

Relaxation Processes and Molecular Motion in Liquids and Gases

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In this paper we extend the time correlation function approach to infrared absorption in an organic liquid or dense gas. We include an interaction energy (coupling) between the ir active vibrational mode and the coupled translational-rotational degrees of freedom to account for collision-induced de-excitation of the vibration (damping). The additional time dependence of the dipole correlation function is a damped exponential and modifies the line shape obtained by earlier treatments. The appearance of a damping term also changes the interpretation of the first few terms in the short-time expansion of the correlation function, which are related to the molecular moment of inertia and the mean-square torque. Our treatment is based on many-body perturbation theory (renormalization of the vibrational energy to second order in the coupling) and can be extended to more general cases.

I. INTRODUCTION

In this paper we extend the discussion of ir molecular absorption in terms of the dipole moment time-correlation function¹ to include the effect of damping of the excited vibrational state.

We take our system to consist of a large number of identical molecules and describe their motion in terms of their *coupled* rotational-translational degrees of freedom. For the sake of simplicity, we assume a single internal degree of freedom (a molecular vibration) which couples to the electric field of the probe beam. Due to the absorption of light from the probe beam, the equilibrium distribution of the system is perturbed. In any macroscopic system such as a liquid or gas, there will be some coupling of the perturbed mode to the other degrees of freedom (the collisions between molecules are not purely elastic), and the system will return to a new equilibrium distribution by redistributing the energy deposited into the vibrational excitation.² This coupling leads to a shift in the vibrational frequency and a line broadening.

In earlier treatments of the line shape of infrared absorption or emission¹ it was assumed that the final vibrational state was sharp, and the density of final states could be written in terms of a delta function expressing energy conservation between the initial and final states of the system. We will show that the inclusion of a coupling energy between the vibrational mode and the rotational-translational degrees of freedom for the molecular system leads to a change in the frequency of the vibrational mode. This effect is a familiar one in many-body theory, where it determines the effect of an interaction on the unperturbed energy levels of a system. The contribution of the coupling to the energy is commonly called self-energy, and the procedure of including its effect on the unperturbed energy spectrum, renormalization. In the situation under study here, the self-energy of the vibrational mode leads to a shift given by the real part of the self-energy [Eq. (10)], and a width proportional to its imaginary part [Eq. (10)], which is the width of the vibrationally excited state. The appearance of a width is directly responsible

for the finite lifetime of the molecular vibration and leads to damping of the vibration. In this manner, the inclusion of the coupling between the internal (vibrational) energy and the translational-rotational states describes the dissipative aspects of the time evolution of the system and leads to irreversibility.³ Physically, it is the interaction between molecules in the liquid in collision processes which leads to the time dependence of the dipole correlation function. The coupled rotational-translational part of the Hamiltonian describes dephasing (soft) collisions, which reorient the molecules without de-excitation. The coupling between rotational-translational states and the vibrational state accounts for de-excitation (energy transfer, strong collision). The analogy to the standard magnetic resonance relaxation times, T_2 and T_1 , our rotational dephasing time $\tau_R = 1/\Gamma_0$, and vibrational relaxation time $\tau_v = 1/\tilde{\gamma}$ is worth mentioning. In our model, we eventually separate the contribution from the soft and strong collisions and treat the time evolution associated with them as independent [Eq. (15)] on the assumption of weak coupling between the vibrational and the translational-rotational modes. A similar situation exists in many other examples of the interaction of a probe with a macroscopic system, and we are drawing on some of the techniques and results developed to describe the role of dissipation on the structure of the phonon spectrum in a crystal,³⁻⁸ observed by inelastic neutron scattering.

The main result of our treatment is the expression [Eq. (16)] for the normalized frequency spectrum of the absorbed light

$$I(\omega) = \int_{-\infty}^{\infty} \exp(-\tilde{\gamma} |t|) G^{(\text{rot})}(t) \exp[i(\omega - \bar{\Omega})t] dt,$$

where $\tilde{\gamma}$ is the mean width of the excited vibrational state, $\bar{\Omega} = \Omega + \delta$ is the mean renormalized vibrational frequency, and $G^{(\text{rot})}(t)$ is the rotational correlation function for the molecular dipole operator. As a consequence of the modified form for the frequency spectrum, the identification of the long time behavior of the time correlation function, obtained by Fourier inversion of the experimental spectrum, is changed. It now con-

