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Theory of infrared and anisotropic Raman band profiles of pure liquids: Product approximation and its extensions

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The theory of infrared and anisotropic Raman spectra of pure van der Waals liquids is developed without introducing any *a priori* factorization of the rotational-vibrational correlation functions. Extensive use is made of the fact that the Hamiltonian of a pure liquid sample is invariant, both under permutations of the molecules and under rotations of the liquid sample as a whole. The total and self-correlation functions are expanded into series. Their leading term corresponds to the product approximation and higher-order terms provide successive corrections. These corrections are shown to be small. Moreover, in spite of the presence of molecular interactions, infrared absorption and anisotropic Raman scattering in pure liquids exhibit mainly monomolecular characteristics of vibrational and rotational motions.

I. INTRODUCTION

Infrared absorption and Raman spectroscopies have been widely used in the last decade to investigate vibrational and rotational motions in molecular liquids. In most theories, infrared or anisotropic Raman correlation functions are assumed to be factorizable into vibrational and rotational contributions. In spite of its success,[1,2] this assumption merits a careful study since vibrations are coupled to rotations and translations through the angle- and position-dependent intermolecular forces and through the angular-momentum-dependent intramolecular forces.

This problem was recently examined for dilute van der Waals solutions by Tarjus and Bratos.[3,4] The theory employs a special form of expansion of the total infrared or anisotropic Raman correlation function info a series. Its leading term represents the product approximation and its higher-order terms represent the successive corrections. The latter were calculated by employing the Langevin equation. In weakly interacting van der Waals solutions at least, they prove to be quite small.

As far as pure liquids are concerned, the investigation is complicated by the presence of resonant vibrational and rotational interactions, even if the factorization of rotational-vibrational correlation functions is assumed.[5] Nevertheless several theories were published and may be presented as follows.

(i) The first paper in which the factorization of the infrared correlation function into its vibrational and rotational components was questioned is that by van Woerkom *et al.*[6] In this theory, the generalized cumulant expansion theorem for noncommuting operators is applied to describe vibrational motions whereas rotational motions are pictured by the monomolecular rotational diffusion model. Moreover, the correlation between resonant and nonresonant vibrational interactions is neglected. The theory then shows that the product approximation introduces errors arising from the fact that the successive time points are not correctly intercorrelated. See also Ref. 7.

(ii) Later on, Lynden Bell[8] presented another theory and calculated vibrational relaxation times for infrared, isotropic, and anisotropic Raman spectra of pure liquids. This theory, in which any *a priori* separation of the rotational-vibrational dynamics is avoided, is based on the Redfield theory well known in NMR. Then, supposing rotational motions to be slow as compared with translational motions, it was shown that the three relaxation times are different from each other.

(iii) More recently, Wang and McHale[9] and McHale[10] calculated the lowest two spectral moments of the infrared, isotropic, and anisotropic Raman spectra of pure liquids. No particular form was imposed on the rotational-vibrational correlation functions. Only the resonant vibrational transfer mechanisms were systematically investigated. The main prediction of this theory is that the first moments of the three spectra differ from each other, an effect termed the noncoincidence effect. However, as shown recently by Bratos and Tarjus,[11] the major part of this effect is obtained even if separability is assumed.

(iv) Finally, Levesque, Weis, and Oxtoby[12] presented a molecular dynamics simulation of liquid HCl testing the validity of the product approximation directly. It results from their calculation that the total and the product correlation functions of both infrared spectra and anisotropic Raman spectra coincide within the accuracy of the molecular dynamics simulation.

The purpose of the present paper is to extend the discussion of the product approximation contained in the Tarjus-Bratos theory of Ref. 4 from dilute solutions to pure liquids. Extensive use is made of the fact that the Hamiltonian of a pure liquid sample is invariant under the operations of two groups: the full N-symmetric and the three-dimensional rotation group. The total- and the self-correlation functions are expanded into series; their leading term corresponds to the product approximation and the higher-order terms to successive corrections. The latter prove to be small in spite of the presence of resonant vibrational and rotational interactions. The product approximation thus remains valid, not only in dilute van der Waals solutions, but also in pure liquids of this class.

II. GENERAL CONSIDERATIONS

A. Description of the system

1. Definition of the model

The system under investigation is a liquid sample containing N identical, diatomic molecules. The basic assumptions of the present model are similar to those employed in Ref. 5. (i) The molecules are executing anharmonic vibration described by the free molecule internal coordinates $n=(n_1,n_2,\ldots,n_N)$. They are perturbed by a stochastic potential $V(n,t)$ expressing molecular interactions. The corresponding semiclassical Hamiltonian can be written

$$\begin{aligned} H(n,t)= & \left[\tfrac{1}{2}\sum_{i=1}^{N} p_i^2+\tfrac{1}{2}\sum_{i=1}^{N} kn_i^2+\tfrac{1}{6}\sum_{i=1}^{N} fn_i^3+\cdots\right] \\ & +\left[\sum_{i=1}^{N} V_i(t)n_i+\tfrac{1}{2}\sum_{i,j=1}^{N} V_{ij}(t)n_in_j\right. \\ & \left.\quad+\tfrac{1}{6}\sum_{i,j,k=1}^{N} V_{ijk}(t)n_in_jn_k+\cdots\right] \\ = & H_0+V(n,t)\ , \end{aligned} \tag{1}$$

etc. As shown in previous papers,[3-5] the existence of these symmetry elements permits a considerable simplification of the calculation; here again, it makes the problem accessible to an analytical treatment.

The terms $V_i(t)$, $V_{ii}(t)$, $V_{iii}(t)$, etc. give rise to environmental fluctuations of the vibrational frequency whereas the terms $V_{ij}(t)$, $V_{ijk}(t)$, etc., generate the resonant intermolecular coupling. (ii) The molecules of the liquid are executing stochastic reorientations and translations. They are described by the ensemble of polar angles $\theta=(\theta_1,\theta_2,\ldots,\theta_N)$ and the ensemble of center-of-gravity coordinates $R=(R_1,R_2,\ldots,R_N)$. (iii) There is no collision-induced scattering. Constructed in this way, the model can account for rotational-vibrational correlations arising from intermolecular forces but not from intramolecular forces. This latter effect is shortly discussed at the end of Sec. V.

