,

$$\hat{I}(\omega)=I(\omega)\Big/\int_{\text{band}}I(\omega)\,d\omega$$

and to a vector $\mathbf{u}=\mathbf{m}^v/\langle(\mathbf{m}^v)^2\rangle^{\frac{1}{2}}$ along the direction of the transition dipole moment. Then Eq. (II.6) reads

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle dt. \quad \text{(II.7)}$$

(Using a normalized spectrum largely eliminates dielectric effects on the local electric field due to the radiation. Only fluctuations about the average local field will affect the normalized spectrum.) This equation expresses the Heisenberg-type description of an infrared band shape: The distribution of absorption frequencies about the vibration frequency is the Fourier transform of the average motion of the transition dipole moment. The classical correspondence of this formula is apparent. If one calculates the motion of the dipole moment classically, then the Fourier transformation produces the classical approximation to the band shape; if a quantum-mechanical calculation of the motion is made, the true quantum spectrum is obtained.

If an experimental spectrum extends over the entire range of rotation-translation frequencies about a band, then the inverse Fourier integral allows us to reconstruct experimentally the average motion of the transition dipole moment:

$$\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle=\int_{\text{band}}\hat{I}(\omega)e^{i\omega t}d\omega. \quad \text{(II.8)}$$

In this way one obtains a clear physical picture of just what an experimental infrared band contour can tell us about molecular motion. The physical meaning of the correlation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ (at least in the classical limit, where measurements do not disturb the system) is the following: Imagine that one could observe the microscopic reorientation of a single molecule in a system of many molecules in thermal equilibrium. Suppose that at a time 0 the vibrating dipole of this molecule points along a direction $\mathbf{u}(0)$. Then we follow the thermal motion of the molecules and at a time later we measure the *projection* of $u(t)$ on the original direction: $\mathbf{u}(0)\cdot\mathbf{u}(t)$. Now we make this measurement again and again, picking out different reference times "0." Finally, we average all of these trajectories $\mathbf{u}(0)\cdot\mathbf{u}(t)$ to obtain the correlation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$.

A slightly different way to view this correlation function is to say that it describes the decay of our knowledge about a system as it approaches equilibrium. Even if we know that a molecule points in a certain direction at time $t=0$, after a long time it is equally likely to be pointing in any direction. Then our initial knowledge is no longer relevant. The correlation function is a quantitative statement of what average predictions may be made after a given time, using our initial knowledge.

Some examples of dipole correlation functions are plotted in Fig. 1 for carbon monoxide. They were obtained by numerical Fourier transformation of several experimental infrared spectra. The curves will become unreliable for times longer than about $(1/\Delta\omega)$, where $\Delta\omega$ is the experimental resolution.

We have simplified the above treatment by neglecting vibrational perturbations (frequency shifts). If we wish to include these perturbations, we must allow the intermolecular potential energy for a vibrationally excited molecule to differ from that of a molecule in its ground state. If we let H_v be the rotation–translation Hamiltonian for the system including the infrared-active molecule in its vth vibrationally excited state, then the function whose Fourier transform gives the band shape is

$$\langle(\boldsymbol{\varepsilon}\cdot\mathbf{m}_v)\,(e^{iH_vt/\hbar}\boldsymbol{\varepsilon}\cdot\mathbf{m}_ve^{-iH_0t/\hbar})\rangle. \qquad \text{(II.9)}$$

Only when $H_v=H_0$ (no frequency shifts) does this reduce to the dipole time correlation function. Thus, in cases when frequency shifts are significant, the simple physical interpretation of the Fourier transform of the spectrum is obscured. This difficulty is reduced if we remove the mean frequency shift from the vibrational band origin; then only the fluctuations of the frequency shift distort the band shape. Generally speaking, the complications from frequency shifts should be more important for larger and heavier molecules. In addition, the problem of overlapping of different vibrational bands becomes serious for any but the simplest of molecules.