tains contributions from the rotational reorientation due to rotational diffusion, as well as from vibrational relaxation (damping). We point out that we expect a Lorentzian line shape from our expression with a width equal to the sum of the widths due to rotational diffusion and vibrational relaxation. Additionally, in the identification of molecular parameters, such as the moment of inertia and the mean-square molecular torque from the short time behavior of the total correlation function, care has to be taken to separate the effects of damping from those of the molecular motion. We illustrate the possible effects of damping on the analysis of vibrational dipole correlation functions by a numerical example based on published data. If we assume, as was done by McClintock *et al.*,⁹ that the vibrational lifetime can be deduced from the additional spectral width of Raman scattered light compared to the Rayleigh width, we have an example of comparable magnitudes of the orientational and vibrational relaxation time. It would be desirable to experimentally confirm the deduced vibrational lifetime by direct measurement. In general, we expect vibrational lifetimes for many larger organic molecules in the range of 10^{-10} – 10^{-12} sec due to the larger number of intramolecular decay channels. Although we deal here with the specific case of vibrational–translation–rotational coupling for a single vibrational mode, our approach can be generalized to deal with more general dissipative mechanisms and different interactions (e.g., Raman scattering).

We mention here in passing, that our assumption of a single vibrational mode excited by the probing radiation and its coupling to only rotational–translational state is highly idealized. It can be expected to hold only for the simplest (diatomic) molecules. The extension of the method used to the more realistic case of relaxation by exciting other (lower) vibrational modes and transferring only part of the energy to rotational–translational degrees of freedom can be done by including additional degrees of freedom in the background modes $[\alpha]$.

II. INFRARED ABSORPTION BY A COUPLED MOLECULAR VIBRATION

We will confine ourselves to the simplest case containing the main features of interest. A system of N molecules with a single vibrational degree of freedom of frequency, Ω , which couples to the electromagnetic field (frequency $\omega \sim \Omega$) and weakly to the coupled rotational–translational states of the molecular system. The total Hamiltonian for the molecular system can be written

$$H_s = H_0 + H_v + \lambda V, \quad (1)$$

in which H_0 describes the energy of the coupled rotational–translational degrees of freedom of the system, H_v the energy in the vibrational mode, and λV describes the interaction energy of the coupling between the

eigenstates of H_0 and H_v and accounts for dissipative effects. The consequences of this coupling will be included to order λ^2 in our discussion of the renormalization of the phonon frequency Ω (weak coupling).

The interaction with the electromagnetic wave of the probe field is described in the standard dipole approximation

$$H_I = \sum_{i=1} (\epsilon \cdot p_i) (e^{-i\omega t} a + e^{i\omega t} a^\dagger), \quad (2)$$

with p_i the vibrational dipole operator for the i th molecule, and the free field Hamiltonian H_{rad} is taken to correspond to a single mode ω of the radiation field of polarization ϵ , in second quantized notation, with $\hbar = c = 1$:

$$H_{\text{rad}} = \omega a^\dagger a. \quad (3)$$

The Hamiltonian describing our total system of N molecules and the probe field is, therefore,

$$H_T = H_s + H_I + H_{\text{rad}}. \quad (4)$$

In the following, we will draw on some of the results of a paper by Brout,¹⁰ in which the effects of dissipative interaction on the line shape in emission are treated, in a way suggested by earlier work by Van Hove⁴ on the approach to statistical equilibrium in a system with a large number of degrees of freedom. The main consequence of size in such systems is the transition from a discrete to a quasicontinuous energy spectrum and the existence of a macroscopic number of states degenerate in energy, as well as weak matrix elements of residual interactions connecting these to any specific state of the system to which a transition may be induced by an external field. After computing the transition probability, we will convert it under certain approximations to a Fourier transform of the vibrational dipole operator correlation function.

Let us consider to first order, the effect of H_I on the state function $\psi(t)$ of the combined system at time t , corresponding to the removal of one photon from the probe field and creation of one vibrational excitation,

$$|\psi(t)\rangle = |\psi(0)\rangle + i \int_0^t dt' \exp[i(H_s + H_{\text{rad}})(t-t')] H_I \times \exp[i(H_s + H_{\text{rad}})t'] |\psi(0)\rangle. \quad (5)$$

