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Raman scattering from pure liquids. Theory of band profiles

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A theory is presented to analyze the Raman scattering from liquids formed by diatomic molecules. This theory is based on the fact that the Hamiltonian of a liquid sample is invariant under the operations of the full N-symmetric group. This symmetry entirely determines the structure of the theory; it is applicable for all vibrational-modulation speeds. Moreover, the notion of coherence and incoherence of a light scattering process is examined. One finds that the isotropic Raman process is partially coherent, and the anisotropic Raman scattering is basically an incoherent process.

I. INTRODUCTION

A considerable interest has been manifested the last few years in studying Raman-band profiles of pure liquids; for review articles on this subject, see Refs. 1 and 2. This difficult problem involves the study of collective vibrational-rotational motions extending over large portions of the macroscopic sample; the complexity of the theoretical analysis increases by an order of magnitude when going from dilute solutions to pure liquids. The early work in this field is due to Valiev,[3] Vincent-Geisse,[4] Döge,[5,6] and Tokuhiro and Rothschild.[7] More recently, the following three directions of investigation have been explored: (i) The theories proposed by Oxtoby,[1,8] Oxtoby, Levesque, and Weis[9] and Levesque, Weis, and Oxtoby[10] are based on the generalized cumulant expansion theorem for noncommuting operators. In principle, these theories are fully quantum mechanical although, in practice, averaging over rotational and translational degrees of freedom is classical; computer simulation may be used for that purpose. (ii) The theories due to Madden and Lynden-Bell,[11] and Lynden-Bell,[12,13] either employ the Redfield equation familiar in nuclear magnetic resonance or apply methods derived from it. In these theories, the vibrational dynamics is described with the help of quantum mechanics whereas the bath dynamics is simulated by stochastic models. (iii) Finally, the theories by Wang,[14,15] Wertheimer,[16-18] and Knauss[19] are based on the Zwanzig-Mori theory of Brownian motion; some of them are fully quantum mechanical and the others analyze vibrational motions quantum mechanically and rotational-translational motions classically. It results from this investigation that vibrational relaxation in liquids is due to three main mechanisms: the environmental fluctuations of vibrational frequency, the resonant transfer of vibrational energy, and population changes. Unfortunately, at the present time, the theory of vibrational relaxation in liquids is only established in its fast modulation limit; this contrasts with the situation in dilute solutions for which an analysis is available for all modulation speeds.

The purpose of this paper is to reexamine the Raman scattering from a diatomic-molecule liquid, the simplest representative molecular system of interest. The theory employs symmetry arguments, the Hamiltonian of a liquid sample being invariant under permutations of identical molecules. This symmetry entirely determines the structure of the theory which is applicable for all modulation speeds. Moreover, the notion of coherence of a light scattering process is carefully examined and is compared to that of a neutron scattering process. It results from the present theory that the isotropic Raman process is partially coherent, and the anisotrpic Raman scattering is a basically incoherent, process. For a preliminary account of this work, see Ref. 20.

II. BASIC FORMULATION

A. Description of the model

The system under investigation is a liquid containing N identical, diatomic molecules. The following model is used to investigate its optical behavior: (i) The molecules in the liquid are executing anharmonic vibrations described by the free-molecule normal coordinate $n=(n_1,n_2,\ldots,n_N)$. They are perturbed by a stochastic potential $V(n,t)$ expressing molecular interaction and the Hamiltonian is

$$\begin{aligned}H(n,t)&=\left(\tfrac{1}{2}\sum_{i=1}^{N}p_i^2+\tfrac{1}{2}\sum_{i=1}^{N}\lambda_i n_i^2+\tfrac{1}{6}\sum_{i=1}^{N}\mu_i n_i^3\right)+\left(\sum_{i=1}^{N}V_i(t)n_i+\tfrac{1}{2}\sum_{ij=1}^{N}V_{ij}(t)n_in_j+\tfrac{1}{6}\sum_{ijk=1}^{N}V_{ijk}(t)n_in_jn_k\right)\\&=H^{(0)}(n)+V(n,t)\,.\end{aligned}\tag{1}$$

The terms $V_i(t)$, $V_{ii}(t)$, $V_{iii}(t)$ provide the coupling between vibrations of a molecule and the bath whereas the terms $V_{ij}(t)$ describe the resonant coupling between them. (ii) The molecules in the liquid are executing stochastic reorientations described by $\theta=(\theta_1, \theta_2, \ldots, \theta_N)$, the ensemble of angular coordinates of the individual molecules. (iii) The correlation between vibrations and rotations is weak. (iv) There is no collision-induced scattering. For the justification of this type of approach see, e.g., Ref. 21.

B. Description of the scattering process

Once the basic properties of the model have been chosen, the formulas relating the isotropic and the anisotropic Raman differential cross sections to appropriate correlation functions must be presented. If, as usual, the $\vec{k}$-dependent spectral features are neglected, one can write

$$\left(\frac{\partial^2\sigma}{\partial\omega\,\partial\Omega}\right)_{\text{iso}}=\frac{1}{2\pi}k_s^4\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\sum_{ij}\langle a_{0i}^{(0)}(0)a_{0j}^{(0)}(t)\rangle\,, \tag{2a}$$

$$\left(\frac{\partial^2\sigma}{\partial\omega\,\partial\Omega}\right)_{\text{ani}}=\frac{1}{2\pi}k_s^4\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\sum_{ij}\langle a_{0i}^{(2)}(0)a_{0j}^{(2)}(t)\rangle\,. \tag{2b}$$

In these equations the $a_{0i}^{(j)}$'s are components of the standard irreducible tensorial sets associated with $\vec{\alpha}_i$, the polarizability tensor of molecule i. These equations only apply if the difference between the external and the internal Maxwellian electric fields is sufficiently small; unfortunately, this assumption is heavily restrictive for polar systems.

