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Infrared and Raman study of liquids. III. Theory of the rotation-vibration coupling effects. Diatomic molecules in inert solutions

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A theory is proposed to explain the effects of the rotation-vibration coupling in the ir and Raman spectra of inert solutions of diatomic molecules. This theory is a stochastic-type theory related to similar theories of NMR spectra. Spectral manifestations of the rotation-vibration interaction are found to depend very strongly on whether an ir, isotropic, or anisotropic Raman spectrum is concerned, on the nature of molecular rotations in the liquid, and on the properties of the solvent-solute interaction forces. Explicit expressions are given for a number of profiles which are perturbed by this interaction.

I. INTRODUCTION

The theories describing the ir and Raman band profiles of diatomic molecules dissolved in inert solutions[1-10] generally imply the following assumptions: (a) The rotation-vibration coupling is negligible; rotational and vibrational motions are statistically independent. (b) There are no solvent-induced components in the dipole-moment vector $\vec{M}$ and in the polarizability tensor $\tilde{\alpha}$ of the active molecule. These assumptions are probably correct in a zero-order theory, but they no longer remain satisfactory if more precise information is required. The purpose of the present paper is to investigate spectral manifestations of the rotation-vibration coupling in the case of diatomic molecules dissolved in inert solvents; for the previous work along similar lines, see Refs. 11–19. The theory we propose is a semiclassical theory of a stochastic type. Spectral manifestation of the rotation-vibration coupling is investigated in detail, and expressions are proposed which reproduce different profiles perturbed by this interaction.[20]

II. BASIC FORMULATION

A. Description of model

The problem to be investigated is the absorption, or the inelastic scattering, of the radiation by a system formed by one active molecule and a large number of nonactive structureless molecules (Fig. 1). The following model is used to investigate this problem: (a) The active molecule is executing anharmonic vibrations coupled to the remaining degrees of freedom of the system. This coupling acts through (i) the solvent-solute interaction, (ii) the rotation-vibration interaction of the solute molecule. Thus its vibrations are describable by the following Hamiltonian:

$$H(r,t)=[(p^2/2\mu)+\tfrac{1}{2}K(r-r_0)^2+\frac{1}{6}f(r-r_0)^3+\cdots]+[H_s(r,t)]\,, \tag{1a}$$

where

$$\begin{aligned} H_s(r,t)&=[V_s(r,t)-V_s(r_0,t)]+\left(\frac{\vec{J}^2(t)}{2I(r)}-\frac{\vec{J}^2(t)}{2I(r_0)}\right)\\ &=\left((r-r_0)\frac{\partial V_s}{\partial r}(r_0,t)+\frac{1}{2}(r-r_0)^2\frac{\partial^2 V_s}{\partial r^2}(r_0,t)+\frac{1}{6}(r-r_0)^3\frac{\partial^3 V_s}{\partial r^3}(r_0,t)+\cdots\right)\\ &\quad+\frac{\vec{J}^2(t)}{2I(r_0)}\left(-(r-r_0)\frac{2}{r_0}+(r-r_0)^2\frac{3}{r_0^2}-(r-r_0)^3\frac{4}{r_0^3}+\cdots\right). \end{aligned} \tag{1b}$$

The stochastic operator $V_s(r,t)$ representing the solvent-solute interaction is such that there are no solvent-induced components in $\vec{M}$, $\tilde{\alpha}$. (b) The active molecule is executing stochastic reorientations described by means of the unit vector $\vec{u}(t)$ for the molecular axis. (c) The vibrations are described with the help of quantum mechanics, $\hbar\omega_V \gg kT$; the reorientations are described with the help of classical mechanics, $\hbar\omega_R \ll kT$. For justification of this approach, see, e.g., Ref. 21;

contrary to Refs. 1–10, vibrations and rotations are no longer considered as independent entities.

B. Description of absorption and scattering processes

Once the basic properties of the model have been chosen the method used for the study of the absorption or the scattering process must still be discussed. It is assumed that (i) the incident beam is either linearly polarized or represents natural light, and (ii) the sample is isotropic. In these circumstances (a) using the fluctuation-dissipation theorem, and (b) repeating the calculations of Refs. 2, 3 with vibrations and rotations kept correlated, the following formulas are easily obtained [compare with Eq. (4) of Ref. 2 and with Eq. (5) of Ref. 3]:

$$I(\omega) \sim \int_{-\infty}^{+\infty} G(t) e^{i\omega t}\, dt\,, \tag{2}$$

where

$$G(t) = G_{\mathrm{ir}}(t) = \langle [\mathrm{Tr}\rho_0 M^H(t) M^H(0)][\vec{u}(t)\vec{u}(0)]\rangle \quad (\mathrm{ir}), \tag{3}$$

$$G(t) = G_i(t) = \langle \mathrm{Tr}\rho_0 \alpha^H(t)\, \alpha^H(0)\rangle \quad (\text{isotropic } R), \tag{4}$$

$$G(t) = G_a(t) = \langle [\mathrm{Tr}\rho_0 \beta^H(t)\beta^H(0)] \times \{\tfrac{3}{2}[\vec{u}(t)\vec{u}(0)]^2 - \tfrac{1}{3}\}\rangle \quad (\text{anisotropic } R). \tag{5}$$

In these equations the trace operator Tr implies the averaging over the vibrational coordinate, characterized by its density matrix ρ_0, and the angle brackets indicate the averages over the stochastic processes $V_s(r,t)$, $\vec{J}^2(t)$, $\vec{u}(t)$. All the other symbols have their usual meaning: $M^H(t)$ is the Heisenberg operator for the magnitude of the dipole-moment vector of the active molecule, $\alpha^H(t)$ the Heisenberg operator for its mean polarizability, and $\beta^H(t)$ that for the magnitude of its anisotropy. The ratio $\alpha^H(0)/\beta^H(0)$ is expressible in terms of the depolarization factor ρ of the band under study; one can show that $\alpha^H(0)/\beta^H(0) = 45\rho/3 - 4\rho$ for linearly polarized light, and $\alpha^H(0)/\beta^H(0) = 45\rho/6 - 7\rho$ for natural light.[3] The correlation function $G_R(t)$ of the complete Raman spectrum is a linear combination, $G_R(t) = AG_i(t) + BG_a(t)$, with coefficients A, B depending on the geometry of the experimental arrangement. These coefficients are displayed in Table I.

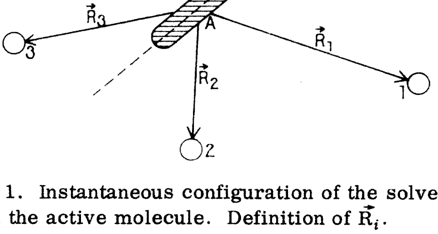

FIG. 1. Instantaneous configuration of the solvent around the active molecule. Definition of $\vec{R}_i$.

Equations (3)–(5) can readily be transformed into a form which makes more recognizable the role of different physical processes influencing the band shape. (i) The Heisenberg equation

$$\frac{d\gamma^H}{dt} = \frac{i}{\hbar}[H^H, \gamma^H] + \frac{\partial \gamma^H}{\partial t}$$

is solved in the adiabatic approximation with $\gamma = M$, α, or β; $\partial\gamma^H/\partial t$ is put equal to zero, as by assumption there are no induced components in γ^H. (ii) The effect of $H_s(r,t)$ in (1a) is calculated with the help of first-order perturbation theory; all terms of order higher than one in the anharmonic force constant f are neglected.[22] (iii) $\theta(t)$ is the angle between $\vec{u}(t)$ and $\vec{u}(0)$, $\omega_{0\alpha}^0$ is the nonperturbed frequency of the $0 \to \alpha$ transition, and $\omega_0 = (K/\mu)^{1/2}$. If points (i)–(iii) are taken into account, Eqs. (3)–(5) take the following form [compare with Eqs. (8), (9), and (16) of Ref. 2 and with Eqs. (8), (9), and (14) of Ref. 3]:

$$G_{\mathrm{ir}}(t) = |\langle 0|M^H(0)|\alpha\rangle|^2 \exp(-i\omega_{0\alpha}^0 t) \times \left\langle \exp\left(-i\int_0^t [\omega_{0\alpha}^1(t') + \omega_{0\alpha}^2(t')]\,dt'\right) \times \cos\left[\int_0^t \omega^3(t')\,dt'\right]\right\rangle, \tag{6}$$

$$G_i(t) = |\langle 0|\alpha^H(0)|\alpha\rangle|^2 \exp(-i\omega_{0\alpha}^0 t) \times \left\langle \exp\left(-i\int_0^t [\omega_{0\alpha}^1(t') + \omega_{0\alpha}^2(t')]\,dt'\right)\right\rangle, \tag{7}$$

TABLE I. Coefficients A, B of the transformation $G(t) = AG_i(t) + BG_a(t)$ relating, at 90° observation and VV and VH configurations, the correlation function $G(t)$ of the complete Raman spectrum to the correlation functions $G_i(t)$ and $G_a(t)$ defined by Eqs. (4) and (5) (see Ref. 3).

	Configuration	A	B
Polarized light	VV	1	$\frac{4}{45}$
	VH	0	$\frac{1}{15}$
Natural light	VV	$\frac{1}{2}$	$\frac{7}{90}$
	VH	0	$\frac{1}{15}$

$$G_a(t)=|\langle 0|\beta^H(0)|\alpha\rangle|^2\exp(-i\omega_{0\alpha}^0 t)\left[\frac{1}{4}\left\langle\exp\left(-i\int_0^t[\omega_{0\alpha}^1(t')+\omega_{0\alpha}^2(t')]\,dt'\right)\right\rangle\right.$$
$$\left.+\frac{3}{4}\left\langle\exp\left(-i\int_0^t[\omega_{0\alpha}^1(t')+\omega_{0\alpha}^2(t')]\,dt'\right)\cos\left(2\int_0^t\omega^3(t')\,dt'\right)\right\rangle\right], \tag{8}$$

$$\omega_{0\alpha}^1(t)=v_\alpha\frac{1}{2\mu\omega_0}\left(-\frac{f}{K}\,\frac{\partial V_s}{\partial r}(r_0,t)+\frac{\partial^2 V_s}{\partial r^2}(r_0,t)-\frac{5\hbar f}{12\mu^2\omega_0^3}\,\frac{\partial^3 V_s}{\partial r^3}(r_0,t)\right)-v_\alpha^2\left(\frac{5\hbar f}{24\mu^3\omega_0^4}\,\frac{\partial^3 V_s}{\partial r^3}(r_0,t)\right), \tag{9}$$

$$\omega_{0\alpha}^2(t)=v_\alpha\frac{\vec{J}^2(t)}{2I(r_0)}\left[\frac{f}{Kr_0}\left(\frac{1}{\mu\omega_0}+\frac{5\hbar}{KI(r_0)}\right)+\frac{3}{I(r_0)\omega_0}\right]$$
$$+v_\alpha^2\left[\frac{\vec{J}^2(t)}{2I^2(r_0)}\left(\frac{5\hbar f}{K^2 r_0}\right)\right], \tag{10}$$

$$\omega^3(t)=\frac{d\theta(t)}{dt}. \tag{11}$$

The physical content of Eqs. (6)–(11) is as follows. The band profile is produced by fluctuations of three stochastic quantities, $\omega_{0\alpha}^1(t)$, $\omega_{0\alpha}^2(t)$, $\omega^3(t)$. These quantities designate the frequency increments due to (a) the solvent-solute interaction, (b) the rotation-vibration interaction of the active molecule, and (c) the component of the angular velocity $\vec{\Omega}(t)$ of the active molecule perpendicular to the plane $\vec{u}(t)$, $\vec{u}(0)$. Contributions (a) and (c) generally predominate and are included, explicitly or implicitly, in the zeroth-order theories.[1-10] Contribution (b) often represents only a small perturbation; the study of its effects on the band profile is the main purpose of the present paper.