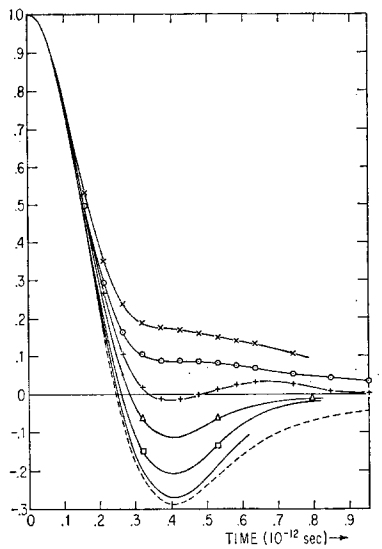

FIG. 1. CO dipole correlation functions in various environments. Spectra were obtained from the following references; $CHCl_3$ and $n-C_7H_{16}$, M, O. Bulanin and N. D. Orlova, Opt. i Spectroskopiya **15**, 112 (1963) [English transl.: Opt. Spectry. **15**, 208 (1963)]; CCl_4, J. Lascombe, P. V. Huong, and M. Josien, Bull. Soc. Chim. (France) **1959**, 1175; A, R. Coulon, L. Galalry, B. Oksengorn, S. Robin, and B. Vodar, J. Phys. Radium **15**, 58, 641 (1954); ×, CO in $CHCl_3$ (liquid); ⊙, CO in CCl_4 (liquid); +, CO in $n-C_7H_{16}$ (liquid), △, CO in argon (gas, 510 amagat); ⊡, CO in argon (gas, 270 amagat); ——, CO in argon (gas, 66 amagat); - - - -, CO free (calculated).

III. PURE ROTATIONAL ABSORPTION

The problem of frequency shifts in rotation–vibration spectra would be avoided by studying pure rotational absorption in the microwave and far infrared region. Calculations analogous to those in the previous section lead to the Heisenberg picture for a pure rotational spectrum:

$$\frac{3\hbar c\sigma(\omega)}{4\pi^2\omega[1-\exp(-\hbar\omega/kT)]}=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}$$

$$\times[\langle\boldsymbol{\mu}_1(0)\cdot\boldsymbol{\mu}_1(t)\rangle+\sum_{i\neq1}\langle\boldsymbol{\mu}_1(0)\cdot\boldsymbol{\mu}_i(t)\rangle]dt, \qquad \text{(III.1)}$$

where $\boldsymbol{\mu}_i$ is the permanent dipole moment of the ith molecule. One difference in the pure rotational case is the presence of interference terms between different dipoles. Such interference terms are absent in the vibrational case because of the assumed lack of coupling between vibrations of different molecules. Of course these interference terms go to zero when there are no interactions between dipolar molecules, as in the case of dilute solutions. The classical limit ($\hbar\omega\ll kT$) of this formula has been obtained by a linear response calculation.[4] As before, we may consider the Fourier inversion of this formula to obtain the correlation

[4] S. Glarum, J. Chem. Phys. **33**, 1371 (1960).

function:

$$\langle \boldsymbol{\mu}_1(0)\cdot\boldsymbol{\mu}_1(t)\rangle+\sum_{i\neq 1}\langle \boldsymbol{\mu}_1(0)\cdot\boldsymbol{\mu}_i(t)\rangle$$

$$=\int_{-\infty}^{\infty}e^{i\omega t}\left(\frac{3\hbar c}{4\pi^2}\right)\frac{\sigma(\omega)\,d\omega}{\omega[1-\exp(-\hbar\omega/kT)]}. \quad \text{(III.2)}$$