C. Coherence and incoherence

Microscopic properties of the scattered light are only partially under the experimentalist's control. This is due, not only to the fact that the microscopic properties of the incident radiation may not be completely known, but also to the impossibility of preparing the scattering system in a well defined quantum state. While the first difficulty may be overcome by employing a laser source, the second is intrinsically unavoidable and imposes the scattered electric field to be considered as a statistical object defined by an ensemble of correlation functions

$$\langle E_s^*(\vec{r}_1t_1)E_s^*(\vec{r}_2t_2)\cdots E_s^*(\vec{r}_mt_m)E_s(\vec{r}_{m+1}t_{m+1})\cdots E_s(\vec{r}_nt_n)\rangle\,, \tag{3}$$

where the variable $E_s(\vec{r}_it_i)$ represents the magnitude of the scattered electric field at $\vec{r}_i, t_i$. This sort of description is required, not only in the present problem, but also in many other problems in optics. For example, second-order correlation functions permit the description of the conventional interference experiments and of the power spectrum of a stationary electromagnetic field whereas higher-order correlation functions are needed in more sophisticated experiments such as the Hanbury-Brown-Twiss experiment. For a detailed discussion, see the textbooks by Born and Wolf[22] and by Crosignani, di Porto and Bertolotti.[23]

On the other side, it is convenient in the present context to consider the liquid sample as an optical source, each molecule representing an elementary radiatior. Its optical properties can, in turn, be related to its physical properties. Then, (i) applying the electromagnetic theory of retarded potentials, (ii) writing $\vec{\alpha}(\vec{r},t)=\sum\vec{\alpha}_i(\vec{r},t)$ where $\vec{\alpha}(\vec{r},t)$ is the total polarizability density at $\vec{r},t$ and $\vec{\alpha}_i(\vec{r},t)$ the contribution to $\vec{\alpha}(\vec{r},t)$ due to molecule i, and (iii) designating by $\vec{\epsilon}_I, \vec{\epsilon}_S$ the unit vectors along the directions of the incident and scattered electric fields, the optical properties of the source can be specified by the ensemble of correlation functions

$$\langle[\vec{\epsilon}_I\vec{\alpha}_{i_1}(\vec{r}_1t_1)\vec{\epsilon}_s][\vec{\epsilon}_I\vec{\alpha}^*_{i_2}(\vec{r}_2t_2)\vec{\epsilon}_j]\cdots[\vec{\epsilon}_I\vec{\alpha}^*_{i_m}(\vec{r}_mt_m)\vec{\epsilon}_s][\vec{\epsilon}_I\vec{\alpha}_{i_{m+1}}(\vec{r}_{m+1}t_{m+1})\vec{\epsilon}_s]\cdots[\vec{\epsilon}_I\vec{\alpha}_{i_n}(\vec{r}_nt_n)\vec{\epsilon}_s]\rangle\,. \tag{4}$$

It is usual to discuss the coherence and incoherence of an optical source by applying the following definitions. An optical source is said to be incoherent if all elementary radiators composing it are statistically independent; it is said to be coherent if there is a fixed phase relation between the wavelets emitted by them.

This general theory can now be applied to the calculation of the differential scattering cross section of a Raman process; in that case, only one- and two-particle second-order polarizability density correlation functions are required. Then, if the source is completely incoherent in the sense defined above, all distinct pair-correlation functions

$$\langle[\vec{\epsilon}_I\vec{\alpha}_i(\vec{r},t)\vec{\epsilon}_s][\vec{\epsilon}_I\vec{\alpha}_j(\vec{r}',t')\vec{\epsilon}_s]\rangle$$

vanish as the averaging over each factor may be performed separately; the distinct pair-correlation functions $\langle\alpha_i(0)\alpha_j(t)\rangle$ and $\langle\vec{\beta}_i(0)\vec{\beta}_j(t)\rangle$ of Eqs. (2a) and (2b) vanish in consequence. It then seems reasonable to call incoherent a Raman process such that distinct pair-correlation functions vanish for all times and to call it partially coherent otherwise. This definition will be retained in what follows.

III. CALCULATION OF CORRELATION FUNCTIONS

A. General considerations

The calculation of the isotropic and anisotropic Raman-band profiles requires, according to Eqs. (2a) and (2b), separate determinations of the correlation functions $\langle a_{0i}^{(0)}(0)a_{0j}^{(0)}(t)\rangle$ and $\langle a_{0i}^{(2)}(0)a_{0j}^{(2)}(t)\rangle$. A convenient procedure consists of (i) developing $a_{0i}^{(0)}$, $a_{0j}^{(0)}$, $a_{0i}^{(2)}$, $a_{0j}^{(2)}$ into Taylor series in the normal coordinates n_i, n_j of molecules, i, j and (ii) of considering the fact that the $a_{0i}^{(0)}$'s, $a_{0j}^{(0)}$'s are invariant under rotations of the molecular frames whereas the $a_{0i}^{(2)}$'s, $a_{0j}^{(2)}$'s undergo a linear transformation with coefficients given by the elements of the Wigner rotation matrix $D^{(2)}(\theta)$. Then, taking the symmetry of the linear rotators into account, the following formulas are readily derived:

$$\left(\frac{\partial^2\sigma}{\partial\omega\,\partial\Omega}\right)_{\mathrm{iso}}=\frac{1}{2\pi}k_s^4\int_{-\infty}^{\infty}dt\,e^{-i\omega t}G^{(0)}(t), \tag{5a}$$

$$\left(\frac{\partial^2\sigma}{\partial\omega\,\partial\Omega}\right)_{\mathrm{ani}}=\frac{1}{2\pi}k_s^4\int_{-\infty}^{\infty}dt\,e^{-i\omega t}G^{(2)}(t), \tag{5b}$$

$$G^{(0)}(t)=\left(\frac{\partial a^{(0)}}{\partial n}\right)_0^2\sum_{ij}\langle n_i(0)n_j(t)\rangle, \tag{5c}$$

$$G^{(2)}(t)=\left(\frac{\partial a^{(2)}}{\partial n}\right)_0^2\sum_{ij}\langle n_i(0)D_{00}^{(2)}(\theta_i(0))n_j(t)D_{00}^{(2)}(\theta_j(t))\rangle\,. \tag{5d}$$

A further simplification of the theoretical description may be obtained by using the assumption of the present model according to which vibrational and rotational motions are only weakly correlated. Then, the four-variable two-time correlation functions of Eq. (5d) may be presented, in the lowest-order approximation, as products of two-variable correlation functions involving either n_i's or $D_{00}^{(2)}(\theta_i)$'s, but not n_i's and $D_{00}^{(2)}(\theta_i)$'s simultaneously; for the discussion of higher-order effects, see Section III D below. The following important intermediate result is obtained in this way:

$$G^{(0)}(t)=\left(\frac{\partial a^{(0)}}{\partial n}\right)_0^2\sum_{ij}\langle n_i(0)n_j(t)\rangle, \tag{6a}$$

$$G^{(2)}(t)=\left(\frac{\partial a^{(2)}}{\partial n}\right)_0^2\sum_{ij}\langle n_i(0)n_j(t)\rangle\langle D_{00}^{(2)}(\theta_i(0))D_{00}^{(2)}(\theta_j(t))\rangle \tag{6b}$$

The problem thus reduces to a separate determination of the vibrational and rotational correlation functions $\langle n_i(0)n_j(t)\rangle$ and $\langle D_{00}^{(2)}(\theta_i(0))D_{00}^{(2)}(\theta_j(t))\rangle$. It should also be noted that, *a priori*, $G^{(2)}(t)$ appears as a sum of products of vibrational and rotational factors rather than a product of a single-vibrational and a single-rotational correlation function, found in dilute solutions; compare with the paper by Bratos and Maréchal.[24]