C. Stochastic treatment of $\omega_{0\alpha}^1(t)$, $\omega_{0\alpha}^2(t)$, $\omega^3(t)$

According to Eqs. (6)–(11), the functions $G_{\text{ir}}(t)$, $G_i(t)$, $G_a(t)$ are determined by three correlated stochastic functions $\omega_{0\alpha}^1(t)$, $\omega_{0\alpha}^2(t)$, $\omega^3(t)$. A complex situation results which is difficult to treat mathematically and to analyze physically. It seems reasonable, under these circumstances, to focus attention on the study of a number of simpler carefully selected limiting situations in which $\omega_{0\alpha}^1(t)$, $\omega_{0\alpha}^2(t)$, $\omega^3(t)$ are either rapidly or slowly modulated; the analysis of complicated intermediate cases is then qualitatively deduced from the study of the limiting cases. The procedure which has been adopted here can be sketched in the following way.

The functions $\omega_{0\alpha}^1(t)$, $\omega_{0\alpha}^2(t)$, $\omega^3(t)$ are economically designated by $\omega_i(t)$, with $i=1,2,3$, and are treated by use of three arguments. (i) To each $\omega_i(t)$ is associated its correlation time τ_i, characterizing the duration of the fluctuations of $\omega_i(t)$. These times are compared with a reference time $\tau\sim 1/\Delta\omega$, the lifetime of the physical process generating the ir or Raman band of half-width $\Delta\omega$ under study. $\omega_i(t)$ is said to be slowly modulated if $\tau_i\gg\tau$; the modulation is considered to be fast if $\tau_i\ll\tau$. (ii) All $\omega_i(t)$'s are assumed to be either slowly or rapidly modulated. The correlation between slowly and rapidly modulated $\omega_i(t)$'s is neglected (see Appendix A). (iii) The time dependence is suppressed in the slowly modulated $\omega_i(t)$'s by writing $\omega_i(t)\to\omega_i$. This dependence is conserved for the $\omega_i(t)$'s which are rapidly modulated, but the condition $\tau_i\ll\tau$ can be used to simplify the calculations. The theory based on these premises represents a generalization to a multidimensional case of well-known one-dimensional theories, e.g., Refs. 21 and 23. It can be shown in particular that, in the one-dimensional case, the well-known slow and fast modulation conditions $(\langle\omega_1^2\rangle)^{1/2}\tau_1\gg 1$, $(\langle\omega_1^2\rangle)^{1/2}\tau_1\ll 1$ are deducible from the conditions $\tau_1\gg\tau$, $\tau_1\ll\tau$. Compare with Appendix B.

It remains to define the limiting cases for which a detailed theory is to be presented. A number of empirical and theoretical arguments are needed for that purpose; they are developed in detail in Secs. III A, IV A, and V A. For simplicity these limits are called the free-rotation and rotational-diffusion limits, according to whether τ_2, $\tau_3\gg\tau$ or τ_2, $\tau_3\ll\tau$, and independently of the value of τ_1.

III. RELAXATION FUNCTIONS, ir SPECTRA

A. Order-of-magnitude estimation of τ_i's

The general properties of ir spectra of diatomic molecules dissolved in inert solutions essentially depend on two physical parameters of the system under study, the moment of inertia $I(r)$ of the active molecule and the energy $V_s(r,t)$ of the solvent-solute interaction. If $I(r)$ and the nonradial component $V_n(r,t)$ of $V_s(r,t)$ are sufficiently small,[24] the ir bands are broad and show characteristic rotational wings; their over-all half-widths $\Delta\omega$ range, typically, from 50 to 200 cm^{-1}. The presence of a certain structure may introduce ambiguity into the definition of the reference time τ. If, as usual, spectral analysis of the band as a whole is desired, and lack of precision in analyzing diffuse spectral details is tolerated, τ can be calculated from the over-all half-width $\Delta\omega$ of the band; this gives τ's of the order of 10^{-13}–10^{-14} sec.[25] The estimation of the correlation times τ_1, τ_2, and τ_3 is more uncertain. Nevertheless, careful analysis of the experimental material leads to the following rough estimation: $\tau_1 \sim 10^{-11}$ sec, $\tau_2 \sim 10^{-12}$–10^{-13} sec, $\tau_3 \sim 10^{-12}$–10^{-13} sec. The comparison of these numbers shows that, for systems under discussion, the conditions $\tau_1 \gg \tau$, $\tau_2 \gg \tau$, $\tau_3 \gg \tau$ approach physical reality.

If $I(r)$ and $V_s(r, t)$ are sufficiently large, the ir spectra have very different characteristics. The bands are moderately broad, symmetrical or slightly asymmetrical, and generally structureless. Their half-widths $\Delta\omega$ range, typically, from 25 to 50 cm^{-1}. The corresponding references times $\tau = 1/\Delta\omega$ are of the order of 10^{-13} sec, longer than in the free-rotation case. The estimation of τ_1, τ_2, and τ_3 is much more uncertain. The main difficulty is that radial and nonradial forces both contribute to $\omega^1_{0\alpha}(t)$ and their effect on τ_1 must somehow be assessed. It is believed that $\tau_1 \sim 10^{-11}$–10^{-13} sec, depending on the relative importance of the nonradial contribution to $\omega^1_{0\alpha}$; $\tau_2 \sim 10^{-13}$–10^{-14} sec, $\tau_3 \sim 10^{-13}$–10^{-14} sec. The numbers certify that the conditions $\tau_1 \gg \tau$, $\tau_2 \ll \tau$, $\tau_3 \ll \tau$ fit, approximately, the experimental data in the present case.

The intermediate situations characterized by conditions $\tau_1 > \tau$, $\tau_2 \sim \tau$, $\tau_3 \sim \tau$ often occur in practice as well. The ir spectra have properties intermediate between those just cited.

B. Free-rotation limit $\tau_1 \gg \tau$, $\tau_2 \gg \tau$, $\tau_3 \gg \tau$

The calculation of $G_{\text{ir}}(t)$ goes through the following steps. (i) Equation (6) is rewritten with $\omega^1_{0\alpha}(t) = \omega^1_{0\alpha}$, $\omega^2_{0\alpha}(t) = \omega^2_{0\alpha}$, $\omega^3(t) = \omega^3$. (ii) The averages over the stochastic processes $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$ are taken separately; this procedure is justified by the fact that $V_n(r, t)$ is small:

$$G_i(t) = |\langle 0 | M^H(0) | \alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\langle\exp(-i\omega^1_{0\alpha}t)\rangle \times \langle\exp(-i\omega^2_{0\alpha}t)\cos(\omega^3 t)\rangle \,. \tag{12}$$

(iii) The average over $\omega^1{}_{0\alpha}$ is made by use of the cumulant expansion theorem, and that over $(\omega^2_{0\alpha}, \omega^3)$ by writing $\omega^2_{0\alpha} = -C(\alpha)\omega'^2$ and $\omega^3 = \omega'$, with

$$P(\omega') = \frac{I_0}{2kT}|\omega'|\exp\left(-\frac{I_0\omega'^2}{2kT}\right).$$

Then, combining points (i)–(iii) one is led to the final result:

$$G_i(t) = |\langle 0 | M^H(0) | \alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\left[\exp\left(\sum_{j=1}^{\infty} \alpha_j(-it)^j\right)\right] \times\left[\frac{1}{1 - i4\beta_r C(\alpha)t}\, {}_1F_1\left(1, \frac{1}{2}, \frac{-\beta_r t^2}{1 - i4\beta_r C(\alpha)t}\right)\right], \tag{13a}$$

$$\frac{1}{I_0} = \frac{1}{I(r_0)} + \frac{1}{I^2(r_0)}\left(\frac{\hbar f r_0}{2\omega_0\mu} + \frac{3\hbar}{2\omega_0} + \frac{11\hbar^2 f}{6K^2 r_0}\right), \tag{13b}$$

$$-C(\alpha) = \frac{v_\alpha I_0^2}{I^2(r_0)}\left[\frac{f}{2Kr_0}\left(\frac{I(r_0)}{\mu\omega_0} + \frac{5\hbar}{K}\right) + \frac{3}{2\omega_0}\right]. \tag{13c}$$

The notation is as follows. The quantity $\alpha_j = (1/j\,!)\langle\omega^1_{0\alpha}\rangle_j$ represents the jth-order cumulant for $\omega^1_{0\alpha}$, ${}_1F_1(1, \frac{1}{2}, z)$ the confluent hypergeometric function of arguments 1, $\frac{1}{2}$, and $z = -[\beta_r t^2/1 - i4\beta_r C(\alpha)t]$, $\beta_r = (kT/2I_0)$, with I_0 being the effective moment of inertia of nonrigid rotator, $I(r_0)$ its equilibrium value, and $C(\alpha)$ the coefficient measuring the strength of the rotation-vibration interaction. The following interpretation can be given to (13a). The relaxation mechanism consists of two approximately independent processes, $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$. This situation is reflected by the structure of $G_{\text{ir}}(t)$, which contains, apart from trivial contributions, two independent factors associated with $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$, respectively. The first of them describes the spread of vibrational frequencies due to V_s and the second describes spectral manifestations of the rotations of a free nonrigid rotator. If the rotation-vibration interaction is weak, i.e., if $C(\alpha) \to 0$, $I_0 \to I(r_0)$, $\beta_r \to [kT/2I(r_0)] = \beta^0_r$, expression (13a) reduces to the simple formula provided by the zero-order theory [compare with Eqs. (11) and (17) of Ref. 2)].