Finally there is the question of dielectric corrections to the local field. As in the vibration–rotation case, these effects are essentially eliminated by using a normalized spectrum. In the present case of pure rotational absorption, a sum rule derived previously[5] is useful:

$$\mu^2=3c\int\sigma(\omega)\,d\omega\Big/[4\pi^2\,(\mathrm{Tr}\mathbf{I}-\mathbf{u}\cdot\mathbf{I}\cdot\mathbf{u})], \quad \text{(III.3)}$$

where $\mathbf{I}$ is the reciprocal moment of inertia tensor for a molecule, and $\mathbf{u}=\boldsymbol{\mu}/|\,\boldsymbol{\mu}\,|$ is a unit vector along the permanent dipole moment of a molecule. Now if we divide Eq. (III.2) by the sum rule [Eq. (III.3)], we obtain

$$\langle \mathbf{u}_1(0)\cdot\mathbf{u}_1(t)\rangle+\sum_{i\neq 1}\langle \mathbf{u}_1(0)\cdot\mathbf{u}_i(t)\rangle$$

$$=\left\{\hbar(\mathrm{Tr}\mathbf{I}-\mathbf{u}\cdot\mathbf{I}\cdot\mathbf{u})\int\frac{e^{i\omega t}\sigma(\omega)\,d\omega}{\omega[1-\exp(-\hbar\omega/kT)]}\right\}\Big/\int\sigma(\omega)\,d\omega \quad \text{(III.4)}$$

and any constant factors arising from internal field corrections will cancel from this equation. Unfortunately, there are at present no experimental results of this type which span the necessary frequency range. Microwave measurements cover only the lower end of the spectrum, whereas far-infrared spectrometers scan the upper parts of the range. We may partially alleviate this difficulty by weighting the intensity defined in Eq. (III.1) by an additional factor of, say, ω^2. This would tend to bring the important parts of the spectrum more completely into the range of far-infrared spectrometers, at least for reasonably light molecules. Then the Fourier inversion gives the second time derivative of the dipole correlation function considered above.

IV. RAMAN BAND SHAPES

In the Heisenberg picture of spectroscopy, a Raman band shape (observed by inelastic light scattering) is the Fourier transform of the average motion of the polarizability tensor of a molecule. Specifically, the depolarized component of a rotational Raman band corresponds to the correlation function

$$c(t)=\mathrm{Tr}\,\langle\boldsymbol{\beta}_1(0)\cdot\boldsymbol{\beta}_1(t)\rangle+\sum_{i\neq 1}\mathrm{Tr}\,\langle\boldsymbol{\beta}_1(0)\cdot\boldsymbol{\beta}_i(t)\rangle, \quad \text{(IV.1)}$$

where $\boldsymbol{\beta}_i$ is the anisotropy of the electric polarizability tensor for the ith molecule, and the trace (Tr) is over the three spatial indices of $\boldsymbol{\beta}$.

[5] R. G. Gordon, J. Chem. Phys. **38**, 1724 (1963).

Similarly, for the depolarized part of a vibration–rotation Raman band, we must consider the correlation function[2]

$$c(t)=\mathrm{Tr}\,\langle\boldsymbol{\beta}^v(0)\cdot\boldsymbol{\beta}^v(t)\rangle, \quad \text{(IV.2)}$$

where $\boldsymbol{\beta}^v$ is the vibrational matrix element of the anisotropy of the polarizability, taken between the two vibrational states involved in the transition. As in the infrared case, interference terms between two different molecules occur for pure rotational bands, but do not occur when vibrational transitions are also involved. To illustrate this general formula for a specific case, a totally symmetric vibration in a symmetric-top or a linear molecule gives a correlation function of the form[2] $\frac{1}{2}\langle 3[\mathbf{u}(0)\cdot\mathbf{u}(t)]^2-1\rangle$, where $\mathbf{u}$ is a unit vector along the axis of the molecule. Correlation functions of this same form are also important in the theory of spin–lattice relaxation.[2]