2. Symmetry properties of the system

The exact Hamiltonian of a liquid sample is invariant under the operations of two different symmetry groups: the permutations of two, three, or several molecules, i.e., the operations of the full N-symmetric group and the rotations of the reference frame, i.e., the operations of the three-dimensional rotation group. This property is also shared with the model Hamiltonian given by Eq. (1) as well as with various probability densities

$$\begin{aligned} & p(R_1^{(1)},\theta_1^{(1)},R_2^{(1)},\theta_2^{(1)},\ldots,R_N^{(1)},\theta_N^{(1)},t_1)\ , \\ & p(R_1^{(1)},\theta_1^{(1)},R_2^{(1)},\theta_2^{(1)},\ldots,R_N^{(1)},\theta_N^{(1)},t_1\ ; \\ & \quad R_1^{(2)},\theta_1^{(2)},R_2^{(2)},\theta_2^{(2)},\ldots,R_N^{(2)},\theta_N^{(2)},t_2)\ , \end{aligned}$$

B. Description of the absorption and scattering processes

It is convenient to start the calculation by expressing the infrared and anisotropic Raman spectral densities in terms of Fourier transforms of the following two correlation functions:

$$G_{\mathrm{ir}}(t)=\sum_{i,j=1}^{N}\langle \mathbf{M}_i(0)\cdot\mathbf{M}_j(t)\rangle=4\pi\left|\frac{\partial M_1}{\partial n_1}\right|^2\sum_{i,j=1}^{N}\langle n_i(0)Y_{10}(\theta_i(0))n_j(t)Y_{10}(\theta_j(t))\rangle\ , \tag{2a}$$

$$G_{\mathrm{ani}}(t)=\sum_{i,j=1}^{N}\mathrm{Tr}\langle \overleftrightarrow{\beta}_i(0)\cdot\overleftrightarrow{\beta}_j(t)\rangle=\frac{8\pi}{3}\left|\frac{\partial \beta_1}{\partial n_1}\right|^2\sum_{i,j=1}^{N}\langle n_i(0)Y_{20}(\theta_i(0))n_j(t)Y_{20}(\theta_j(t))\rangle\ . \tag{2b}$$

In these equations $\mathbf{M}_i$, $\overleftrightarrow{\beta}_i$, and $Y_{lm}(\theta_i)$ represent the transition dipole moment, the anisotropic component of the Raman polarizability tensor, and the spherical harmonics associated with the molecule i, respectively. These equations only apply if local-field effects are sufficiently small; this assumption, as well as assumption (iii) of Sec. I A, may be restrictive for strongly polar or strongly polarizable systems.

The correlation function $G_{\mathrm{ir}}(t)$ and $G_{\mathrm{ani}}(t)$ given by Eqs. (2a) and (2b) can be expressed in a compact form by designating $Y_{10}(\theta_i)$ and $Y_{20}(\theta_i)$ by a unique symbol $Y_{u0}(\theta_i)$, where $u=1$ for infrared and $u=2$ for anisotropic Raman spectra. The normalized correlation functions may also be denoted by a unique symbol $G_u(t)$, $u=1$ referring to an infrared, and $u=2$ to an anisotropic Raman spectrum. This convention will be respected in what follows.

C. Series expansion of correlation functions

1. Frequency matrix $\Omega(t)$ and its properties

The central part of the problem is to analyze the motions of a set of N-coupled vibrating rotators evolving in a spatially and temporally disordered medium. The basic equations describing the time evolution of the normal coordinates $n_i(t)$, $i=1,2,\ldots,N$, can be obtained by (i) choosing a basic set composed of nonexcited and monoexcited vibrational wave functions of H_0, (ii) defining an $N\times N$ frequency matrix $\Omega(t)$, where $\hbar\Omega_{st}(t)=V_{st}(t)-\delta_{st}V_{00}(t)$, $s,t=1,2,\ldots,N$, and (iii) suppressing in the Hamiltonian matrix all elements which connect vibrational states of different degrees of excitation. The formal resolution of the Heisenberg equation then leads to the following expressions:

$$\langle n_i(0)Y_{u0}(\theta_i(0))n_j(t)Y_{u0}(\theta_j(t))\rangle$$
$$=|(n_1)_{01}|^2e^{i\omega_0t}\Big\langle Y_{u0}(\theta_i(0))Y_{u0}(\theta_j(t)) \times\left[\exp_0 i\int_0^t dt_1\,\Omega(t_1)\right]\Big\rangle\ ; \tag{3}$$

$$\Omega_{ij}=\frac{1}{2\mu\omega_0}\left[\frac{\partial^2V}{\partial n_i\,\partial n_j}\right]_{n=0},\quad i\neq j\ ; \tag{4a}$$

$$\Omega_{ii}=\frac{1}{2\mu\omega_0}\left[-\frac{f}{k}\left[\frac{\partial V}{\partial n_i}\right]_{n=0}+\left[\frac{\partial^2V}{\partial n_i^2}\right]_{n=0}\right], \tag{4b}$$

where ω_0 is the vibrational frequency of the free molecule. The presence in Eq. (3) of a time-ordered exponential makes the subsequent calculation comparatively difficult.

2. Matrix $X_u(t)$ and its properties

The potential $V(n,t)\equiv V(n,R(t),\theta(t))$ depends on the translational and rotational variables R, θ. A glance at Eqs. (3) and (4) then shows that the variables $\{Y_{u0}(\theta_i(t))\}$ and $\{n_i(t)\}$, $i=1,\ldots,N$, are coupled to each other through the angle- and position-dependent frequency matrix $\Omega(t)\equiv\Omega(R(t),\theta(t))$. Infrared and anisotropic Raman correlation functions thus cannot be factorized rigorously into their rotational and vibrational components. However, generalizing the procedure developed in Ref. 4, it is legal to write

$$\Big\langle[P_u(t,0)]\left[\exp_0\left[i\int_0^t dt_1\,\Omega(t_1)\right]\right]\Big\rangle=X_u(t)\Big\langle\left[\exp_0\left[i\int_0^t dt_1\,\Omega(t_1)\right]\right]\Big\rangle, \tag{5a}$$

$$G_u(t)=4\pi e^{i\omega_0t}\mathrm{Tr}\left\{X_u(t)\Big\langle\left[\exp_0\left[i\int_0^t dt_1\,\Omega(t_1)\right]\right]\Big\rangle\right\}, \tag{5b}$$

where $[P_u(t,0)]_{ij}=Y_{u0}(\theta_i(t))Y_{u0}(\theta_j(0))$. The $N\times N$ matrix $X_u(t)$ is chosen as to transform Eq. (5a) to an identity. This matrix can be found be expanding the time-ordered exponential and by collecting the terms of the same power in $\Omega(t)$. The results are as follows:

