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Relaxation of rotational angular momentum of polar diatomic molecules in simple liquids

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The relaxation processes of rotational angular momentum of polar diatomic molecules diluted in simple liquids are analyzed by applying a non-Markovian relaxation theory to the study of the binary time autocorrelation function of the angular momentum. This non-Markovian theory was previously applied to the study of the infrared and Raman spectroscopy, and also to the analysis of the rotational energy relaxation processes. We have obtained non-Markovian evolution equations for the two-time j-level angular momentum correlation components involved in the angular momentum correlation function. In these equations, the time-dependent angular momentum transfer rates and the pure orientational angular transfer rates are given in terms of the binary time autocorrelation function of the diatomic-solvent anisotropic interaction. The non-Markovian evolution equations converge to Markovian ones in the long time limit, reaching the angular momentum transfer rates in the usual time-independent form. Alternative time scales for the angular relaxation processes, relative to the individual rotational processes as well as to the global decay correlations, are introduced and analyzed. The theory is applied to the study of the angular momentum relaxation processes of HCl diluted in liquid SF_6, a system for which rotational energy relaxation and infrared and Raman spectroscopy was previously analyzed in the scope of the same theory.

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I. INTRODUCTION

The study of the angular momentum relaxation processes and the analysis of the orientational correlation functions has contributed significantly to the understanding of the molecular dynamics in condensed phases [1–5]. However, while for the molecular orientational processes we can obtain direct experimental data from the infrared and Raman spectra, for the angular momentum relaxation we must appeal to indirect procedures which often only give a partial representation of these processes.

The angular momentum correlation time and the orientational correlation time are connected by the so-called Hubbard relation [1,5], so when the orientational times can be estimated from the infrared and Raman data, the Hubbard relation gives an indirect measure of the angular correlation time. Furthermore, when the spin-rotation coupling is the dominant nuclear-spin relaxation channel, the angular correlation time can be indirectly estimated from the experimental NMR data [4–6]. The connection between the short time behavior of the angular momentum correlation function and the absorption shape in the far wings provides interesting information about the angular momentum relaxation processes [2,3]. Moreover, the femtosecond pump-probe LIF measurements give valuable information about the progressive effect of the solvent friction on the rotational motion of solute molecules in liquid solvents, a molecular process closely related to the time fluctuations of the angular momentum [7].

Though all the above experimental methods are certainly very useful, they present some limitations in order to provide a complete description of the angular momentum relaxation processes, particularly for light diatomic molecules in liquid phase [8]. In this work we present a quantum non-Markovian theory for the autocorrelation function of the angular momentum of a heteronuclear diatomic molecule immersed in a nonpolar liquid. This theory has been deduced from a more general framework for the diatomic vibrorotational relaxation that was previously applied to the study of the infrared and Raman spectra [9], and also to the energy relaxation processes [12], providing, in this way, a consistent connection with the experimental spectral data [10,11].

In this theory the binary time autocorrelation function of the angular momentum has been written in terms of the two-time j-level angular momentum correlation components, functions which give a measure of the individual angular correlation of each j level at present time with the initially assumed j-level of the diatomic. We have deduced non-Markovian master equations for the two-time j-level angular components in which the angular momentum transfer rates are given, in terms of the binary time autocorrelation function of the diatomic-solvent anisotropic interaction. This non-Markovian evolution equation converges for long times (LTL) toward the Markovian limit, where the angular transfer rates reach the usual time-independent form. We have introduced different time scales for the angular momentum relaxation processes which have been discussed and comparatively analyzed.

The structure of this paper is as follows. In Sec. II we summarized the theoretical relations of the general theory. In Sec. III we introduce the binary time autocorrelation function of the angular momentum in terms of the two-time j-level angular correlation components. In Sec. IV we deduce the non-Markovian evolution equations for the two-time j-level angular correlation components. In Sec. V we study the properties of the angular momentum transfer rates. In Sec. VI we analyze the LTL and the exponential decay representation for its angular momentum correlation function. In Sec. VII we apply the theory to the study of the angular momentum processes of HCl diluted in liquid SF_6. Finally, in Sec. VIII we present a brief summary and some conclusions.

II. THEORETICAL BACKGROUND

In the scope of the analysis of diluted solutions of diatomic polar molecules in a dense nonpolar fluid a theoretical approach [9] has been recently developed to calculate the autocorrelation function,

$$C_K(t) = \langle\langle \mathbf{D}^{(K)}(t) \cdot \mathbf{D}^{(K)}(0)\rangle\rangle = \sum_{q=-K}^{K} (-1)^q \langle\langle D_q^{(K)}(t) D_{-q}^{(K)}(0)\rangle\rangle, \tag{1}$$

for an irreducible tensor $\mathbf{D}^{(K)}$ of rank K, such as the permanent dipole moment or the polarizability of the solute molecule. According to the noninitial correlation hypothesis [9] and assuming that the diatomic is in its vibrational ground state, the correlation function $C_K(t)$ can be written as

$$C_K(t) = \sum_{j_f j_i} \sum_{j_l j_k} \sigma_{j_i}^0 D_{j_f j_i}^{(K)} D_{j_l j_k}^{(K)} \langle \hat{U}^{(K)}(t,0)\rangle_{j_l j_k}^{j_f j_i}, \tag{2}$$

where $\sigma_{j_i}^0$ is the equilibrium population of the rotational j_i level, $D_{j_a j_b}^{(K)}$ are the reduced matrix elements of the $\mathbf{D}^{(K)}$ tensor in the sense of the Wigner Eckart theorem, and $\langle \hat{U}^{(K)}(t,0)\rangle_{j_l j_k}^{j_f j_i}$ are the K-rank irreducible matrix elements of the reduced evolution superoperator (RES) $\langle \hat{U}(t,0)\rangle = \mathrm{Tr}_B[\exp(i\hat{L}t)\rho_B^0]$ in the tensor basis (of the Liouville space)

$$|j_i, j_f; KQ) = \sum_{m_i} \sum_{m_f} (-1)^{j_i - m_i} \sqrt{2K+1} \begin{pmatrix} j_i & j_f & K \\ m_i & m_f & -Q \end{pmatrix} |j_i m_i\rangle \times \langle j_f m_f|, \tag{3}$$

