Rotational relaxation matrix for fast non-Markovian collisions

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(Received 15 March 1999)

By using the Zwanzig-Mori theory, the rotational relaxation Γ matrix of the sudden approximation is corrected for rotational adiabaticity, off-energy shell scattering, and initial bath-molecule correlations. Expressions derived for the case of a linear rotator perturbed by fast binary collisions are shown to satisfy all known fundamental relations; in addition, the Γ matrix is symmetric and positive definite in line space. The general case of non-Markovian relaxation of an arbitrary molecular rth rank tensor is treated, which substantially expands the scopes of the impact scalar $(r=0)$ relaxation. A model of Γ is developed compatible with the known data on the N_2-N_2 potential and is shown to fit well a variety of different relaxation characteristics $(r=0,1,2)$ measured in compressed room-temperature nitrogen. [S1050-2947(99)09509-8]

PACS number(s): 34.10.+x, 33.70.Jg

I. INTRODUCTION

Apart from the academic interest, collisional mixing of rotovibrational lines is required for a number of spectroscopic applications, including gas diagnostics and the physics of planetary atmospheres. The main achievements in this field are due to the concept of the relaxation matrix $\hat{\Gamma}$ that accounts for collisional correlation between different radiative transitions. Concurrent with theoretical advances, many models of $\hat{\Gamma}$ have been developed (see book [1] and reviews [2,3]) exploiting the scattering approach. Among them, the infinite-order sudden approximation (IOSA) and its extensions hold much promise as a basis for modeling. To treat the inelastic rotational $J \rightarrow J'$ transitions, the IOSA assumes that both the collision duration t_0 and the associated Massey parameter $\eta \equiv t_0 \omega_{JJ'}$ are negligible. This oversimplification results in broadening coefficients of the isotropic Raman $Q_1(J)$ lines of linear molecules [4] calculated using the IOSA not decreasing with J (except for the very lowest transitions) and diverging increasingly from the experimental data; allowance for finite η is thus required. It was with such an intent that De Pristo *et al.* [5] developed the energy-corrected sudden approximation (ECSA), which generated much interest among spectroscopists [1–3]. However, their proposed correction [5] is semiempirical, and its form was postulated rather than rigourously derived. For this reason, ECSA interaction lengths deduced from experiment by using different models are scattered [6] and are difficult to correlate with intermolecular potential parameters. Moreover, for optical transitions induced by nonscalar $(r \neq 0)$ photon-molecule coupling, the sudden approximations are feasible only for the off-diagonal elements of the rotational relaxation matrix $\hat{\Gamma}$ [7], and their accuracy for diagonal elements is questionable.

Binary collisions are treated by scattering theory as isolated impacts, which leaves out details of intracollisional evolution. It has been realized that broadband spectroscopies are promising tools for probing this evolution, especially when the frequency ω is sufficiently detuned from the band center (see the recent publications [8,9], and references therein). This requires the use of off-energy-shell scattering amplitudes to account for incomplete (non-Markovian) collisions [10], whereas the general impact approach to rotational relaxation [11] operates with a conventional S matrix. Moreover, the fundamental sum rules [12] for the relaxation matrix elements hold generally only in the more realistic non-Markovian picture in which frequency-dependent relaxation matrices $\hat{\Gamma}(r;\omega)$ appear. Such matrices have thus far been elaborated only for weak interactions by using the perturbation theory (see [13] and references therein). The task is further complicated by the problem of initial molecule-bath correlations [9,10], whose neglect in the scattering approaches can give rise to violations of the detailed-balance properties of the computed spectra. For this reason also, the theoretical description should be revised.

Based on the Zwanzig-Mori formalism [14], the present treatment simultaneously incorporates rotational adiabaticity (finite η), non-Markovian effects, and initial correlations into the IOSA scheme. All known fundamental relations are satisfied for the $\hat{\Gamma}(r;\omega)$ matrix so obtained; further, the calculation of its secular part also poses no problem. Some preliminary results have been reported recently by the author [15]. Although only the case of a nonvibrating rotator is considered here, extensions to more complicated cases seem to be straightforward.