V. CORRELATION FUNCTIONS AT SHORT TIMES

The main reason for Fourier analysis of a band shape is so that we may consider separately the short- and long-time motion of the molecular system. The behavior of a correlation function at short times is best displayed by considering a power series in the time. For example, for a dipolar (infrared) band, if the correlation function is analytic in the time, then

$$\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle=\sum_{n=0}^{\infty}\frac{t^n}{n!}\left[\frac{d^n}{dt^n}\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle\right]_{t=0}. \quad \text{(V.1)}$$

The time derivatives may be performed using the Heisenberg equation of motion

$$d\mathbf{u}/dt=(i/\hbar)[H,\mathbf{u}],$$

giving

$$\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle=\sum_{n=0}^{\infty}\frac{(it)^n}{n!\hbar^n}$$

$$\times\langle\mathbf{u}(0)\cdot[H,[H,\cdots[H,\mathbf{u}(0)]\cdots]]\rangle. \quad \text{(V.2)}$$

The coefficients in this time series are identified as frequency moments of the spectrum, by expanding Eq. (II.8) and interchanging the order of summation and integration:

$$\langle\mathbf{u}(0)\cdot\mathbf{u}(t)\rangle=\int e^{i\omega t}\hat{I}(\omega)\,d\omega=\sum_{n=0}^{\infty}\frac{(it)^n}{n!}\int\omega^n\hat{I}(\omega)\,d\omega. \quad \text{(V.3)}$$

Comparing Eq. (V.2) and (V.3), we have

$$M(n)\equiv\int\omega^n\hat{I}(\omega)\,d\omega$$

$$=\hbar^n\langle\mathbf{u}(0)\cdot[H,[H,\cdots[H,\mathbf{u}(0)]\cdots]]\rangle. \quad \text{(V.4)}$$

Each coefficient in the time series is an equilibrium property of the molecular system, and may be evaluated without solving any equations of motion. Some of the lower moments have been computed previously[1] for

infrared and Raman bands, and therefore we may immediately write down the first few terms in the time expansion of these correlation functions. For example, for an infrared band of a linear molecule, polarized along the axis, the time series in the classical limit, begins

$$\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle = 1-(kT/I)t^2 + [\tfrac{1}{3}(kT/I)^2 + (24I^2)^{-1}\langle(\mathbf{O}V)^2\rangle]t^4 + O(t^6), \quad \text{(V.5)}$$

where k is Boltzmann's constant, T is the temperature, I is the moment of inertia, and $\langle(\mathbf{O}V)^2\rangle$ is the mean-square torque on a molecule due to the other molecules. As another example of the time series, we may consider the correlation function describing both the Raman band shape and some of the spin relaxation properties of a linear molecule.[2] Using the Raman frequency moments computed previously,[1] we may write down the short-time behavior of this correlation function:

$$\tfrac{1}{2}\langle 3[\mathbf{u}(0)\cdot\mathbf{u}(t)]^2 - 1\rangle = 1-(3kT/I)t^2 + [4(kT/I)^2 + (8I^2)^{-1}\langle(\mathbf{O}V)^2\rangle]t^4 + O(t^6). \quad \text{(V.6)}$$

The first point to note is that the initial *curvatures* (second moments) of these correlation functions depend only on the *temperature* of the system and the molecular *moment of inertia*, but not on the intermolecular forces. This invariance occurs because the second moment is entirely a kinetic-energy effect, and in the classical limit the kinetic energy is determined by the temperature alone, through the equipartition theorem.

The effects of intermolecular forces are first seen in the terms of order t^4, for classical systems. The hindering of the rotation *increases* the coefficient of t^4 by an amount proportional to the mean-square torque on a molecule, which is necessarily a positive quantity. Thus the rotational correlation function for interacting molecules initially lies *above* that of free molecules, and the magnitude of the deviation increases initially as t^4. Therefore the actual decay of the rotational correlation function for hindered rotors is *slower* than the decay for free rotors, at least in the initial period of decay.