where $|jm\rangle$ are the usual rotor eigenstates, Tr_B is the partial trace over the bath coordinates (those of the solvent and the solute molecules, except the solute vibration-rotation), ρ_B^0 is the equilibrium density operator of the bath, and $\hat{L}$ is the Liouville superoperator of the total system. The time evolution of the RES can be deduced by using the Kubo cumulant expansion method [9,12,13] with a partial time-ordering cumulant prescription (PTOC) leading to the following master equation for the K-rank matrix elements of the RES [12],

$$\frac{d}{dt}\langle \hat{U}^{(K)}(t,0)\rangle_{j_l j_k}^{j_f j_i} = -i\omega_{j_l j_k} \langle \hat{U}^{(K)}(t,0)\rangle_{j_l j_k}^{j_f j_i} - \sum_{j_p j_r} [\hat{G}^{(K)}(t)]_{j_l j_k}^{j_p j_r} \langle \hat{U}^{(K)}(t,0)\rangle_{j_p j_r}^{j_f j_i}, \tag{4}$$

with the initial condition

$$\langle \hat{U}^{(K)}(t=0,0)\rangle_{j_l j_k}^{j_f j_i} = \delta_{j_f j_l} \delta_{j_i j_k}, \tag{5}$$

where $\omega_{j_l j_k}$ are the rotational transition frequencies and $[\hat{G}^{(K)}(t)]_{j_l j_k}^{j_p j_r}$ are the K-rank irreducible matrix elements of the PTOC relaxation superoperator. The Markovian limit, which holds when the temporal scales of the vibrorotational processes are large compared with those associated to the fluctuations of the solute-solvent interaction, is characterized by the Markovian relaxation superoperator $\hat{R}$ [9], whose K-rank irreducible matrix elements are given by

$$(\hat{R}^{(K)})_{j_l j_k}^{j_p j_r} = \lim_{t\to\infty} [\hat{G}^{(K)}(t)]_{j_l j_k}^{j_p j_r}, \tag{6}$$

which are the long time limit of the PTOC matrix elements.

The particular form of the relaxation matrix depends upon the model adopted for the vibrorotation bath interaction. As usual [9,12,14,15] here we assume that the anisotropic interaction Hamiltonian is a sum of effective binary potentials, each one expanded in Legendre polynomial P_L. With this assumption the PTOC relaxation matrix can be written as additive L contribution in the following form [see Eqs. (8)–(12) of Ref. [12]]:

$$[\hat{G}^{(K)}(t)]_{j_l j_k}^{j_p j_r} = \sum_{L=1}^{\infty} [\hat{G}^{(K)}(t;L)]_{j_l j_k}^{j_p j_r}, \tag{7}$$

where the anisotropic components $(L > 0)$ are given by

$$\begin{aligned}
[\hat{G}^{(K)}(t;L)]_{j_l j_k}^{j_p j_r} = {} & \delta_{j_f j_l} \delta_{j_i j_k} \sum_{j_n} \hbar^{-2} \Phi^{(L)}(t, \omega_{j_k j_n}) [j_i]^{-1} \bar{C}_{j_i j_n}^{(L)} \bar{C}_{j_n j_k}^{(L)} \\
& + \delta_{j_f j_l} \delta_{j_i j_k} \sum_{j_n} \hbar^{-2} \Phi^{(L)}(t, \omega_{j_l j_n})^{*} [j_f]^{-1} \bar{C}_{j_f j_n}^{(L)} \bar{C}_{j_n j_l}^{(L)} \\
& - \bar{C}_{j_l j_f}^{(L)} \bar{C}_{j_i j_k}^{(L)} (-1)^K \hbar^{-2} \begin{Bmatrix} j_f & j_k & K \\ j_i & j_f & L \end{Bmatrix} \\
& \times [\Phi^{(L)}(t, \omega_{j_k j_i}) + \Phi^{(L)}(t, \omega_{j_l j_f})^{*}],
\end{aligned} \tag{8}$$

with $[j] = 2j+1$ and

$$\bar{C}_{j_f j_i}^{(L)} = \sqrt{[j_f][j_i]} \begin{pmatrix} j_f & L & j_i \\ 0 & 0 & 0 \end{pmatrix}, \tag{9}$$

$$\Phi^{(L)}(t,\omega) = \int_{-t}^{t} d\tau \exp(i\omega\tau) \Phi^{(L)}(\tau), \tag{10}$$

$$\Phi^{(L)}(t) = \frac{\lambda_L^2}{2L+1} \phi^{(L)}(t). \tag{11}$$

In these equations λ_L^2 accounts for the strength of the interaction and $\phi^{(L)}(t)$ is a normalized time autocorrelation function $[\phi^{(L)}(0) = 1]$, which collects all the temporal dependence of the L-anisotropic interaction component. Both λ_L^2 and $\phi^{(L)}(t)$ can be calculated by appropriate liquid models, by molecular dynamics simulations, or by fitting between theoretical and experimental spectral results.

III. ANGULAR MOMENTUM CORRELATION FUNCTION

The relaxation processes of the angular momentum will be described by means of the binary time autocorrelation function

$$C_J(t) = \langle\langle \vec{J}(0)^2\rangle\rangle^{-1} \langle\langle \vec{J}(t) \cdot \vec{J}(0)\rangle\rangle, \tag{12}$$

where $\vec{J}$ is the intrinsic angular momentum of the diatomic. The angular momentum is a tensor of rank $K=1$ whose spherical components J_q are given in the irreducible tensor basis (3) by [16]

$$|J_q) = \sum_j \langle j\|J\|j\rangle \sqrt{3}|j,j;1,q), \tag{13}$$

where $\langle j\|J\|j\rangle$ are the reduced matrix elements

$$\langle j\|J\|j\rangle = \sqrt{[j]j(j+1)}, \tag{14}$$

being $\Delta j=0$ its j-selection rule. Therefore, from Eq. (2) we obtain that the correlation function (12) can be approximated by the expression

$$C_J(t) = \langle\langle \vec{J}(0)^2\rangle\rangle^{-1} \sum_{j_i}\sum_{j_k} \sigma^0_{j_i} \langle j_i\|J\|j_i\rangle\langle j_k\|J\|j_k\rangle\langle \hat{U}^{(1)}(t,0)\rangle^{j_ij_i}_{j_kj_k}, \tag{15}$$

where

$$\langle\langle \vec{J}(0)^2\rangle\rangle = \mathrm{Tr}\{\vec{J}^2\sigma^0\} = \sum_j \sigma^0_j j(j+1)\hbar^2 \tag{16}$$

is the equilibrium average of the square angular momentum.