B. Vibrational correlation functions

1. Symmetry considerations

The exact Hamiltonian of a liquid sample is invariant under permutations of two, three, or several molecules, i.e., under the operations of the full N-symmetric group. This is also true for the approximate Hamiltonian of Eq. (1) as well as for the probability densities $p(R_1^{(1)}\theta_1^{(1)}R_2^{(1)}\theta_2^{(1)}\ldots R_N^{(1)}\theta_N^{(1)},t_1)$, $p(R_1^{(1)}\theta_1^{(1)}R_2^{(1)}\theta_2^{(1)}\ldots R_N^{(1)}\theta_N^{(1)},t_1;R_1^{(2)}\theta_1^{(2)}R_2^{(2)}\theta_2^{(2)}\ldots R_N^{(2)}\theta_N^{(2)},t_2)$, etc. The potential $V(n,t)\equiv V(n,\theta(t),\vec{R}(t))$ entering into $H(n,t)$ is stochastic through the time dependence of $\theta(t)$, $\vec{R}(t)$ and not through its functional form. The existence of these symmetry elements simplifies the calculations to an extent which makes the problem accessible to mathematical analysis.

2. Equation of motion for $n_i(t)$

The basic problem to examine is that of the vibrational dynamics of a set of N-coupled vibrators evolving in a spatially and temporally disordered medium. Its counterpart in an ordered crystalline phase has been carefully examined by Born and Huang, Davydov, and many others. It is convenient to start by writing the Heisenberg equations of motion for the variables n_i. Then, (i) choosing a basic set of vibrational wave functions $|s\rangle$ of $H(0)$, $s=0,1,2\ldots,N$, such that $|0\rangle$ describes the ground vibrational states, whereas $|s\rangle$ for $s\neq0$ denotes a state in which the sth molecule is monoexcited, (ii) constructing column matrices A_i, $i=1,2,\ldots,N$, where $(A_i)_s=(n_i)_{0s}$, $s=1,2,\ldots,N$, (iii) defining a $N\times N$ frequency matrix where $\hbar\Omega_{st}=V_{st}(n,t)-\delta_{st}V_{00}(n,t)$, $s,t=1,2,\ldots,N$, and (iv) suppressing all matrix elements which connect vibrational states of different degrees of excitation, there results

$$\begin{aligned}\frac{dn_i}{dt}=\frac{i}{\hbar}[H,n_i]&\Rightarrow\frac{d}{dt}(n_i)_{s0}=\frac{i}{\hbar}\sum_t[H_{st}(n_i)_{t0}-(n_i)_{s0}H_{00}]=i\omega_0(n_i)_{s0}+i\sum_t\Omega_{st}(n_i)_{t0}\\&\Rightarrow\frac{dA_i(t)}{dt}=i[\omega_0I+\Omega(t)]A_i(t)\Rightarrow A_i(t)=e^{i\omega_0t}\,\exp_0\left(i\int_0^t d\tau\,\Omega(\tau)\right)A_i(0)\,.\end{aligned} \tag{7}$$

In this equation, ω_0 is the vibrational frequency of the free molecule, the ordered exponential prescribes a chronological ordering and depends on a matrix argument. The energy relaxation processes have been eliminated by neglecting the matrix elements $V_{0s}(n,t)$; this is allowed in the present case since the excited vibrational levels are widely separated. Then, using Eq. (7) it is easy to express the vibrational correlation functions in terms of appropriate matrix elements of the ordered exponential. Since in all cases of practical interest only the ground vibrational states is thermally populated, the component $\langle n_i(0)n_j(t)\rangle_{\omega_0}$ of $\langle n_i(0)n_j(t)\rangle$ describing a fundamental transition can be written in the form

$$\begin{aligned}\langle n_i(0)n_j(t)\rangle_{\omega_0} &= \sum_s \langle [n_i(0)]_{0s}[n_j(t)]_{s0}\rangle \\ &= [n_i(0)]_{0i}[n_j(0)]_{j0} \\ &\quad\times e^{i\omega_0 t}\left\langle \exp_0\left(i\int_0^t d\tau\,\Omega(\tau)\right)_{ij}\right\rangle . \qquad (8)\end{aligned}$$

3. *Frequency matrix and its properties*

The results of the preceding analysis by no means represent the decisive step in the present calculation; handling ordered exponentials is difficult and not easily practicable. In fact, the decisive element of this theory is provided by the symmetry arguments enumerated in Sec. III B 1; the following statements relating to the frequency matrix $\Omega(t)$ can easily be proved. (i) All diagonal elements of the matrices $\langle\Omega(t)\rangle$, $\langle\Omega(t)\Omega(t')\rangle$, $\langle\Omega(t)\Omega(t')\Omega(t'')\rangle,\ldots$ are equal to each other and all nondiagonal elements are equal too. This can be understood intuitively by noticing that all molecules, or all pairs of molecules, or all triples of molecules, etc.... play the same role on the average. More formally, the n-time probability densities $p(\vec{R}_1^{(1)}\theta_1^{(1)},\vec{R}_2^{(1)}\theta_2^{(1)},\ldots\vec{R}_N^{(1)}\theta_N^{(1)},t_1;\vec{R}_1^{(2)}\theta_1^{(2)},\vec{R}_2^{(2)}\theta_2^{(2)}\ldots\vec{R}_N^{(2)}\theta_N^{(2)},t_2;\ldots\vec{R}_1^{(n)}\theta_1^{(n)},\vec{R}_2^{(n)}\theta_2^{(n)}\ldots\vec{R}_N^{(n)}\theta_N^{(n)},t_n)$ are invariant under the operations of the full N-symmetric group, which justifies the above statement. (ii) The matrices $X,Y\cdots$ having all diagonal elements equal and all nondiagonal elements equal have a number of remarkable mathematical properties. It can be easily seen that the linear combinations $\lambda X+\mu Y$, the product XY, and the inverse X^{-1} conserve this property and that X and Y commute. Moreover, these matrices can always be diagonalized whatever their order may be; two different eigenvalues exist, a nondegenerate eigenvalue $X_{11}+(N-1)X_{12}$ and a $(N-1)$-fold degenerate eigenvalue $X_{11}-X_{12}$, where N is the order of the matrix; the transformation matrix does not depend on the particular values of the matrix elements. One concludes that the averaged frequency matrix and averaged products of it are comparatively simple objects; their simplicity may be exploited as follows.