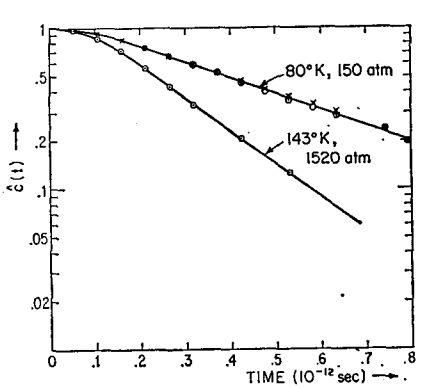

FIG. 2. Dipole correlation functions for carbon monoxide. $\langle\hat{u}(0)\cdot\hat{u}(t)\rangle$ for liquid CO computed from infrared spectra. X, fundamental vibration (1←0), from infrared spectra of G. Ewing, J. Chem. Phys. **37**, 2250 (1962). +, (first overtone, 2←0) and ⊙, (2nd overtone, 3←0) from infrared measurements of H. Vu, M. R. Atwood, and B. Vodar, J. Chem. Phys. **38**, 2671 (1963).

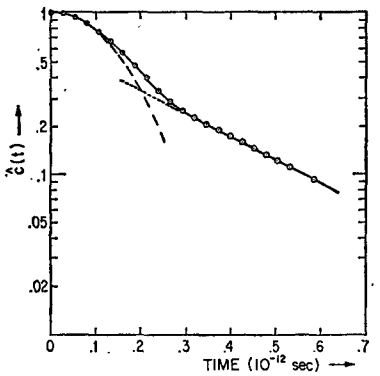

FIG. 3. Dipole correlation function $\langle\hat{u}(0)\cdot\hat{u}(t)\rangle$ for liquid methane (98°K) computed from infrared data of G. E. Ewing, J. Chem. Phys. **40**, 179 (1964).

The classical invariance of the second moment provides a convenient check on the completeness of the frequency range of an experimental band shape. If the second moment is far below its classical value, then one may suspect that measurements were not carried far enough into the "wings" of the band, and the correlation function obtained by Fourier transformation in such a case would be incorrect. On the other hand, if an experimental second moment considerably exceeds the calculated value, then it is likely that the fluctuations of the vibrational frequency shift are a significantly broadening factor in the spectrum.

The lower moments of a spectrum are simple properties[1] of the molecular system essentially because they describe the short-time behavior of the motion. On the other hand, if one wants to describe the time development to longer times, many more higher moments are needed in the power series. These higher moments are naturally more complicated equilibrium properties, since they describe the very complicated motion at longer times. Thus computational difficulties limit the usefulness of the time expansion to the consideration of relatively short times.

VI. CORRELATION FUNCTIONS AT LONG TIMES

At long times it becomes impractical to follow the dynamics either analytically or numerically, due to the extreme complexity of the molecular trajectories. However, this very complexity suggests that the actual reorientation process may be simulated at long times by a stochastic (Markov) process. Then all of the correlation functions should approach exponential decay at long times. It is very interesting, therefore, to find experimental rotational correlation functions that do indeed behave exponentially at long times (Figs. 2–4).

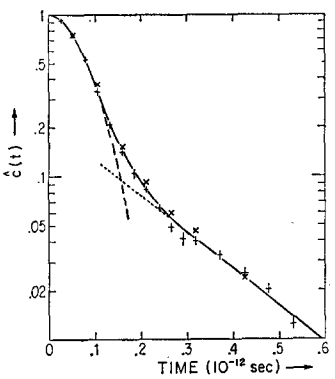

FIG. 4. P_2 correlation function

$\langle P_2[\hat{u}(0)\cdot\hat{u}(t)]\rangle$

for liquid methane (95°K), computed from Raman band shapes obtained by J. H. Harrold, Ref. 11, +; and C. A. Plint, Ref. 12, ×.