We introduce the correlation time associate to $C_J(t)$ [Eq. (15)] in the usual form

$$\tau_J = \int_0^\infty dt C_J(t), \tag{17}$$

which gives a measure of the global time scale for the relaxation processes of the angular momentum.

We define the two-time j-level angular momentum correlation components in terms of the irreducible matrix elements of the RES

$$C_J(t,j_k|0,j_i) = \langle \hat{U}^{(1)}(t,0)\rangle^{j_ij_i}_{j_kj_k}, \tag{18}$$

which give a measure of the angular momentum correlation between the single j_k level at time $t>0$ and the assumed initial ($t=0$) j_i level of the diatomic. Due to the initial conditions of the RES (5), the two-time j-level angular momentum components satisfy the property

$$C_J(0,j_k|0,j_i) = \delta_{j_kj_i}, \tag{19}$$

so the autocorrelation function $C_J(t,j_i|0,j_i)$ gives information about the lifetime of the angular momentum in the single j_i level, while the cross-correlation functions $C_J(t,j_k|0,j_i)$ ($j_k\neq j_i$) give information about the angular momentum transfer processes between different j levels.

In terms of the two-time j-level angular momentum components (18) the time correlation function of the angular momentum (15) can be written as

$$C_J(t) = \langle\langle \vec{J}(0)^2\rangle\rangle^{-1} \sum_{j_i}\sum_{j_k} \langle j_k\|J\|j_k\rangle C_J(t,j_k|0,j_i)\langle j_i\|J\|j_i\rangle\sigma^0_{j_i}, \tag{20}$$

where $C_J(t)$ results of the average effect produced by all the j-level pairs of the angular momentum connected by the two-time j-level components. Associated to each j level we define an angular momentum relaxation time as

$$\tau_j = \int_0^\infty dt C_J(t,j|0,j), \tag{21}$$

which gives a selective measure of the relaxation time scale for the angular momentum in each j level. Then, focusing our attention in the binary time autocorrelation function $C_J(t)$, the detailed description of the angular momentum relaxation processes has been regarded to the knowledge of the two-time j-level angular momentum components (18).

IV. NON-MARKOVIAN TIME EVOLUTION EQUATIONS

The time evolution equations for the two-time j-level angular momentum correlation components $C_J(t,j_k|0,j_i)$ [Eq. (18)] can be obtained from the non-Markovian equations (4) by selecting the $K=1$ rank and the j-selection rule $\Delta j=0$. Thus, taking into account that the $\Delta j=0$ transition has even parity, that the remainder allowed $K=1$ transitions $\Delta j=\pm 1$ have odd parity, and that the reduced matrix elements of the PTOC superoperators (7) and (8) do not mix j transitions of different parity, we obtain the evolution equations

$$\frac{d}{dt}C_J(t,j_k|0,j_i) = -[T_J(t)]^{-1}_{j_k}C_J(t,j_k|0,j_i) + \sum_{j_l(\neq j_k)} P^{(J)}_{j_lj_k}(t)C_J(t,j_l|0,j_i), \tag{22}$$

where $P^{(J)}_{j_lj_k}(t)$ are the time-dependent angular momentum transfer rate

$$P^{(J)}_{j_lj_k}(t) = -[\hat{G}^{(1)}(t)]^{j_lj_l}_{j_kj_k}, \tag{23}$$

while $[T_J(t)]_{j_k}$ is the time-dependent angular momentum relaxation time of the j_k level

$$\frac{1}{[T_J(t)]_{j_k}} = [\hat{G}^{(1)}(t)]^{j_kj_k}_{j_kj_k}, \tag{24}$$

which gives a measure of the transient time scales associated to the angular momentum relaxation in each j level.

V. ANGULAR MOMENTUM TRANSFER RATES

From Eqs. (7), (8), and (23) it is deduced that the angular momentum transfer rates can be written as the additive contributions due to the L-anisotropic components of the interaction

$$P^{(J)}_{j_lj_k}(t) = \sum_{L=1}^{\infty} P^{(J)}_{j_lj_k}(t;L), \tag{25}$$

where each L component is given by

$$P^{(J)}_{j_lj_k}(t;L) = -[\hat{G}^{(1)}(t;L)]^{j_lj_l}_{j_kj_k}, \tag{26}$$

which from Eqs. (8)–(11) can be written as

$$P^{(J)}_{j_lj_k}(t;L) = \Theta^{(J,L)}_{j_lj_k}\phi^{(L)}(t;\omega_{j_lj_k}), \tag{27}$$

and where $\Theta^{(J,L)}_{j_lj_k}$ is the L-static coupling factor,

$$\Theta^{(J,L)}_{j_l j_k} = -\begin{Bmatrix} j_l & j_l & 1 \\ j_k & j_k & L \end{Bmatrix} |\bar{C}^{(L)}_{j_l j_k}|^2 \frac{\hbar^{-2}\lambda_L^2}{(2L+1)}, \tag{28}$$

while

$$\phi^{(L)}(t;\omega) = \int_{-t}^{t} dt \exp(i\omega t)\phi^{(L)}(t) \tag{29}$$

is the L-dynamic time-dependent coupling function.

In a similar way, from Eqs. (24), (7), and (8) we obtain for the time-dependent relaxation time

$$\frac{1}{[T_J(t)]_{j_k}} = \sum_{L=1}^{\infty}\left\{\sum_{j_n(\neq j_k)} \Theta^{(J^2,L)}_{j_k j_n}\phi^{(L)}(t;\omega_{j_k j_n})\right\} + \frac{1}{[T_J^{(M)}(t)]_{j_k}}, \tag{30}$$

where $\Theta^{(J^2,L)}_{j_n j_k}$ is the L-static coupling factor

$$\Theta^{(J^2,L)}_{j_k j_n} = [j_k]^{-1}|\bar{C}^{(L)}_{j_n j_k}|^2 \frac{\hbar^{-2}\lambda_L^2}{(2L+1)}, \tag{31}$$

defined in Ref. [12] for the L component of the time-dependent transition rates

$$P_{j_k j_n}(t;L) = \Theta^{(J^2,L)}_{j_k j_n}\phi^{(L)}(t;\omega_{j_k j_n}), \tag{32}$$

while $[T_J^{(M)}(t)]_{j_k}$, which is given by

$$\frac{1}{[T_J^{(M)}(t)]_{j_k}} = \sum_{L=2}^{\infty} \Theta^{(M,L)}_{j_k}\phi^{(L)}(t;0), \tag{33}$$

and

$$\Theta^{(M,L)}_{j_k} = |\bar{C}^{(L)}_{j_k j_k}|^2 \frac{\hbar^{-2}\lambda_L^2}{(2L+1)}\left([j_k]^{-1} + \begin{Bmatrix} j_k & j_k & 1 \\ j_k & j_k & L \end{Bmatrix}\right) \tag{34}$$

is the time-dependent M-relaxation time, which is associated to the pure reorientational [zero-frequency component of the dynamics function (29)] relaxation processes of the angular momentum. From the selection rules for the $3j$ symbols appearing in Eq. (34) it follows that only the even L components of the anisotropic interaction contribute to the pure orientational relaxation of the angular momentum.