II. RELAXATION MATRIX

A. Liouville space metric

The line-space (or projection) formalism exploited in the present derivation (for details, see book [14]) is based on the notion of the Liouville space $\mathcal{L}$ spanned by the quantum-mechanical operators of the total ''molecule (a) + bath (B)'' system. Caution is required at the first step, as the metric in $\mathcal{L}$ cannot be defined uniquely in the quantum case. As is shown below, the conventional definition of the scalar product $(A|C)$ of two Liouville vectors A and C, namely,

$$(A|C) \equiv \mathrm{Tr}\, \rho A^{\dagger} C, \tag{1}$$

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(ρ is the total density matrix) leads to spurious effects. Consider the spectral function $S(\omega)$ of a rigid rotator perturbed by binary collisions, namely,

$$S(\omega)=\pi^{-1}\lim_{\varepsilon\to 0}\int_0^\infty (A(0)|A(t))\exp(-izt)dt, \quad (2)$$

where the ''complex'' frequency $z=\omega-i\varepsilon$ lies in the lower half-plane ($\varepsilon\geqslant 0$). The total system has a continuous energy spectrum and, because of molecule-bath coupling, time correlation functions [such as $(A(0)|A(t))$] vanish at long times. Their absolute values are assumed to be integrable over infinite time intervals, thus ensuring the analyticity of $S(z)$ in the lower half plane. The total Liouville superoperator $\hat{L}$ governs the time evolution of A: $A(t)=\exp(iHt/\hbar)A(0)\exp(-iHt/\hbar)\equiv\exp(i\hat{L}t)A(0)$. For the case that A is the molecular dipole moment, the real part $S'(\omega)$ of the spectral function [Eq. (2)] defines the far-infrared absorption profile. As collisions become more frequent, the formation of a new, progressively narrowed quasi-Lorentzian band centered at $\varpi=(A|\hat{L}|A)$ is predicted by the line-space formalism [1,14]. In the eigenbasis of H, one has

$$\varpi=\sum_{fi}(\rho_{ii}-\rho_{ff})\omega_{fi}|A_{if}|^2/2>0. \quad (3)$$

In other words, a new long-lasting quantum mode appears at positive ϖ; of course, this is impossible from a physical standpoint. One can rigorously show that $S'(-\omega)=S'(\omega)\exp(-\hbar\omega/kT)$. This fundamental detailed-balance relation may be lost when one uses the projection technique: for example, the artifact peak formation at $\varpi\neq 0$, which arises from the use of metric (1), is inconsistent with detailed balance, and the metric must therefore be modified. For this reason, the symmetrized metric [13]

$$(A|C)=\mathrm{Tr}\,\rho[A^\dagger C+CA^\dagger]/2, \quad (4)$$

was adopted previously. In this case, the even real spectral function $F'(\omega)=[S'(\omega)+S'(-\omega)]/2$ is generated by Eqs. (2) and (4). For a particular case, its relation to the observable response poses no problem, so that the detailed-balance relation can be incorporated exactly into the response profile from the very beginning. In the symmetrized approach, the motionally narrowed band becomes correctly centered at $\varpi=\Sigma_{fi}(\rho_{ii}+\rho_{ff})\omega_{fi}|A_{if}|^2/2=0$. Moreover, the parity of $F'(\omega)$ is not violated by the neglect of initial correlations. One may expect that, in contrast to the Fano or scattering-theory treatments, possible inaccuracies caused by this neglect will be partially suppressed. As has been noted [9], such neglect in the conventional treatment leads to the artifact of negative band-wing intensity [16].

Naturally, a change of metric also affects the form of the relaxation matrix.

B. Fano-Mori superoperator

The dynamic subspace $\mathcal{L}_D$ in $\mathcal{L}$ is spanned by the vectors $|\tilde{\mathbf{k}})=|KI_B)$, where I_B is the identity operator acting on the bath wave functions. The transition operator K transforms the rotator eigenstates; generally, it is an irreducible tensor of rank r whose explicit form [17]

$$K_\sigma^{(r)}=\sum_{m_im_f}(-1)^{J_f-m_f}\begin{pmatrix} J_f & r & J_i\\ m_f & -\sigma & -m_i\end{pmatrix}\times|J_fm_f\rangle\langle J_im_i|\equiv|f\rangle\langle i|, \quad (5)$$

follows from the representation of the molecular operator $A^{(r)}$,

$$A_\sigma^{(r)}=\sum_k A'_kK\equiv\sum_{fi}|f\rangle\langle f\|A^{(r)}\|i\rangle\langle i|, \quad (6)$$