C. Rotational-diffusion limit $\tau_1 \gg \tau$, $\tau_2 \ll \tau$, $\tau_3 \ll \tau$

The calculation of $G_{\text{ir}}(t)$ involves, in this limit, the following essential steps. (i) Equation (6) is rewritten with $\omega^1_{0\alpha}(t) = \omega^1_{0\alpha}$, $\omega^2_{0\alpha}(t)$, $\omega^3(t)$. (ii) Stochastic processes $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$ are assumed to be noncorrelated; this assumption is justified by the fact that, in the present case, $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$ have very different modulation speeds:

$$G_{\text{ir}}(t) = |\langle 0 | M^H(0) | \alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\langle\exp(-i\omega^1_{0\alpha}t)\rangle \times\left\langle\exp\left[-i\int_0^t \omega^2_{0\alpha}(t')\,dt'\right]\cos\left[\int_0^t \omega^3(t')\,dt'\right]\right\rangle. \tag{14}$$

(iii) The averages over $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$ are calculated, the former by using the cumulant-expansion theorem and the latter by a theorem related to it.[26] Moreover, all terms of order higher than two are neglected in the series over $(\omega^2_{0\alpha}, \omega^3)$. It can be shown, in fact, that if $\tau_2 \ll \tau$, $\tau_3 \ll \tau$ they are much smaller than its first- and second-order terms; the proof is omitted here. (iv) $\omega^2_{0\alpha}(t)$, $\omega^3(t)$ are taken to be Markovian-Gaussian and the corresponding correlation functions to be single exponentials.[27–29] Combining points (i)–(iv) the following result is obtained:

$$G_{\text{ir}}(t) = |\langle 0|M^{H}(0)|\alpha\rangle|^{2}\exp(-i\omega^{0}_{0\alpha}t)\left[\exp\left(\sum_{j=1}^{\infty}\alpha_{j}(-it)^{j}\right)\right]$$
$$\times\left(\exp\left\{iC(\alpha)\frac{2kT}{I_0}t+i^{2}\alpha_{J}\tau_{J}\left[\frac{t}{\tau_J}-1+\exp\left(-\frac{t}{\tau_J}\right)\right]+i^{2}\alpha_{R}\tau_{R}\left[\frac{t}{\tau_R}-1+\exp\left(-\frac{t}{\tau_R}\right)\right]\right\}\right), \qquad (15a)$$

$$\tau_J = \tau_2 , \qquad (15b)$$

$$\tau_R = \tau_3 , \qquad (15c)$$

$$\alpha_J = \langle(\omega^{2}_{0\alpha})^{2} - \langle\omega^{2}_{0\alpha}\rangle^{2}\rangle\tau_2 , \qquad (15d)$$

$$\alpha_R = \langle(\omega^{3})^{2}\rangle\tau_3 . \qquad (15e)$$

Equation (15a) suggests the following physical interpretation. Two approximately independent quantities, $\omega^{1}_{0\alpha}$ and $(\omega^{2}_{0\alpha}, \omega^{3})$, determine the band shape. This situation is reflected in the structure of $G_{\text{ir}}(t)$ containing, apart from trivial contributions, two independent factors. The first of them, associated with $\omega^{1}_{0\alpha}$, describes the spread of vibrational frequencies due to V_s and the second, related to $(\omega^{2}_{0\alpha}, \omega^{3})$, describes spectral manifestations of strongly perturbed rotations of a nonrigid rotator. If the rotation-vibration interaction is absent, i.e., if $C(\alpha)\to 0$, $I_0 \to I(r_0)$, $\alpha_J \to 0$, the well-known zero-order formula for $G_{\text{ir}}(t)$ is easily obtained [compare with Eqs. (11) and (20) of Ref. 2].

IV. RELAXATION FUNCTIONS, ISOTROPIC RAMAN SPECTRA

A. Order-of-magnitude estimation of τ_i's

The general characteristics of isotropic Raman spectra essentially depend on two physical parameters of the system under study, the rotation-vibration coupling constant $C(\alpha)$ and the energy $V_s(r,t)$ of the solvent-solute interaction. If $C(\alpha)$ is sufficiently large and if the solvent is exceptionally inert (e.g., SF_6) the bands of the spectrum are narrow and distinctly asymmetrical, and their half-widths $\Delta\omega$ are of the order of a few wave numbers. The reference times τ are of the order of 10^{-12} sec, which is much longer than in ir. The correlation times τ_1, τ_2 can be analyzed as in Sec. III A. The following estimate is obtained in this way: $\tau_1 \sim 10^{-11}$–10^{-12} sec, $\tau_2 \sim 10^{-11}$ sec. As a rule, $\omega^{1}_{0\alpha}(t)$'s are very small and there is no need for a very precise determination of τ_1. One concludes that the conditions $\tau_1 \gg \tau$, $\tau_2 \gg \tau$ fit, approximately, the experimental data for these systems.

If the solvent-solute interaction energy $V_s(r,t)$ were to gradually increase, one would observe first, a spectacular narrowing of the isotropic Raman band; if $V_s(r,t)$ were further increased, a new broadening of the band would occur. The bands are symmetrical or slightly asymmetrical. Typically, their half-widths $\Delta\omega$ range between a fraction of a wave number and a few wave numbers; the corresponding τ's may be quite long: $\tau \sim 10^{-10}$–10^{-12} sec. Estimated values of τ_1 range from 10^{-11} to 10^{-13} sec: The long-time end of this interval is approached if $V_r(r,t)$ determines the behavior of $\omega^{1}_{0\alpha}(t)$, and its short-time end is approached if $V_n(r,t)$ predominates. Finally, $\tau_2 \sim 10^{-13}$–10^{-14} sec. It is then easily seen that two limits $\tau_1 \gg \tau$, $\tau_2 \ll \tau$ and $\tau_1 \ll \tau$, $\tau_2 \ll \tau$ must be considered.

B. Free-rotation limit $\tau_1 \gg \tau$, $\tau_2 \gg \tau$

The calculation of $G_i(t)$ goes through the following steps. (i) Equation (7) is rewritten with $\omega^{1}_{0\alpha}(t) = \omega^{1}_{0\alpha}$, $\omega^{2}_{0\alpha}(t) = \omega^{2}_{0\alpha}$. (ii) The averages over the stochastic processes $\omega^{1}_{0\alpha}$ and $\omega^{2}_{0\alpha}$ are made separately; this procedure is justified by the fact that $V_n(r,t)$ is small:

$$G_i(t) = |\langle 0|\alpha^{H}(0)|\alpha\rangle|^{2}\exp(-i\omega^{0}_{0\alpha}t)\langle\exp(-i\omega^{1}_{0\alpha}t)\rangle$$
$$\times\langle\exp(-i\omega^{2}_{0\alpha}t)\rangle . \qquad (16)$$

(iii) The averaging over $\omega^{1}_{0\alpha}$ is made by use of the cumulant expansion theorem, and that over $\omega^{2}_{0\alpha}$ by writing $\omega^{2}_{0\alpha} = -C(\alpha)\omega'^{2}$,

$$P(\omega') = \frac{I_0}{2kT}|\omega'|\exp\left(\frac{I_0\omega'^{2}}{2kT}\right).$$

Then, combining points (i)–(iii) one is led to the final result:

$$G_i(t) = |\langle 0|\alpha^{H}(0)|\alpha\rangle|^{2}\exp(-i\omega^{0}_{0\alpha}t)$$
$$\times\left[\exp\left(\sum_{j=1}^{\infty}\alpha_j(-it)^{j}\right)\right]\left(\frac{1}{1-i4\beta_r C(\alpha)t}\right). \qquad (17)$$

The following interpretation can be given to Eq. (17). The relaxation mechanism consists of two approximately independent processes $\omega^{1}_{0\alpha}$ and $\omega^{2}_{0\alpha}$. This situation is reflected in the structure of $G_i(t)$ containing, apart from trivial contributions, two independent factors associated with $\omega^{1}_{0\alpha}$ and $\omega^{2}_{0\alpha}$, respectively. These factors describe the spread of vibrational frequencies produced by the solvent-solute interactions and by the rotation-vibration interactions, respectively. If the rotation-vibration interaction is weak, i.e., if $C(\alpha) \to 0$, expression (17) reduces to the simple formula provided by the zero-order theory [compare with Eq. (11) of Ref 3].

C. Rotational-diffusion limits $\tau_1 \gg \tau$, $\tau_2 \ll \tau$ and $\tau_1 \ll \tau$, $\tau_2 \ll \tau$

The calculation of $G_i(t)$ depends on whether the conditions $\tau_1 \gg \tau$, $\tau_2 \ll \tau$ or the conditions $\tau_1 \ll \tau$, $\tau_2 \ll \tau$ apply. The procedure utilized in the first case can be sketched as follows. (i) Equation (7) is rewritten with $\omega^1_{0\alpha}(t) = \omega^1_{0\alpha}$, $\omega^2_{0\alpha}(t)$. (ii) Stochastic processes $\omega^1_{0\alpha}$ and $\omega^2_{0\alpha}$ are considered to be noncorrelated; this assumption is justified by the fact that, in this limit, $\omega^1_{0\alpha}$ and $\omega^2_{0\alpha}$ have very different modulation speeds:

$$G_i(t) = |\langle 0 \,|\, \alpha^H(0) \,|\, \alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\langle \exp(-i\omega^1_{0\alpha}t)\rangle \times \left\langle \exp\left[-i\int_0^t \omega^2_{0\alpha}(t')\,dt'\right]\right\rangle . \tag{18}$$

(iii) The averages over $\omega^1_{0\alpha}$, $\omega^2_{0\alpha}$ are calculated with the help of the cumulant expansion theorem. The modulation of $\omega^2_{0\alpha}$ being fast, all terms of order higher than two in $\omega^2_{0\alpha}$ can be neglected in this expansion; the proof is omitted here. (iv) $\omega^2_{0\alpha}$ is taken to be a Markovian-Gaussian process and its correlation function a single exponential.[27-29] This leads to the following result valid in the case $\tau_1 \gg \tau$, $\tau_2 \ll \tau$:

$$G_i(t) = |\langle 0 \,|\, \alpha^H(0) \,|\, \alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\left[\exp\left(\sum_{j=1}^{\infty} \alpha_j(-it)^j\right)\right]\left(\exp\left\{iC(\alpha)\frac{2kT}{I_0}t + i^2\alpha_J\tau_J\left[\frac{t}{\tau_J} - 1 + \exp\left(-\frac{t}{\tau_J}\right)\right]\right\}\right). \tag{19}$$

