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Theory of infrared and Raman spectra of diluted van der Waals solutions: Simple product approximation and its extension

G. Tarjus and S. Bratos
Laboratoire de Physique Théorique des Liquides (Equipe associée au Centre National de la Recherche Scientifique), Université Pierre et Marie Curie, Tour 16, 4 place Jussieu, F-75230 Paris Cedex 05, France

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The theory of infrared and anisotropic Raman spectra of diatomic molecules dissolved in inert solvents is reexamined without any *ad hoc* factorization of rotational-vibrational correlation functions. The total correlation function is expanded into a series. Its leading term represents the simple product approximation and its higher-order terms the successive corrections. An order-of-magnitude estimation of corrective terms is presented. They prove to be small, in weakly interacting van der Waals solutions at least, and their spectral effects by no means conspicuous.

I. INTRODUCTION

The theory of infrared and anisotropic Raman spectra of molecular liquids is usually based on the assumption that the total correlation functions may be factorized into their vibrational and rotational factors.[1,2] Constructed in this way, the theory provides a satisfactory description of a vast body of infrared and Raman data; see the review papers in Refs. 3 and 4. In spite of its success, this assumption should be investigated. In fact, vibrational degrees of freedom are coupled to rotational and translational degrees of freedom of the liquid sample through the angle- and position-dependent intermolecular forces and through the angular-momentum-dependent intramolecular forces. As, in turn, rotational and translational degrees of freedom are coupled to each other, one concludes that vibrational and rotational motions are necessarily correlated unless there is no vibrational relaxation. The product approximation, its validity, and its limitations thus merit a careful study.

In spite of its importance, this problem has been examined only by a limited number of authors. The first paper in which the separability of the total infrared correlation function into its vibrational and rotational factors was questioned is that of Van Woerkom *et al.*[5] Their theory employs the generalized cumulant expansion method and rotational motions are described by the isotropic rotational diffusion model. This theory indicates that the product approximation introduces errors arising from inadequate correlations of a given oscillator at several time points. Similar conclusions were also reached by other authors.[6] Later, Lynden-Bell calculated vibrational relaxation times in infrared, isotropic, and anisotropic Raman spectra of pure liquids by employing the Redfield theory well known in NMR; separation of vibrational and rotational motions was avoided.[7] Then, supposing rotational motions to be slow in the time scale of interest, she showed that the three relaxation times are different from each other. More recently, Wang and McHale[8] and McHale[9] calculated the lowest two spectral moments of the isotropic and anisotropic Raman and of the infrared spectra of a pure liquid without postulating the separability of the rotational-vibrational correlation functions. They predicted the first moments of the three spectra to be different; this effect was termed as the noncoincidence effect. However, as shown recently by Bratos and Tarjus,[10] the major part of this effect is obtained even if separability is assumed. Finally, Levesque, Weis, and Oxtoby[11] presented a molecular dynamics simulation of liquid HCl and tested the validity of the product approximation directly. They found that the total and the product correlation functions coincide within the accuracy of the molecular dynamics simulation. Unfortunately, no systematic analysis of this problem has yet been published.

The purpose of the present paper is to reexamine the theory of infrared and anisotropic Raman spectra of a diatomic molecule dissolved in an inert solvent by avoiding any *ad hoc* factorization of the rotational-vibrational correlation function. The total correlation function is expanded into a series. Its leading term is shown to be the simple product correlation function whereas higher-order terms appear as successive corrections to this simple product approximation. These corrections are small and their spectral effect by no means spectacular. For a preliminary account of this work, see Ref. 12.

II. GENERAL CONSIDERATIONS

A. Basic formulation

The system under consideration is a diatomic molecule dissolved in an inert solvent formed by N molecules. The following model is used to investigate the problem. (i) The active molecule is executing quantum-mechanical vibrations described by the free molecule vibrational coordinate n. The vibrations are coupled to the remaining degrees of freedom of the system through an angle- and position-dependent intermolecular potential. (ii) The active molecule as well as the solvent molecules execute stochastic reorientations and translations. The active molecule is characterized by its polar angles θ,ϕ and by its center of gravity coordinates $\vec{R}$ whereas the solvent molecules are characterized by their Eulerian angles Θ_i and by their center of gravity coordinates $\vec{R}_i$, $i=1,2,\ldots,N$. (iii) Collision-induced processes are absent. Under these conditions the Hamiltonian of the system can be written

$$H(n,t)=(p^2/2\mu+\tfrac{1}{2}kn^2+\tfrac{1}{6}fn^3+\cdots)+V(n,t)\ , \tag{1}$$

where $V(n,t)$ represents the solvent-solute interaction. For justification of this approach, see e.g., Ref. 13.