and the Wigner-Eckart theorem [18]. The coefficients $A'_k=\langle f\|A^{(r)}\|i\rangle$ are the reduced rotational matrix elements [18] of $A^{(r)}$. Due to the isotropy of space, $(A^{(r)}|B^{(r')})\sim\delta_{rr'}$, and from Eq. (4) on, the usual scalar contraction operation $(A^{(r)},C^{(r)})\equiv\Sigma_\sigma A_{-\sigma}^{(r)}C_\sigma^{(r)}(-1)^\sigma$ shall be implied. For brevity, we shall occasionally drop tensor ranks. The norm n_k of $|\tilde{\mathbf{k}})$ ($n_k=n_{if}=\sqrt{(\tilde{\rho}_{aii}+\tilde{\rho}_{aff})/2}$) is given by the diagonal matrix elements of the reduced rotational density matrix $\tilde{\rho}_a\equiv\mathrm{Tr}_B\,\rho$. Averaging over the bath states (Tr_B) then converts ρ into a scalar operator diagonal in the spherical-harmonics basis; because of this the $|\tilde{\mathbf{k}})$ set is orthogonal [13]. In principle, $\tilde{\rho}_{aJJ}$ may deviate from the rotational Boltzmann factors ρ_{aJJ} of a free rotator; the difference will, however, be neglected since it produces smaller terms nonlinear in the buffer-gas number density.

The projection technique reduces the spectrum calculation to matrix inversion, that is,

$$F(\omega)=\pi^{-1}\lim_{\varepsilon\to 0}\langle\langle A|R^{-1}|A\rangle\rangle=\lim_{\varepsilon\to 0}\sum A_k^*A_{k'}(R^{-1})_{kk'}, \quad (7)$$

in the line space $\mathcal{L}_S$ spanned by the transition operators K [Eq. (5)]; the weights A_k and the relaxation matrix elements $\Gamma_{kk'}$ are defined in terms of the scalar product of Eq. (4): $A_k\equiv(\tilde{\mathbf{k}}|A)=n_kA'_k$. Further, note that the matrix $R_{kk'}(z)=i(z-\omega_k)\delta_{kk'}+\Gamma_{kk'}(z)$ contains the molecular self-frequencies $\omega_k=\omega_{fi}$.

The explicit form of the rotational Γ-matrix element has been shown [13] to be

$$\Gamma_{if}^{i'f'}(z)=(1/2n_{if}n_{i'f'})\int_0^\infty \exp(-izt)\mathrm{Tr}\,\rho[(|f\rangle\langle i|)^\dagger\hat{M}(t)\times|f'\rangle\langle i'|+(\hat{M}(t)|f'\rangle\langle i'|)(|f\rangle\langle i|)^\dagger]dt, \quad (8)$$

where $z=\omega-i\varepsilon$ $(\varepsilon>0)$, and the superoperator

$$\hat{M}(t)=\hat{L}_1^\dagger\exp(i\hat{L}t)\hat{L}_1 \quad (9)$$

transforms the vectors in $\mathcal{L}$. Here $\hat{L}_1$ is the anisotropic molecule-bath coupling: $\hat{L}_1=(W-W^\times)/\hbar$, where W acts on the ket vectors, while $W^\times$ is the complex adjoint of W, and acts on the bra vectors.

The terms constituting matrix element (8) can be classified as ''outer'' (i.e., containing WW or $W^\times W^\times$) and ''middle'' (containing $WW^{\times}$ or $W^{\times}W$). The technique will be demonstrated for the integrand of the outer WW term, which can be written as

$$\begin{aligned}2\hbar^2 n_{if} n_{i'f'} \Gamma^{WW}_{out}(t) &= \mathrm{Tr}\,\rho\{|i\rangle\langle Wf|\exp(i\hat{L}t)W|f'\rangle\langle i'| \\ &\quad + [\exp(i\hat{L}t)W|f'\rangle\langle i'|]|i\rangle\langle Wf|\} \\ &= \sum_{\alpha\beta\sigma n} \langle n\sigma|\rho|i\alpha\rangle\langle f\alpha|W\exp(iHt)W|f'\beta\rangle \\ &\quad \times\langle i'\beta|\exp(-iHt/\hbar)|n\sigma\rangle + \langle f\sigma|W\rho|n\alpha\rangle \\ &\quad \times\langle n\alpha|\exp(iHt)W|f'\beta\rangle\langle i'\beta|\exp(-iHt/\hbar)|i\sigma\rangle,\end{aligned} \tag{10}$$

where the Greek letters label bath states.

The IOSA assumes the bath motion to be much faster than rotation. Conventionally, it neglects the rotational energy H_a in the total Hamiltonian $H = H_a + H_B + W$ when it enters the evolution operators, and does the same for the anisotropic part of the interaction potential W in the density matrix (neglect of initial correlations) resulting in $\rho = \rho_a \rho_B$. Both approximations are unnecessary in the present approach, resulting in the energy-and-frequency-corrected sudden approximation (EFCSA).