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

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

$$\{P_u(t,0)y\}_A=\langle P_u(t,0)y\rangle-\langle P_u(t,0)\rangle\langle y\rangle\ , \tag{7b}$$

$$\{P_u(t,0)yz\}_A=\langle P_u(t,0)yz\rangle-(\langle P_u(t,0)\rangle\langle yz\rangle+\langle P_u(t,0)y\rangle\langle z\rangle+\langle P_u(t,0)z\rangle\langle y\rangle)$$
$$+\langle P_u(t,0)\rangle(\langle y\rangle\langle z\rangle+\langle z\rangle\langle y\rangle),\ \text{etc.}\ , \tag{7c}$$

where $y,z,\ldots$ represent any relevant scalar or matrix dynamical variable of the system. The problem thus reduces to that of calculating the trace of the matrix

$$\left\{X_u(t)\Big\langle\left[\exp_0\left[i\int_0^t dt_1\,\Omega(t_1)\right]\right]\Big\rangle\right\},$$

with $u=1$ or 2.

The correlation function $G_u(t)$ appears in the form of a power series of the frequency matrix $\Omega(t)$. Its leading term is proportional to the trace of

$$\langle P_u(t,0)\rangle\Big\langle\left[\exp_0\left[i\int_0^t dt_1\,\Omega(t_1)\right]\right]\Big\rangle$$

which is the product of the rotational correlation matrix associated with $Y_{u0}(\theta)$ and the vibrational correlation matrix. This term constitutes the product approximation and will be said, for economy of language, to represent the zero-order theory. The next terms of the series provide successive corrections of this product theory and the corresponding approximations will be designated as first-, second-order, etc., theories.

3. Total- and self-correlation functions $G_u(t)$ and $G_{su}(t)$

The expressions (5)—(7) for $G_u(t)$ are matrix expressions of a very high order; thus they cannot be employed such as they stand. Fortunately, the permutational symmetry imposes on all ensemble-averaged products built from $P_u(t,0)$ and $\Omega(t)$ a special form such that their diagonal elements are equal to each other as are their nondiagonal elements. These matrices are known to admit a nondegenerate and a $(n-1)$-fold degenerate root where n is their order.[5] Four quantities thus appear in subsequent calculations: $x_{u,1}(t)$, $x_{u,2}(t)$, and $\lambda_1(t)$, $\lambda_2(t)$, representing the roots of matrices $X_u(t)$ and

$$\ln\left\{\left\langle\left[\exp_0\left[i\int_0^t dt_1\,\Omega(t_1)\right]\right]\right\rangle\right\}.$$

Then, supposing the potential energy V be pairwise additive,

$$V=\frac{1}{2}\sum_i\sum_{j\,(\neq i)}v_{ij}=\sum_i\sum_{j\,(>i)}v_{ij}\;,$$

the following results may be derived, valid in the large N limit:

$$G_u(t)=4\pi e^{i\omega_0 t}x_{u,2}(t)e^{\lambda_2(t)}\;, \tag{8}$$

$$\begin{aligned}\lambda_2(t)=iN\int_0^t dt_1\langle\omega_{12}(t_1)\rangle-N\int_0^t dt_1\int_0^{t_1}dt_2[\langle\Delta\omega_{12}(t_1)\Delta\omega_{12}(t_2)\rangle+\langle\Delta\bar{\omega}_{12}(t_1)\Delta\bar{\omega}_{12}(t_2)\rangle\\+N\langle\Delta\omega_{12}(t_1)\Delta\omega_{13}(t_2)\rangle]+\cdots\;,\end{aligned} \tag{9}$$

$$\begin{aligned}x_{u,2}(t)=\{P_{u,11}(t,0)\}_A+iN\int_0^t dt_1[\{P_{u,11}(t,0)\omega_{12}(t_1)\}_A+\{P_{u,12}(t,0)\bar{\omega}_{12}(t_1)\}_A]\\-N\int_0^t dt_1\int_0^{t_1}dt_2([\{P_{u,11}(t,0)\omega_{12}(t_1)\omega_{12}(t_2)\}_A+\{P_{u,11}(t,0)\bar{\omega}_{12}(t_1)\bar{\omega}_{12}(t_2)\}_A\\+\{P_{u,12}(t,0)\omega_{12}(t_1)\bar{\omega}_{12}(t_2)\}+\{P_{u,12}(t,0)\bar{\omega}_{12}(t_1)\omega_{12}(t_2)\}_A]\\+N[\{P_{u,11}(t,0)\omega_{12}(t_1)\omega_{13}(t_2)\}_A+\{P_{u,12}(t,0)\omega_{23}(t_1)\bar{\omega}_{12}(t_2)\}_A+\{P_{u,12}(t,0)\bar{\omega}_{12}(t_1)\omega_{13}(t_2)\}_A\\+\{P_{u,12}(t,0)\bar{\omega}_{23}(t_1)\bar{\omega}_{13}(t_2)\}_A])+\cdots\;,\end{aligned} \tag{10}$$

$$\Omega_{ii}=\sum_{j\,(\neq i)}\omega_{ij}=\sum_{j\,(\neq i)}\frac{1}{2\mu\omega_0}\left[-\frac{f}{K}\left[\frac{\partial v_{ij}}{\partial n_i}\right]_0+\left[\frac{\partial^2 v_{ij}}{\partial n_i^2}\right]_0\right]\;, \tag{11a}$$

$$\Omega_{ij}=\bar{\omega}_{ij}=\frac{1}{2\mu\omega_0}\left[\frac{\partial^2 v_{ij}}{\partial n_i\partial n_j}\right]_0\;, \tag{11b}$$

where $\Delta\omega_{ij}=\omega_{ij}-\langle\omega_{ij}\rangle$, $\Delta\bar{\omega}_{ij}=\bar{\omega}_{ij}-\langle\bar{\omega}_{ij}\rangle$. The physical meaning of Eqs. (8)–(11) is as follows. In spite of the presence of resonant molecular interactions, the zero-order correlation function $G_u^{(0)}(t)$ still is equal to the simple product of the monomolecular rotational correlation function $\langle Y_{u0}(\theta_1(t))Y_{u0}(\theta_1(0))\rangle$ and the monomolecular vibrational function $\langle n_1(0)n_1(t)\rangle\sim e^{-\lambda_2(t)}$; compare with Ref. 5. The cross correlation functions vanish in this level of approximation. Infrared and anisotropic Raman spectra of pure liquids thus exhibit, basically, monomolecular characteristics of vibrational-rotational motions.