We shall use the following notation to describe the eigenstates of the coupled system:

$$\phi([\alpha], N, n) = |[\alpha]; N; n\rangle. \quad (6)$$

The collective index $[\alpha]$ stands for a particular set of quantum numbers describing the coupled rotational–translational degrees of freedom, N and n enumerate the number of phonons and photons, respectively. We note that because of the dissipative term λV in H_s , the molecular time evolution operator $\exp(iH_s t')$ can connect different states $\langle [\alpha']; N' |, |[\alpha]; N \rangle$, and it is precisely this fact which leads to a shift in the phonon

frequency Ω and its smearing out over an energy range $\bar{\gamma}$ [corresponding to a finite lifetime $\tau \sim (1/\bar{\gamma})$]. Due to the coupling of the phonon to the residual degrees of freedom, the final state in the absorption is no longer sharp (we do not obtain a delta function response at the free-space phonon frequency), and we can no longer use the Gordon approach¹ directly. Instead, we insert complete sets of states between the time development operators and the interaction term in (4) and project the wavefunction unto a final state $\langle \psi_f |$:

$$\langle \psi_f | = \langle [\alpha_f]; N^f; n-1 |. \quad (7)$$

To find the transition amplitude from the initial (unperturbed) state $\psi(0)$ —we imagine the probe field turned on at $t=0$ —to the particular final state $\langle \psi_f |$, we set

$$\begin{aligned} T_{fi} &= \langle \psi_f | \psi(t) \rangle \\ &= (-i) \sum_{N'} \sum_{[\alpha], [\alpha']} \int_0^t dt' \langle [\alpha_f]; N^f | \exp[iH_s(t-t')] \\ &\quad \times | [\alpha]; N+1 \rangle \langle N+1; n-1 | H_I | N; n \rangle \\ &\quad \times \langle [\alpha]; N | \exp(iH_s t') | [\alpha']; N' \rangle \\ &\quad \times \langle [\alpha']; N'; n | \psi(0) \rangle \exp(i\omega t') \exp[i\omega(n-1)t]. \quad (8) \end{aligned}$$

In (8) we explicitly used the fact that H_I couples only the vibrational mode directly to the photon and perturbs the phonon population. The transitions occurring in the system under the action of the weak coupling term λV before and after the probe field interaction H_I are included in the matrix element

$$\langle [\alpha_f]; N^f | \exp[iH_s(t-t')] | [\alpha]; N+1 \rangle$$

and

$$\langle [\alpha]; N | \exp(iH_s t') | [\alpha']; N' \rangle.$$

It is the existence of these energy conserving processes which, as stressed by Van Hove,³ lead to dissipation and irreversibility.

Expansion of these matrix elements leads to the approximate expression, valid to second order in λ ,³

$$\begin{aligned} &\langle [\alpha_f]; N^f | \exp[iH_s(t-t')] | [\alpha]; N+1 \rangle \\ &= \exp\{i[\Omega + \Sigma(\alpha_f)](t-t')\} \\ &\quad \times \langle [\alpha_f]; N^f-1 | \exp[iH_s(t-t')] | [\alpha]; N \rangle, \\ \Sigma(\alpha_f) &= \delta(\alpha_f) + i\gamma(\alpha_f). \quad (9) \end{aligned}$$

The self-energy of the phonon $\Sigma(\alpha_f)$ and its real and imaginary parts, the shift $\delta(\alpha_f)$ and width $\gamma(\alpha_f)$, are defined by

$$\begin{aligned} \delta(\alpha_f) &= \lambda^2 \sum_{\alpha''; N''} \{ P\{ | \langle \alpha_f; N^f | V | \alpha''; N'' \rangle |^2 / [E_{\alpha_f} - E_{\alpha''} + \Omega(N^f - N'')] \} \\ &\quad - P\{ | \langle \alpha_f; N^f-1 | V | \alpha''; N'' \rangle |^2 / [E_{\alpha_f} - E_{\alpha''} + \Omega(N^f - N'' - 1)] \} \}, \\ \gamma(\alpha_f) &= \pi\lambda^2 \sum_{\alpha''; N''} [| \langle \alpha_f; N^f | V | \alpha''; N'' \rangle |^2 \delta(E_{\alpha_f} + \Omega(N^f - N'')) \\ &\quad - | \langle \alpha_f; N^f-1 | V | \alpha''; N'' \rangle |^2 \delta(E_{\alpha_f} - E_{\alpha''} + \Omega(N^f - N'' - 1))] \quad (10) \end{aligned}$$

and describe the difference in renormalization of the state of the system corresponding to N^f and N^f-1 phonons and the set of quantum numbers $[\alpha_f]$ from the ensemble of rotational-translational states. As pointed out in Ref. 10, the quantities defined in (9) introduce a *complex* phase shift in the transition amplitude and lead to a shift in the phonon frequency and the appearance of a width. In order to find the transition probability for the absorption process, we form the absolute square of T_{fi} and sum over final states of the molecular system since we do not observe them. We obtain for the transition probability for absorption $P_{N \rightarrow N+1}(\omega; t)$