Intrinsically, the EFCSA is similar to the adiabatic approximation [19] used in quantum chemistry. Instead of electrons, the translational motion plays the role of a rapid subsystem, while rotation is analogous to nuclear molecular motion. Since traces are invariant to the choice of basis, we may choose the bath basis to be an eigenbasis of $H'_B = H_B + W$ at fixed orientation $\Omega_a = (\theta_a, \phi_a)$ of the molecular axis in the laboratory frame. Due to the isotropy of space, the translational energy eigenvalues ε_α are independent of Ω_a and the basic EFCSA equation reads

$$\langle n\alpha(\Omega_a)|H|m\beta(\Omega_a)\rangle \approx \delta_{nm}\delta_{\alpha\beta}(E_n + \varepsilon_\alpha), \tag{11}$$

where E_n is the rotational energy of the n state. The neglected off-diagonal terms are of order $|\omega_{mn}/\omega_{\beta\alpha}|$ [19]; statistically, this ratio is converted into the Massey parameter η. The use of such an Ω_a-adjusted bath basis greatly simplifies the calculation. One finds directly that

$$2\hbar^2 n_{if} n_{i'f'} \Gamma^{WW}_{out}(t) = \delta_{ii'}\langle f|X|f'\rangle, \tag{12}$$

where

$$\begin{aligned}X &= \rho_{aii}\,\mathrm{Tr}_B\, U(t) \sum_{J'm'} \exp[i(E_{J'} - E_i)t/\hbar] \\ &\quad \times|J'm'\rangle\langle J'm'|V(t) + \mathrm{Tr}_B\, V(-t)\sum_{J'm'} \rho_{aJ'J'} \\ &\quad \times\exp[i(E_{J'} - E_i)t/\hbar]|J'm'\rangle\langle J'm'|U(-t).\end{aligned} \tag{13}$$

Two operators acting in the total space, namely, $V(t) = W\exp(-iH'_B t/\hbar)\rho'_B$ and $U(t) = W\exp(iH'_B t/\hbar)$, appear in the last equation, with $\rho'_B = \exp(-\beta H'_B)/Z'_B$ and $\beta = 1/kT$. Neither operator contains differential operators in the rotational subspace; they can be written as the scalar contractions

$$V(t) = \sum_L [v^{(L)}(t), C^{(L)}(\Omega_a)], \tag{14}$$

$$U(t) = \sum_{L'} [u^{(L')}(t), C^{(L')}(\Omega_a)], \tag{15}$$

where $C^{(L)}(\Omega_a)$ is a spherical harmonic normalized to $\sqrt{4\pi/(2L+1)}$; $v^{(L)}(t)$ and $u^{(L')}(t)$ are tensor operators in the bath space. However, only the scalar contractions of $v^{(L)}$ and $u^{(L)}$ of the same rank L survive averaging over the bath variables. In fact, X is a scalar operator with respect to molecular rotations, and one arrives at the formula

$$\Gamma^{WW}_{out}(t) = \delta_{ii'}\delta_{ff'}\langle f|X(t)|f\rangle, \tag{16}$$

in which

$$\begin{aligned}\langle f|X(t)|f\rangle &= \sum_{LJ'} \Pi^2_{J'} \begin{pmatrix} J_f & L & J' \\ 0 & 0 & 0 \end{pmatrix}^2 \exp(i\omega_{J'J_i}t)[\rho_{aii}F_L(t) \\ &\quad + \rho_{aJ'J'}F_L(-t)],\end{aligned} \tag{17}$$

with $\Pi_{ab\ldots c} = \sqrt{(2a+1)(2b+1),\ldots,(2c+1)}$. The functions $F_L(t)$, given by

$$F_L(t) = (2L+1)^{-1}\,\mathrm{Tr}_B(u^{(L)}(t), v^{(L)}(t)), \tag{18}$$

characterize the bath motion at fixed molecular orientation. Similarly, the outer term proportional to $W^{\times}W^{\times}$ can also be shown to be entirely diagonal. The total outer contribution

$$\begin{aligned}&2\hbar^2 n_{if} n_{i'f'} \Gamma^{i'f'}_{if}(r;\omega)_{outer} \\ &= \delta_{ii'}\delta_{ff'}\int_0^\infty \exp(-i\omega t)\sum_{LJ'} \begin{pmatrix} J' & L & J_f \\ 0 & 0 & 0 \end{pmatrix}^2 \exp(i\omega_{J'J_i}t) \\ &\quad \times[\rho_{aii}F_L(t) + \rho_{aJ'J'}F_L(-t)] + \begin{pmatrix} J' & L & J_i \\ 0 & 0 & 0 \end{pmatrix}^2 \\ &\quad \times\exp(i\omega_{J'J_f}t)[\rho_{aff}F_L(-t) + \rho_{aJ'J'}F_L(t)]dt\end{aligned} \tag{19}$$