The question may be raised, however, whether the higher-order terms modify this conclusion. The following statement can be proven. The infrared and anisotropic Raman self-correlation functions $G_{su}(t)$, $u=1,2$, may be written, as $G_u(t)$, in the form of series. Their expressions are obtained by eliminating in Eqs. (8)–(10) all terms involving $P_{u,ij}(t,0)$ with $i\neq j$. The results are as follows:

$$G_{su}(t)=4\pi e^{i\omega_0 t}x_{su,2}(t)e^{\lambda_2(t)}\;, \tag{12}$$

$$\begin{aligned}x_{su,2}(t)=\{P_{u,11}(t,0)\}_A+iN\int_0^t dt_1\{P_{u,11}(t,0)\omega_{12}(t_1)\}_A\\-N\int_0^t dt_1\int_0^{t_1}dt_2[\{P_{u,11}(t,0)\omega_{12}(t_1)\omega_{12}(t_2)\}_A+\{P_{u,11}(t,0)\bar{\omega}_{12}(t_1)\bar{\omega}_{12}(t_2)\}_A\\+N\{P_{u,11}(t,0)\omega_{12}(t_1)\omega_{13}(t_2)\}_A]+\cdots\;.\end{aligned} \tag{13}$$

Comparing Eqs. (8)–(11) to Eqs. (12)–(13) then shows that the total- and self-correlation functions coincide in the zero-order, but not in the higher-order theories. Infrared absorption and anisotropic Raman scattering processes in pure liquids are not rigorously monomolecular. However, as shown in what follows, the correction terms remain quite small in van der Waals liquids.

III. CALCULATION OF CORRELATION FUNCTIONS

A. Dynamic variables and their equation of motion

1. Choice of dynamic variables

According to the preceding sections, the calculation of infrared and anisotropic Raman correlation functions requires the determination of one-, two-, three-time, etc., correlation functions involving the spherical harmonics $Y_{u0}(\theta_i)$ and the elements $\Omega_{ii}(t)=\sum_{j\neq i}\omega_{ij}(t)$ and $\Omega_{ij}(t)=\bar{\omega}_{ij}(t)$, $i,j=1,\ldots,N$ of the frequency matrix Ω. It is convenient to express the angular dependence of $\omega_{ij}(t)$ and $\bar{\omega}_{ij}(t)$ by developing them into a series of products of spherical harmonics $Y_{m\mu}(\theta_i)Y_{n\nu}(\theta_j)$. Considering the translational and rotational invariance of v_{ij}, one finds[13]

$$v_{ij}=\sum_{\substack{m,n,\\ \mu,\nu}}\sum_{l=|m-n|}^{m+n}\sum_{\lambda=-l}^{l}\begin{bmatrix} m & n & l\\ \mu & \nu & \lambda\end{bmatrix}h_{mnl}(n_i,n_j,R_{ij})\times Y_{l\lambda}(\hat{\mathbf{R}}_{ij})Y_{m\mu}(\theta_i)Y_{n\nu}(\theta_j)\ , \tag{14}$$

$$h_{mnl}(n_i,n_j,R_{ij})=h_{mnl}(n_j,n_i,R_{ji})=h^{*}_{mnl}(n_i,n_j,R_{ij})\ , \tag{15a}$$

$$h_{mnl}(n_i,n_j,R_{ij})=(-1)^{m+n}h_{mnl}(n_i,n_j,R_{ij})\ , \tag{15b}$$

where R_{ij} and $\hat{\mathbf{R}}_{ij}$ represent the length and the polar angles of the vector $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$. Truncated at an appropriate level, this expansion provides a convenient description of two-body forces. The quantities ω_{ij} and $\bar{\omega}_{ij}$ may then be written,

$$\omega_{ij}=\sum_{\substack{m,n,\\ \mu,\nu}}\sum_{l=|m-n|}^{m+n}\sum_{\lambda=-l}^{l}\begin{bmatrix} m & n & l\\ \mu & \nu & \lambda\end{bmatrix}g^{mn}_{l\lambda}(\mathbf{R}_{ij})\times Y_{m\mu}(\theta_i)Y_{n\nu}(\theta_j)\ , \tag{16a}$$

$$\bar{\omega}_{ij}=\sum_{\substack{m,n,\\ \mu,\nu}}\sum_{l=|m-n|}^{m+n}\sum_{\lambda=-l}^{l}\begin{bmatrix} m & n & l\\ \mu & \nu & \lambda\end{bmatrix}\bar{g}^{mn}_{l\lambda}(\mathbf{R}_{ij})\times Y_{m\mu}(\theta_i)Y_{n\nu}(\theta_j)\ , \tag{16b}$$

$$g^{mn}_{l\lambda}(\mathbf{R}_{ij})=\frac{1}{2\mu\omega_0}\left[-\frac{f}{k}\frac{\partial h_{mnl}}{\partial n_i}(n_i=n_j=0,R_{ij})+\frac{\partial^2 h_{mnl}}{\partial n_i^2}(n_i=n_j=0,R_{ij})\right]Y_{l\lambda}(\hat{\mathbf{R}}_{ij})\ , \tag{17a}$$

$$\bar{g}^{mn}_{l\lambda}(\mathbf{R}_{ij})=\frac{1}{2\mu\omega_0}\frac{\partial^2 h_{mnl}}{\partial n_i\partial n_j}(n_i=n_j=0,R_{ij})Y_{l\lambda}(\hat{\mathbf{R}}_{ij})\ . \tag{17b}$$

This analysis allows a proper selection of dynamic variables of the problem. According to Eqs. (8)–(11) and (16), these variables are the spherical harmonics $\{Y_{l\lambda}(\theta_i)\}_{l,\lambda=-l,\dots,l}$ including $Y_{u0}(\theta_i)$, $i=1,2,\dots,N$, and the functions

$$\{g^{mn}_{l\lambda}(\mathbf{R}_{ij}),\bar{g}^{mn}_{l\lambda}(\mathbf{R}_{ij})\}_{m\le n;l=n-m,\dots,n+m;\lambda=-l,\dots,l}\ ,$$

$i,j=1,2,\dots,N$. The former describe the reorientations of the molecules, whereas the latter contains information about their translations.