By introducing the definition of the time-dependent rotational lifetime $[T_1(t)]_{j_k}$ given in Ref. [12],

$$\frac{1}{[T_1(t)]_{j_k}} = \sum_{j_n(\neq j_k)}\left\{\sum_{L=1}^{\infty} P_{j_k j_n}(t;L)\right\}, \tag{35}$$

we can write [see Eqs. (31) and (32)] the time-dependent angular momentum relaxation time (30) as

$$\frac{1}{[T_J(t)]_{j_k}} = \frac{1}{[T_1(t)]_{j_k}} + \frac{1}{[T_J^{(M)}(t)]_{j_k}}, \tag{36}$$

an expression in which we can identify the elastic and the inelastic contributions [15] to the angular momentum relaxation processes, that is, the contribution due to pure reorientational relaxation and the contribution due to population relaxation or T_1 processes, respectively.

From the properties of the $3j$ and $6j$ symbols appearing in $\Theta^{(J,L)}_{j_l j_k}$ [Eq. (28)], it is easy to show that the L-static coupling factor satisfies the symmetry relation

$$\Theta^{(J,L)}_{j_l j_k} = \Theta^{(J,L)}_{j_k j_l}, \tag{37}$$

while from Eqs. (28) and (31) we have

$$\Theta^{(J,L)}_{j_l j_k} = \Theta^{(L)}_{j_l j_k}\Theta^{(J^2,L)}_{j_l j_k}, \tag{38}$$

where

$$\Theta^{(L)}_{j_l j_k} = -[j_l]\begin{Bmatrix} j_l & j_l & 1 \\ j_k & j_k & L \end{Bmatrix}, \tag{39}$$

which satisfies the symmetry relation

$$\Theta^{(L)}_{j_l j_k}[j_k] = [j_l]\Theta^{(L)}_{j_k j_l}.$$

Then, by taking into account Eqs. (27) and (32) we obtain the relation

$$P^{(J)}_{j_l j_k}(t;L) = \Theta^{(L)}_{j_l j_k}P_{j_l j_k}(t;L), \tag{40}$$

which shows the close connection between the transition rates of the T_1 processes (32) and the angular momentum transfer rate (22).

The rotational j levels coupled by the L-static factors (28) are selected by the $3j$ and $6j$ symbols appearing in $\Theta^{(J,L)}_{j_l j_k}$. For the first two terms of the anisotropic interaction $L=1,2$ we have the j-selection rules: $j_k = j_l \pm L$, while the corresponding static factors are

$$\Theta^{(J,1)}_{j_l j_l+1} = -\frac{\hbar^{-2}\lambda_1^2}{3}\sqrt{\frac{j_l(j_l+2)}{(2j_l+1)(2j_l+3)}}, \tag{41}$$

$$\Theta^{(J,2)}_{j_l j_l+2} = \frac{\hbar^{-2}\lambda_2^2}{5}\frac{-3}{2(2j_l+3)}\sqrt{\frac{j_l(j_l+1)(j_l+2)(j_l+3)}{(2j_l+1)(2j_l+5)}}, \tag{42}$$

the remaining L-static factors can be obtained from the symmetry relation (37). On the other hand, the j dependence of the $L=1,2$ components of the time-dependent relaxation time (30) can be obtained from both the explicit form of the coupling factors $\Theta^{(J^2,L)}_{j_l j_l \pm L}$ given in Ref. [12] [Eqs. (32)–(34)], and the $L=2$ factor (34),

$$\Theta^{(M,2)}_{j_l} = \frac{\hbar^{-2}\lambda_2^2}{5}\frac{3}{(2j_l+3)(2j_l-1)}, \tag{43}$$

which determines the first L-anisotropic contribution to the pure orientational angular momentum processes.

As in previous works [10,12], we have considered an exponential decay function

$$\phi_r^{(L)}(t) = \exp(-t/t_{C;L}), \tag{44}$$

for the real part of the L-correlation function $\phi^{(L)}(t)$, where $t_{C;L}$ is the correlation time for the L-anisotropic interaction. The imaginary part $\phi_i^{(L)}(t)$ was determined by following the method proposed in Ref. [17], where the relation between the Fourier transforms of the real $\phi_r^{(L)}(t)$ and the imaginary $\phi_i^{(L)}(t)$ parts of an equilibrium correlation function

$$\phi_i^{(L)}(\omega) = -\, i \tanh\left(\frac{\beta\hbar\omega}{2}\right)\phi_r^{(L)}(\omega) \tag{45}$$

is used to calculate the imaginary part $\phi_i^{(L)}(t)$, that is,

$$\phi_i^{(L)}(t) = u(t)\sum_{n=0}^{\infty}\left\{\frac{4\gamma}{\gamma^2-(2n+1)^2\pi^2}\left[\exp\left(-\frac{|t|}{t_{C;L}}\right) - \exp\left(-\frac{(2n+1)\pi}{\beta\hbar}|t|\right)\right]\right\}, \tag{46}$$

with $u(t)=1$, if $t>0$, $u(t)=-1$ if $t<0$, $u(0)=0$, and $\gamma=\beta\hbar t_{C;L}^{-1}$.