4. *Averaging over the process $\theta(t)$, $\vec{R}(t)$ and final formulas*

Averaging of the ordered exponential of Eq. (8) over the stochastic process $\theta(t)$, $\vec{R}(t)$ can most conveniently be carried out by applying the cumulant expansion technique; see the papers by Kubo[25] and Van Kampen.[26] The application of these techniques is particularly simple in the present case where all operators commute after averaging. Thus generalized cumulants may be replaced by ordered cumulants and ordered exponentials by ordinary exponentials. Then, diagonalizing all $N\times N$ matrices, the following final result is obtained:

$$\langle n_i(0)n_i(t)\rangle = \frac{1}{N}|(n_1)_{01}|^2 e^{i\omega_0 t}[e^{\lambda_1(t)}+(N-1)e^{\lambda_2(t)}]\,, \tag{9a}$$

$$\langle n_i(0)n_j(t) = \frac{1}{N}|(n_i)_{01}|^2 e^{i\omega_0 t}(e^{\lambda_1(t)}-e^{\lambda_2(t)}),\quad i\neq j \tag{9b}$$

$$\begin{aligned}\lambda_1(t) = {}& i\int_0^t dt'[\langle\Omega_{11}(t')\rangle+(N-1)\langle\Omega_{12}(t')\rangle] \\ &+ i^2\int_0^t dt'\int_0^{t'} dt''\{\langle\Delta\Omega_{11}(t')\Delta\Omega_{11}(t'')\rangle \\ &\qquad + (N-1)[\langle\Delta\Omega_{11}(t')\Delta\Omega_{12}(t'')\rangle+\langle\Delta\Omega_{12}(t')\Delta\Omega_{11}(t'')\rangle+\langle\Delta\Omega_{12}(t')\,\Delta\Omega_{12}(t'')\rangle] \\ &\qquad + (N-1)(N-2)\langle\Delta\Omega_{12}(t')\Delta\Omega_{13}(t'')\rangle\}+\cdots\,,\end{aligned} \tag{10a}$$

$$\begin{aligned}\lambda_2(t)=i\int_0^t dt'[\langle\Omega_{11}(t')\rangle-\langle\Omega_{12}(t')\rangle]\\ +i^2\int_0^t dt'\int_0^{t'} dt''[\langle\Delta\Omega_{11}(t')\Delta\Omega_{11}(t'')\rangle-\langle\Delta\Omega_{11}(t')\Delta\Omega_{12}(t'')\rangle-\langle\Delta\Omega_{12}(t')\Delta\Omega_{11}(t'')\rangle\\ -(N-1)\langle\Delta\Omega_{12}(t')\Delta\Omega_{12}(t'')\rangle-(N-2)\langle\Delta\Omega_{12}(t')\Delta\Omega_{13}(t'')\rangle]+\cdots\,.\end{aligned} \tag{10b}$$

In these equations, $\Delta\Omega_{ij}=\Omega_{ij}-\langle\Omega_{ij}\rangle$. It can easily be shown that $\lambda_1(t)$ is expressible in terms of cumulants of a scalar variable $\omega_1=\Omega_{11}+\sum_{j=2}^{N}\Omega_{1j}$. However, this simplification does not apply beyond the terms of second order in $\Delta\Omega_{ij}$; no simple expressions of this kind were found for $\lambda_2(t)$. The mathematical structure of solutions (9a) and (9b) is remarkably simple and is entirely conditioned by symmetry.

C. Rotational correlation functions

1. Equation of motion for $D_{00}^{(2)}(\theta_i(t))$

The basic problem, according to Eq. (5d), is to study the rotations of a set of N-coupled diatomic rotators forming a liquid sample. This problem has first been examined by Kivelson and Keyes.[26,27] To simplify the notation, the function $D_{00}^{(2)}(\theta_i(t))$ will be designated by $a_i(t)$, $i=1,2,\ldots,N$. The problem may then be treated by (i) constructing a sequence of matrix variables $A^{(1)T}=(a_1,a_2,\ldots,a_N)$, $A^{(2)T}=(a_1,\dot a_1,a_2,\dot a_2\ldots,a_N,\dot a_N)$, $A^{(3)T}=(a_1,\dot a_1,\ddot a_1,a_2,\dot a_2,\ddot a_2,\ldots a_N,\dot a_N,\ddot a_N)$, etc. and (ii) by assuming that either $A^{(1)}$, or $A^{(2)}$, or else $A^{(3)}$, etc., satisfy the simple Langevin equation

$$\frac{dA^{(n)}(t)}{dt}=-Q^{(n)}A^{(n)}(t)+F^{(n)}(t)\,, \tag{11}$$

where $Q^{(n)}$ is the $nN\times nN$ constant friction matrix and $F^{(n)}$ the random force associated with $A^{(n)}(t)$; the dots in quantities like $\dot a_i$ and $\ddot a_i$ indicate time derivatives and $n=1,2,3$, etc. The approximations of this sequence are called the one-variable, two-variable, three-variable, etc., theory, respectively; they have been shown to converge, if $n\to\infty$, to an exact solution of the present problem.[28] It leading terms describe a small-step rotational diffusion and a large-step extended diffusion, respectively. The free rotation limit is of no interest here; this motion does not occur in systems in which molecular interaction is large enough to produce nonnegligible collective vibrational and rotational effects.

2. Friction matrix and its properties

Here again, the symmetry imposes severe restrictions on the form of the friction matrix $Q^{(n)}$; the following statements can readily be proved.

(i) A correlation matrix $R^{(n)}(t)=\langle A^{(n)}(t)A^{(n)T}(0)\rangle$ can be thought of as an array of $n\times n$ matrices $R_{ij}^{(n)}(t)$ associated with molecules i,j. Then, all submatrices $R_{ii}^{(n)}(t)$ are equal to each other and all submatrices $R_{ij}^{(n)}(t)$, $i\neq j$, are equal too. This can be understood intuitively by noticing that all molecules, or all pairs of molecules, play the same role on the average. More formally, the two-time probability density $p(\vec{\mathrm{R}}_1^{(1)}\theta_1^{(1)},\vec{\mathrm{R}}_2^{(1)}\theta_2^{(1)}\ldots\vec{\mathrm{R}}_N^{(1)}\theta_N^{(1)},t_1;\vec{\mathrm{R}}_1^{(2)}\theta_1^{(2)},\vec{\mathrm{R}}_2^{(2)}\theta_2^{(2)}\ldots\vec{\mathrm{R}}_N^{(2)}\theta_N^{(2)},t_2)$ is invariant under the operations of the full N-symmetric group, which justifies the above statement. (ii) The matrices $X(t)$ formed by $N\times N$ submatrices $X_{ij}(t)$ of order $n\times n$ and such that all $X_{ii}(t)$ are equal and all $X_{ij}(t)$, $i\neq j$, are equal too, have a number of remarkable mathematical properties. It can first be shown that $X^{-1}(t)$ and $\int_{-\infty}^{\infty}dt\,X(t)$ conserve this property. Moreover, they can be diagonalized whatever N may be, provided n is small or moderately large. There exist n nondegenerate roots obtainable by diagonalizing the matrix $X_{11}+(N-1)X_{12}$, as well as $n(N-1)$-fold degenerate roots calculable by diagonalizing the matrix $X_{11}-X_{12}$; they are of order n rather that of order nN, and the diagonalization does not represent any difficulty for small or moderate n's. (iii) The friction matrix $Q^{(n)}$ is related to the corresponding correlation matrix $R^{(n)}(t)$ through the relation

$$(Q^{(n)})=\left[\left(\int_0^{+\infty}dt\,R^{(n)}(t)\right)[R^{(n)}(0)^{-1}]\right]^{-1}.$$