$$\begin{aligned} P_{N \rightarrow N+1}(\omega; t) &= \sum_{[\alpha_f], N^f} | T_{fi} |^2 = \sum_{\alpha_f, \alpha'} \sum_{\alpha'', \alpha'''} \sum_{N', N''} \sum_{N'''} \int_0^t dt' \int_0^t dt'' U^*(\alpha_f, N^f-1 \leftarrow \alpha, N; t-t') m^* \cdot \epsilon \\ &\quad \times U^*(\alpha, N \leftarrow \alpha', N'; t') \langle \alpha', N', n | \psi(0) \rangle \langle \psi(0) | \alpha'', N'', n' \rangle U(\alpha'', N'' \leftarrow \alpha'', N; t'') m \cdot \epsilon \\ &\quad \times U(\alpha'', N \leftarrow \alpha_f, N^f-1; t-t'') \exp\{i[\omega - \Omega'(\alpha_f)](t-t'') - \gamma(\alpha_f)(2t-t'-t'')\}. \quad (11) \end{aligned}$$

Here, we have introduced the abbreviations

$$\begin{aligned} U(\alpha, N; \alpha', N'; t) &= \langle \alpha; N | \exp(-iH_s t) | \alpha'; N' \rangle, \\ n^{1/2} m(0) \cdot \epsilon &= \langle N+1; n-1 | H_I | N; n \rangle, \\ \Omega'(\alpha_f) &= \Omega + \delta[\alpha_f] \quad (12) \end{aligned}$$

for the time-evolution operator U , the phonon-photon transition matrix element in the molecular rest system $m(0)$, which changes the phonon population at time t' and the renormalized phonon frequency Ω' . The phonon-photon transition matrix element has been normalized to unit photon flux. We recognize the operator $|\psi(0)\rangle\langle\psi(0)|$

as the density matrix for the initial state of the total system (molecules plus radiation field), and on the basis of the standard assumption of uncorrelated states (random phases for the different state vectors composing it), we obtain

$$\langle [\alpha']; N'; n | \psi(0) \rangle \langle \psi(0) | [\alpha'']; N''; n' \rangle = \delta_{\alpha'\alpha''} \delta_{N'N''} \delta_{nn'} P_{\alpha'; N'; n} \quad (13)$$

with $P_{\alpha'; N'; n}$ the equilibrium probability of the state vector $|[\alpha']; N'; n\rangle$. Performing the sum over $[\alpha_f]$, $N^f - 1$ by closure after replacing $\delta(\alpha_f)$, $\gamma(\alpha_f)$ by their ensemble average values $\bar{\delta}$, $\bar{\gamma}$, as they are slowly varying functions of $[\alpha_f]$ near the equal energy surface in phase space $[E_{\alpha_f} + (N^f - 1)\Omega] = (E_{\alpha} + N^f\Omega)$, we reduce (11) to the form

$$P_{N \rightarrow N+1}(\omega; t) = \int_0^t dt' \int_0^t dt'' \sum_{[\alpha']; N'} P_{\alpha'; N'; n} \langle [\alpha']; N' | m^*(t'') \cdot \epsilon m(t') \cdot \epsilon | [\alpha']; N' \rangle \\ \times \exp[i(\omega - \bar{\Omega})(t' - t'')] \exp[-\bar{\gamma}(2t - t' - t'')], \\ m(t') \cdot \epsilon = \exp(-iH_0 t') H_I \exp(iH_0 t'). \quad (14)$$

We have introduced the mean renormalized phonon frequency $\bar{\Omega} = \Omega + \bar{\delta}$ and used closure on the sums over $[\alpha'']$, $[\alpha''']$, N'' . We now eliminate the coupling between the set of rotational-translational modes $[\alpha']$ and the phonons on the basis of the weak coupling hypothesis by approximating

$$\sum_{[\alpha']; N'} P_{[\alpha']; N'} \langle [\alpha']; N' | m^*(t'') \cdot \epsilon m(t') \cdot \epsilon | [\alpha']; N' \rangle = P_N \exp(-\bar{\gamma} | t'' - t' |) \sum_{[\alpha']} P_{[\alpha']} \langle [\alpha'] | (m(t'' - t') \cdot \epsilon)_0, \\ (m(0) \cdot \epsilon)_0 | [\alpha'] \rangle = P_N \exp(-\bar{\gamma} | t'' - t' |) \text{Tr}[\rho_0 (m^*(t'' - t') \cdot \epsilon)_0 (m(0) \cdot \epsilon)_0]. \quad (15)$$