VI. MARKOVIAN LIMIT

A. Long time limit

When the Fourier transforms $\phi^{(L)}(\omega)=\lim \phi^{(L)}(t\to\infty;\omega)$ of the L-anisotropic components correlation function $\phi^{(L)}(t)$ are well defined [Eq. (29)], the time-dependent transfer rates (25) and (27) and the time-dependent relaxation times (30) and (33) converge in the long time limit towards their usual time-independent form,

$$P_{j_lj_k}^{(J)} = \lim_{t\to\infty} P_{j_lj_k}^{(J)}(t) = \sum_{L=1}^{\infty} P_{j_lj_k}^{(J)}(L) = \sum_{L=1}^{\infty}\Theta_{j_lj_k}^{(J,L)}\phi^{(L)}(\omega_{j_lj_k}), \tag{47}$$

$$\frac{1}{(T_J)_{j_k}} = \lim_{t\to\infty}\frac{1}{[T_J(t)]_{j_k}} = \sum_{L=1}^{\infty}\left\{\sum_{j_n(\neq j_k)}\Theta_{j_kj_n}^{(J^2,L)}\phi^{(L)}(\omega_{j_kj_n})\right\} + \sum_{L=2}^{\infty}\Theta_{j_k}^{(M,L)}\phi^{(L)}(0). \tag{48}$$

Alternatively, by combining Eq. (6) and Eqs. (23) and (24), the above equations can be deduced from the more general relations,

$$P_{j_lj_k}^{(J)} = -\,(\hat{R}^{(1)})_{j_kj_k}^{j_lj_l} = -\lim_{t\to\infty}[\hat{G}^{(1)}(t)]_{j_kj_k}^{j_lj_l}, \tag{49}$$

$$\frac{1}{(T_J)_{j_k}} = (\hat{R}^{(1)})_{j_kj_k}^{j_kj_k} = \lim_{t\to\infty}[\hat{G}^{(1)}(t)]_{j_kj_k}^{j_kj_k}. \tag{50}$$

On the other hand, by taking the limit process in Eqs. (32)–(36) we obtain

$$\frac{1}{(T_J)_{j_k}} = \frac{1}{(T_1)_{j_k}} + \frac{1}{(T_J^{(M)})_{j_k}}, \tag{51}$$

where $(T_J^{(M)})_{j_k}$ is given by

$$\frac{1}{(T_J^{(M)})_{j_k}} = \sum_{L=2}^{\infty}\Theta_{j_k}^{(M,L)}\phi^{(L)}(0), \tag{52}$$

while $(T_1)_{j_k}$ is given by Eqs. (40) and (43) of Ref. [12].

From Eqs. (45) and (47) it can be deduced that the L component of the angular transfer rate is given by

$$P_{j_lj_k}^{(J)}(L) = \Theta_{j_lj_k}^{(J,L)}\phi_r^{(L)}(\omega_{j_lj_k})\left\{1+\tanh\left(\frac{\beta\hbar\omega_{j_lj_k}}{2}\right)\right\}, \tag{53}$$

then, due to the symmetry of both the L-static coupling factor (37) and the function $\phi_r^{(L)}(\omega)=\phi_r^{(L)}(-\omega)$ ($\phi_r^{(L)}(t)$ is an even function of t) we obtain

$$P_{j_lj_k}^{(J)}(L) = P_{j_kj_l}^{(J)}(L)\exp(\beta\hbar\omega_{j_lj_k}), \tag{54}$$

which is the detailed balance condition for the angular transfer rates.

By combining Eqs. (49) and (50) and (23) and (24), it follows that the long time limit of the master equations (22) are

$$\frac{d}{dt}C_J(t,j_k|0,j_i) = -\,(T_J)_{j_k}^{-1}C_J(t,j_k|0,j_i) + \sum_{j_l(\neq j_k)}P_{j_lj_k}^{(J)}C_J(t,j_l|0,j_i), \tag{55}$$

which are the Markovian evolution equations for the two-time j-level angular momentum correlation components (18).

B. Exponential representation

In the Markovian limit, the binary time autocorrelation function of the angular momentum (20) can be written in an alternative form. By introducing the set of functions

$$C_{j_k}(t) = \|\vec{J}(0)^2\|^{-1}\sum_{j_i}C_J(t,j_k|0,j_i)\langle j_i\|J\|j_i\rangle\sigma_{j_i}^0, \tag{56}$$

which are the components of the column vector $\mathbf{C}(t)$, by collecting $\mathbf{J}$ to the elements $\langle j_k\|J\|j_k\rangle$, we can write the binary time autocorrelation function (20) as

$$C_J(t) = \mathbf{J}\cdot\mathbf{C}(t). \tag{57}$$

From Eqs. (55) and (56) it follows that $\mathbf{C}(t)$ satisfies the time evolution equation

$$\frac{\partial\mathbf{C}(t)}{\partial t} = -\,\mathbf{R}^{(J)}\mathbf{C}(t), \tag{58}$$

where the elements of the matrix $\mathbf{R}^{(J)}$ are given by $R_{j_kj_k}^{(J)}=(T_J)_{j_k}^{-1}$ and $R_{j_kj_l}^{(J)}=-P_{j_lj_k}^{(J)}$, while the initial conditions are [see Eqs. (19) and (56)] $C_{j_k}(0)=\langle\langle\vec{J}(0)^2\rangle\rangle^{-1}\langle j_k\|J\|j_k\rangle\sigma_{j_k}^0$.

As the eigenvectors $\mathbf{Y}_\alpha$ of the matrix $\mathbf{R}^{(J)}$, $\mathbf{R}^{(J)}\mathbf{Y}_\alpha=\gamma_\alpha\mathbf{Y}_\alpha$, form a basis of the vector space generated by the solutions of Eq. (58), the time dependence of $\mathbf{C}(t)$ can be written as

$$\mathbf{C}(t) = \sum_\alpha C_\alpha\exp(-\,\gamma_\alpha t)\mathbf{Y}_\alpha, \tag{59}$$

where C_α are the coefficients of $\mathbf{C}(0)$ in the $\mathbf{Y}_\alpha$ basis.