Then, using the arguments which have been presented above, the conclusion may easily be reached that the friction matrix $Q^{(n)}$ is composed of N identical $n\times n$ submatrices $Q_{ii}^{(n)}$ and of $N(N-1)$ identical submatrices $Q_{ij}^{(n)}$, $i\neq j$. The simplicity of its structure is exploited below.

3. Solution of the Langevin equation and final formulas

The solution of the Langevin equation (11) produces a correlation matrix of the form $R^{(n)}(t)=\exp(-Q^{(n)}t)R^{(n)}(0)$ and the problem finally reduces to the calculation of the elements of that matrix; this last problem requires the diagonalization of $Q^{(n)}$. Eventually, applying the results of the preceding section, the following one-variable approximation correlation functions are obtained:

$$\langle a_i(0)a_i(t)\rangle = \frac{1}{N}\{[\langle a_1(0)^2\rangle + (N-1)\langle a_1(0)a_2(0)\rangle]e^{-\rho_1 t} + (N-1)[\langle a_1(0)^2\rangle - \langle a_1(0)a_2(0)\rangle]e^{-\rho_2 t}\}, \tag{12a}$$

$$\langle a_i(0)a_j(t)\rangle = \frac{1}{N}\{\langle[a_1(0)^2\rangle + (N-1)\langle a_1(0)a_1(0)\rangle]e^{-\rho_1 t} - [\langle a_1(0)^2\rangle - \langle a_1(0)a_2(0)\rangle]e^{-\rho_2 t}\},\ i \neq j. \tag{12b}$$

In these equations ρ_1 is the nondegenerate and ρ_2 the $(N-1)$-fold degenerate root of the friction matrix. The n-variable approximation gives similar results but each exponential is replaced by n of them. The mathematical structure of the rotational correlation functions (12a) and (12b) is strikingly similar to that of the vibrational correlation functions (9a) and (9b); the essential role of the symmetry in these problems may be appreciated by this comparison.

D. Rotation-vibration correlation effects

This section may be concluded by briefly discussing the effect of the rotation-vibration correlations on $G^{(2)}(t)$, the correlation function associated with an anisotropic Raman spectrum. A convenient procedure is to use Eq. (7) for $A_i(t)$ and to construct a matrix $P(t)$ such that $P_{ji}(t) = D_{00}^{(2)}(\theta_i(0))\, D_{00}^{(2)}(\theta_j(t))$, $i,j = 1,2,\ldots,N$. There results

$$\begin{aligned} G^{(2)}(t) &= \left(\frac{\partial a^{(2)}}{\partial n}\right)_0^2 \sum_{ij} (n_{0i})(n_{j0}) e^{i\omega_0 t} \left\langle \exp_0\left(i\int_0^t d\tau\, \Omega(\tau)\right)_{ij} P_{ji}(t) \right\rangle \\ &= \left(\frac{\partial a^{(2)}}{\partial n}\right)_0^2 (n_{01})^2 e^{i\omega_0 t}\, \mathrm{Tr}\left\langle P(t) \exp_0\left(i\int_0^t d\tau\, \Omega(\tau)\right) \right\rangle \\ &= \left(\frac{\partial a^{(2)}}{\partial n}\right)_0^2 (n_{01})^2 e^{i\omega_0 t}\, \mathrm{Tr}\left\langle P(t) + i\int_0^t dt'\, P(t)\Delta\Omega(t') + \cdots \right\rangle \left\langle \exp_0\left(i\int_0^t dt'\, \Omega(t')\right)\right\rangle \\ &= (G^{(2)}(t))_0 + (G^{(2)}(t))_1 + \cdots . \end{aligned} \tag{13}$$

This expansion can be proven by (i) considering the identity

$$\langle y e^{ix}\rangle = \frac{1}{i}\lim_{\lambda\to 0}\frac{d}{d\lambda}\langle e^{i(x+\lambda y)}\rangle ,$$

where x, y are stochastic variables and (ii) generalizing it to the case of an ordered exponential of operators which commute after averaging. For other papers on this subject see Van Woerkom, de Bleyser *et al.*,[29] and Lynden-Bell.[12,13] The simplified theory presented here is that associated with $(G^{(2)}(t))_0$; it thus represents a correct zero-order theory of $G^{(2)}(t)$.

IV. RAMAN SPECTRA OF PURE LIQUIDS

A. Isotropic Raman spectra

Spectral properties of the scattered light may be described either by the correlation function $G^{(0)}(t)$ or by its Fourier transform; compare with Eqs. (5a), (6a), and (9a). The following results are obtained from the present theory: (i) The total, self- and distinct pair-correlation functions $G^{(0)}(t)$, $G_S^{(0)}(t)$, $G_D^{(0)}(t)$ have, in the large-N limit, the following analytical form:

$$G^{(0)}(t) = \frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\alpha}{\partial n}\right)_0^2 e^{i\omega_0 t} e^{\lambda_1(t)}, \tag{14a}$$

$$G_S^{(0)}(t) = \frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\alpha}{\partial n}\right)_0^2 e^{i\omega_0 t} e^{\lambda_2 t}, \tag{14b}$$

$$G_D^{(0)}(t) = \frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\alpha}{\partial n}\right)_0^2 e^{i\omega_0 t}\left(e^{\lambda_1(t)} - e^{\lambda_2(t)}\right), \tag{14c}$$

where α is the mean polarizability of a diatomic molecule and $\lambda_1(t)$, $\lambda_2(t)$ are given by Eqs. (10a) and (10b). (ii) The total correlation function $G^{(0)}(t)$ always has a single exponential form although the $\langle n_i(0)n_j(t)\rangle$'s contain two exponentials if $i \neq j$; typically, it exhibits a monotonic time decay (Fig. 1). (iii) The self-correlation function $G_S^{(0)}(t)$ of a pure liquid and the correlation function $G_{\rm iso}^{(0)}(t)$ of a dilute isotopic solution coincide after normalization. This statement can be proved by noticing that Ω_{12} is of the order of $(1/N)\Omega_{11}$ and can safely be neglected in the expression for $\lambda_2(t)$. The tacit assumption is that the rotational-translational molecular dynamics of the liquid sample is not altered in a significant way by the isotropic substitution. The decay of $G_S^{(0)}(t)$ most often is monotonic and similar to that of $G^{(0)}(t)$ (Fig. 2). (iv) The distinct