2. *Equation of motion*

A major difficulty of the present investigation is to study correlation functions involving the many correlated monomolecular and bimolecular dynamic variables $\{Y_{l\lambda}(\theta_i)\}_{l\neq 0}$, $\{g^{mn}_{l\lambda}(\mathbf{R}_{ij}),\bar{g}^{mn}_{l\lambda}(\mathbf{R}_{ij})\}$ over several time points. The difficulty may be overcome, at least in principle, by collecting all the dynamic variables in one column matrix $U(t)$ and assuming $U(t)$ to obey the simple Langevin equation

$$\frac{dU(t)}{dt}=-\Gamma U(t)+F(t)\ , \tag{18}$$

where Γ is a constant transport matrix and $F(t)$ a Gaussian random force. $U(t)$ is thus a Gaussian process,[14] as are all the various variables $Y_{l\lambda,l\neq 0}(\theta_i)$, $g^{mn}_{rp}(\mathbf{R}_{ij})$, $\bar{g}^{mn}_{rp}(\mathbf{R}_{ij})$. As a consequence, the three-time, four-time, etc., correlation functions involved in the calculation are all expressible in terms of products of one- and two-time correlation functions. The use of a simple Langevin equation to describe the time evolution of coupled rotational and translational variables was discussed earlier.[4]

B. Symmetry arguments

1. *Rotational invariance*

Considering the rotational symmetry of the system under study, one shows readily that the functions $\{Y_{m\mu}\}$, $\{g^{pq}_{m\mu}\}$, $\{\bar{g}^{pq}_{m\mu}\}$, $\mu=-m,\dots,m$, form bases for the same irreducible representation, usually designated by $\mathscr{D}^{(m)}$, of the three-dimensional rotation group. Applying standard arguments of group theory then leads to the following equations:

$$\langle Y_{m\mu}(\theta_i)\rangle=\delta_{m0}\delta_{\mu 0}(\sqrt{4\pi})^{-1}\ , \tag{19a}$$

$$\langle g^{pq}_{m\mu}(\mathbf{R}_{ij})\rangle=\delta_{m0}\delta_{\mu 0}\langle g^{pq}_{00}(R_{ij})\rangle=\delta_{m0}\delta_{\mu 0}\delta_{pq}\langle g^{pp}_{00}(R_{ij})\rangle\ , \tag{19b}$$

$$\langle Y_{m\mu}(\theta_i(t_1))Y_{n\nu}(\theta_j(t_2))\rangle=\delta_{nm}\delta_{\nu(-\mu)}(-1)^{\mu}\langle Y_{m0}(\theta_i(t_1))Y_{m0}(\theta_j(t_2))\rangle\ , \tag{19c}$$

$$\langle Y_{m\mu}(\theta_i(t_1))g^{rs}_{n\nu}(\mathbf{R}_{kl}(t_2))\rangle=\delta_{nm}\delta_{\nu(-\mu)}(-1)^{\mu}\langle Y_{m0}(\theta_i(t_1))g^{rs}_{m0}(\mathbf{R}_{kl}(t_2))\rangle\ , \tag{19d}$$

$$\langle g^{pq}_{m\mu}(\mathbf{R}_{ij}(t_1))g^{rs}_{n\nu}(\mathbf{R}_{kl}(t_2))\rangle=\delta_{nm}\delta_{\nu(-\mu)}(-1)^{\mu}\langle g^{pq}_{m0}(\mathbf{R}_{ij}(t_1))g^{rs}_{m0}(\mathbf{R}_{kl}(t_2))\rangle\ , \tag{19e}$$

where δ_{mn} is the Kronecker symbol. Similar formulas apply, mutatis mutandis, to $\bar{g}^{pq}_{m\mu}$. According to these formulas, the system of coupled equations (18) reduces to a number of independent simple Langevin equations associated with the sets of variables $\{\{g^{pp}_{00}(R_{ij}),\bar{g}^{pp}_{00}(R_{ij})\}_p\}_{i<j}$ and, for $m\neq 0$, $\{\{Y_{m0}(\theta_i)\}_i$, $\{\{g^{pq}_{m0}(\mathbf{R}_{ij})$, $\bar{g}^{pq}_{m0}(\mathbf{R}_{ij})\}_{p\le q}\}_{i<j}\}$. However, contrary to what is true for dilute solutions, the complexity of the calculation still keeps the problem out of handling. This is due to the existence of a large number of coupled variables. Their number varies as N^2, where N is the number of molecules in the liquid sample.

2. *Permutational invariance*

The decisive step of the calculation consists in using symmetry arguments resulting from the invariance of the system under permutations, as described in Sec. II A 2. The following procedure may be employed. (i) For given m, i, and $j>i$, the variables $\{g_{m0}^{pq}(\mathbf{R}_{ij}),\bar{g}_{m0}^{pq}(\mathbf{R}_{ij})\}_{p\leq s}$ are collected into a column matrix $G_{m0}(\mathbf{R}_{ij})$. (ii) These $[N(N-1)/2]$ column matrices $G_{m0}(\mathbf{R}_{12}),G_{m0}(\mathbf{R}_{13}),\ldots,G_{m0}(\mathbf{R}_{1N}),G_{m0}(\mathbf{R}_{23}),\ldots,G_{m0}(\mathbf{R}_{2N}),\ldots,G_{m0}(\mathbf{R}_{(N-1)N})$ are collected together with the N variables $Y_{m0}(\theta_1)$, $Y_{m0}(\theta_2),\ldots,Y_{m0}(\theta_N)$, into a single-column matrix. This latter matrix obeys a simple Langevin equation. (iii) The symmetry imposes severe restriction on the form of the friction and correlation matrices denoted by $\Gamma^{(m)}$ and $R^{(m)}(t)$, respectively; see Figs. 1(a) and 1(b). The $(Y-Y)$ part of these matrices contains two different elements, the $(Y-G)$ or $(G-Y)$ part contains two different submatrices, and the $(G-G)$ part contains three different submatrices; the $(Y-G)$, $(G-Y)$, and $(G-G)$ matrices have a different structure for odd and even values of m. Their symmetry is high enough to permit an exact, analytical block diagonalization for all N. (iv) Three different blocks, noted $\gamma_1^{(m)},\gamma_2^{(m)},\gamma_3^{(m)}$, are found for the friction matrix: $\gamma_1^{(m)}$ occurs once, $\gamma_2^{(m)}$ occurs $(N-1)$ times, whereas $\gamma_3^{(m)}$ occurs $(N-2)(N-1)/2$ times for odd values of m and $N(N-3)/2$ times for even values of m; see Figs. 2(a) and 2(b). The case $m=0$ belongs to this latter class. (v) The block diagonalization of the correlation matrix leads to the following one-, two-, three-, and four-particle correlation functions:

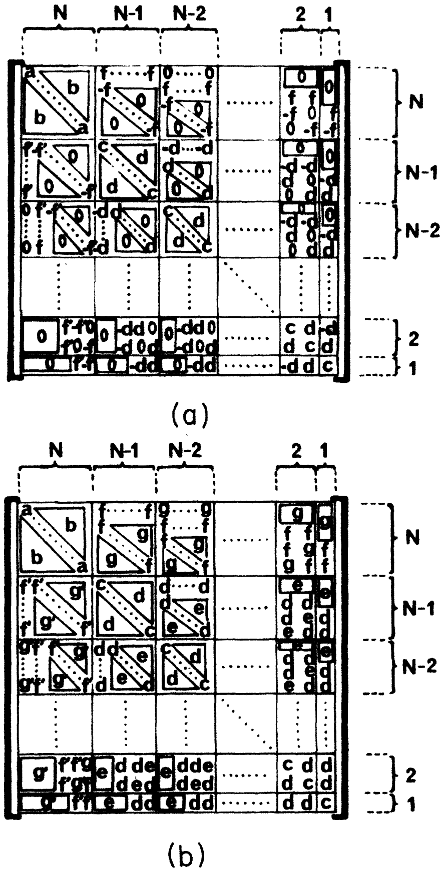

FIG. 1. General form of the friction matrix $\Gamma^{(m)}$: (a) odd values of m; (b) even values of m.

$$\langle Y_{m0}(\theta_1(t))Y_{m0}(\theta_1(0))\rangle=\frac{1}{N}R_{y_1}^{(m)}(t)+\frac{N-1}{N}R_{y_2}^{(m)}(t),\quad m\neq 0 \tag{20}$$

$$\langle Y_{m0}(\theta_1(t))Y_{m0}(\theta_2(0))\rangle=\frac{1}{N}R_{y_1}^{(m)}(t)-\frac{1}{N}R_{y_2}^{(m)}(t),\quad m\neq 0 \tag{21}$$

$$\langle \underline{G}_{m0}(\mathbf{R}_{12}(t))\underline{G}_{m0}(\mathbf{R}_{12}(0))^T\rangle=\frac{2}{N(N-1)}\underline{\underline{R}}_{g_1}^{(m)}(t)+\frac{2}{N}\underline{\underline{R}}_{g_2}^{(m)}(t)+\frac{N-3}{N-1}\underline{\underline{R}}_{g_3}^{(m)}(t),\quad m\text{ even} \tag{22a}$$

$$=\frac{2}{N}\underline{\underline{R}}_{g_2}^{(m)}(t)+\frac{N-2}{N}\underline{\underline{R}}_{g_3}^{(m)}(t),\quad m\text{ odd} \tag{22b}$$

$$\langle \underline{G}_{m0}(\mathbf{R}_{12}(t))\underline{G}_{m0}(\mathbf{R}_{13}(0))^T\rangle=\frac{2}{N(N-1)}\underline{\underline{R}}_{g_1}^{(m)}(t)+\frac{N-4}{N(N-2)}\underline{\underline{R}}_{g_2}^{(m)}(t)-\frac{N-3}{(N-1)(N-2)}\underline{\underline{R}}_{g_3}^{(m)}(t),\quad m\text{ even} \tag{23a}$$

$$=\frac{1}{N}\underline{\underline{R}}_{g_2}^{(m)}(t)-\frac{1}{N}\underline{\underline{R}}_{g_3}^{(m)}(t),\quad m\text{ odd} \tag{23b}$$

$$\langle \underline{G}_{m0}(\mathbf{R}_{12}(t))\underline{G}_{m0}(\mathbf{R}_{34}(0))^T\rangle=\frac{2}{N(N-1)}\underline{\underline{R}}_{g_1}^{m}(t)-\frac{4}{N(N-2)}\underline{\underline{R}}_{g_2}^{(m)}(t)+\frac{2}{(N-1)(N-2)}\underline{\underline{R}}_{g_3}^{(m)}(t),\quad m\text{ even} \tag{24a}$$

$$=\underline{\underline{0}},\quad m\text{ odd} \tag{24b}$$

$$\langle Y_{m0}(\theta_1(t))\underline{G}_{m0}(\mathbf{R}_{12}(0))\rangle=\frac{1}{N}\underline{\underline{R}}_{x_1}^{(m)}(t)+\frac{N-2}{N}\underline{\underline{R}}_{x_2}^{(m)}(t),\quad m\text{ even}\neq 0 \tag{25a}$$

$$=\underline{\underline{R}}_{x_2}^{(m)}(t),\quad m\text{ odd} \tag{25b}$$

$$\langle Y_{m0}(\theta_1(t))\underline{G}_{m0}(\mathbf{R}_{23}(0))\rangle=\frac{1}{N}\underline{\underline{R}}_{x_1}^{(m)}(t)-\frac{2}{N}\underline{\underline{R}}_{x_2}^{(m)}(t),\quad m\text{ even}\neq 0 \tag{26a}$$

$$=\underline{\underline{0}},\quad m\text{ odd}\,. \tag{26b}$$

$$
(a)\quad \begin{cases} \gamma_1^{(m)} = \left(g_1^{(m)} \right) \\[2ex] \gamma_2^{(m)} = \begin{bmatrix} y_2^{(m)} & x_2^{(m)} \\ x_2^{(m)\prime} & g_2^{(m)} \end{bmatrix} \\[2ex] \gamma_3^{(m)} = \left(g_3^{(m)} \right) \end{cases}
$$

$$
(b)\quad \begin{cases} \gamma_1^{(m)} = \begin{bmatrix} y_1^{(m)} & x_1^{(m)} \\ x_1^{(m)\prime} & g_1^{(m)} \end{bmatrix} \\[2ex] \gamma_2^{(m)} = \begin{bmatrix} y_2^{(m)} & x_2^{(m)} \\ x_2^{(m)\prime} & g_2^{(m)} \end{bmatrix} \\[2ex] \gamma_3^{(m)} = \left(g_3^{(m)} \right) \end{cases}
$$

FIG. 2. Matrices $\gamma_1^{(m)},\gamma_2^{(m)},\gamma_3^{(m)}$ deduced from $\Gamma^{(m)}$ by block diagonalization: (a) odd values of m, $y_1=a+(N-1)b$, $y_2=a-b$, $g_2=c+(N-2)d$, $g_3=c-2d$, $x_2^{(\prime)}=f^{(\prime)}$; (b) even values of m, $y_1=a+(N-1)b$, $y_2=a-b$, $g_1=c+2(N-2)d+[(N-2)(N-3)/2]e$, $g_2=c+(N-4)d-(N-3)e$, $g_3=c-2d+e$, $x_1^{(\prime)}=2f^{(\prime)}+(N-2)g^{(\prime)}$, $x_2^{(\prime)}=f^{(\prime)}-g^{(\prime)}$.