By substituting Eq. (59) into Eq. (57) it follows that the angular momentum correlation function can be written as

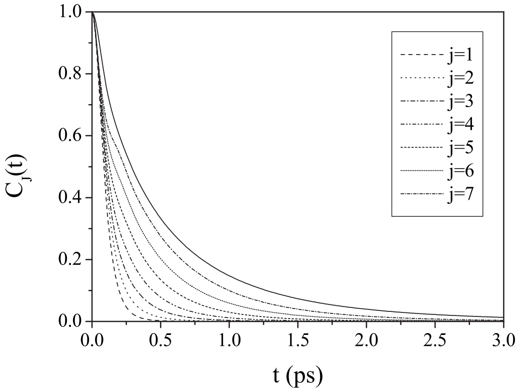

FIG. 1. The time correlation function of angular momentum (solid line) and the first seven two-time j-level correlation components $C_J(t,j|0,j)$ of HCl in liquid SF_6.

$$C_J(t)=\sum_\alpha W_\alpha \exp(-\gamma_\alpha t), \tag{60}$$

where the real part of γ_α defines the exponential decay times

$$T_\alpha^{(J)}=(\mathrm{Re}\{\gamma_\alpha\})^{-1}, \tag{61}$$

while

$$W_\alpha=C_\alpha \mathbf{J}\cdot\mathbf{Y}_\alpha \tag{62}$$

gives the weight of each exponential term. From the normalization of $C_J(t)$ $[C_J(0)=1]$ it follows $\mathbf{J}\cdot\mathbf{C}(0)=1$, and therefore

$$\sum_\alpha W_\alpha=1. \tag{63}$$

Finally, from the definition for the correlation time (17) we have

$$\tau_J=\sum_\alpha W_\alpha T_\alpha^{(J)}, \tag{64}$$

so the Markovian correlation time τ_J results from averaging the exponential decay times (61) over the exponential amplitudes (62).

VII. ANGULAR MOMENTUM RELAXATION OF HCl IN LIQUID SF_6

We apply the present theory to the study of the angular momentum relaxation processes of HCl diluted in liquid SF_6 at $T=293$ K, a system for which the infrared and Raman spectra were calculated and compared with the available experimental data [10,11], and for which the rotational energy relaxation processes, or T_1 processes, were also studied [12]. We have performed all the calculation of this application taking the value of the rotational constant $B_0=10.44$ cm^{-1} and using the statistical parameters of the anisotropic interaction for $L=1,2$: $\overline{\lambda_1^2}=73.95$, $\overline{\lambda_2^2}=38.58$, $t_{C;1}=0.091$ ps, $t_{C;2}=0.097$ ps, which were obtained by using a microscopic cell model for the liquid [10].

In Fig. 1 we have represented the angular momentum correlation function $C_J(t)$ together with the first seven two-time j-level angular momentum correlation components $C_J(t,j|0,j)$ $(j=1-7)$ of HCl in SF_6. Both $C_J(t,j|0,j)$ and $C_J(t)$ were obtained by solving numerically the non-Markovian differential equations (22) with the j-quantum numbers truncated at $j_{\max}=20$. As it can be appreciated, the time correlation function $C_J(t)$ presents a simple decay behavior with a correlation time (17) of $\tau_J=0.512$ ps, which is shorter than the rotational energy correlation time [12] $\tau_E=2.85$ ps, being the angular momentum relaxation of HCl in SF_6 is clearly more rapid than the rotational energy relaxation (compare Fig. 1 of this paper with Fig. 1 of Ref. [12]). The first two-time j-level components $C_J(t,j|0,j)$ also present a simple decay behavior; however, for high j values the two-time components show a region of inflection at $t\sim 0.1-0.2$ ps, the same effect was observed in the conditional probabilities of the energy relaxation processes [12]. In Fig. 1 it is shown as the two-time functions $C_J(t,j|0,j)$ decay more slowly as the j-quantum number increases its value, this behavior being confirmed by the values of the angular momentum relaxation times τ_j (21) collected in Table I $(j=1-8)$ and plotted in Fig. 2, which are in the subpicosecond time scale, and they are shown to increase systematically with the j-quantum number.

In Table I we have also collected the Markovian values of the relaxation times τ_j^M (21), which are not very different from the non-Markovian ones, indicating this fact that the memory effects must be small in the angular momentum relaxation. In fact, the effective area of the difference between the Markovian and the non-Markovian functions $C_J(t)$ only represents 3% of the correlation time τ_J [the area of $C_J(t)$]. These effects are more pronounced in the first stage of the relaxation, where as it is shown in Fig. 3 the inverse of the time-dependent relaxation time $[T_J(t)]_j$ [Eq. (30)] presents a transient oscillating behavior that converges to the stationary regime approximately at $t\sim 0.4$ ps. The same behavior can be observed in the L components of the angular momentum transfer rates $P_{jj\pm 1}^{(J)}(t;1)$ and $P_{jj\pm 2}^{(J)}(t;2)$. Thus, those compo-

TABLE I. Relaxation times (in ps) for HCl in liquid SF_6.

j/α	1	2	3	4	5	6	7	8
τ_j	0.093	0.114	0.140	0.180	0.234	0.307	0.397	0.501
τ_j^M	0.064	0.100	0.145	0.202	0.272	0.355	0.451	0.560
$(T_J)_j$	0.061	0.091	0.129	0.179	0.242	0.318	0.405	0.506
$(T_J^{(M)})_j$	0.289	1.213	2.600	4.448	6.759	9.532	12.768	16.465
$T_\alpha^{(J)}$	0.058	0.089	0.131	0.185	0.250	0.329	0.420	0.524

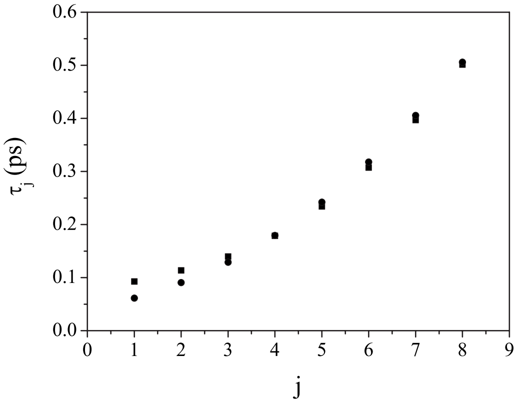

FIG. 2. Relaxation times of HCl in SF$_6$: τ_j (squares) and $(T_J)_j$ (circles).

nents $C_J(t,j|0,j)$ of the correlation function $C_J(t)$, which relaxes more rapidly, will be more affected by the non-Markovian effects than the slower ones. In fact, while the effective area of the difference between the Markovian and the non-Markovian functions $C_J(t,1|0,1)$ represents 43% of τ_1 [the area of $C_J(t,1|0,1)$], the effective area of the difference for $C_J(t,8|0,8)$ only represents 11% of τ_8.