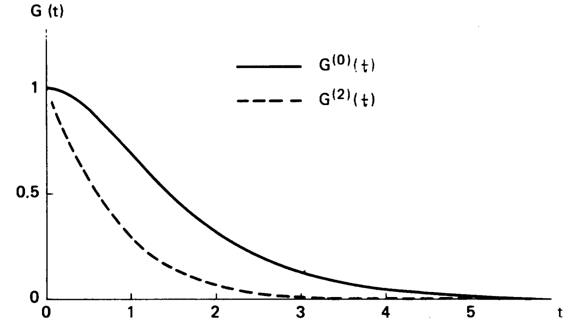

FIG. 1. Total isotropic and anisotropic Raman correlation functions of a pure liquid. Purely periodic factors are not reproduced. Only the cumulants up to the second order are considered in the expression for $\lambda_1(t)$ and $\lambda_2(t)$ and an exponential form is given to the second-order cumulant. One has $\langle \Sigma_j \Omega_{1j}(t)\rangle = \alpha_1$, $\langle \Omega_{11}(t)\rangle = \gamma_1$, $\langle \Sigma_j \Delta\Omega_{1j}(0)\Sigma_k \Delta\Omega_{1k}(t)\rangle = \alpha_2 \exp(-\alpha_2' t)$, $\langle \Delta\Omega_{11}(0)\Delta\Omega_{11}(t)\rangle = \gamma_2 \exp(-\gamma_2' t)$. ($\omega_0 = \alpha_1 = \gamma_1 = 0T^{-1}$, $\alpha_2 = 1T^{-2}$, $\gamma_2 = 0.5T^{-2}$, $\alpha_2' = 1T^{-1}$, $\gamma_2' = 0.5T^{-1}$, and $\rho_2 = 1T^{-1}$.) T is expressed in arbitrary time units.

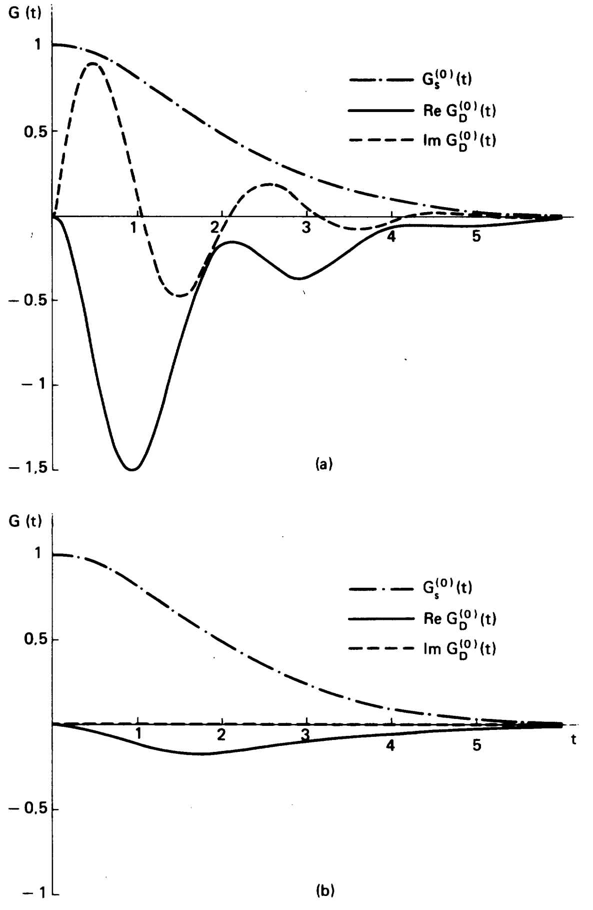

FIG. 2. Self- and distinct-pair isotropic Raman correlation functions of a pure liquid. The real and imaginary part of the pair-correlation functions are both considered. If $\alpha_1 - \gamma_1 > \sqrt{\alpha_2}$ or $\sqrt{\gamma_2}$, $G_D^{(0)}(t)$ has an oscillatory behavior. $\lambda_1(t)$ and $\lambda_2(t)$ have the same form as in Fig. 1. ($\omega_0 = \gamma_1 = 0T^{-1}$, $\alpha_2 = 1T^{-2}$, $\gamma_2 = 0.5T^{-2}$, $\alpha_2' = 1T^{-1}$, $\gamma_2' = 0.5T^{-1}$ [Figs. (a) and (b)]; $\alpha_1 = 3T^{-1}$ [Fig. (a)] or $\alpha_1 = 0.01T^{-1}$ [Fig. (b)]).

pair-correlation function $G_D^{(0)}(t)$ is generally nonvanishing. Thus the isotropic Raman scattering is a partially coherent process, contrary to what is frequently stated. Nevertheless, although $G_D^{(0)}(t)$ contributes to the spectral intensity at a frequency ω, its contribution to the integrated intensity vanishes; in fact, $\lim_{t\to 0} G_D^{(0)}(t) = 0$. The time dependence of $G_D^{(0)}(t)$ is complicated and may be oscillatory (Fig. 2). (v) The correlation function $G^{(0)}(t)$ has two simple limits, the slow and the fast modulation limits; they are defined by the inequalities $\tau_1 \gg \tau$ and $\tau_1 \ll \tau$, where τ_1 indicates the correlation time of $\Omega(t)$, and $\tau \sim 1/\Delta\omega_{1/2}$ is the reference time. Then, if $\alpha_1 = \langle \omega_1(0)\rangle$, $\alpha_2 = \langle \omega_1(0)^2\rangle - \langle \omega_1(0)\rangle^2$, $\beta = \int_0^\infty dt \langle \Delta\omega_1(0)\Delta\omega_1(t)\rangle$, etc., one finds

$$G^{(0)}(t) = \frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\alpha}{\partial n}\right)_0^2 \exp(i\omega_0 t)\exp(i\alpha_1 t - \tfrac{1}{2}\alpha_2 t^2 + \cdots), \quad \tau_1 \gg \tau \tag{15a}$$

$$G^{(0)}(t) = \frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\alpha}{\partial n}\right)_0^2 \exp(i\omega_0 t)\exp(i\alpha_1 t - \beta t), \quad \tau_1 \ll \tau . \tag{15b}$$

The corresponding spectral density is either an asymmetric distorted Gaussian ($\tau_1 \gg \tau$) or a Lorentzian ($\tau_1 \ll \tau$) (Fig. 3). No simple expressions exist to describe the band profiles outside these two limits.