Rotational diffusion is the most widely applied stochastic model for the behavior of rotational correlation functions at long times. If the molecular reorientation process is simulated by random small-angle jumps, then the average rotational motion follows a diffusion-type equation.[6–8] The slopes at long times of the logarithm of the correlation function are then related to the constants in the rotational diffusion equation. The rotational diffusion of a linear molecule or of a spherical-top molecule is characterized by a single rotational diffusion constant. This is the case for those systems (CO, CH_4) for which appropriate spectroscopic band shapes have been measured. It would be interesting to analyze the spectra of asymmetric molecules, in which the diffusion is characterized by a tensor.[6,8] A good example of this type would be ethylene, since the principal axes of the diffusion-constant tensor are then determined by the symmetry of the molecule. Then, by studying the various infrared bands, which are polarized along the three axes of the molecule, one would be able to completely determine the entire rotational diffusion-constant tensor.

Even in liquids, however, the rotational diffusion equation fails to describe one aspect of the long-time behavior of the experimental rotational correlation functions: The limiting long-time exponential curves do not extrapolate back to unity at time $t=0$. The extrapolated initial amplitudes are greater than unity for CO, and less than unity for liquid CH_4. This failure of the diffusion equation appears to arise mainly from the failure of the assumption of infinitesimal angular-diffusion steps.

In gases and some solutions (Fig. 1), the rotational correlation functions have not reached exponential decay even at the longest times permitted by the experimental resolution. In these cases, the usual small-angle rotational diffusion equation is quite inappropriate, and one must take into account rotation through large angles.

VII. DISCUSSION

In order to illustrate further how the Heisenberg picture assists in the understanding of spectra, we consider the case of liquid methane. Infrared[9] and Raman[10–12] spectra have been observed. Qualitative examination of these band contours, in the frequency spectrum, has led to discordant conclusions about the nature of molecular rotation in liquid methane. It was claimed that the Raman spectrum proves free rotation,[10] whereas the infrared spectrum was claimed to demonstrate highly hindered rotation.[9]

This apparent discrepancy is resolved if we consider the Fourier transforms of these band shapes, given in Figs. 3 and 4. For an initial period of about 10^{-13} sec, both correlation functions (solid curves) are indistinguishable from those of the free rotational motion (dashed curves). Intermolecular torques have yet to build up a measurable effect on the motion.

In an intermediate time region, from about 1 to 3×10^{-13} sec, the intermolecular torques produce significant hindering of the rotation, so that the actual reorientation takes place more slowly than the free rotational motion.

At longer times (greater than about 3×10^{-13} sec), the rotational motion has become so complicated by the intermolecular torques, that the average correlation is indistinguishable from that of random, exponential decay (dotted curves).

It is important to note that this time pattern of behavior is shown by *both* the infrared and Raman correlation functions, over the same ranges of time. In contrast, the frequency description of the band shape obscures the similarity in the meaning of the infrared and Raman results. Since the Raman correlation function (P_2) decays faster than the infrared function (P_1), it has fallen to a much smaller numerical value by the time the exponential description becomes valid. Therefore, the Raman frequency spectrum resembles the free rotational spectrum considerably more than the infrared one does. It is this difference which apparently led to the difference in the interpretation of the infrared[9] and Raman[10] bands. It is apparent that the Heisenberg (time) description of band shapes reveals their dynamical meaning much more clearly than does the Schrödinger (frequency) description.

[6] F. Perrin, J. Phys. Radium **5**, 497 (1934).
[7] W. H. Furry, Phys. Rev. **107**, 7 (1957).
[8] L. D. Favro, Phys. Rev. **119**, 53 (1960).
[9] G. E. Ewing, J. Chem. Phys. **40**, 179 (1964).
[10] B. Crawford, H. L. Welsh, and J. H. Harrold, Can. J. Phys. **30**, 81 (1952).
[11] J. H. Harrold, thesis, Toronto, 1949.
[12] C. A. Plint, thesis, Toronto, 1953.