To proceed further, the formulas describing the infrared and anisotropic Raman processes must be presented. As usual, infrared and anisotropic Raman spectral densities can be expressed in terms of Fourier transforms of the following two correlation functions:

$$G_{\mathrm{ir}}(t)=\langle\vec{M}(0)\cdot\vec{M}(t)\rangle$$
$$=4\pi\left|\frac{\partial M}{\partial n}\right|^2\langle n(0)n(t)Y_{10}(\theta(0))Y_{10}(\theta(t))\rangle\ , \tag{2a}$$

$$G_{\mathrm{ani}}(t)=\mathrm{Tr}\langle\overleftrightarrow{\beta}(0)\cdot\overleftrightarrow{\beta}(t)\rangle$$
$$=\frac{8\pi}{3}\left|\frac{\partial\beta}{\partial n}\right|^2\langle n(0)n(t)Y_{20}(\theta(0))Y_{20}(\theta(t))\rangle\ . \tag{2b}$$

In these equations, $\vec{M}$ and $\overleftrightarrow{\beta}$ are the dipole moment and the anisotropic component of the polarizability tensor, respectively, of the active molecule and $Y_{lm}(\theta,\phi)$ are spherical harmonics. The correlation functions entering into Eqs. (2a) and (2b) can be expressed in a compact form by designating $Y_{10}(\theta)$ and $Y_{20}(\theta)$ by a unique symbol $Y_{u0}(\theta)$ where $u=1$ for infrared and $u=2$ for anisotropic Raman spectra.

The problem then reduces to that of calculating the components of $G_{\mathrm{ir}}(t)$ and $G_{\mathrm{ani}}(t)$ corresponding to the fundamental vibrational transition of the dissolved molecule. It is convenient to start by writing the Heisenberg equation of motion for the variable n. Then, by neglecting the energy relaxation processes which play a negligible role in the case of diatomic molecules where vibrational energy levels are widely spaced, the following formulas may be obtained:[14]

$$\langle n(0)n(t)Y_{u0}(\theta(0))Y_{u0}(\theta(t))\rangle=|n_{01}|^2\exp(i\omega_0t)\left\langle Y_{u0}(\theta(0))Y_{u0}(\theta(t))\exp\left[i\int_0^t dt_1\Omega(t_1)\right]\right\rangle\ , \tag{3}$$

$$\Omega(t)=\frac{1}{2\mu\omega_0}\left[-\frac{f}{k}\frac{\partial V}{\partial n}(n=0,t)+\frac{\partial^2V}{\partial n^2}(n=0,t)\right]\ , \tag{4}$$

where $u=1,2$. Conceived in this way, the theory can account for the rotation-vibration correlation effects arising from intermolecular forces. The correlation effects due to intramolecular forces are neglected; this point will be briefly discussed later in this paper.

B. Series expansion for $G_{\mathrm{ir}}(t)$ and $G_{\mathrm{ani}}(t)$

The potential $V(n,t)\equiv V(n,\{\vec{R}(t)-\vec{R}_i(t)\},\{\Theta_i(t)\},\theta(t),\phi(t))$ is stochastic through the time dependence of the variables $\vec{R},\vec{R}_i,\Theta_i,\theta,\phi$ and not through its functional form. Therefore, according to Eqs. (3) and (4), the variables $Y_{u0}(\theta(t))$ and $n(t)$ depend stochastically on each other through the angle- and position-dependent frequency increment $\Omega(t)\equiv\Omega(\{\vec{R}(t)-\vec{R}_i(t)\},\{\Theta_i(t)\},\theta(t),\phi(t))$. As a consequence, infrared and anisotropic Raman correlation functions cannot rigorously be factorized into rotational and vibrational functions. Still, they can be written in the form

$$\left\langle P_u(t,0)\exp\left[i\int_0^t dt_1\Omega(t_1)\right]\right\rangle$$
$$=X_u(t)\left\langle\exp\left[i\int_0^t dt_1\Omega(t_1)\right]\right\rangle\ , \tag{5}$$

where the function $X_u(t)$ is chosen as to transform Eq. (5) into an identity. The last factor on the right-hand side of Eq. (5) is the standard vibrational correlation function[1] whereas $P_u(t,0)$ denotes the product $Y_{u0}(\theta(t))Y_{u0}(\theta_u(0))$. $X_u(t)$ can be found by (i) expanding the exponential $\exp[i\int_0^t dt_1\Omega(t_1)]$ into a series and (ii) collecting the terms of the same power in the variable $\Omega(t)$. The following result may be reached in this way:

$$X_u(t)=\sum_{n=0}^{\infty}X_u^{(n)}(t)=\sum_{n=0}^{\infty}i^n\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n[P_u(t,0)\Omega(t_1)\Omega(t_2)\cdots\Omega(t_n)]_A\ , \tag{6}$$

$$[P_u(t,0)]_A=\langle P_u(t,0)\rangle\ , \tag{7a}$$

$$[P_u(t,0)\Omega(t_1)]_A=\langle[P_u(t,0)-\langle P_u(t,0)\rangle][\Omega(t_1)-\langle\Omega(t_1)\rangle]\rangle\ , \tag{7b}$$

$$[P_u(t,0)\Omega(t_1)\Omega(t_2)]_A=\langle[P_u(t,0)-\langle P_u(t,0)\rangle][\Omega(t_1)-\langle\Omega(t_1)\rangle][\Omega(t_2)-\langle\Omega(t_2)\rangle]\rangle\ , \tag{7c}$$