is the same for any relaxation rank, and is expressible in terms of the one-sided Fourier transforms $\Phi^{\pm}_L(x)$ defined via

$$\Phi^{\pm}_L(x) = \hbar^{-2}\int_0^\infty \exp(-ixt)F_L(\pm t)dt. \tag{20}$$

The middle terms generate the following matrix element:

$$\begin{aligned}\Gamma^{i'f'}_{if}(r;\omega)_{middle} &= -(1/2\hbar^2 n_{if} n_{i'f'})\int_0^\infty \exp(-i\omega t)\,\mathrm{Tr}\,\rho \\ &\quad \times\{(K^{(r)}_{if}W\exp(iHt), K^{(r)}_{f'i'}W\exp(-iHt)) \\ &\quad + (\exp(-iHt)WK^{(r)}_{if}, \exp(iHt)WK^{(r)}_{f'i'}) \\ &\quad + (\exp(iHt)WK^{(r)}_{f'i'}, \exp(-iHt)WK^{(r)}_{if}))\} \\ &\quad + (\exp(iHt)K^{(r)}_{f'i'}W\exp(-iHt), K^{(r)}_{if}W).\end{aligned} \tag{21}$$

For clarity, the subscripts of the $K^{(r)}$ operator explicitly indicate the rotational transition. The use of the EFCSA and the spherical-harmonic expansion of the operators V and U simplifies the last formula. After performing the intermediate summation

$$\sum_{\sigma m_i m_f m_i' m_f'} (-1)^{\sigma+m_i+m_f+m_{i'}+m_{f'}+r+L}\begin{pmatrix} J_f & r & J_i \\ m_f & -\sigma & -m_i \end{pmatrix} \times\begin{pmatrix} J_f' & r & J_i' \\ -m_f' & \sigma & m_i' \end{pmatrix}\times\begin{pmatrix} J_i' & L & J_i \\ -m_i' & M & m_i \end{pmatrix} \times\begin{pmatrix} J_f & L' & J_f' \\ -m_f & -M' & m_f' \end{pmatrix} =(-1)^M\delta_{LL'}\delta_{MM'}\begin{Bmatrix} J_i & J_f & r \\ J_f' & J_i' & L \end{Bmatrix}/(2L+1), \tag{22}$$

one obtains

$$\Gamma_{if}^{i'f'}(r;\omega)_{middle}=-(2n_{if}n_{i'f'})^{-1}\Pi_{J_iJ_fJ_i'J_f'}(-1)^r \times\sum_L \begin{pmatrix} J_i' & L & J_i \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} J_f & L & J_f' \\ 0 & 0 & 0 \end{pmatrix} \times\begin{Bmatrix} J_i & J_f & r \\ J_f' & J_i' & L \end{Bmatrix}[\rho_{aii}\Phi_L(\omega-\omega_{f'i}) +\rho_{ai'i'}\Phi_L(\omega-\omega_{fi'})+\rho_{aff}\Phi_L^*(\omega_{fi'}-\omega) +\rho_{af'f'}\Phi_L^*(\omega_{f'i}-\omega)]dt. \tag{23}$$

Note that this term also contributes to the secular matrix elements. It has been derived using the property $F_L^*(t)=F_L(-t)$ (see the Appendix), which implies the integrability of $|F_L(t)|$; in so doing, the frequency may finally be taken to be real. The real part of $\Gamma_{if}^{i'f'}(r;\omega)_{middle}$ can be given in terms of the double-sided Fourier transforms

$$\Phi_L'(x)=\mathrm{Re}\,\Phi_L(x)=(1/2\hbar^2)\int_{-\infty}^{\infty}\exp(-ixt)F_L(t)dt. \tag{24}$$

Like $S'(\omega)$, these quantities obey the relation $\Phi_L'(-x)=\exp(-\hbar\beta x)\Phi_L'(x)$ (see the Appendix), and by using it, one arrives at the following result:

$$\mathrm{Re}\,\Gamma_{if}^{i'f'}(r;\omega)_{middle}=-(2n_{if}n_{i'f'})^{-1}\Pi_{J_iJ_fJ_i'J_f'}(-1)^r \times\sum_L \begin{pmatrix} J_i' & L & J_i \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} J_f & L & J_f' \\ 0 & 0 & 0 \end{pmatrix} \times\begin{Bmatrix} J_i & J_f & r \\ J_f' & J_i' & L \end{Bmatrix}[1+\exp(-\hbar\beta\omega)] \times[\rho_{aff}\Phi_L'(\omega_{fi'}-\omega) \times\exp(\hbar\beta\omega)+\rho_{aii}\Phi_L'(\omega-\omega_{f'i})]. \tag{25}$$