The procedure utilized in the case $\tau_1 \ll \tau$, $\tau_2 \ll \tau$ is slightly different and can be described as follows. (i) The sum $\omega^1_{0\alpha}(t) + \omega^2_{0\alpha}(t)$ is considered as a new stochastic function $\omega^4_{0\alpha}(t)$ characterized by the correlation time τ_4. Its modulation is supposed to be fast, $\tau_4 \ll \tau$, an assumption consistent with the fact that, separately, $\omega^1_{0\alpha}(t)$ and $\omega^2_{0\alpha}(t)$ are rapidly modulated. (ii) Equation (7) is transformed by applying the cumulant expansion theorem. Only terms up to second order need be retained, a consequence of the fast-modulation condition $\tau_4 \ll \tau$. (iii) $\omega^4_{0\alpha}(t)$ is supposed to be a Markovian-Gaussian process, which implies that its correlation function is a single exponential.[27-29] Combining points (i)–(iii) one is led to the following result valid in the case $\tau_1 \ll \tau$, $\tau_2 \ll \tau$:

$$G_i(t) = |\langle 0 \,|\, \alpha^H(0) \,|\, \alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t) \times \left(\exp\left\{-i\left(\alpha_1 - C(\alpha)\frac{2kT}{I_0}\right)t + i^2\alpha_{VJ}\tau_{VJ}\left[\frac{t}{\tau_{VJ}} - 1 + \exp\left(-\frac{t}{\tau_{VJ}}\right)\right]\right\}\right), \tag{20a}$$

$$\tau_{VJ} = \tau_4 , \tag{20b}$$

$$\alpha_{VJ} = \langle(\omega^1_{0\alpha} + \omega^2_{0\alpha})^2 - \langle\omega^1_{0\alpha} + \omega^2_{0\alpha}\rangle^2\rangle . \tag{20c}$$

The following physical interpretation can be given to Eqs. (19) and (20): the band profile is determined either by a unique strongly coupled two-component process $(\omega^1_{0\alpha}, \omega^2_{0\alpha})$ (case $\tau_1 \ll \tau$, $\tau_2 \ll \tau$) or by two approximately independent processes $\omega^1_{0\alpha}$ and $\omega^2_{0\alpha}$ (case $\tau_1 \gg \tau$, $\tau_2 \ll \tau$). This situation is reflected in the structure of $G_i(t)$ containing, apart from trivial contributions, a single factor in the former and two in the latter case. $G_i(t)$ describes the spread of vibrational frequencies due to solvent-solute and rotation-vibration interactions, respectively. If this second interaction is small, i.e., if $C(\alpha) \to 0$, $I_0 \to I(r_0)$, $\alpha_J \to 0$, the well-known zero-order formula for $G_i(t)$ is easily obtained from (19) [compare with Eq. (11) of Ref. 3].

V. RELAXATION FUNCTION, ANISOTROPIC RAMAN SPECTRA

A. Order-of-magnitude estimation of τ_i's

The general properties of anisotropic Raman spectra of diatomic molecules dissolved in an inert solvent essentially depend on two physical parameters of the system under consideration—the moment of inertia $I(r)$ of the active molecule and the energy $V_s(r, t)$ of the solvent-solute interaction. If $I(r)$ and the nonradial component $V_n(r, t)$ of $V_s(r, t)$ are sufficiently small, the bands are broad and exhibit a characteristic three-component structure. The ratio between the peak intensity of the central component and those of the side wings varies greatly from one spectrum to another; most frequently, the central peak is more prominent here than in ir. The over-all half-width $\Delta\omega$ of these bands ranges, typically, from 100 to 400 cm^{-1}, and that of their central components is of the order of 5–50 cm^{-1}. In presence of such a band structure, choice of the characteristic time τ essentially depends on the purpose of the study one is concerned with. Accordingly, if a rough analysis of the band as a whole or a more precise study of its central component is required, τ will be calculated either from the over-all half-width $\Delta\omega$ of the band or from that of its central component; this gives τ's of the order of 10^{-13}–10^{-14} sec and 10^{-12}–10^{-13} sec, respectively. On the other hand the estimate of the correlation times τ_1, τ_2, τ_3 gives the values indicated in Sec. III A: $\tau_1 \sim 10^{-11}$ sec, $\tau_2 \sim 10^{-12}$–10^{-13} sec, $\tau_3 \sim 10^{-12}$–10^{-13} sec. Comparing these numbers one is led to the conclusion that the conditions $\tau_1 \gg \tau$, $\tau_2 \gg \tau$, $\tau_3 \gg \tau$ are adequate for reproducing, roughly, the over-all structure of anisotropic Raman bands of this class, but may be insufficient in certain cases for a detailed quantitative description of their fine structure.

If $I(r)$ and $V_s(r,t)$ are sufficiently large, the anisotropic Raman spectra have very different characteristics. The bands are moderately broad, symmetrical or slightly asymmetrical and generally structureless. Their half-widths $\Delta\omega$ are, typically, of the order of 50 cm^{-1}. The corresponding reference times $\tau = 1/\Delta\omega$ are of the order of 10^{-13} sec, larger than in the free-rotation limit. The estimation of the correlation times τ_1, τ_2, and τ_3 leads to the values given in Sec. III A: $\tau_1 \sim 10^{-11}$–10^{-13} sec, depending on the relative importance of the nonradial contribution to $\omega^1_{0\alpha}$, $\tau_2 \sim 10^{-13}$–10^{-14} sec, and $\tau_3 \sim 10^{-13}$–10^{-14} sec. These numbers indicate that the conditions $\tau_1 \gg \tau$, $\tau_2 \ll \tau$, $\tau_3 \ll \tau$ fit, approximately, the experimental data of this class of systems.

The intermediate situations are characterized by conditions $\tau_1 > \tau$, $\tau_2 \sim \tau$, $\tau_3 \sim \tau$ and often occur in practice. The anisotropic Raman spectra then have properties intermediate between those just cited.

B. Free-rotation limit $\tau_1 \gg \tau$, $\tau_2 \gg \tau$, $\tau_3 \gg \tau$

The calculation of $G_a(t)$ goes through the following steps. (i) Equation (8) is rewritten with $\omega^1_{0\alpha}(t) = \omega^1_{0\alpha}$, $\omega^2_{0\alpha}(t) = \omega^2_{0\alpha}$, $\omega^3(t) = \omega^3$. (ii) The averages over stochastic processes $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$ are made separately; this procedure is justified by the fact that $V_n(r,t)$ is small:

$$G_a(t) = |\langle 0|\beta^H(0)|\alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\langle\exp[-i\omega^1_{0\alpha}t]\rangle \times \langle[\exp(-i\omega^2_{0\alpha}t)][\tfrac{1}{4}+\tfrac{3}{4}\cos(2\omega^3 t)]\rangle . \tag{21}$$

(iii) The average over $\omega^1_{0\alpha}$ is performed by use of the cumulant expansion theorem, and that over $(\omega^2_{0\alpha}, \omega^3)$ by writing $\omega^2_{0\alpha} = -C(\alpha)\omega'^2$, $\omega^3 = \omega'$,

$$P(\omega') = \frac{I_0}{2kT}\,|\omega'|\exp\left(-\frac{I_0\omega'^2}{2kT}\right).$$

Then, combining points (i)–(iii) one is led to the following final result:

$$G_a(t) = |\langle 0|\beta^H(0)|\alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\left[\exp\left(\sum_{j=1}^{\infty}\alpha_j(-it)^j\right)\right]\left\{\frac{-1}{1-i4\beta_r C(\alpha)t}\left[\frac{1}{4}+\frac{3}{4}\,{}_1F_1\left(1,\ \frac{1}{2},\ \frac{-4\beta_r t^2}{1-i4\beta_r C(\alpha)t}\right)\right]\right\}. \tag{22}$$

This expression merits some comment. The correlation function $G_a(t)$ appears as a sum of two contributions. The comparison with Eqs. (13a) and (17) shows that, apart from the nonessential factor $\frac{1}{4}|\langle 0|\beta^H(0)|\alpha\rangle|^2$, the first term is just the correlation function of an isotropic Raman band. The second term is similar to, but not identical with, the correlation function of an ir band; the difference is (i) in the nonessential factor $\frac{3}{4}|\langle 0|\beta^H(0)|\alpha\rangle|^2$ and (ii) in the fact that the hypergeometric function ${}_1F_1$ depends on the argument $-4\beta_r t^2/1 - i4\beta_r C(\alpha)t$ in Raman and on the argument $-\beta_r t^2/1 - i4\beta_r C(\alpha)t$ in ir.[30] Thus the analysis given in Secs. III A and IV A can be reproduced word for word and does not need to be repeated here. In particular, if $C(\alpha) \to 0$, $I_0 \to I(r_0)$, $\beta_r \to \beta^0_r$, Eq. (22) reduces to the simple formula predicted by the zero-order theory [compare with Eqs. (11) and (15) of Ref. 3].