$G_{\mathrm{ir}}(t)$ and $G_{\mathrm{ani}}(t)$ thus appear in the form of a series in $\Omega(t)$. Its leading term, proportional to

$$X_u^{(0)}(t)\left\langle\exp\left[i\int_0^t dt_1\Omega(t_1)\right]\right\rangle\ ,$$

is the well-known product of rotational and vibrational functions commonly used in the theories of infrared and Raman spectra of liquids. For economy of language, it will be said to represent the zero-order theory. The next terms of the series provide successive corrections of this simple product theory. These approximations will be designated as first-order, second-order, etc., theories. It must be emphasized, however, that Eqs. (6) and (7) do not provide a perturbation expansion in powers of an appropriate coupling parameter, e.g., the intermolecular rotation-vibration interaction potential. In fact, the rotational and the vibrational correlation functions are calculated with the full Hamiltonian containing rotation-vibration coupling terms. The rotation-vibration correlation effects are thus present, to an important part, even in the zero-order theory.

III. CALCULATION OF CORRELATION FUNCTIONS

A. Dynamic variables

According to the preceding section, the calculation of the infrared and anisotropic Raman correlation functions requires the determination of the one-time, two-time, three-time, etc., correlation functions. These functions involve the spherical harmonics $Y_{u0}(\theta)$ and the frequency increment $\Omega(\{\vec{R}-\vec{R}_i\},\{\Theta_i\},\theta,\phi)$. It is convenient to proceed as follows. (i) The solvent-solute interaction potential $V(n,t)$ is expressed as a sum of all possible pair interaction terms between the active molecule and solvent molecules. (ii) The energy of interaction v between the active diatomic molecule and ith solvent molecule can be expanded into a series of spherical harmonics $Y_{l\lambda}(\theta,\phi)$:[15]

$$v(n,\vec{R}-\vec{R}_i,\Theta_i,\theta,\phi)=\sum_l \sum_{\lambda=-l}^{l} h_{l\lambda}(n,\vec{R}-\vec{R}_i,\Theta_i)Y^*_{l\lambda}(\theta,\phi) \, . \tag{8}$$

Truncated at an appropriate level, this expansion provides a good description of intermolecular forces. The familiar expressions for the short-range repulsion, the long-range dispersion, and the dipole-dipole interaction forces may serve as an illustration:

$$h^{\mathrm{REP}}_{00}=\sqrt{4\pi}\epsilon e^{-r_i/\sigma} \, , \tag{9}$$

$$h^{\mathrm{DISP}}_{00}=-\sqrt{4\pi}\frac{3}{2}\frac{E_I E_{Ii}}{E_I+E_{Ii}}\frac{\alpha\alpha_i}{r_i^6} \, , \tag{10}$$

$$h^{\mathrm{DD}}_{11}=\sqrt{2\pi/3}\frac{\mu\mu_i}{r_i^3}\{\sin\theta_i e^{i\phi_i}-3\sin\theta_{\hat{r}_i}e^{i\phi_{\hat{r}_i}}[\cos\theta_i\cos\theta_{\hat{r}_i}+\sin\theta_i\sin\theta_{\hat{r}_i}\cos(\phi_{\hat{r}_i}-\phi_i)]\} \, , \tag{11a}$$

$$h^{\mathrm{DD}}_{10}=\sqrt{4\pi/3}\frac{\mu\mu_i}{r_i^3}\{\cos\theta_i-3\cos\theta_{\hat{r}_i}[\cos\theta_i\cos\theta_{\hat{r}_i}+\sin\theta_i\sin\theta_{\hat{r}_i}\cos(\phi_{\hat{r}_i}-\phi_i)]\} \, , \tag{11b}$$

$$h^{\mathrm{DD}}_{1-1}=-\sqrt{2\pi/3}\frac{\mu\mu_i}{r_i^3}\{\sin\theta_i e^{-i\phi_i}-3\sin\theta_{\hat{r}_i}e^{-i\phi_{\hat{r}_i}}[\cos\theta_i\cos\theta_{\hat{r}_i}+\sin\theta_i\sin\theta_{\hat{r}_i}\cos(\phi_{\hat{r}_i}-\phi_i)]\} \, , \tag{11c}$$

where $r_i=|\vec{R}-\vec{R}_i|$ is the distance between the two molecules and (θ_i,ϕ_i) and $(\theta_{\hat{r}_i},\phi_{\hat{r}_i})$ are the polar angles of the dipole moment of the ith solvent molecule and of the vector $\vec{r}_i=\vec{R}-\vec{R}_i$, respectively; all other symbols have their usual meaning.[16] (iii) The solvent-induced frequency increment Ω may be written in a form similar to that of Eq. (8). One finds

$$\Omega(\{\vec{R}-\vec{R}_i\},\{\Theta_i\},\theta,\phi)=\sum_l \sum_{\lambda=-l}^{l} g_{l\lambda}(\{\vec{R}-\vec{R}_i\},\{\Theta_i\})Y^*_{l\lambda}(\theta,\phi) \, , \tag{12}$$

$$g_{l\lambda}(\{\vec{R}-\vec{R}_i\},\{\Theta_i\})=\frac{1}{2\mu\omega_0}\sum_{i=1}^{N}\left[-\frac{f}{k}\frac{\partial h_{l\lambda}}{\partial n}(n=0,\vec{R}-\vec{R}_i,\Theta_i)+\frac{\partial^2 h_{l\lambda}}{\partial n^2}(n=0,\vec{R}-\vec{R}_i,\Theta_i)\right] . \tag{13}$$