Remarkably, Eqs. (23) and (25) have exactly the same form as those obtained by the perturbation approach [13], differing only in the definition of the bath functions $\Phi_L(x)$. Perturbation theory may be used for large rotational energy gaps, i.e., for high values of J, whereas the EFCSA is applicable for low or moderate J values. Therefore, one may hope that some hybrid model can be developed to cover the entire J domain. We note also that no assumption has been made on the perturber structure, so that the derived results may equally be applied to molecule-atom and molecule-molecule collisions. Physically, the IOSA holds when $|\omega_{JJ'}|$ is much smaller than the half width t_0^{-1} of $\Phi_L(\omega)$ (i.e., $\eta\ll 1$), and then one may set $\Phi_L(\omega_{JJ'})\approx\Phi_L(0)$. If, additionally, one assumes collisions to be Markovian (i.e., $\omega\approx 0$), the IOSA cross sections can be expressed in terms of the quantities (generally complex) $\tilde{q}_L=2\Phi_L(0)$. Their real parts $q_L=2\Phi_L'(0)$ define the so-called basic $(0\to L)$ transition rates.

C. Fundamental properties of the EFCSA matrix

1. Sum rules

Sum rules can be obtained [12] for any tensor A that is diagonal in coordinate representation:

$$-\sum_{k'\neq k} A_{k'}\Gamma_{kk'}(\omega)=-\sum_{k'\neq k} A_{k'}\Gamma_{k'k}(\omega)=A_k\Gamma_{kk}(\omega). \tag{26}$$

In the EFCSA case, they can be verified straightforwardly by carrying out the summations over the rotational quantum numbers (see Ref. [13] for details).

2. Matrix symmetry

It follows from Eq. (23) that the EFCSA matrix is symmetric, i.e.,

$$\Gamma_{if}^{i'f'}(r;\omega)=\Gamma_{i'f'}^{if}(r;\omega). \tag{27}$$

As shown below, this symmetry ensures that the non-negative character of $\Gamma'(r,\omega)=\mathrm{Re}\,\Gamma(r,\omega)$, i.e.,

$$\langle B|\Gamma'|B\rangle=\sum_{k'k} B_{k'}\Gamma_{k'k}'B_k\geqslant 0, \tag{28}$$

holds for any line-space vector $B^{(r)}$ expandable in the line-space basis of $A^{(r)}$. Hence, both tensors have coincident relaxation matrices and, by using the sum rules for $A^{(r)}$, one obtains

$$\langle B|\Gamma'|B\rangle=-1/2\sum_{k'\neq k} A_{k'}A_k\Gamma_{k'k}'(B_k/A_k-B_{k'}/A_{k'})^2. \tag{29}$$

Explicitly, A_k and $A_{k'}$ are given by

$$A_k=n_k(-1)^{J_i}\begin{pmatrix} J_i & r & J_f \\ 0 & 0 & 0 \end{pmatrix}\Pi_{J_iJ_f}, \tag{30a}$$

$$A_{k'}=n_{k'}(-1)^{J_i'}\begin{pmatrix} J_i' & r & J_f' \\ 0 & 0 & 0 \end{pmatrix}\Pi_{J_i'J_f'}. \tag{30b}$$

The coefficient $-A_{k'}A_k\Gamma'_{k'k}(k\neq k')$ is positive as can be seen from Eqs. (25) and (30), so that inequality (28) holds.

3. Time-reversal relation

The EFCSA Γ matrix obeys the time-reversal equation (the Ben-Reuven relation [17])

$$\Gamma_{fi}^{f'i'}(r;\omega)=\Gamma_{if}^{i'f'*}(r;-\omega). \tag{31}$$

For narrow Q branches, one can use the Markov limit ($\omega\rightarrow 0$), in which case the corresponding block, as seen from Eq. (31), consists of real matrix elements.