Here $(m(t) \cdot \epsilon)_0 = \exp(iH_0 t) m(0) \cdot \epsilon \exp(-iH_0 t)$, and P_N is the probability for the state with N phonons,

$$\rho_0 = \sum_{[\alpha']} P_{[\alpha']} | [\alpha'] \rangle \langle [\alpha'] |$$

is the equilibrium density matrix for the coupled rotational-translational degrees of freedom alone, and we have used the invariance of the trace under time displacement (ergodic hypothesis). The factor $\exp(-\bar{\gamma} | t'' - t' |)$ accounts for the probability of decay of the vibrational state,¹¹ and $\text{Tr}[\rho_0 (m^*(t'' - t') \cdot \epsilon)_0 (m \cdot \epsilon)_0]$ is the rotational correlation function $G^{(\text{rot})}(t'' - t')$ used by Gordon¹ for the nondissipative case. It describes the time evolution of the transition-dipole operator under the action of H_0 alone since we have accounted for the damping term by extracting $\exp(-\bar{\gamma} | t'' - t' |)$. In accordance with our weak coupling hypothesis, this crucial step amounts to treating the collisions, which lead to the two types of processes considered (orientational dephasing and rotational-vibrational coupling) as *independent*, and the motion corresponding to them as uncorrelated. In a calculation going beyond this decoupling approximation, one would have to keep the correlations between the parts of the density matrix corresponding to these two processes (in the intermediate region, collisions can contribute to both mechanisms). The extension to this case would seem to be most conveniently done in a density matrix approach,¹² working directly with the equation of motion for ρ , the total density matrix, and decoupling in higher order. We hope to return to this extension in future work.

We now substitute (15) into (13) and obtain the transition probability (frequency spectrum) for absorp-

tion by the molecular system

$$P_{N \rightarrow N+1}(\omega; t) = P_N \int_0^t dt' \int_0^t dt'' \exp(-\bar{\gamma} | t'' - t' |) \\ \times G^{(\text{rot})}(t'' - t') \exp[i(\omega - \bar{\Omega})(t' - t'')] \\ \times \exp\{-2\bar{\gamma}[t - (t' + t'')/2]\}. \quad (14')$$

Introducing new integration variables $\tau = t' - t''$; $T = (t' + t'')/2$ and letting $t \rightarrow \infty$, we obtain our final result for the frequency distribution of the absorption spectrum $I(\omega)$:

$$I_N(\omega) = \frac{P_N}{2\bar{\gamma}} \int_{-\infty}^{\infty} d\tau \exp(-\bar{\gamma} | \tau |) \\ \times G^{(\text{rot})}(\tau) \exp[i(\omega - \bar{\Omega})\tau]. \quad (16)$$

We note in (16), that the center of the line has been displaced by $\bar{\delta}$ from the free-space vibrational frequency Ω and that the purely rotational correlation function for the motion of the vibrational transition dipole moment is modified by the damping factor $\exp(-\bar{\gamma}\tau)$, which refers to the loss processes introduced by the coupling. We will discuss this additional structure of the correlation function and its effect on the interpretation of experimental absorption spectra in the next section.

III. RELAXATION INFORMATION IN THE FREQUENCY SPECTRUM

As pointed out by Gordon,¹ Fourier analysis of the frequency distribution of the absorption or Raman spectrum allows the construction of the correlation function of the appropriate operator, to which the perturbing lightwave couples. For absorption (emission)

by a vibrational mode, the appropriate operator is the matrix element of the transition dipole operator $m(0)$ defined in the molecular rest system. Its time evolution is determined by molecular rotation and it is possible to differentiate two distinct time regimes, in which the molecular motion can be pictured in a straightforward manner. For very short times, one can expand the correlation function as a power series in t and relate its first few coefficients to molecular properties such as moments of inertia and mean molecular torques. For very long times, the path of the normalized transition moment on the surface of the unit sphere can be simulated by a stochastic process and leads to exponential decay (rotational diffusion¹³). The intermediate time regime involves complicated paths for the motion and eludes a simple dynamical description.

The construction of the short- and long-time rotational correlation function by Gordon¹ from various absorption and Raman spectra published in the literature, was a major step in coordinating different sets of data and contributed greatly to the unification of information on rotational molecular motion from seemingly disparate data on Raman spectra and absorption spectra as well as nuclear quadrupole relaxation times.