The above analysis allows a proper selection of the dynamic variables of the problem. According to Eqs. (6), (7), and (12), these variables are the spherical harmonics $Y^*_{l\lambda}(\theta,\phi)$, including $Y_{u0}(\theta)$, and the functions $g_{l\lambda}(\{\vec{R}-\vec{R}_i\},\{\Theta_i\})$. The former enter into both $\Omega(t)$ and $p(t,0)$ and describe the reorientations of the active molecule. The latter contain informations about rotational-translation motions of the solvent particles.

B. Equation of motion

A major difficulty of the present theory is to study correlation functions containing several times and involving the many dynamic variables $Y^*_{l\lambda}(t)$, $g_{l\lambda}(t)$. The difficulty may be overcome by collecting all the p variables $g_{00}(t)$, $g_{l\lambda,l\neq 0}(t)$, $Y^*_{l\lambda,l\neq 0}(t)$ in a column matrix $U(t)$ and supposing $U(t)$ to obey the simple Langevin equation:

$$\frac{dU(t)}{dt}=-\Gamma U(t)+F(t) \, , \tag{14}$$

where Γ is a constant $p\times p$ transport matrix and $F(t)$ a Gaussian random force. $U(t)$ is thus a Gaussian process as are all variables following a simple Langevin equation with a Gaussian random force.[17] So it is with the various variables g_{00}, $g_{l\lambda,l\neq 0}$, $Y^*_{l\lambda,l\neq 0}$. As a consequence, the three-time, four-time, etc., correlation functions occuring in the calculation are all reducible to products of one- and two-time correlation functions.

The use of the simple Langevin equation (14) may be questioned. It is justified, however, whenever molecules execute diffusionlike motions; free rotationlike motions are of no interest in the present context where intermolecular rotation-vibration correlations are investigated. If desired, the theory can be improved by assuming that either $[U(t),dU(t)/dt]$ or $[U(t),dU(t)/dt,d^2U(t)/dt^2]$, etc., satisfy a simple Langevin equation; extended diffusionlike motions are usually examined in this way. However, this additional effort does not seem to be justified at the present time when precise experimental data are still missing.

C. Symmetry considerations

The exact Hamiltonian of a liquid sample is invariant under rotations of the reference frame, i.e., under the operations of the full three-dimensional rotation group. This is also true for the approximate Hamiltonian of Eq. (1) as well as for the probability densities $p(\{\vec{R}^{(1)}-\vec{R}_i^{(1)}\},\{\Theta_i^{(1)}\},\theta^{(1)},\phi^{(1)},t_1)$, $p(\{\vec{R}^{(1)}-\vec{R}_i^{(1)}\},\{\Theta_i^{(1)}\},\theta^{(1)},\phi^{(1)},t_1;\{\vec{R}^{(2)}-\vec{R}_i^{(2)}\},\{\Theta_i^{(2)}\},\theta^{(2)},\phi^{(2)},t_2)$, etc. This rotational invariance is just the mathematical statement of the isotropy of an ordinary liquid sample. The existence of these symmetry elements permits a further simplification of the problem. Indeed, considering the rotational invariance of the intermolecular potential V and, hence of the frequency increment Ω, one may readily show that the functions $\{g_{l\lambda}\}$ and $\{Y_{l\lambda}\}$, $\lambda=-l, -(l-1),\ldots,l$, form bases for the same irreducible representation of the rotation group; any rotation R_Ω of the reference frame transforms $g_{l\lambda}$ and $Y_{l\lambda}$ according to the formulas

$$R_\Omega Y_{l\lambda}=\sum_{\lambda'=-l}^{l} D^{(l)}_{\lambda'\lambda}(\Omega)Y_{l\lambda'}\ , \tag{15a}$$

$$R_\Omega g_{l\lambda}=\sum_{\lambda'=-l}^{l} D^{(l)}_{\lambda'\lambda}(\Omega)g_{l\lambda'}\ , \tag{15b}$$

where $D^{(l)}_{\lambda'\lambda}$ represent the Wigner rotation matrices. Then, using Eqs. (15a) and (15b) and applying usual arguments of group theory, one can deduce the following set of equations:

$$\langle Y^*_{l\lambda}\rangle=\delta_{l0}\delta_{\lambda 0}\sqrt{4\pi}\ , \tag{16a}$$

$$\langle g_{l\lambda}\rangle=\delta_{l0}\delta_{\lambda 0}\langle g_{00}\rangle\ , \tag{16b}$$

$$\langle Y^*_{l\lambda}(t_1)Y^*_{l'\lambda'}(t_2)\rangle=\delta_{ll'}\delta_{\lambda(-\lambda')}(-1)^\lambda\langle Y_{l0}(t_1)Y_{l0}(t_2)\rangle, \tag{17a}$$

$$\langle g_{l\lambda}(t_1)g_{l'\lambda'}(t_2)\rangle=\delta_{ll'}\delta_{\lambda(-\lambda')}(-1)^\lambda\langle g_{l0}(t_1)g_{l0}(t_2)\rangle\ , \tag{17b}$$

$$\begin{aligned} Y^*_{l\lambda}(t_1)g_{l'\lambda'}(t_2)\rangle&=\langle g_{l'\lambda'}(t_1)Y^*_{l\lambda}(t_2)\rangle\\ &=\delta_{ll'}\delta_{\lambda\lambda'}\langle Y_{l0}(t_1)g_{l0}(t_2)\rangle\ . \end{aligned} \tag{17c}$$