C. Rotational-diffusion limit $\tau_1 \gg \tau$, $\tau_2 \ll \tau$, $\tau_3 \ll \tau$

The calculation of $G_a(t)$ involves, in this limit, the following steps. (i) Equation (8) is rewritten with $\omega^1_{0\alpha}(t) = \omega^1_{0\alpha}$, $\omega^2_{0\alpha}(t)$, $\omega^3(t)$. (ii) Stochastic processes $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$ are considered to be noncorrelated; this assumption is justified by the fact that, in the present case, $\omega^1_{0\alpha}(t)$ and $(\omega^2_{0\alpha}(t), \omega^3(t))$ have very different modulation speeds:

$$G_a(t) = |\langle 0|\beta^H(0)|\alpha\rangle|^2 \exp(-i\omega^0_{0\alpha}t)\langle\exp(-i\omega^1_{0\alpha}t)\rangle \times\left\langle\left[\exp\left(-i\int_0^t \omega^2_{0\alpha}(t')\,dt'\right)\right]\times\left[\tfrac{1}{4}+\tfrac{3}{4}\cos\left(2\int_0^t \omega^3(t')\,dt'\right)\right]\right\rangle. \tag{23}$$

(iii) The averages over $\omega^1_{0\alpha}$ and $(\omega^2_{0\alpha}, \omega^3)$ are calculated, the former using the cumulant expansion theorem and the latter a theorem related to it.[31] Moreover, all terms of order higher than 2 are neglected in the series over $(\omega^2_{0\alpha}, \omega^3)$. It can be shown, in fact, that if $\tau_2 \ll \tau$, $\tau_3 \ll \tau$, they are much smaller than its first- and second-order terms; the proof is omitted here. (iv) $\omega^2_{0\alpha}(t)$ and $\omega^3(t)$ are taken to be Markovian-Gaussian and the corresponding correlation functions to be single exponentials.[27-29] Combining points (i)–(iv) the following result is obtained:

$$G_a(t) = |\langle 0|\beta^H(0)|\alpha\rangle|^2 \exp(-i\omega_{0\alpha}^0 t)\left[\exp\left(\sum_{j=1}^{\infty}\alpha_j(-it)^j\right)\right]\left(\exp\left\{iC(\alpha)\frac{2kT}{I_0}t + i^2\alpha_J\tau_J\left[\frac{t}{\tau_J}-1+\exp\left(\frac{t}{\tau_J}\right)\right]+i^2 3\alpha_R\tau_R\left[\frac{t}{\tau_R}-1+\exp\left(\frac{t}{\tau_R}\right)\right]\right\}\right). \quad (24)$$

Apart from the nonessential factor $|\langle 0|\beta^H(0)|\alpha\rangle|^2$, Eq. (24) differs from Eq. (15a) valid in ir in that α_R is replaced by $3\alpha_R$; this difference is easily explained by the elementary theory of rotational diffusion. The following interpretation can be given to (24). Two approximately independent processes, $\omega_{0\alpha}^1$ and $(\omega_{0\alpha}^2, \omega^3)$, determine the band shape. This situation is reflected in the structure of $G_a(t)$ containing, besides trivial contributions, two independent factors. The first of them, associated with $\omega_{0\alpha}^1$, describes the spread of vibrational frequencies due to V_s and the second, related to $(\omega_{0\alpha}^2, \omega^3)$, spectral manifestations of strongly perturbed rotations of a nonrigid rotator. If the rotation-vibration interaction is absent, i.e., if $C(\alpha)\to 0$, $I_0 \to I(r_0)$, $\alpha_J \to 0$, the well-known formula for $G_a(t)$ is easily obtained [compare with Eqs. (11) and (19) of Ref. 3].

VI. POSITION AND PROFILE OF SPECTRAL BANDS

A. Method of calculation

The method of calculating the position of spectral bands essentially depends on how the band center is defined. In what follows, the band center will be assumed to correspond to the first moment $(\omega_1)_0$ of the band. $(\omega_1)_0$ is simply related to the correlation function, e.g.,[9,19]

$$(\omega_1)_0 = i\,\frac{G'(0)}{G(0)}\,.$$

Thus the study of the influence of the rotation-vibration interaction on the band position reduces to the derivation of (13a), (15a), (17), (19), (20a), (22), and (24).

The calculation of the intensity-distribution function $I(\omega)$ is considerably more elaborate. According to (2), it involves Fourier transformation of the correlation functions (13a), (15a), (17), (19), (20a), (22), and (24). In the simplest cases, this can be done analytically: The results are shown in Tables II–IV. The calculation is facilitated by considering the following three points: (i) The Fourier transform of a product of two functions is given by the convolution integral over Fourier transforms of separate factors. (ii) In calculating the Fourier transform of (17) and those of (13a) and (22), with $\alpha_j = 0$, the order of integrations over ω' and t is interchanged. Treating the "functions" $\delta[f(x)]$ in the usual way,[32] one is easily led to the final result. (iii) In the case of rotational diffusion, i.e., (15a), (19), (20a) and (24), it is sufficient to consider that part of $G(t)$ corresponding to $t \gg \tau_J$, τ_{VJ} of τ_R; the short-time portion of these functions only affects $I(\omega)$ far in the wings. If the analytical treatment is impracticable, and this is the case for the majority of complicated situations, numerical integration remains necessary.

TABLE II. ir band profiles. The non-normalized band profiles of the $0 \to v_\alpha$ ir bands of solutions. The parameters $\beta_v = \alpha_2$, β_r, C, α_J, and α_R are defined in Eqs. (13a)–(13c) and (15a)–(15e) of the next text. Finally, $\theta(x)$ is the Heaviside step function $[\theta(x)=1, x\le 0$ and $\theta(x)=0, x>0]$ and $H(a,x)$ is the Voigt function $\{H(a,x) = (a/\pi)\int_{-\infty}^{\infty} e^{-t^2}dt/[(x-t)^2+a^2]\}$. All these expressions refer to the shifted band origin ω_c. In calculating $I(\Delta\omega)$ in the rotational diffusion limit, the short-time portion of $G(t)$ has been neglected.

Broadening mechanism	Profile $I(\omega-\omega_c) = I(\Delta\omega)$
Free classical rotation	$\frac{\pi}{4\beta_r C}\left[\theta\left(\Delta\omega-\frac{1}{4C}\right)\right]\left(\frac{1-(1-4C\Delta\omega)^{1/2}}{(1-4C\Delta\omega)^{1/2}}\right)\exp\left(\frac{-[1-(1-4C\Delta\omega)^{1/2}]^2}{16C^2\beta_r}\right)$
Rotational diffusion	$\frac{2(\alpha_R+\alpha_J)}{(\alpha_R+\alpha_J)^2+\Delta\omega^2}$
Rotational diffusion and $V_s(r,t)$	$\left(\frac{\pi}{\beta_v}\right)^{1/2} H\left(\frac{\alpha_R+\alpha_J}{2(\beta_v)^{1/2}}, \frac{\Delta\omega}{2(\beta_v)^{1/2}}\right)$

TABLE III. Isopropic Raman band profiles. The non-normalized band profiles of the $0 \rightarrow v_\alpha$ isotropic Raman bands of solutions. The parameters $\beta_v = \alpha_2$, β_r, C, α_J, and α_{JV} are defined in Eqs. (17), (19), and (20) of the text. $\theta(x)$ is the Heaviside step function, $H(x,a)$ the Voigt function, and Erfc(x) the complementary error function [Erfc$(x) = \int_x^\infty e^{-t^2} dt$]. All these expressions refer to the shifted band origin ω_c. In calculating $I(\Delta\omega)$ in the rotational-diffusion limit, the short-time portion of $G(t)$ has been neglected.

Broadening mechanism	Profile $I(\omega - \omega_c) = I(\Delta\omega)$
Free classical rotation	$\frac{\pi}{2\beta_r C}[\theta(\Delta\omega)] \exp\left(-\frac{\lvert\Delta\omega\rvert}{4\beta_r C}\right)$
Free classical rotation and $V_s(r,t)$	$\frac{\sqrt{\pi}}{2\beta_r C} \mathrm{Erfc}\left[\frac{1}{2(\beta_v)^{1/2}}\left(\Delta\omega + \frac{\beta_v}{2\beta_r C}\right)\right] \exp\left[\frac{1}{4\beta_r C}\left(\Delta\omega + \frac{\beta_v}{4\beta_r C}\right)\right]$
Rotational diffusion	$\frac{2\alpha_J}{\alpha_J^2 + \Delta\omega^2}$
Rotational diffusion and $V_s(r,t)$ [Eq. (20)].	$\frac{2\alpha_{VJ}}{\alpha_{VJ}^2 + \Delta\omega^2}$
Rotational diffusion and $V_s(r,t)$[Eq. (19)].	$\left(\frac{\pi}{\beta_v}\right)^{1/2} H\left(\frac{\alpha_J}{2(\beta_v)^{1/2}}, \frac{\Delta\omega}{2(\beta_v)^{1/2}}\right)$

B. ir spectra

The rotation-vibration coupling affects the band position and deforms its profile. It is never the principal shape-determining relaxation mechanism, but rather represents a secondary perturbing process. The band shift is equal to $-C(\alpha)(2kT/I_0)$ and does not depend on the nature of molecular rotations. The perturbation of the band profile, on the contrary, strongly depends on the nature of this motion; the following cases can be envisioned theoretically. (a) Rotation is similar to free rotation. The theory predicts that one of the two wings will become narrower and more intense and the other will become broader and less intense (compare with Table II and Fig. 2). The position of the gap between the two wings remains unchanged in spite of the over-all shift of the band; the rotation-vibration interaction is, in fact, inoperative at low rotational frequencies appearing around the gap. (b) Rotation is similar to rotational diffusion. The rotation-vibration interaction broadens the band but the increase of its half-width is quite small. Here again, this can be explained by the low angular velocities characterizing the rotational diffusion and making the rotation-vibration interaction ineffective. Different possible cases are illustrated in Table II and Fig. 3. (c) Rotations are of an intermediate type. The spectral perturbations are, qualitatively speaking, inter-

TABLE IV. Anisotropic Raman band profiles. The non-normalized band profiles of the $0 \rightarrow v_\alpha$ anisotropic Raman bands of solutions. The parameters $\beta_v = \alpha_2, \beta_r$, C, α_J, and α_R are defined in Eqs. (22) and (24) of the text. Finally, $\theta(x)$ is the Heaviside step function and $H(a,x)$ the Voigt function. All these expressions refer to the shifted band origin ω_c. In calculating $I(\Delta\omega)$ in the rotational-diffusion limit, the short-time portion of $G(t)$ has been neglected.

Broadening mechanism	Profile $I(\omega - \omega_c) = I(\Delta\omega)$
Free classical rotation	$\frac{1}{4}\left[\frac{\pi}{2\beta_r C}[\theta(\Delta\omega)] \exp\left(-\frac{\Delta\omega}{4\beta_r C}\right)\right]$ $+ \frac{3}{4}\left\{\frac{\pi}{4\beta_r C}\left[\theta\left(\Delta\omega - \frac{1}{C}\right)\right]\left(\frac{1-(1-C\Delta\omega)^{1/2}}{1-C\Delta\omega^{1/2}}\right) \exp\left[\frac{[1-(1-C\Delta\omega)^{1/2}]^2}{4C^2\beta_r}\right]\right\}$
Rotational diffusion	$\frac{2(3\alpha_R + \alpha_J)}{(3\alpha_R + \alpha_J)^2 + \Delta\omega^2}$
Rotational diffusion and $V_s(r,t)$	$\left(\frac{\pi}{\beta}\right)^{1/2} H\left(\frac{3\alpha_R + \alpha_J}{2(\beta_v)^{1/2}}, \frac{\Delta\omega}{2(\beta_v)^{1/2}}\right)$

mediate between those described in (a) and (b); see Fig. 4. The effects are complex, however, and escape a simple analysis. All these conclusions are in excellent agreement with the existing experimental material; see, e.g., Refs. 33–36.