Although some reference is made in Gordon's work to the occurrence of vibrational frequency shifts and ensuing complications in the construction of the correlation function, the coupling of the perturbed mode to background modes is not considered. Inclusion of this coupling, which is invariably present in any large system, necessarily leads to some damping and consequently information concerning the relaxation of the system to equilibrium *must* be contained in the experimental spectrum.⁹ This is the central point of this paper. The calculations in Ref. 1 were based on the assumption of infinitely long-lived states for the infrared active vibrations, equivalent to δ functions in the density of states. The broadening of the line shape studied experimentally is then due *only* to rotational diffusion (the loss of information due to successive dephasing of the induced transition moment caused by reorientation of the molecule in soft collisions) such that the resulting Lorentzian linewidth reflects only this aspect of molecular motion. The presence of a large number of interacting molecules and the resulting quasi-continuous energy spectrum inevitably leads to dissipation, an aspect of the irreversible return to equilibrium of macroscopic collections of particles. We have included this effect by allowing for an interaction energy (coupling) between the phonon and the residual degrees of freedom of the system (de-excitation of the molecular vibration by strong collisions). Our final formula (16) contains, therefore, both the finite lifetime of the excited vibrational state due to its interaction with the medium, as well as a level shift, and the rotational dephasing of the correlation function $G^{\text{rot}}(l''-l') = \langle m^{*}(l''-l') \cdot m(0) \rangle$. We now demonstrate how the form

of Eq. (15) allows the extraction of information on the dominant relaxation in a straightforward manner. We start by Fourier inverting (15) and normalizing by dividing by

$$G^{\text{rot}}(0) = \frac{\tilde{\gamma}}{P_N} (2\pi)^{-1} \int_{-\infty}^{\infty} I(\omega) d\omega,$$

$$\frac{G^{\text{rot}}(\tau) \exp(-\tilde{\gamma}\tau)}{G^{\text{rot}}(0)} = g^{\text{rot}}(\tau) \exp(-\tilde{\gamma}\tau)$$

$$= \int_{-\infty}^{\infty} \exp[-i(\omega - \bar{\Omega})\tau] I(\omega) d\omega \bigg/ \int_{-\infty}^{\infty} I(\omega) d\omega. \quad (17)$$

We also have for the normalized correlation function

$$g^{\text{rot}}(\tau) = \langle m^{*}(\tau) \cdot m(0) \rangle / \langle m^{*}(0) \cdot m(0) \rangle. \quad (18)$$

The angle brackets in (18) indicate averaging over the ensemble of coupled rotational-translational states (eigenstates of H_0) only. For short times, we use the classical expansion

$$g^{\text{rot}}(\tau) = 1 - a\tau^2 + b\tau^4 \dots, \quad (19)$$

where a , b are related to the molecular moment of inertia I and the mean-square molecular torque $\langle (OV)^2 \rangle$ by

$$a = kT/I,$$

$$b = \frac{1}{3}(kT/I)^2 + (24I^2)^{-1} \langle (OV)^2 \rangle, \quad (20)$$

as shown by Gordon.¹ The appearance of the damping factor $\exp(-\tilde{\gamma}\tau)$ modifies the expansion and leads to reinterpretation of the molecular properties derived by neglecting dissipative effects. The effective coefficients of the τ^2 and τ^4 terms, a' and b' , are now given by

$$a' = a + (\tilde{\gamma}^2/2), \quad b' = b + a(\tilde{\gamma}^2/2) + (\tilde{\gamma}^2/4) \quad (21)$$

and will lead to considerable changes in the calculated molecular moment of inertia and mean-square torque if $\tilde{\gamma}^2/2$ is of comparable magnitude to a and $a\tilde{\gamma}^2/2$ comparable to b .

Turning to long times, where rotational diffusion is assumed to be a valid description of the time evolution of the correlation function, we find

$$\lim_{\tau \rightarrow \infty} g^{\text{rot}}(\tau) \exp(-\tilde{\gamma}\tau)$$

$$= \exp[-(\Gamma_0 + \tilde{\gamma})\tau]$$

$$= \int_{-\infty}^{\infty} \exp[-i(\omega - \bar{\Omega})\tau] I(\omega) d\omega \bigg/ \int_{-\infty}^{\infty} I(\omega) d\omega. \quad (17')$$

The resulting line shape is still Lorentzian and corresponds to a total width at half-maximum Γ ($\tau_R = 1/\Gamma_0$ is the rotational dephasing time),

$$\Gamma = \Gamma_0 + \tilde{\gamma}, \quad (22)$$

reflecting the independence of the two broadening

mechanisms—rotational diffusion and relaxation—in our model.