B. Anisotropic Raman spectra

Here again, the spectra may be described, according to Eqs. (5b), (6b), (9b), and (12a), and (12b), either by the correlation function $G^{(2)}(t)$ or by its Fourier transform. The following results are obtained from the present zero-order theory, i.e., for sufficiently weak vibration-rotation correlation. (i) If the molecules execute a small-step rotational diffusion, i.e., if the one-variable theory is used to describe the rotations, the total, self- and distinct pair-correlation functions $G^{(2)}(t)$, $G_S^{(2)}(t)$, $G_D^{(2)}(t)$ can be written

$$G^{(2)}(t) = \frac{2}{15}\frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\beta}{\partial n}\right)_0^2 \times e^{i\omega_0 t}\left[e^{\lambda_2(t)+\rho_2(t)} + \frac{g}{N}\left(e^{\lambda_1(t)+\rho_1(t)} - e^{\lambda_2(t)+\rho_2(t)}\right)\right], \tag{16}$$

$$G^{(2)}(t) = \frac{2}{15}\frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\beta}{\partial n}\right)_0^2 e^{i\omega_0 t} e^{\lambda_2 t + \rho_2(t)}, \tag{17a}$$

$$G_S^{(2)}(t) = G^{(2)}(t), \tag{17b}$$

$$G_D^{(2)}(t) = 0 . \tag{17c}$$

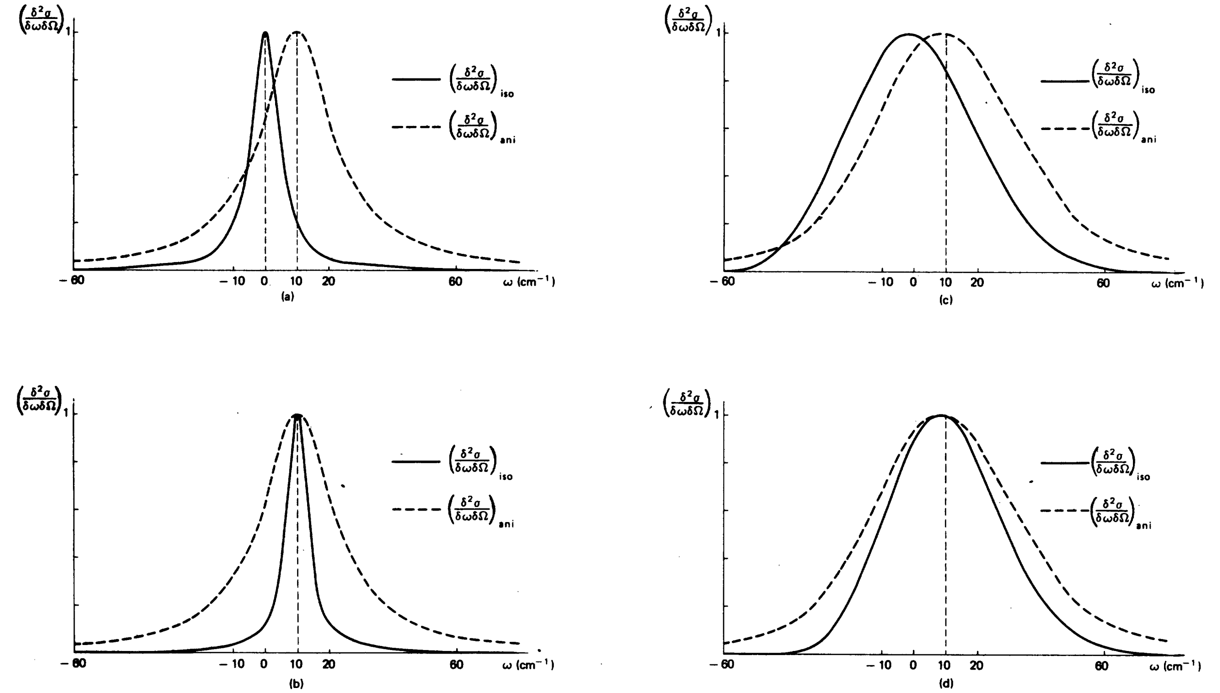

FIG. 3. Isotropic and anisotropic Raman-band profiles of a pure liquid [Figs. (a) and (c)] and of an isotopically diluted solution [Figs. (b) and (d)]; both the slow [Figs. (c) and (d)] and the fast [Figs. (a) and (b)] modulation limits are considered. The positions of isotropic and anisotropic Raman bands do not coincide in liquids but coincide in solutions. The correlation functions are those of Eqs. (15a), (15b) and (18a), (18b). ($\omega_0 = \alpha_1 = 0T^{-1}$, $\gamma_1 = 1T^{-1}$, $\rho_2 = 1T^{-1}$ [Figs. (a), (b), (c), and (d)]; $\beta = 0.5T^{-1}$, $\delta = 0.4T^{-1}$ [Figs. (a) and (b)]; $\alpha_2 = 4T^{-2}$, $\gamma_2 = 3T^{-2}$, $\alpha_3 = 1.8T^{-3}$, $\gamma_3 = 1.2T^{-3}$ [Figs. (c) and (d)]). The time unit is $1/6\pi\, 10^{-11}$ sec.

Here, β is the anisotropy of the molecule, $g = \langle \sum_j a_1(0) a_j(0)\rangle / \langle a_1(0)^2\rangle$ the Frolich-Kirkwood correlation factor, $\lambda_1(t), \lambda_2(t)$ are given by Eqs. (10a) and (10b), and $\rho_1(t) = -\rho_1 t, \rho_2(t) = -\rho_2 t$. Similar results are obtained in the two-, three-, etc. variable theory of rotational motions except that the exponentials $e^{\rho_1(t)}, e^{\rho_2(t)}$ are replaced by a linear combination of two, two, three, etc. of them. Equation (17a) represents the large-N limit of Eq. (16a); in fact, the correlation factor g is of the order of 10^0 in the systems under consideration and $g/N \sim 10^{-23}$. (ii) The distinct pair-correlation function $G_D^{(2)}(t)$ is of the order of $(1/N)G_S^{(2)}(t)$ and vanishes in the large-N limit. Thus, contrary to an isotropic Raman process which is partially coherent, the anisotropic Raman scattering is a purely incoherent process. As a consequence, the total correlation function $G^{(2)}(t)$, the self-correlation function $G_S^{(2)}(t)$, and the correlation function $G_{iso}^{(2)}(t)$ of an isotopically dilute solution coincide. Their time decay is generally monotonic, but faster than in isotropic spectra (Fig. 1). (iii) The correlation function $G^{(2)}(t)$ has two simple limits according to whether vibrational motions are modulated slowly or rapidly; only rapidly modulated rotational motions are of interest in the present context. Then, if $\gamma_1 = \langle \Omega_{11}(0)\rangle$, $\gamma_2 = \langle \Omega_{11}^2(0)\rangle - \langle \Omega_{11}(0)\rangle^2$, $\delta = \int_0^\infty dt \langle \Delta\Omega_{11}(0)\Delta\Omega_{11}(t)\rangle$, etc. one can write