C. Isotropic Raman spectra

The rotation-vibration coupling affects the position and the shape of isotropic Raman bands. According to circumstances, it may either be the principal shape-determining mechanism or represent a secondary perturbing process. The band shift is equal to $-C(\alpha)(2kT/I_0)$ and does not depend on the nature of molecular rotations. The perturbing effect of this interaction on the band profile is, on the contrary, strongly influenced by the precise nature of vibrational and rotational motions; the following cases can be envisioned theoretically. (a) Rotation is similar to free rotation. If the rotation-vibration interaction is the only relaxation mechanism available, this perturbation spreads an originally very narrow line into a strongly asymmetrical band. Compare with

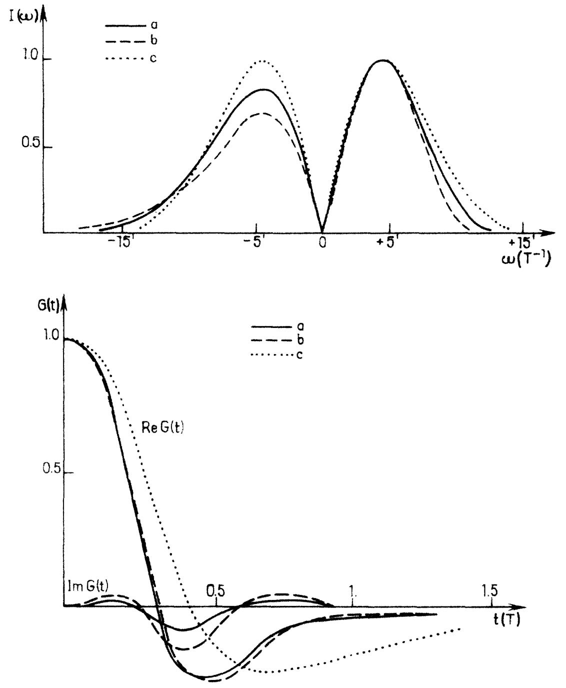

FIG. 2. Effect of the rotation-vibration coupling on ir spectra: free rotation, no vibrational broadening. Profiles a and b and the corresponding correlation functions are associated with the $0\rightarrow1$, $0\rightarrow2$ transitions perturbed by the rotation-vibration coupling, and curve c reproduces the same quantities in the absence of this perturbation. Calculations are made by use of Eq. (13) of the text [$\beta_r=10T^{-2}$; $C(\alpha)=0.01$, 0.02, $0T$]. T is measured in arbitrary time units.

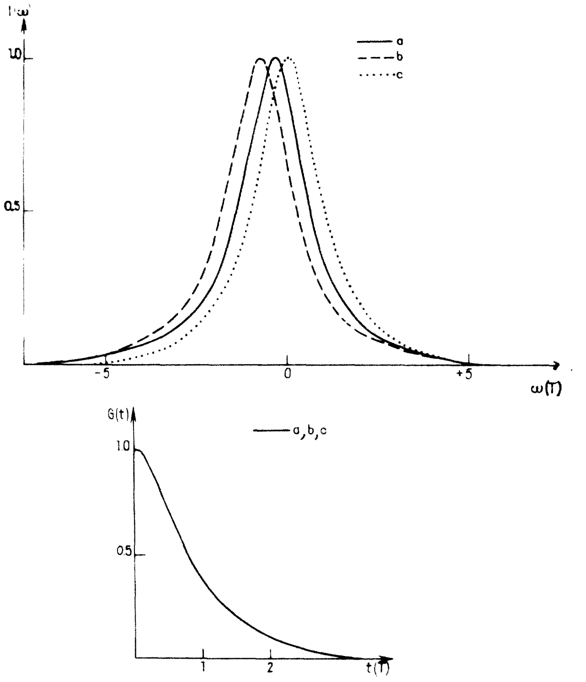

FIG. 3. Effect of the rotation-vibration coupling on ir spectra: rotational diffusion, no vibrational broadening. Profiles a and b and the corresponding correlation functions are associated with the $0\rightarrow1$, $0\rightarrow2$ transitions perturbed by the rotation-vibration coupling, and curves c repoduce the same quantities in the absence of this perturbation; the correlation functions refer to the shifted band origin. Calculations are made by using Eqs. (15) of the text [$\delta=(2kT/I_0)\,C(\alpha)=0.4$, 0.8, $0T^{-1}$; $\alpha_J=0.004$, 0.016, $0T^{-1}$; $\alpha_R=1T^{-1}$; $\tau_R=\tau_J=0.025T$].

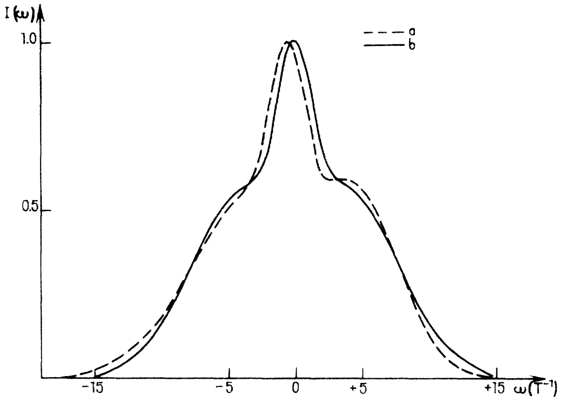

FIG. 4. Effect of the rotation-vibration coupling on ir spectra: intermediate rotations and vibrational broadening. Profile a shows spectral manifestations of the rotation-vibration coupling in the case of a $0\rightarrow1$ band. These effects are absent in profile b. The calculations are made by means of the superposition approximation (Ref. 2): $G(t)=(1-\xi)G_{FR}(t)+\xi G_{RD}(t)$; here $G_{FR}(t)$, $G_{RD}(t)$ are given by Eqs. (13) and (15), respectively. ($\xi=0.35$; $\alpha_2=0.5T^{-2}$; $\alpha_3=0.02T^{-3}$; $\beta_r=10T^{-2}$; $C(\alpha)=0.01$, $0T$; $\delta=0.4$, $0T^{-1}$; $\alpha_J=0.004$, $0T^{-1}$; $\alpha_R=1T^{-1}$; $\tau_J=\tau_R=0.025T$.)

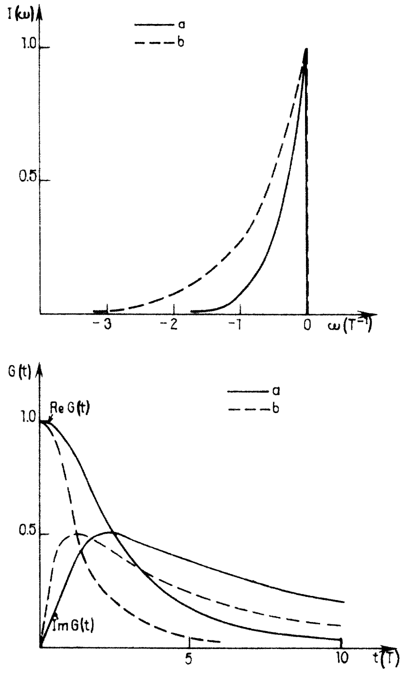

FIG. 5. Effects of the rotation-vibration coupling on isotropic Raman spectra: free rotation, no vibrational broadening. The profiles a and b and the corresponding correlation functions are associated with the $0 \rightarrow 1$, $0 \rightarrow 2$ isotropic Raman transitions perturbed by the rotation-vibration coupling. In the absence of this perturbation the band reduces to a δ function. Calculations are made by using Eq. (17) of the text ($\beta_r = 10T^{-2}$; $C(\alpha) = 0.01$, $0.02T$).

Table III and Fig. 5. The existence of the high-frequency edge in $I(\omega)$ is characteristic of theories treating molecular rotations classically. It disappears in more accurate quantum-mechanical theories, but this effect is not treated here. The symmetry of this band may be gradually restored by the presence of vibrational relaxation processes. Compare with Table III and Fig. 6. (b) Rotation is similar to rotational diffusion. If the solvent-solute interaction $V_s(r,t)$ is sufficiently large to transform free rotation to rotational diffusion, but small enough to keep slow vibrational relaxation processes, the band is strongly narrowed and becomes symmetrical. Its structure is entirely

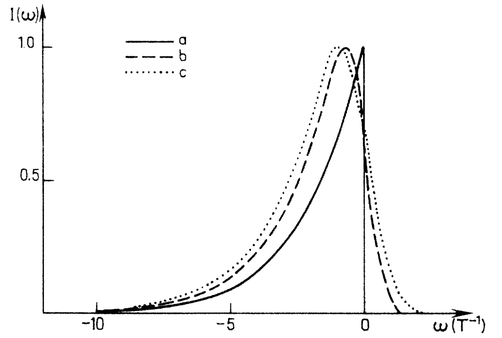

FIG. 6. Effect of the rotation-vibration coupling on isotropic Raman spectra: free rotation, vibrational broadening. The profiles a–c illustrate the increasing effect of vibrational relaxation. Calculations are made with the help of Eq. (17) of the text. ($\alpha_2 = 0$, 0.15, $0.30T^{-2}$; $\beta_r = 10T^{-2}$; $C = 0.05T$.)