According to these expressions, the system of p coupled equations (14) splits into a number of independent simple Langevin equations associated with the functions $\{g_{00}\}$ and with the pairs $\{g_{10},Y_{10}\}$, $\{g_{20},Y_{20}\}$, etc. The complexity of the calculation reduces correspondingly.

D. Theoretical expressions for $G_{\rm ir}(t)$ and $G_{\rm ani}(t)$

The final formulas for the infrared and anisotropic Raman correlation functions $G_{\rm ir}(t)$ and $G_{\rm ani}(t)$ may readily be deduced from the above analysis. More specifically, one has to calculate the quantities $\langle\exp[i\int_0^t dt_1\Omega(t_1)]\rangle$, $X_u^{(0)}(t)$, $X_u^{(1)}(t)$, $X_u^{(2)}(t),\ldots,u=1,2$ by employing methods sketched earlier in this paper. The procedure contains the following elements. (i) The vibrational relaxation function is expressed by employing the cumulant expansion technique:

$$\left\langle\exp\left[i\int_0^t dt_1\Omega(t_1)\right]\right\rangle=\exp[\lambda(t)]\ , \tag{18}$$

$$\lambda(t)=i\int_0^t dt_1\langle\Omega(t_1)\rangle+i^2\int_0^t dt_1\int_0^t dt_2\langle(\Omega(t_1)-\langle\Omega(t_1)\rangle)(\Omega(t_2)-\langle\Omega(t_2)\rangle)\rangle+\cdots\ . \tag{19}$$

(ii) The Gaussian property of the dynamic variables is used in calculating successive terms of $\lambda(t)$ and $X_u(t)$. Then, applying Eqs. (16) and (17), one obtains the following formulas:

$$\begin{aligned} \lambda(t)=&\,i\left[\frac{\langle g_{00}\rangle}{\sqrt{4\pi}}+\sum_{l\,(\neq 0)}(2l+1)\langle g_{l0}Y_{l0}\rangle\right]t\\ &+i^2\int_0^t dt_1\int_0^{t_1}dt_2\left[\frac{1}{4\pi}C^{(0)}_{gg}(t_1-t_2)\right.\\ &\left.+\sum_{l\,(\neq 0)}(2l+1)[C^{(l)}_{gg}(t_1-t_2)C^{(l)}_{yy}(t_1-t_2)+C^{(l)}_{gy}(t_1-t_2)C^{(l)}_{gy}(t_1-t_2)]\right]+\cdots\ , \end{aligned} \tag{20}$$

$$X_u^{(0)}(t)=C^{(u)}_{yy}(t)\ , \tag{21a}$$

$$X_u^{(1)}(t)=i\int_0^t dt_1[C^{(u)}_{gy}(t-t_1)C^{(u)}_{yy}(t_1)+C^{(u)}_{yy}(t-t_1)C^{(u)}_{gy}(t_1)]\ , \tag{21b}$$

$$\begin{aligned} X_u^{(2)}(t)=i^2\int_0^t dt_1\int_0^t dt_2[&C^{(u)}_{yy}(t-t_1)C^{(u)}_{gg}(t_1-t_2)C^{(u)}_{yy}(t_2)+C^{(u)}_{gy}(t-t_1)C^{(u)}_{gy}(t_1-t_2)C^{(u)}_{yy}(t_2)\\ &+C^{(u)}_{gy}(t-t_1)C^{(u)}_{yy}(t_1-t_2)C^{(u)}_{gy}(t_2)+C^{(u)}_{yy}(t-t_1)C^{(u)}_{gy}(t_1-t_2)C^{(u)}_{gy}(t_2)]\ , \end{aligned} \tag{21c}$$

where $u=1,2$. In these expressions, $C^{(0)}_{gg}(t)$ denotes the autocorrelation function of the variable $[g_{00}(t)-\langle g_{00}\rangle]$ whereas $C^{(l)}_{gg}(t)$, $C^{(l)}_{yy}(t)$, and $C^{(l)}_{gy}(t)$, $l\neq 0$, denote the correlation functions built on the variables $g_{l0}(t)$ and $Y_{l0}(t)$, $l\neq 0$. The fact that only $C^{(1)}_{gg}(t)$, $C^{(1)}_{yy}(t)$, and $C^{(1)}_{gy}(t)$ enter into $X_1^{(0)}$, $X_1^{(1)}$, $X_1^{(2)}$, etc., and generate corrections to $G_{\rm ir}(t)$ is a consequence of the symmetry, i.e., of the isotropy of the liquid sample. The same statement applies, *mutatis mutandis,* to an anisotropic Raman spectrum. (iii) The calculation of various two-time correlation functions involves the diagonalization of 1×1 or 2×2 transport matrices associated with $\{g_{00}\}$ and $\{g_{l0}, Y_{l0}\}$, $l\neq 0$, respectively; compare with Sec. III C. Then, denoting the corresponding eigenvalues by λ_0 and $\lambda_{l\alpha}$, $\alpha=1,2$, performing in Eqs. (20) and (21) the integration over the time and designating the normalized infrared and anisotropic Raman correlation functions by $G_1(t), G_2(t)$, one finally finds