$$G^{(2)}(t) = \frac{2}{15}\frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\beta}{\partial n}\right)_0^2 \exp(i\omega_0 t) \times \exp(i\gamma_1 t - \tfrac{1}{2}\gamma_2 t^2 + \cdots)\exp(-\rho_2 t), \quad \tau_1 \gg \tau \tag{18a}$$

$$G^{(2)}(t) = \frac{2}{15}\frac{N\hbar}{2\mu\omega_0}\left(\frac{\partial\beta}{\partial n}\right)_0^2 \exp(i\omega_0 t)\exp(i\gamma_1 t - \delta t) \times \exp(-\rho_2 t), \quad \tau_1 \ll \tau\,. \tag{18b}$$

The corresponding spectral density has either an asymmetrically distorted Voigt profile ($\tau_1 \gg \tau$) or a Lorentzian profile ($\tau_1 \ll \tau$) (Fig. 3). No simple expressions describing band shapes exist outside of these two limits.

C. Raman analysis of molecular dynamics of liquids

The following experiments are suggested by the present theory (Fig. 4). (i) Determination of self- and distinct pair-vibrational-correlation function. The isotropic Raman spectrum is recorded for a

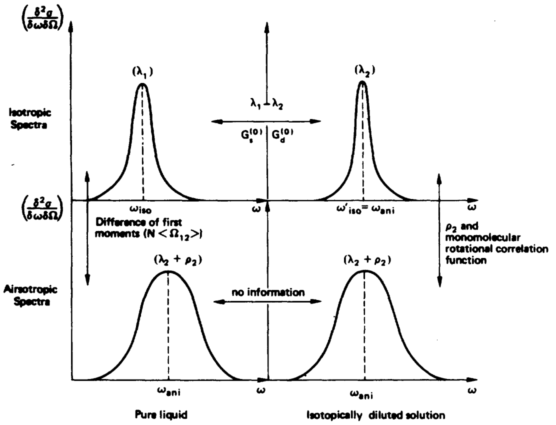

FIG. 4. Comparison of information contained in isotropic and anisotropic Raman spectra of a pure liquid and of an isotopically diluted solution.

pure liquid and for a dilute isotopic solution. Then the Fourier-inverted solution spectrum gives $G_S^{(0)}(t)$ whereas the Fourier-inverted liquid-solution difference spectrum gives $G_D^{(0)}(t)$. This procedure depends critically on the fact, proved earlier in this section, that the self-correlation function of a liquid and the correlation function of a dilute isotopic solution are equal to each other; moreover, the bands of the two species must be spectrally separated. See also the proposals by Van Woerkom *et al.*,[29] Lynden-Bell,[12] Oxtoby,[1] and Wertheimer.[17] (ii) Determination of vibrational and rotational self-correlation functions. Isotropic and anisotropic Raman spectra are recorded for a dilute isotopic solution. Then, application of the standard *VV*-*VH* separation technique furnishes the desired information.[24] It should be pointed out, however, that it is not permissible to apply this technique to pure liquids. The reason is that the vibrational correlation functions which enter into $G^{(0)}(t)$ and $G^{(2)}(t)$, respectively, differ from each other. (iii) Role of environmental fluctuations of vibrational frequency and of resonant transfers of vibrational energy in a vibrational relaxation process. The first moments M_G, M_S, M_L of an isotropic Raman band are measured for a gas, a dilute isotopic solution and for a pure liquid. Then,

$$M_G - M_S = \hbar\langle\Omega_{11}\rangle, \tag{19a}$$

$$M_S - M_L = N\hbar\langle\Omega_{12}\rangle \tag{19b}$$

provides the desired information. The information contained in Eq. (19b) can also be obtained, in principle, by comparing the first moments of an isotropic and of an anisotropic Raman spectrum of a liquid; however, the presence of the rotation-vibration correlations makes this information somewhat less reliable.

V. DISCUSSION

The present theory represents a generalization of the Bratos-Maréchal theory of Raman-band profiles of dilute van der Waals solutions.[24] However, the following points should be mentioned.

As far as vibrational correlation functions are concerned, the results of the present theory are in excellent agreement with those obtained by other authors. The formula (10a) reduces to that proposed by Oxtoby[1] and extends its validity to all modulation speeds. The expressions for the vibrational half-width given by Wertheimer[16] are deducible from Eq. (10a) if the modulation is assumed to be fast. The important result of Wang,[14] who showed that the pair-correlation functions do not contribute to the integrated intensity of isotropic Raman bands, is also rederived. An overall agreement is found between the predictions of this theory and the qualitative description due to Döge.[5,6] Finally, the effect of the rotation-vibration correlation on the first moment of an anisotropic Raman band has recently been investigated by Wang *et al.*[15]; this effect is also described by Eq. (13). On the other hand, the results obtained here for the slow and intermediate modulation regimes are entirely novel. This is also true for the present discussion of coherence and incoherence of a Raman scattering process.

As far as rotational correlation functions are concerned, the theory elaborated here parallels closely that proposed by Kivelson and Keyes[26,27]; this latter theory provides an analysis of Rayleigh scattering from pure liquids. However, there exists an important difference between the Rayleigh and Raman scattering processes: the self- and distinct pair-rotational correlation functions enter in the former case whereas only the self-rotational correlation functions are involved in the latter. A similar sort of vibrational decoupling was also observed by Thibeau *et al.*[30] in their study of the depolarized collision-induced Rayleigh and Raman scattering from dense fluids.

This paper may be concluded by briefly comparing the notions of coherence and incoherence in light and neutron scattering experiments.[31] These notions are required whenever the microscopic properties of a wave are incompletely defined. Two sources of uncertainty exist in the case of neutrons; one is related to the fact that the elementary scattering act between a neutron and a nucleus is usually outside the experimentalist's control and the second is related to the impossibility of preparing a liquid sample in a well-determined quantum state. Only the first of these two elements is built into the definition of a coherent and incoherent component of a scattered neutron wave. On the other hand, only one single element of uncertainty is present in light scattering. The elementary scattering act between a photon and a molecule being perfectly well known, the uncertainty comes exclusively from the impossiblity of preparing the liquid sample in a given quantum state. Thus the notions of coherence and incoherence have a different meaning in these two experiments.

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