In Table I and in Fig. 2 it can be appreciated as the angular momentum relaxation times τ_j [Eq. (21)] and $(T_J)_j$ [Eq. (50)] take similar values for the first j-quantum numbers, a fact that contrasts with the results obtained for the analogous times of the energy relaxation processes [see Eqs. (21) and (25), and Fig. 2 of Ref. [12]]. On the other hand, in Table I it can be also observed the main contributions to the relaxation times $(T_J)_j$ come from the rotational energy relaxation contributions [the first term of Eq. (51)]. In this table we can observe the values of the M-relaxation times $(T_J^{(M)})_j$, which are generated by the $L=2$ anisotropic interaction term, are much larger than the corresponding energy relaxation times $(T_1)_j$, reaching values of several picoseconds with increasing j.

In Fig. 4 we have represented the first angular momentum relaxation times τ_j [Eq. (21)], together with the energy relaxation times τ_j^E [Eq. (21) of Ref. [12]], the dephasing times associated to the rotational absorption R-branch $\tau^{0\text{-}0}_{1;R;j}$, to the rotational Q-dispersion branch $\tau^{0\text{-}0}_{2;Q;j}$ and to the rotational S-dispersion branch $\tau^{0\text{-}0}_{2;S;j}$ [10]. As it can be appreciated, the angular momentum times τ_j present values comparable to the energy relaxation times τ_j^E and to the rotational dephasing times, being τ_j the smaller ones unless for the $j=1,2$ values of $\tau^{0\text{-}0}_{2;Q;1}$ and $\tau^{0\text{-}0}_{2;Q;2}$. A similar situation can be observed in Fig. 5, where the plotted values of τ_j are comparable and smaller (again unless for $j=1,2$) to the vibrorotational dephasing times of both the anisotropic S-dispersion branch $\tau^{1\text{-}0}_{2;S;j}$ and the anisotropic Q-branch $\tau^{1\text{-}0}_{2;Q;j}$. Also the relaxation times of the angular momentum τ_j remain comparable to the dephasing times of the isotropic Q-branch $\tau^{1\text{-}0}_{0;Q;j}$, however, the values of the last ones are clearly greater for the first values of the j-quantum numbers number. In this way, the angular momentum relaxation of the first j levels proceeds more rapidly than their energy relaxation, or the dephasing processes involved in the infrared and Raman spectra.

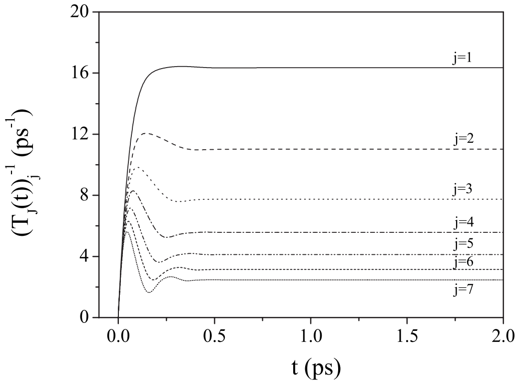

FIG. 3. Inverse of the time-dependent relaxation times $[T_J(t)]_j$ (in ps^{-1}) of HCl in liquid SF$_6$.

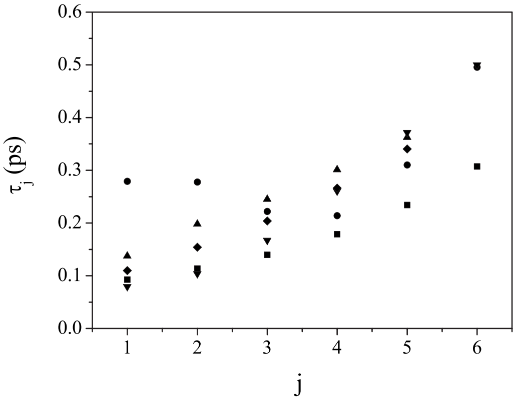

FIG. 4. Relaxation times τ_j (squares), rotational energy lifetimes τ_j^E (circles), and rotational dephasing times of HCl in SF$_6$: $\tau^{0\text{-}0}_{1;R;j}$ (up triangles), $\tau^{0\text{-}0}_{2;Q;j}$ (down triangles), $\tau^{0\text{-}0}_{2;S;j}$ (rhombus).

As the time correlation function $C_J(t)$ is essentially Markovian, we can describe the angular momentum relaxation by means of the exponential decay times $T_\alpha^{(J)}$ [Eq. (61)] and their respective weights W_α [Eq. (62)]. With such a purpose we have calculated the eigenvalues and the eigenvectors of the $\mathbf{R}^{(J)}$ matrix [see the equations following Eq. (58)], taking for its representation the maximum of the j-quantum number

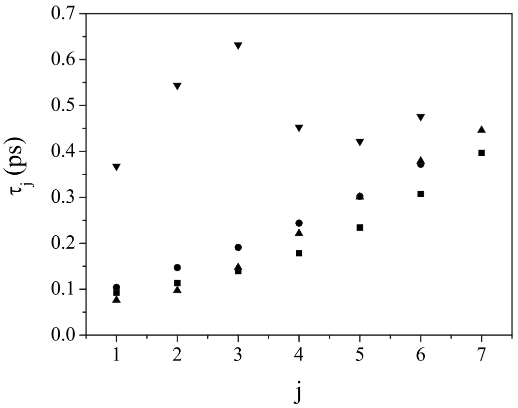

FIG. 5. Relaxation times τ_j (squares) and vibrorotational dephasing times of HCl in SF$_6$: $\tau^{1\text{-}0}_{2;S;j}$ (circles), $\tau^{1\text{-}0}_{2;Q;j}$ (up triangles), $\tau^{1\text{-}0}_{0;Q;j}$ (down triangles).

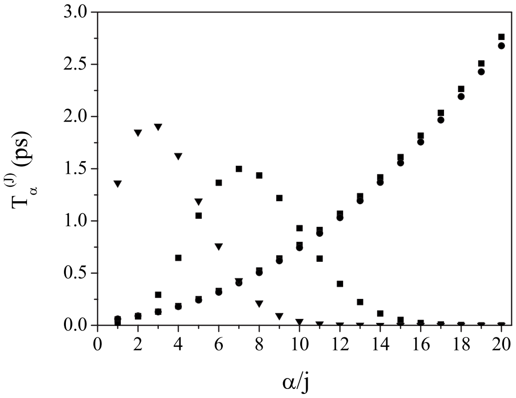

FIG. 6. Exponential decay times $T_\alpha^{(J)}$ (squares) and relaxation times $(T_J)_j$ (circles) of HCl in SF$_6$ together with the exponential weights W_α (up triangles) and the thermal populations $[j]\sigma_j^0$ (down triangles). Time values in ps.