$$\begin{aligned} G_u(t) = &\left\{ \left[\sum_{\alpha=1,2} x_{u\alpha} e^{-\lambda_{u\alpha} t} \right] + i \left[\sum_{\alpha,\beta=1,2} y_{u\alpha\beta} \left[\frac{e^{-\lambda_{u\alpha}t} - e^{-\lambda_{u\beta}t}}{\lambda_{u\beta}-\lambda_{u\alpha}} \right] \right] \right. \\ &\left. - \left[\sum_{\alpha,\beta=1,2} \sum_{i=1,2} z^{(i)}_{u\alpha\beta} \left[\frac{t e^{-\lambda_{u\alpha}t}}{\lambda_{u\beta}-(-1)^i \lambda_{u\alpha}} - \frac{e^{-\lambda_{u\alpha}t} - e^{-\{[1-(-1)^i]\lambda_{u\alpha}+\lambda_{u\beta}\}t}}{[\lambda_{u\beta}-(-1)^i\lambda_{u\alpha}]^2} \right] \right] + \cdots \right\} \\ &\times \exp(i\omega_0 t) \exp\left\{ i(\Delta\omega\, t) - \left[\sum_{l} \sum_{\alpha,\beta=1,2} \Gamma_{l\alpha\beta} \left[\frac{t}{\lambda_{l\alpha}+\lambda_{l\beta}} - \frac{1-e^{-(\lambda_{l\alpha}+\lambda_{l\beta})t}}{(\lambda_{l\alpha}+\lambda_{l\beta})^2} \right] \right] + \cdots \right\} \\ = &\, G_u^{(0)}(t) + G_u^{(1)}(t) + G_u^{(2)}(t) + \cdots, \quad u=1,2 . \end{aligned} \tag{22}$$

All parameters entering into this equation are calculated from the transport matrices; the resulting expressions are lengthy and are not reproduced here. It should be noticed that Eq. (22) is valid for positive times; for negative times, $G_u(t)$ is equal to $G_u(|t|)^*$.

E. Convergence of the series for $G_{\rm ir}(t)$ and $G_{\rm ani}(t)$

The formulas (21a)–(21c) can be easily generalized to include higher-order terms. Then, noticing that the ith-order contribution to the infrared correlation function $G_1(t)$ is obtained by multiplying $X_1^{(i)}(t)$ by the vibrational correlation function $\langle \exp[i \int_0^t dt_1 \Omega(t_1)] \rangle$, one finds readily that these contributions differ from each other by a factor of the order of $g_{10}\tau$. Similarly, the successive contributions to $G_2(t)$ differ by a factor of the order of $g_{20}\tau$. The convergence thus depends on $\tau_u = \Delta\omega_{u1/2}^{-1}$, the characteristic time of the experiment, and on $g_{u0} = \sqrt{\langle g_{u0}^2 \rangle / 4\pi}$, the magnitude of $g_{u0}(t)/\sqrt{4\pi}$, $u=1,2$. If $g_{u0}\tau \ll 1$, a reduced number of terms of the series will suffice to reproduce $G_u(t)$ as in Eq. (22). On the other hand, if $g_{u0}\tau > 1$, the series will diverge and the present theory will no longer remain applicable.

Finally, the use of the particular form of the series expansion employed in this paper can be questioned. For example, a method that might appear to be more straightforward, is to expand the total rotational-vibrational correlation function in the frame of the generalized cumulant expansion method and to introduce an appropriate averaging operation. Proceeding this way, one finds easily[18]

$$\left\langle\!\!\left\langle \exp\left[i \int_0^t dt_1 \Omega(t_1) \right] \right\rangle\!\!\right\rangle = \exp\left[i \int_0^t dt_1 \langle\langle \Omega(t_1) \rangle\rangle_c + i^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \langle\langle \Omega(t_1)\Omega(t_2) \rangle\rangle_c + \cdots \right], \tag{23}$$

$$\langle\langle A \rangle\rangle = \langle P_u(t,0) A \rangle \langle P_u(t,0) \rangle^{-1} . \tag{24}$$

Unfortunately, this procedure is not easily used and its convergence is far from being obvious. In a number of model calculations, expressions of this type were found to contain exponentials which increase with time. This circumstance strongly handicaps the applicability of this method.