In these expressions, $R_{y_i}^{(m)}(t)$, $\underline{\underline{R}}_{\,g_i}^{(m)}(t)$, and $\underline{\underline{R}}_{\,x_i}^{(m)}(t)$ are calculable from $\exp(-\gamma_i^{(m)}t)$, $i=1,2,3$. This calculation requires the diagonalization, for each value of m, of three matrices $\gamma_1^{(m)},\gamma_2^{(m)},\gamma_3^{(m)}$, the order of which is independent of the number of molecules N. In this way, the complexity of the calculation is reduced by a factor on the order of N^2.

The physical meaning of the three matrices $\gamma_1,\gamma_2,\gamma_3$ is as follows. In the large-N limit and the absence of an accidental cancellation, γ_1 describes coupled collective rotations and translations of molecules; γ_2 describes coupled monomolecular rotations and bimolecular and trimolecular translations; finally, γ_3 describes translations of a given pair in pure liquids.

C. Final expressions for $G_{su}(t)$ and $G_u(t)$

The final expressions for the infrared and anisotropic Raman self- and total-correlation functions $G_{su}(t)$ and $G_u(t)$ may now be deduced from the two-time correlation functions calculated in Sec. III B. The Gaussian characteristics of various dynamic variables are considered in this calculation as are the symmetry properties described by Eqs. (19)–(26). The correlation functions $G_{su}(t)$ and $G_u(t)$ can then be expressed in terms of elements of the matrices $R_{y_{1,2}}^{(m)}(t),\underline{\underline{R}}_{\,g_{1,2,3}}^{(m)}(t),\underline{\underline{R}}_{\,x_{1,2}}^{(m)}(t)$. Finally the matrices $\gamma_1^{(m)},\gamma_2^{(m)},\gamma_3^{(m)}$ are diagonalized and the large-N limit of the resulting expressions is determined. In their final form, $G_{su}(t)$ and $G_u(t)$ involve only exponential and polynomial functions of time. Unfortunately, they are too long to be reproduced here.

On the other hand, it can easily be shown that $x_{su,2}^{(n)}(t),x_{u,2}^{(n)}(t)$, $n\geq 1$, and the corrections to the product approximation are different from zero only if the expansion (14) of the pair potential v_{ij} contains at least one spherical harmonic of rank u: $y_{u\lambda}(\theta_i)$, $y_{u\lambda}(\theta_j)$, or $y_{u\lambda}(\hat{\mathbf{R}}_{ij})$. This is a consequence of the Gaussian character of the dynamic variables as well as of the rotational invariance of the system under consideration. As in the case of dilute van der Waals solutions,[3,4] the convergence of the series for $G_u(t)$, $u=1,2$ depends on the product $g_u\tau_u$, where τ_u is the characteristic time of the experiment and g_u the order of magnitude of these components of the resonant transfer and of the environmental fluctuation terms which contain at least one spherical harmonic of rank u. If $g_u\tau_u \ll 1$, a reduced number of terms of the series will suffice to reproduce $G_u(t)$: if $g_u\tau_u > 1$, the series will diverge and the present theory will no longer remain applicable. For discussion of the particular form of the series expansion employed in this work, see Ref. 4.

IV. ORDER OF MAGNITUDE ESTIMATION OF CORRECTIVE TERMS

A. Method of estimation

The purpose of this section is to present an order of magnitude estimation of terms neglected by the product approximation and accounted for by the present theory. The method includes the following steps. (i) The pair interaction potential is written as a superposition of Lennard-Jones, dipole-dipole, dipole-induced dipole, etc., potentials; site-site potentials are not employed. (ii) The contributions to $\{g_{l\lambda}^{mn}\}_{m\leq n}$ and $\{\bar{g}_{l\lambda}^{mn}\}_{m\leq n}$, associated with different types of molecular interactions, are assumed to be statistically independent from each other; for example, for $l=0$, the short-range repulsion and the long-range dispersion contributions are assumed to be uncorrelated. (iii) The correlations between rotational motions of different molecules are considered explicitly, as are the correlations between their translational motions. On the contrary, correlations between rotational and translational motions are neglected. (iv) The various moments of $g_{lo}^{mn},\bar{g}_{lo}^{mn}$ are estimated with the help of the lattice-gas model.[15] (v) Finally, the correlation times of the rotational and translational two-time correlation functions are estimated by using a method described in Ref. 16. This method, in which the inverse of the correlation time is expressed in terms of an integral going through a plateau region, is justified if molecular motions are diffusionlike as tacitly assumed in Eq. (18).

B. Choice of the system

The choice of the system to be studied is dictated by two conflicting conditions. The intermolecular couplings must be large enough to generate nonnegligible rotational-vibrational correlations. On the other hand, they should not be as strong as those produced by medium strong or strong hydrogen bonds which cannot be accounted for by the present theory. Finally, liquid HCl was selected. Infrared and Raman spectra were recorded at different temperatures by Wang and Fleury,[17] Perchard *et al.*,[18] Chesnoy *et al.*,[19] and Andreani *et al.*[20] Moreover, Levesque, Weis, and Oxtoby[12] performed a molecular dynamics simulation of liquid HCl at temperature $T=196$ K. To make the comparison easier, this latter temperature was used in the present estimation. For simplification, only the long-range dispersion and the dipole-dipole interaction forces were assumed to contribute to the environmental fluctuation and to the resonant transfer processes. The contribution of the short-range forces was found to be small in similar circumstances.[12] The parameters entering into the calculation were chosen as follows. The Lennard-Jones parameters were taken from Ref. 21 and the rotational and translational diffusion constants from Refs. 12 and 22, respectively. The spectroscopic parameter l_μ, defined by Levesque, Weis, and Oxtoby[12] was obtained from the value of $[\partial\mu/\partial\mu]$ in pure HCl liquid;[19] the corresponding parameter l_D was determined by fitting the isotropic Raman spectra.[18] Finally the lattice-gas parameter ρ_0 was chosen equal to the close-packed density for HCl. The conclusions resulting from this estimation are discussed in Sec. V.