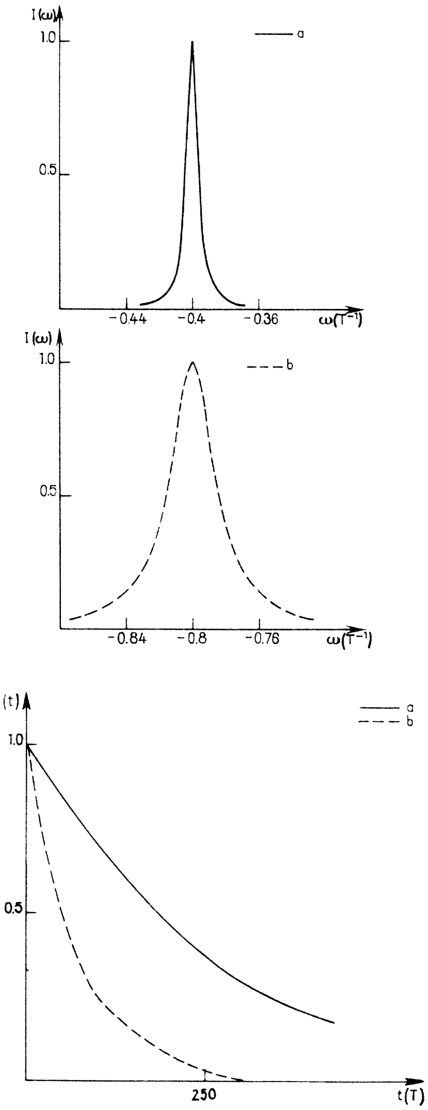

FIG. 7. Effect of the rotation-vibration coupling on isotropic Raman spectra: rotational diffusion, no vibrational broadening. The profiles a and b and the corresponding correlation functions are associated with the $0 \rightarrow 1$, $0 \rightarrow 2$ isotropic Raman transitions perturbed by the rotation-vibration coupling; the correlation functions refer to the shifted band origin. In the absence of this perturbation the band reduces to a δ function. Calculations are made using Eq. (19) of the text [$\delta = (2kT/I_0)$ $C(\alpha) = 0.4$, $0.8T^{-1}$; $\alpha_J = 0.004$, $0.016T^{-1}$; $\tau_J = 0.025T$].

generated by vibration-rotation interaction. Compare with Table III and Figs. 7 and 8. When $V_s(r, t)$ is further increased, the band is broadened again, but its detailed behavior depends on whether the modulation of $\omega_{0\alpha}^{1}(t)$ is fast or slow. In the former case the band remains narrow and symmetrical; in the latter case it is broadened and not necessarily symmetrical. Compare with Table III and Fig. 9. (c) Rotations are of an intermediate type. The spectral perturbations are, qualitatively speaking, intermediate between those described in (a) and (b). All these conclusions are in excellent overall agreement with the existing Raman data; see, e.g., Refs. 37–43.

D. Anisotropic Raman spectra

The rotation-vibration coupling affects the position and the shape of anisotropic Raman bands. Its perturbing action differs on the band center and on the wings, and cannot always be considered as a secondary one. The band shift is equal to $-C(\alpha)(2kT/I_0)$ and does not depend on the nature of molecular rotations. The perturbation of the band profile, on the contrary, strongly depends on the nature of this motion; the following cases

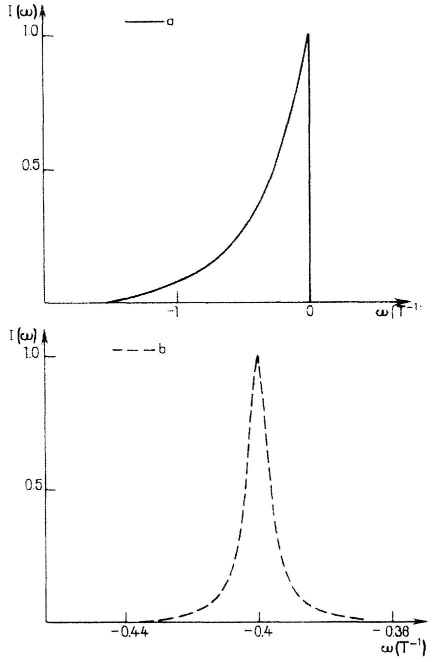

FIG. 8. Effect of the rotation-vibration coupling on isotropic Raman spectra. Illustration of the motion-narrowing effect. Calculations are made using Eqs. (17) and (19) of the text; compare with Refs. 15 and 16. [Free rotation limit, profile a: $\beta_r = 10T^{-2}$; $C(\alpha) = 0.01T^{-1}$. Rotational-diffusion limit, profile b: $\alpha_J = 0.004T^{-1}$; $\delta = 0.4T^{-1}$; $\tau_J = 0.025T$.]

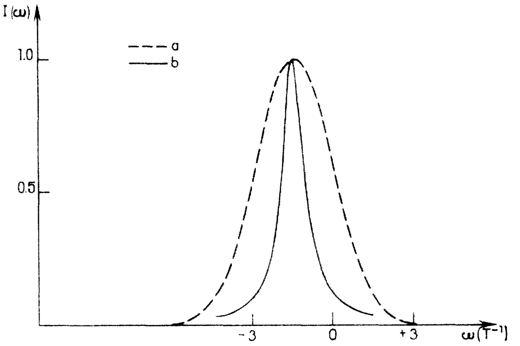

FIG. 9. Effect of the rotation-vibration coupling on isotropic Raman spectra: rotational diffusion, vibrational broadening. The mode of action of the vibrational perturbation depends on the modulation speed of $\omega_{0\alpha}^{1}(t)$; profile a corresponds to a slow modulation of $\omega_{0\alpha}^{1}(t)$ and profile b to a fast modulation. Calculations are made with the help of Eqs. (19) and (20) of the text. [Profile a: $\alpha_1 = -1T^{-1}$, $\alpha_2 = 1T^{-2}$; $\delta = (2kT/I_0)\ C(\alpha) = 0.4T^{-1}$; $\alpha_J = 0.004T^{-1}$; $\tau_J = 0.025T$. Profile b: $\alpha_1 = -1T^{-1}$; $\tau_{VJ} = 0.010T$; $\delta = 0.4T^{-1}$; $\alpha_{VJ} = 0.5T^{-1}$.]

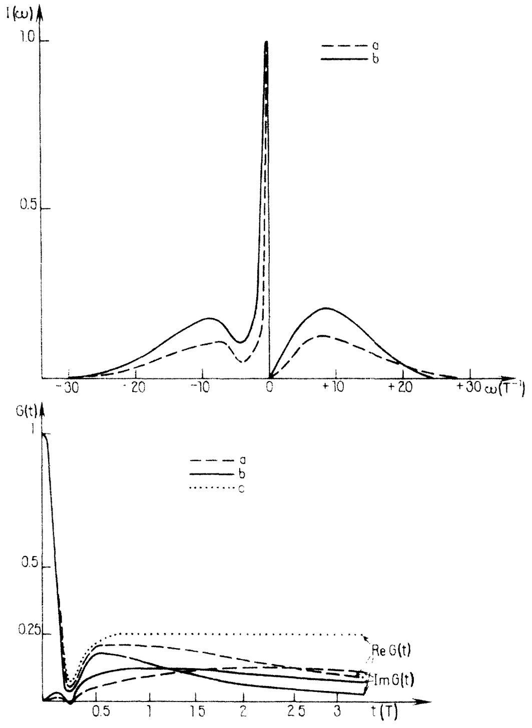

FIG. 10. Effect of the rotation-vibration coupling on anisotropic Raman spectra: free rotation, no vibrational broadening. Profiles a and b and the corresponding correlation functions are associated with the 0→1, 0→2 anisotropic Raman transitions perturbed by the rotation-vibration coupling. Curve c represents the correlation function in the absence of this perturbation; the corresponding theoretical profile is not calculated, as its central branch is a δ function ($\beta_r = 10T^{-2}$; $C(\alpha) = 0.01, 0.02, 0T$).

can be envisioned theoretically. (a) Rotation is similar to free rotation. If solvent-induced relaxation mechanisms are not operating, the rotation-vibration interaction spreads the originally very narrow central component into a strongly asymmetrical band; its behavior is essentially that of an isotropic Raman band. Furthermore, the coupling makes one of two wings narrower and more intense, and the other broader and less intense. Compare with Table IV and Fig. 10. If the solvent-induced relaxation mechanisms are operating, they may restore the symmetry of the central component; see Fig. 11. (b) Rotation is similar to rotational diffusion. The rotation-vibration interaction broadens the band, but the increase of its half-width is quite small; the explanation is the same as in Sec. VIB. Different possible cases are illustrated in Table IV and Fig. 12. (c) Rotations are of an intermediate type. The spectral perturbations are, qualitatively speaking, intermediate between those described in (a) and (b). Yet the difference in the evolution of the band center and of the wings, when going from the free rotation to the rotational-diffusion limits, must be stressed. All these conclusions are in excellent over-all agreement with the existing Raman data; see, e.g., Refs. 37–43.

E. Comments

The following comments can be made about the present theory. This theory can be viewed as representing a generalization of two sorts of theories. It introduces the rotation-vibration coupling effects into the elementary theories of the ir and Raman spectra of diatomic solutions.[1–10] On the other hand, this theory replaces, in the case of dilute solutions, the theories which have been proposed to describe the rotation-vibration coupling effects in the Raman spectra of dilute or moderately dense gases.[11–18] Many results of the moment-analysis theory[19] are also reproduced, although the theories are formally entirely different.

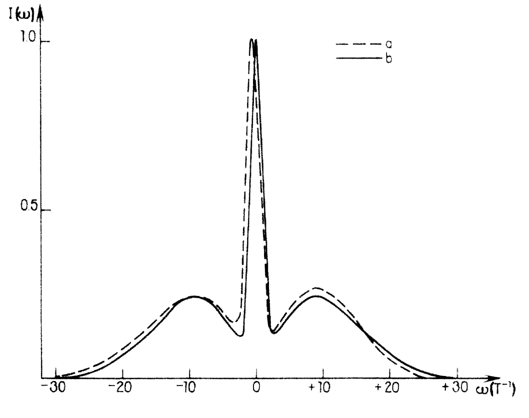

FIG. 11. Effect of the rotation-vibration coupling on anisotropic Raman spectra: free classical rotation and vibrational broadening. Profile a is associated with the $0 \rightarrow 1$ anisotropic Raman transition perturbed by the rotation-vibration interaction, and curve b reproduces the same quantities in the absence of this perturbation. The calculations are made by applying Eq. (22) of the text [$\alpha_2 = 0.5T^{-2}$; $\alpha_3 = 0.02T^{-3}$; $\beta_r = 10T^{-2}$; $C(\alpha) = 0.01, 0T$].