If we use Fig. 3 from Ref. 1 for the dipole correlation function of liquid methane at 98°K, we find: $a' = 1.16 \times 10^{26} \text{ sec}^{-2}$; $b' = 1.04 \times 10^{52} \text{ sec}^{-4}$, and $(\Gamma_0 + \bar{\gamma}) = 5.55 \times 10^{11} \text{ sec}^{-1}$. Although we do not have a value for $\bar{\gamma}$ in CH_3 from independent measurements, we will take an average vibrational relaxation time from a recent measurement,⁹ $\bar{\gamma} \simeq 10^{11} \text{ sec}^{-1}$. This would reduce the deduced rotational width by 20% ($\Gamma_0 = 4.55 \times 10^{11} \text{ sec}^{-1}$) but would have a very small effect ($\sim 0.01\%$) on the calculated moment of inertia as $\bar{\gamma}^2/2 \ll a$. Note, however, should the phonon lifetime decrease by an order of magnitude, its effect on the calculated molecular moment of inertia would increase rapidly. In practice, we can directly extract the various parameters a , b , $\bar{\gamma}$, and Γ_0 by using the experimentally determined total correlation function $\exp(-\bar{\gamma}\tau) g^{(\text{rot})}(\tau) = C(t)$ and fitting it for both short and long times.

If we consider the limiting cases of $\tau_r = 1/\bar{\gamma} \ll 1/\Gamma_0$, we note that the rotational correlation function will be close to one, and a logarithmic plot of $C(t)$ should directly reveal the linewidth $\bar{\gamma}$ as the slope of the resulting straight line. In this case, no information concerning molecular reorientation can be inferred from the spectrum as the rapid decay of the excited phonon prevents the dephasing mechanism of the dipole moment to come into play. For the opposite case of $\Gamma_0 \gg \bar{\gamma}$, the treatment of Ref. 1 is relevant as the damping factor is of order 1 and rotational diffusion predominates. The intermediate case $\Gamma_0 \sim \bar{\gamma}$ is the one of greatest interest and can reasonably be expected to occur in many organic molecules. It is in this case, that our approach is directly applicable and allows the determination of the dominant relaxation rate responsible for dissipative broadening.

IV. DISCUSSION AND POSSIBLE APPLICATIONS

We have shown how to formulate the problem of the absorption of infrared radiation by a single vibrational mode in a system of interacting molecules. The many-body nature of the problem leads to the appearance of a level shift and linewidth (due to the uncertainty in the phonon eigenfrequency), which crucially affects the frequency distribution of the absorbed light. Our result is expressed in terms of the rotational correlation function of the dipole operator of the infrared active vibration and a damping term, which accounts for the finite lifetime of the phonon due to its coupling to the rotational-translation degrees of freedom.

Our formalism can be readily extended to treat light scattering^{9,14} (i.e., the Raman process), and the interaction of other probe fields (particle beams) with elementary excitations (excitons, phonons, magnons, etc.) in molecular systems, in which residual interactions lead to coupling between the particular excita-

tion perturbed by the probe field and the background modes, provided the coupling energy is small compared to the energy of the excitation. Important information about relaxation phenomena and their rates due to energy transfer, nonradiative decay, and vibrational-rotational coupling can thus be obtained directly from absorption measurements and light scattering. We intend to return to these subjects in a future publication.

APPENDIX

The contribution of dissipative processes to line broadening can be obtained differently from the renormalization viewpoint of the paper by a straightforward phenomenological extension of Gordon's¹¹ treatment. We start with the expression for the frequency distribution of the absorption spectrum with the argument of the delta function being complex rather than real as in Gordon's approach. The presence of a finite imaginary part in the argument of the delta function removes the characteristic singularity and leads to a function of finite width in frequency space. We, therefore, must replace Gordon's energy-conserving delta function by the following expression:

$$\Delta(\omega - z) = (1/\pi) \{ \text{Im}z / [(\omega - \text{Re}z)^2 + (\text{Im}z)^2] \}, \quad (\text{A1})$$

recognizing that in the limit of $\text{Im}z \rightarrow 0$ this reduces to the Dirac delta function $\delta(\omega - \text{Re}z)$. We, therefore, have

$$I_N(\omega) = P_N \sum_{i,f} \rho_i \langle i | \epsilon \cdot m^* | f \rangle \langle f | \epsilon \cdot m | i \rangle \times \Delta(\omega_f - \omega_i - \omega + \Omega + \Sigma), \quad (\text{A2})$$

where ω is the frequency of the radiation, Ω is the vibrational frequency in the absence of coupling, and $\Sigma = \bar{\delta} + i\bar{\gamma}$ (assumed to be the same for all states) contains the effect of coupling and leads to a linewidth $\bar{\gamma}$ and vibrational frequency shift $\bar{\delta}$. We obtain for $I_N(\omega)$ using the renormalized phonon frequency $\bar{\Omega} = \Omega + \bar{\delta}$,

$$I_N(\omega) = P_N \int_{-\infty}^{\infty} dt \exp[-i(\omega - \bar{\Omega})t - \gamma |t|] \times \sum_{i,f} \rho_i \langle i | \epsilon \cdot m^* | f \rangle \langle f | \exp(i\omega_f t) \epsilon \cdot m \exp(-i\omega_i t) | i \rangle, \quad (\text{A3})$$

where we have Fourier transformed the Lorentzian using Cauchy's theorem. This led to the appearance of the absolute value of time $|t|$ in the damping term.