4. Dispersion relations

According to Eq. (8), any element of the exact relaxation matrix $\Gamma(z)$ is an analytic function in the lower half plane; hence, its real and imaginary parts are interrelated via the Kramers-Kronig formulas. Thus, for example, the imaginary part $\Gamma''(\omega)$ (for brevity, we drop the matrix indices) is given via the principal value of the integral

$$\Gamma''(\omega)=-P\frac{1}{\pi}\int_{-\infty}^{\infty}\Gamma'(\omega')(\omega'-\omega)^{-1}d\omega'. \tag{32}$$

For practical implementation, it therefore suffices to model only $\Gamma'(\omega)=\lim_{\varepsilon\rightarrow 0}\mathrm{Re}\,\Gamma(z)$, and then to evaluate $\Gamma''(\omega)$. Effectively, the EFCSA decouples the bath motion from the rotational motion. This leads to dispersion relations for the bath spectral functions. Apparently, each Lth term $\Phi_L(z)$ of the EFCSA $\Gamma(z)$ of Eq. (23) is also analytic in the lower half plane. Because of the detailed balance and dispersion relations, the modeling of $\Phi_L(\omega)$ is accomplished once one fixes its symmetrized real part $\tilde{\Phi}'_L(\omega)=[\Phi'_L(\omega)+\Phi'_L(-\omega)]/2$.

D. Particular cases

1. Raman bands

For isotropic Raman bands ($r=0, i=f=J, i'=f'=J'$), the Markov theory may be used, and one obtains the real symmetric matrix ($J\neq J'$),

$$\Gamma_{JJ}^{J'J'}(0,0)=\Gamma_{J'J'}^{JJ}(0,0)$$
$$=-2\sqrt{\frac{\rho_J}{\rho_{J'}}}\Pi_{JJ'}\sum_L\begin{pmatrix}J'_i & L & J_i\\ 0 & 0 & 0\end{pmatrix}^2\Phi'_L(\omega_{JJ'}). \tag{33}$$

The conventional (unsymmetrized) relaxation matrix elements are

$$\tilde{\Gamma}_{JJ'}\equiv -W_{JJ'}=\Gamma_{JJ}^{J'J'}(0,0)\sqrt{\frac{\rho_{J'}(2J'+1)}{\rho_J(2J+1)}}, \tag{34}$$

where $W_{JJ'}$ represents the $J\rightarrow J'$ transition rate, which obeys the detailed-balance relation

$$\rho_J(2J+1)W_{JJ'}=\rho_{J'}(2J'+1)W_{J'J}. \tag{35}$$

The functions Φ'_L can be related with the basic upward ($0\rightarrow L$) transition rates q_L given by

$$q_L=2\Phi'_L(\omega_{0L}). \tag{36}$$

When one uses these rates as the input parameters (known, say, from experiment), the ECSA matrix becomes

$$\Gamma_{JJ}^{J'J'}(0,0)=-\sqrt{\frac{\rho_J}{\rho_{J'}}}\Pi_{JJ'}$$
$$\times\sum_L\begin{pmatrix}J' & L & J\\ 0 & 0 & 0\end{pmatrix}^2\Phi'_L(\omega_{JJ'})q_L/\Phi'_L(\omega_{0L}). \tag{37}$$

The same procedure applied to Eq. (23) results in the element

$$\mathrm{Re}\,\Gamma_{if}^{i'f'}(r;\omega)=-(-1)^r[1+\exp(-\hbar\beta\omega)]/2n_{if}n_{i'f'}$$
$$\times\sum_L\begin{pmatrix}J'_i & L & J_i\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}J_f & L & J'_f\\ 0 & 0 & 0\end{pmatrix}$$
$$\times\begin{Bmatrix}J_i & J_f & r\\ J'_f & J'_i & L\end{Bmatrix}\Pi_{J_iJ_fJ'_iJ'_f}q_L$$
$$\times[\rho_f\Phi'_L(\omega_{fi'}-\omega)\exp(\hbar\beta\omega)$$
$$+\rho_i\Phi'_L(\omega-\omega_{f'i})]/\Phi'_L(\omega_{0L}), \tag{38}$$

originating from the middle terms. Apart from frequency arguments, the form of Eqs. (23) and (38) is the same as that given by the IOSA [20,21]. To enforce the unitarity of the scattering matrix, the diagonal IOSA terms in the scalar case ($r=0$) are obtained from summation of the inelastic transition rates. However, such terms do not directly appear in the IOSA [20], and the secular part of its general Γ matrix is not properly obtained. The same applies to the energy-corrected IOSA matrix [5].