APPENDIX A

The purpose of this Appendix is to show that, if two classical dynamic variables $A(t)$, $B(t)$ contain very different frequencies in their Fourier expansion, their correlation is weak. The proof uses stochastic arguments and goes as follows. (i) Let $A(t)$, $B(t)$ be two stochastic functions, stationary over all time intervals of practical interest; for simplicity, they are assumed to be real and to

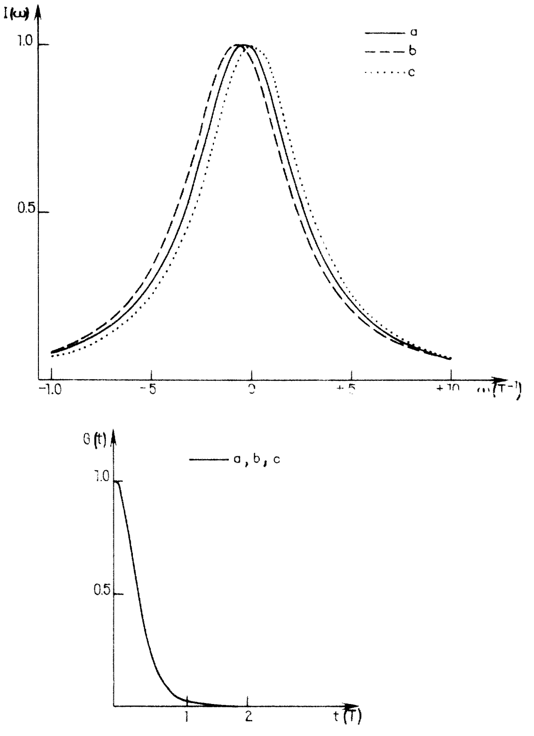

FIG. 12. Effect of the rotation-vibration coupling on anisotropic Raman spectra: rotational diffusion, no vibrational broadening. The profiles a and b and the corresponding correlation functions are associated with the $0 \rightarrow 1$, $0 \rightarrow 2$ anisotropic Raman transition perturbed by the rotation-vibration coupling, and curves c reproduce the same quantities in the absence of this perturbation; the correlation functions refer to the shifted band origin. Calculations are made with the help of Eq. (24) of the text [$\delta = (2kT/I_0)\ C(\alpha) = 0.4,\ 0.8,\ 0T^{-1}$; $\alpha_J = 0.004,\ 0.016,\ 0T^{-1}$; $\alpha_R = 1T^{-1}$; $\tau_J = \tau_R = 0.025T$].

have zero mean value. Their Fourier transforms are written $A[\omega]$, $B[\omega]$. (ii) The correlation functions involving $A(t)$, $B(t)$ are $G^{AA}(t) = \langle\langle A(t)A(0)\rangle\rangle$, $G^{AB}(t) = \langle\langle A(t)B(0)\rangle\rangle$, $G^{BA}(t) = \langle\langle B(t)A(0)\rangle\rangle$, $G^{BB}(t) = \langle\langle B(t)B(0)\rangle\rangle$. The Fourier transforms of $G^{AA}(t)$, $G^{AB}(t)$, $G^{BA}(t)$, $G^{BB}(t)$ are $G^{AA}[\omega]$, $G^{AB}[\omega]$, $G^{BA}[\omega]$, $G^{BB}[\omega]$. (iii) The stationary property of $A(t)$, $B(t)$ implies that the averaged products of Fourier components $A[\omega]$, $B[\omega]$ are related as follows (see Ref. 44):

$$\langle A[\omega]A[\omega']\rangle = G^{AA}[\omega]\delta(\omega+\omega'),$$

$$\langle A[\omega]B[\omega']\rangle = G^{AB}[\omega]\delta(\omega+\omega'), \text{ etc.}$$

Considering points (i)–(iii) and applying the Schwartz inequality gives the following estimate for $|G^{AB}(t)|$ [or $|G^{BA}(t)|$]:

$$|G^{AB}(t)| = \left|\int_{-\infty}^{\infty} G^{AB}[\omega]e^{-i\omega t}\,d\omega\right| = \left|\int_{-\infty}^{\infty}\langle A[\omega]B[-\omega]\rangle\, e^{-i\omega t}\,d\omega\right| \leqslant \int_{-\infty}^{\infty}|\langle A[\omega]B^*[\omega]\rangle|\,d\omega$$

$$\leqslant \int_{-\infty}^{\infty}(\langle A[\omega]A^*[\omega]\rangle\langle B[\omega]B^*[\omega]\rangle)^{1/2}d\omega \rightarrow |G^{AB}(t)| \leqslant \int_{-\infty}^{\infty}(G^{AA}[\omega]G^{BB}[\omega])^{1/2}d\omega\ .$$

Conclusions

If the overlap S between these subspaces of the ω space, in which $G^{AA}[\omega]$, $G^{BB}[\omega]$ are essentially nonvanishing, tends to zero, $G^{AB}(t)$ tends to zero as well; this also holds true for the correlation coefficient

$$r = \frac{G^{AB}(0)}{(G^{AA}(0)G^{BB}(0))^{1/2}}\ .$$

On the other hand, S will generally be small if $A(t)$, $B(t)$ have very different correlation times; thus in these circumstances the correlation between $A(t)$, $B(t)$ is weak.

APPENDIX B

The purpose of this Appendix is to rederive, by applying the method of Sec. II C, the slow- and fast-modulation conditions $(\langle\omega_1^2\rangle)^{1/2}\tau_1 \gg 1$, $(\langle\omega_1^2\rangle)^{1/2}\tau_1 \ll 1$ familiar, e.g., in the theory of NMR relaxation.[21,23] The derivation implies the following steps. (i) Let $G(t) = \langle\exp[-i\int_0^t \omega_1(t')\,dt']\rangle$ be the correlation function under study and τ, τ_1 the correlation times of $G(t)$, $\omega_1(t)$, respectively; for simplicity, one puts $\langle\omega_1\rangle = 0$. (ii) To express τ in terms of $\langle\omega_1^2\rangle$ and τ_1, one recalls that τ is that time for which the mean square deviation of the random function $\int_0^t \omega_1(t')dt'$ becomes comparable to unity. In the slow-modulation limit $\tau \gg \tau_1$, $\omega_1(t) \rightarrow \omega_1$, which gives

$$\left\langle\left[\int_0^{\tau}\omega_1(t)\,dt\right]^2\right\rangle = \langle\omega_1^2\rangle\tau^2 \sim 1 \rightarrow \tau \sim \frac{1}{(\langle\omega_1^2\rangle)^{1/2}}$$

$$\tau_1 \gg \tau \rightarrow \tau_1 \gg \frac{1}{(\langle\omega_1^2\rangle)^{1/2}} \rightarrow (\langle\omega_1^2\rangle)^{1/2}\tau_1 \gg 1. \quad \text{Q.E.D.}$$

In the fast-modulation limit $\tau_1 \ll \tau$ and over the major portion of the time interval of interest $(\tau_1 \ll t)$ this gives

$$\left\langle\left[\int_0^{\tau}\omega_1(t)\,dt\right]^2\right\rangle = \int_0^{\tau}\int_0^{\tau}\langle\omega_1(t)\omega_1(t')\rangle\,dt\,dt'$$

$$\simeq 2\langle\omega_1^2\rangle\tau\tau_1 \sim 1 \rightarrow \tau \sim \frac{1}{\langle\omega_1^2\rangle\tau_1}\ ,$$

$$\tau_1 \ll \tau \rightarrow \tau_1 \ll \frac{1}{\langle\omega_1^2\rangle\tau_1} \rightarrow (\langle\omega_1^2\rangle)^{1/2}\tau_1 \ll 1. \quad \text{Q.E.D.}$$

The conclusion is that, in the one-dimensional case, the existence of the conditions $\tau_1 \gg \tau$, $\tau_1 \ll \tau$ implies the existence of the conditions $(\omega_1^2)^{1/2}\tau_1 \gg 1$, $(\omega_1^2)^{1/2}\tau_1 \ll 1$.

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[20] In order to keep the terminology as close as possible to that generally adopted, the term "rotation-vibration interaction" refers, in this paper, exclusively to the interaction resulting from the r dependence of the moment of inertia $I(r)$ of the active molecule. For other types of interaction coupling vibrational and rotational motions see Ref. 24.

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[22] If greater accuracy is desired, the formulas given by J. L. Dunham [Phys. Rev. 41, 713 (1932), 713, 721] and R. M. Herman and S. Short [J. Chem. Phys. 48 1266 (1968); 50, 572 (1969) 572] can be used.

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[24] If r is the vibrational coordinate of the active molecule θ, ψ its polar coordinates, and $\vec{R}$ the ensemble of translational coordinates, the radial component $V_r(r,t)$ of $V_s(r,t)$ and its nonradial component $V_n(r,t)$ are generally given by the following definitions: $V_r(r,\vec{R}) = (1/4\pi) \times \int \int V_s(r,\theta,\psi,\vec{R}) \sin\theta\, d\theta\, d\psi$, $V_n(r,\theta,\psi,\vec{R}) = V_s(r,\theta,\psi,\mathrm{R}) - V_r(r,\vec{R})$. Correspondingly, $V_s(r,t) = V_s[r,\theta(t),\psi(t),\vec{R}(t)]$; $V_r(r,t) = V_r[r,\vec{R}(t)]$; $V_n(r,t) = V_n[r,\theta(t);\psi(t),\vec{R}(t)]$.

[25] If a more complete analysis is required, a more selective choice of the characteristic time τ is necessary. τ can be taken to be equal to $1/\Delta\omega$, where $\Delta\omega$ is the width of the narrowest spectral detail to be interpreted. The values $\tau \sim 10^{-13}$ sec are found in this way.

[26] $\langle e^{ix} \cos y\rangle = \langle [1 - ix + (i^2x^2/2!) + \cdots][1 - (y^2/2!) + \cdots]\rangle = 1 - i\langle x\rangle + (i^2/2!)\langle x^2\rangle + (i^2/2!)\langle y^2\rangle + \cdots = e^K \rightarrow K = -i\langle x\rangle + (i^2/2!)(\langle x^2\rangle - \langle x\rangle^2) + (i^2/2!)\langle y^2\rangle + \cdots$.

[27] This is the Doob theorem. A more accurate assumption is to take the vectors $[\omega_{0\,\alpha}^{\,2}(t), d\omega_{0\,\alpha}^{\,2}/dt]$, $[\omega^3(t), d\omega^3(t)/dt]$ to be Markovian-Gaussian and the corresponding correlation functions linear combinations of two exponentials (Refs. 28 and 29).

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[31] $\langle e^{ix}(\frac{1}{4} + \frac{3}{4}\cos 2y)\rangle = \langle [1 + ix + (i^2x^2/2!) + \cdots](\frac{1}{4} + \frac{3}{4} - \frac{3}{2}y^2 + \cdots)\rangle = 1 + i\langle x\rangle + (i^2/2!)\langle x^2\rangle + (3i^2/2)\langle y^2\rangle + \cdots \rightarrow e^K = -i\langle x\rangle + (i^2/2!)(\langle x^2\rangle - \langle x\rangle^2) + (3i^2/2)(\langle y^2\rangle) + \cdots$.

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