IV. ORDER OF MAGNITUDE ESTIMATION OF CORRECTIVE TERMS OF $G_{\rm ir}(t)$ AND $G_{\rm ani}(t)$

This section is relative to the order of magnitude estimation of terms neglected by the simple product approximation and accounted for by the present theory. The procedure contains the following steps. (i) The solvent-solute interaction potential is written as a superposition of a Lennard-Jones, dipole-dipole, dipole-induced dipole, dipole-quadrupole, etc., potentials. Site-site potentials are not employed. (ii) The correlations between translational motions of solute and solvent molecules are considered explicitly as are the correlations between their rotational motions. On the contrary, correlations between rotational and translational motions are neglected. The spectral effect of this assumption turns out to be comparatively small. (iii) The lattice-gas model is used to calculate $\langle g_{l0}^2 \rangle$ where $l=0,1,2,\ldots$. The method employed in this paper follows closely that proposed earlier by Guillot, Bratos, and Birnbaum.[19] (iv) The correlation times of $C_{gg}^{(l)}(t)$, $C_{yy}^{(l)}(t)$, where $l=0,1,2,\ldots$, are calculated by a formula described by Berne and Pecora.[20] This formula in which the inverse of the correlation time is expressed in terms of an integral going through a plateau region is employed in conditions similar to those described in the above cited paper by Guillot, Bratos, and Birnbaum. Its use is justified if molecular motions are diffusionlike as it is tacitly assumed in Eq. (14).

This method was applied to the estimation of the infrared spectrum of a diluted solution of HCl in SO_2, a spectrum recorded by Perrot and Lascombe.[21] The choice of the system was dictated by two conflicting requirements. The intermolecular forces must be sufficiently large to generate important intermolecular rotational-vibrational correlations. However, they must be weaker than hydrogen bonds which cannot be accounted for by the present theory. Only the attractive dispersion and the dipole-dipole interaction forces were assumed to contribute to the frequency increment $\Omega(t)$ of HCl in SO_2; the contribution of the Pauli repulsion forces was found to be small in similar circumstances.[11] The parameters entering into the calculation were chosen as follows. The Lennard-Jones parameters for HCl were taken from Ref. 16, and those for SO_2 from the recent molecular dynamics data.[22] In turn, rotational diffusion constants were estimated from the experiment,[21,23] whereas translational diffusion constants were calculated from the Stokes formula. The spectroscopic parameter l_μ, defined by Levesque, Weis, and Oxtoby,[11] was estimated by considering the values $\partial\mu/\partial n$ for HCl in diluted gas and in pure liquid;[24] the corresponding parameter l_D was then determined by fitting the isotropic Raman spectral data.[21] Finally, the lattice-gas parameter ρ_0 was chosen so as to correspond to the close-packed density for SO_2. The estimations reached in this way are discussed in the next section.

V. RESULT AND DISCUSSION

The infrared and anisotropic Raman spectra may be calculated by Fourier transforming the correlation functions $G_u(t)$, $u=1,2$, given by Eq. (22). The following conclusions may be reached from this theory.

(i) The zero-order theory coincides with the simple product theory. This theory in which the correlation function is split into two independent factors associated with rotational and vibrational motions is thus a correct lowest-order theory. It gives an exact integrated intensity. (ii) The first-order theory generates a spectral density which is illustrated qualitatively in Fig. 1. Superposed to the spectral density of the zero-order theory it produces, in essence, a small frequency shift. (iii) The second-order theory generates a spectral density which is illustrated qualitatively in Fig. 2. Superposed to the spectral density of the zero-order theory it produces, in essence, a small broadening or narrowing of the band. The combined effect of these two corrections is shown in Fig. 3. (iv) The size of the effect is illustrated, in the case of an infrared spectrum of a diluted solution of HCl in SO_2, on Fig. 4. The half-width of the HCl stretching band calculated by the complete theory exceeds that produced by the simple product theory by $\sim 8\%$ whereas the band centers remain unchanged; this value may increase or decrease for a half according to the choice of l_μ which is largely uncertain. The product $g_{10}\tau$ is of the order of 0.2. The effects missing in the simple product approximation are thus comparatively small and may escape observation. This is true even in the present case where intermolecular forces are quite large. (v) The magnitude of successive corrections to $G_{\mathrm{ir}}(t), G_{\mathrm{ani}}(t)$ as well as their convergence vary when going, for a given system, from an infrared to an anisotropic Raman spectrum. The components of $V(n,t)$ contributing to $X_1(t)$ are different from those contributing to $X_2(t)$. The isotropy of the liquid sample contributes essentially to this effect. One concludes from this discussion that the rotation-vibration correlation effects missing in the simple product approximation are, in weakly interacting van der Waals solutions at least, small and by no means conspicuous.