$j_{\max}=30$. The first values of the exponential times $T_\alpha^{(J)}$ are shown in Table I, where it can be noted as $T_\alpha^{(J)}$ present similar values to the first relaxation times τ_j [Eq. (21)] and $(T_J)_j$ [Eq. (30)]. In Fig. 6 we can observe the similitude between the exponential times $T_\alpha^{(J)}$ and the relaxation times $(T_J)_j$ over a longer range of α/j. However, as it was previously observed for the energy relaxation processes [12], it is convenient to take into account that there exists a clear discrepancy between the weights W_α and the thermal populations $[j]\sigma_j^0$. Figure 6 shows the displacement of the weights W_α from the thermal populations $[j]\sigma_j^0$ toward high j/α values. While the maximum of $[j]\sigma_j^0$ is located at $j=3$, with a representative relaxation time of $(T_J)_3=0.129$ ps, the maximum of W_α is located at $\alpha=7$, increasing the representative times to values close to $T_7^{(J)}=0.420$ ps, which is in accord with a global correlation time of $\tau_J=0.512$ ps [see Eq. (64)].

VIII. SUMMARY AND CONCLUSIONS

We have developed a non-Markovian theory for the angular momentum relaxation of a heteronuclear diatomic molecule immersed in a nonpolar fluid. This theory has been deduced from a more general non-Markovian formalism for the diatomic vibrorotational relaxation, which was previously applied to the study of the infrared and Raman spectra, and also to the analysis of the rotational energy relaxation. With this procedure, we have settled an interesting connection between the angular momentum processes and both the infrared and Raman spectroscopy, and the T_1 processes.

The theory has been focused on the binary time correlation function of the diatomic angular momentum, which was expressed in terms of the so-called two-time j-level angular momentum correlation components (18), giving these components a measure of the angular momentum correlation between two particular j-levels at two different times. We have deduced non-Markovian time evolution equations for the two-time j-level correlation components, whose coefficients define the time-dependent angular momentum transfer rates and the time-dependent angular momentum relaxation times, both expressed as the additive contributions determined by the two-time correlation functions of the different orders of the anisotropic interaction. We have analyzed the Markovian long time limit, obtaining a detailed balance condition for the angular transfer rates when the time correlation functions of the anisotropic interaction are appropriate quantum functions.

Three new alternative time scales for the angular momentum relaxation have been introduced in this work: (i) The angular momentum relaxation times τ_j, which give a measure of the decay scale of the two-time j-level correlation components $C_J(t,j|0,j)$. (ii) The relaxation times $(T_J)_j$ given by the long time limit of the time-dependent angular momentum relaxation times, obtained from the coefficients of the Markovian evolution equations. (iii) The exponential decay times $T_\alpha^{(J)}$, which allows one to write the Markovian correlation function $C_J(t)$ as a weighted superposition of exponential decay terms.

The theory has been applied to the study of the angular momentum relaxation of HCl diluted in liquid SF$_6$ at $T=293$ K. We have calculated and analyzed both the non-Markovian and the Markovian two-time j-level correlation components and the corresponding angular momentum correlation functions. We found that the angular momentum relaxation proceeds on the whole in the subpicosecond time scale ($\tau_J=0.512$ ps), being clearly more rapid than the energy relaxation processes ($\tau_E=2.85$ ps). Additionally, the angular momentum relaxation takes place more slowly when the j-quantum number is increased, a behavior also observed in the energy relaxation processes and in the infrared and Raman dephasing processes. The non-Markovian effects were observed non-negligible only at very short times, mainly affecting the lower j levels, those with the shorter relaxation times.

The relaxation times τ_j of the angular momentum of HCl present comparable values to those dephasing times associated to both pure rotational and vibrorotational Raman and infrared spectroscopy. Only the isotropic Raman dephasing times and the rotational energy relaxation times τ_j^E are clearly greater than the angular momentum relaxation times. Also, we have compared the values of the three types of j-level relaxation times introduced in this work. We have found that for the HCl in SF$_6$, τ_j, $(T_J)_j$, and $T_\alpha^{(J)}$ also present comparable values (when they are ordered in the same increasing order). However, like in the previous work on energy relaxation [12], the exponential weights W_α differ clearly from the thermal populations $[j]\sigma_j^0$, being the maximum of the distribution W_α shifted to higher decay times $T_\alpha^{(J)}$.

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[1] P. S. Hubbard, Phys. Rev. **131**, 1155 (1963).
[2] D. K. Green and J. G. Powles, Proc. Phys. Soc. London **85**, 87 (1965).
[3] J. E. Anderson and W. H. Gerritz, J. Chem. Phys. **53**, 2584 (1970).
[4] D. Kivelson, Mol. Phys. **28**, 321 (1974).
[5] A. I. Burshtein and S. I. Temkin, *Spectroscopy of Molecular Rotation in Gases and Liquids* (Cambridge University Press, Cambridge, England, 1994).
[6] R. Shafer and R. G. Gordon, J. Chem. Phys. **58**, 4131 (1973).
[7] J. S. Baskin, M. Gupta, M. Chachisvilis, and A. H. Zewail, Chem. Phys. Lett. **275**, 437 (1997).
[8] *Molecular Cryospectroscopy*, edited by R. Clark and R. Hester, Advances in Spectroscopy (Wiley, New York, 1995), Vol. 23.
[9] A. Padilla, J. Pérez, and A. Calvo Hernández, J. Chem. Phys. **111**, 11015 (1999).
[10] A. Padilla, J. Pérez, and A. Calvo Hernández, J. Chem. Phys. **111**, 11026 (1999).
[11] A. Padilla, J. Pérez, and A. Calvo Hernández, J. Chem. Phys. **113**, 4290 (2000).
[12] A. Padilla, J. Pérez, and A. Calvo Hernández, J. Chem. Phys. **117**, 6599 (2002).
[13] S. Mukamel, Chem. Phys. **37**, 33 (1979).
[14] J. Jang and R. M. Stratt, J. Chem. Phys. **113**, 5901 (2000).
[15] J. Jang and R. M. Stratt, J. Chem. Phys. **113**, 11212 (2000).
[16] R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).
[17] J. A. White, S. Velasco, A. Calvo Hernández, and D. Luis, Phys. Lett. A **130**, 237 (1988).