Since the states $|f\rangle$ and $|i\rangle$ are eigenfunctions of the translational-rotational Hamiltonian H_0 , we can write

$$I_N(\omega) = P_N \int_{-\infty}^{\infty} dt \exp[-i(\omega - \bar{\Omega})t - \bar{\gamma} |t|] \times \sum_{i,f} \rho_i \langle i | \epsilon \cdot m^* | f \rangle \langle f | \exp(iH_0 t) \epsilon \cdot m \exp(-iH_0 t) | i \rangle. \quad (\text{A4})$$

The time evolution of the molecular dipole moment

$m(0)$ in the presence of a coupling λV is given by

$$m(t) = \exp[i(H_0 + \lambda V)t]m(0) \exp[-i(H_0 + \lambda V)t]. \quad (\text{A5})$$

Since we have already included the coupling by re-normalizing the vibrational energy in a phenomenological way, we will neglect the effect of λV in $m(t)$. The shift $\bar{\Omega} - \Omega = \bar{\delta}$ and width $\bar{\gamma}$ represent corrections to the vibrational frequency and must, therefore, be proportional to even powers of λV , i.e., are at least of order λ^2 . The processes neglected in the time evolution of $m(t)$ correspond to the coupled motion through λV of the translational-rotational and vibrational degrees of freedom. The substitution of the uncoupled rotational correlation function

$$G^{(\text{rot})}(t) = \sum_i \rho_i \langle i | [\epsilon \cdot m(t)]_0 [\epsilon \cdot m^*(0)]_0 | i \rangle$$

with

$$[\epsilon m(t)]_0 = \exp(iH_0 t) [\epsilon \cdot m(0)]_0 \exp(-iH_0 t)$$

for the correlation function

$$G(t) = \sum_{i,N} \rho_{i,N} \langle i, N | \epsilon \cdot m(t) \epsilon \cdot m^*(0) | i, N \rangle$$

in the presence of coupling

$$\{m(t) = \exp[i(H_0 + \lambda V)t]m(0) \exp(-iH_0 + \lambda V)t\}$$

is equivalent to the decoupling approximation made in Eq. (15) in Sec. II. Within this approximation we finally arrive at

$$I_N(\omega) = P_N \int_{-\infty}^{\infty} dt \exp[-i(\omega - \bar{\Omega})t - \gamma |t|] G^{(\text{rot})}(t) \quad (\text{A6})$$

corresponding to Eq. (16) in Sec. II.

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Dilute Solution Theory of Polymer Crystal Growth: A Kinetic Theory of Chain Folding

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A kinetic theory of polymer crystallization from dilute solution is formulated for linear chain molecules of finite molecular weight (monodisperse). Two models of crystal growth are considered; both are essentially "regular" chain folding type models. Formulas for the crystal growth rates are derived as a function of the fundamental rate constants associated with the various states of molecular crystallization. These rate constants are evaluated as a function of polymer concentration, molecular weight, crystallization temperature, and crystal thickness. Consideration of finite molecular weight molecules requires an understanding of how these molecules are incorporated into the crystal and what happens to chain ends. Attention is focused on these problems and a description of how "cilia" are formed in polymer crystals is given. A remarkable aspect of cilia formation is that the uncrystallized portion of a chain molecule which dangles in the solution can participate in nucleating a new growth strip (fold plane) on the crystal face—a kind of "self-nucleating" mechanism.

I. INTRODUCTION

Linear chain molecules crystallize from dilute solution in the form of thin lamellae, or plates, which usually have well-defined crystallographic features.¹⁻⁴ Electron and low angle x-ray diffraction studies have shown that solution grown polymer crystals are typically about 100 Å thick and that the chains are oriented with their molecular axes perpendicular to the basal plane of the lamella. Since the crystal is composed of

chain molecules with lengths which may exceed by many times the crystal thickness, the conclusion is drawn that a chain molecule must traverse the lamella several times and in the process it must "fold" back on itself. The chain folding phenomena has been observed in a wide variety of synthetic organic polymers,^{1,5} as well as macromolecules of biological interest⁶⁻⁹ and at least one inorganic polymer (selenium).¹⁰

The concept of chain folding, a revolutionary idea less than 15 years ago, is now widely accepted as a