V. RESULTS AND DISCUSSION

A. Results

The infrared and anisotropic Raman spectra may be calculated by Fourier transforming the correlation functions $G_u(t)$, $u=1,2$, obtained in Secs. II and III. The following conclusions may then be drawn from the present theory.

(i) The zero-order theory coincides with the product theory. This theory, in which the infrared and anisotropic Raman functions are factorized into their rotational and vibrational components, is thus a correct lowest-order theory. Moreover, it gives an exact integrated intensity.

(ii) Superposed to the spectral density given by the zero-order theory, the spectral density produced by the first-order correction generates, in essence, a small frequency shift; in turn, the spectral density produced by the second-order correction generates a small broadening of the band. The combined effect of these two corrections is illustrated in Fig. 3.

(iii) The magnitude of the successive corrections, as well as the convergence of their series, vary when going, for a given liquid sample, from its infrared to its anisotropic Raman spectra. The components of the interaction potential $V(n,t)$ contributing to $X_1(t)$ are different from those contributing to $X_2(t)$. This result is related, within the Gaussian property expression by Eq. (18), to the rotational invariance of the liquid sample.

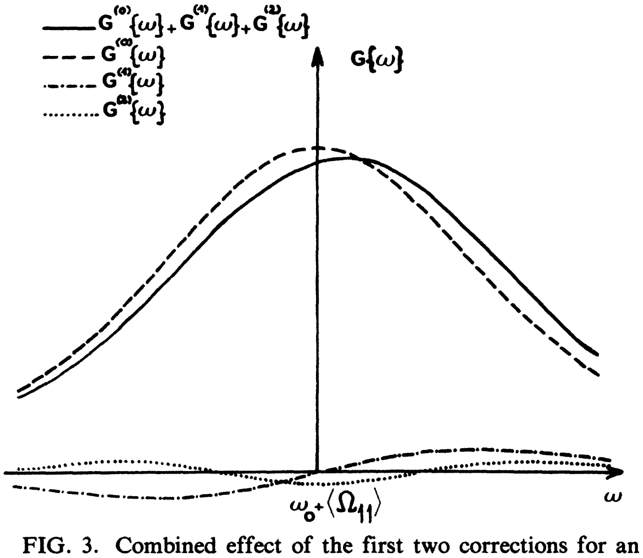

FIG. 3. Combined effect of the first two corrections for an infrared spectrum of a representative van der Waals liquid. Results are similar for an anisotropic Raman spectrum.

(iv) The difference between the complete and the product theory is illustrated, for the infrared spectrum of pure HCl, in Fig. 4. The half-width of the HCl stretching band calculated by the complete theory exceeds that obtained from the product theory by ~6% whereas the band center remains unchanged. However, one may note that decorrelating rotations from translations and attributing the Gaussian characteristics to various dynamic variables of the problem leads to a relatively poor approximation for the absolute value of the first spectral moments. In this case, the angle averaging of the dipole-dipole interaction potential is not correctly executed (see, e.g., Ref. 21, pp. 985–988). Nevertheless, the statement that the spectral effects missing in the product approximation are comparatively small, even for relatively large intermolecular forces, still holds true.

(v) In the zero-order theory, the self- and total-

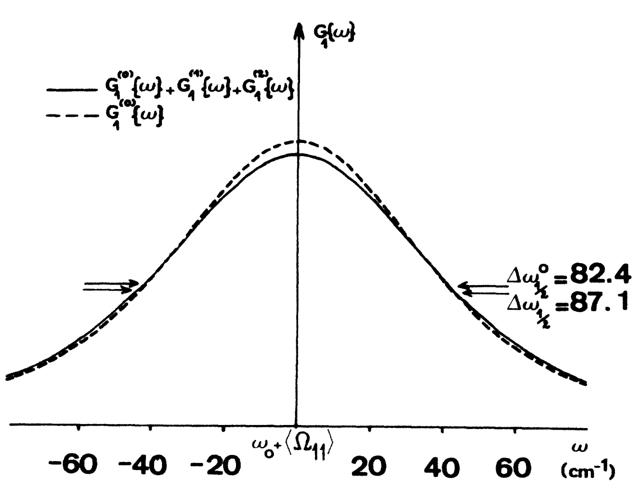

FIG. 4. Spectral effect of corrections to the product approximation for the infrared spectrum of pure HCl at $T=196$ K.

correlation functions coincide. This is no longer exact in the complete theory but difference remains unexpectedly small. The effect is illustrated for the infrared spectrum of a pure HCl liquid sample at $T=196$ K: in the complete theory, the half-width calculated from the self-correlation function differs from that calculated from the total-correlation function by less than one percent; the band centers are equal too. One concludes that the rotational-vibrational effects missing in the product approximation are small, not only in dilute van der Waals solutions, but also in pure van der Waals liquids. Moreover, in spite of the presence of resonant vibrational and rotational couplings, infrared and anisotropic Raman spectra remain mainly monomolecular.

This section may be concluded by briefly mentioning the effect of the intramolecular rotational-vibrational coupling. For a diatomic molecule, it arises from centrifugal effects. The corresponding contribution to the resonant transfer terms Ω_{ij} vanishes whereas its contribution to the environmental fluctuation terms Ω_{ii} is invariant under rotations of the reference frame. This latter contribution may thus be incorporated into the invariant term $G_{00}(R_{ij})$ of Eqs. (22)–(24). It results that the intramolecular coupling contributes to the vibrational relaxation factor $\exp\lambda_2(t)$ but not to $x_{u,2}(t)=1,2$; it does not introduce any correction to the product approximation. This conclusion is similar to that reached, in similar circumstances, for van der Waals solutions.[4,23]

B. Comparison with literature

The early papers by van Woerkom *et al.*[6] and Bell[7,8] do not lend themselves to an easy comparison. Various assumptions present in these theories do not allow a proper characterization of spectral effects missing in the product approximation. Moreover, one may note that the generalized cumulant expansion applied by van Woerkom *et al.* may be poorly convergent in some cases.[4] The comparison is easier with the papers of Wang and McHale.[9,10] The theoretical expressions for the two lowest infrared and anisotropic Raman spectral moments given by these authors are essentially similar to those derived here. However, the most significant comparison is that with the molecular dynamics simulation performed by Levesque, Weis, and Oxtoby[12] for pure HCl. Their calculation shows that the total rotational-vibrational correlation functions are indistinguishable from those given by the product approximation, within the uncertainty of the simulation. This conclusion certainly is compatible with those reached in this paper. Finally the comparison with our previous papers[3,4] on dilute van der Waals solutions shows that the quality of the product approximation is similar in solutions and pure liquids.

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