The previous work on this problem is scarce and does not lend itself to an easy comparison. This is particularly true for the early papers by Van Woerkom *et al.*[5] and Lynden-Bell.[6,7] The discussion is easier for the theory by Wang and McHale.[8,9] Their theoretical expressions for

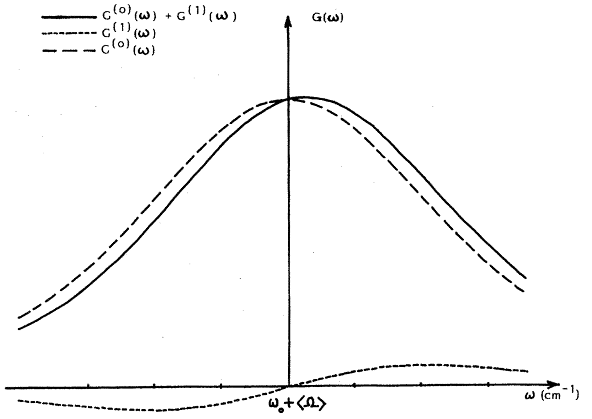

FIG. 1. Effect of the first-order correction on an infrared spectrum. The figure illustrates qualitatively rotation-vibration correlation effects for a representative van der Waals solution.

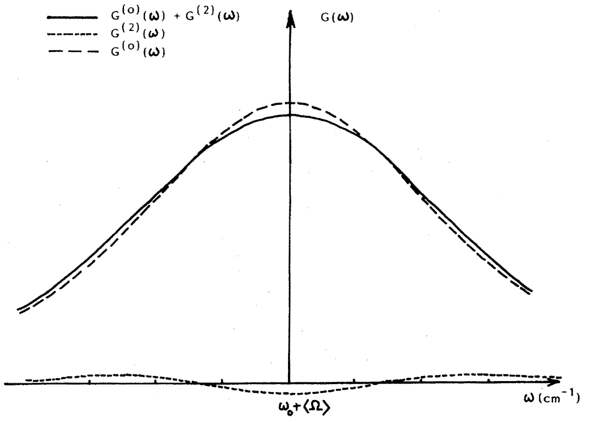

FIG. 2. Effect of the second-order correction on an infrared spectrum. The figure illustrates qualitatively rotation-vibration correlation effects for a representative van der Waals solution.

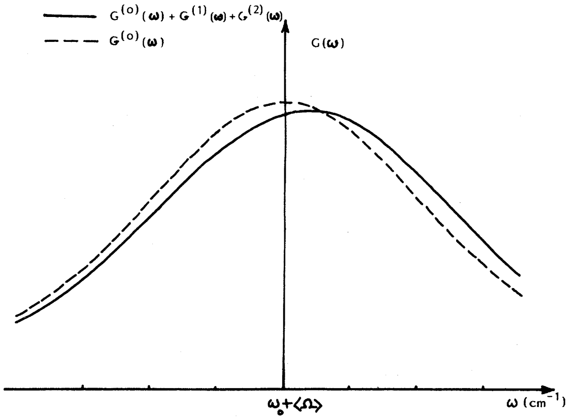

FIG. 3. Combined effect of the first two corrections in the case of an infrared spectrum. Results are similar for an anisotropic Raman spectrum.

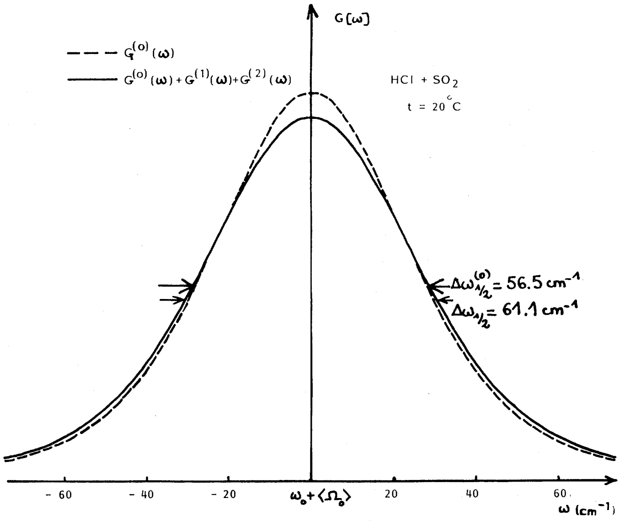

FIG. 4. Rotation-vibration correlation effect in the case of the infrared spectrum of a diluted solution of HCl in SO_2, at room temperature. The correspnding experimental value of $\Delta\omega_{1/2}$ is 61 cm^{-1} (Ref. 21).

the two lowest infrared and anisotropic Raman spectral moments turn out to be similar to those predicted by the present theory. However, the most significant comparison probably is that with the recent work by Levesque, Weis, and Oxtoby.[11] These authors state that the simple product and the exact correlation functions for infrared and anisotropic Raman spectra of the liquid HCl are indistinguishable from each other, within the uncertainty of simulation. This conclusion does not contradict those reached here as the corrections of a few percent are difficult to bring out in standard molecular dynamics calculations. Nevertheless, an additional theoretical work would be required to settle this problem definitively.

This paper may be concluded by briefly mentioning the intramolecular coupling effect which has up till now been neglected. For a diatomic molecule, it is due to centrifugal forces. It may then easily be seen that the corresponding contribution to $\Omega(t)$ can be incorporated into the invariant term g_{00} of Eqs. (12) and (13). The intramolecular coupling thus contributes to $\lambda(t)$, but not to $X_u(t)$, $u=1,2$. The simple product correlation function remains valid. This conclusion is comparable to that reached, in similar circumstances, by Bratos and Chestier.[14]

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