2. Relaxation of irreducible angular-momentum tensors

The tensors of interest are the rotational angular momentum $\mathbf{J}$ itself ($r=1$) and $\{\mathbf{J}\otimes\mathbf{J}\}^{(2)}$ ($r=2$); the latter appears in the depolarized Raman Q_0-branch shapes. For both cases, the radiation selection rules are the same as that for the isotropic Raman case ($i=f=J$, $i'=f'=J'$), and hence Markov theory may be used. The corresponding IOSA matrix is given by Eq. (38) with $\omega_{jj'}=\omega=0$. Examination of the diagonal elements of $\Gamma(r;0)$ shows them to contain both r-dependent elastic (with the zero-frequency arguments) and inelastic terms, which are independent of r [see Eq. (19)]. This allows a comparison of the present expressions with the known IOSA expressions [20,21], even though in the IOSA approach all terms are proportional to $\Phi'_L(0)$. The off-diagonal elements in both approaches are of the same structure, but the relative nonadiabatic contributions to the secular part disagree drastically. Due to shortcomings of the conventional IOSA Γ matrix, it annuls **J** [7,20], with the consequence that **J** is macroscopically conserved in this approximation. Such an unphysical result does not appear in the present formulation. Numerical examples are presented in the following section.

III. MODELING OF SPECTRAL CHARACTERISTICS

The translational spectral functions $\tilde{\Phi}_L'(\omega)$ are the basic EFCSA characterisitics; to calculate them, some realistic approximations can be exploited. In the first place, classical dynamics applies in most cases. Moreover, the general behavior of $\tilde{\Phi}_L'(\omega)$ is known from collision-induced spectra, and one can reconstruct $\tilde{\Phi}_L'(\omega)$ by calculating its leading moments $M_L^{(2n)}$ $(n=0,1,2\dots)$. This is a much simpler task than solving exactly the quantum or classical equations. Besides, the shape is determined by the relative moments $m_L^{(2n)}$, which are not particularly sensitive to the approximations employed [8]. To obtain $m_L^{(2n)}$ the anisotropy of H_B' may be neglected, and the perturbation theory results [13] then appear. Using the Legendre expansion in the case of a point perturber

$$W=\sum_L W_L(R)[C^{(L)}(\Omega),C^{(L)}(\Omega_a)]$$

$$=\sum_L W_L(R)P_L(\cos\theta_a'), \tag{39}$$

with the supposedly short-ranged coefficients $W_L(R)$ described by a unique core parameter R_0 [i.e., W_L is assumed to have the form $W_L\sim\exp(R/R_0)$], one obtains [22] $m_L^{(2)}\sim 1+(R_0/\sigma)^2L(L+1)\equiv\kappa^2(\chi,L)$, where σ characterizes the position of the repulsion-wall and $\chi=(R_0/\sigma)^2$. Typically, the ratio χ is of the order 0.01. The above approximations are incorporated in the formula

$$\tilde{\Phi}_L'(\omega)\approx C(\hbar\beta\omega)\Phi_L'(0)\varphi(\omega/\kappa), \tag{40}$$

where the factor C ensures the detailed-balance relation. The known models $\{C(x)=\exp(x/2);\ \ C(x)=2/[1+\exp(-x)]\}$ were found to have almost the same accuracy for our purposes.

The even shape functions φ are quasi-Lorentzian near the maxima, and decrease exponentially in the wings. Such behavior is typical for collision-induced translational spectra, and is well approximated by [23]

$$\varphi(x)=\exp[\gamma-\sqrt{\gamma^2+(\omega/\omega_0)^2}]. \tag{41}$$

To complete the EFCSA we specify that

$$q_L=A\exp(-\alpha\beta E_L) \tag{42}$$

that reasonably fits with $\alpha\approx 2$, the basic room temperature rates measured in nitrogen [24] (see Fig. 1). Although pure

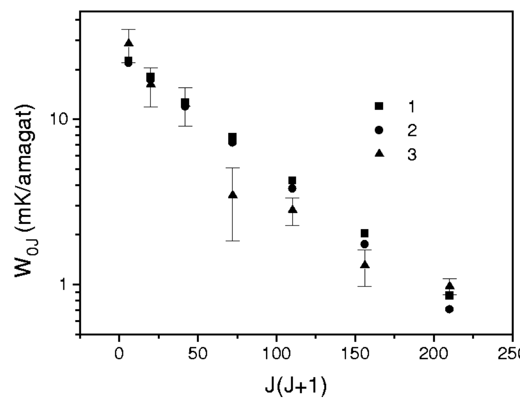

FIG. 1. Collisional $0\rightarrow J$ transition rates in nitrogen ($T=298$ K): 1—this paper, 2—exponential energy-gap model [28], and 3—measurements [24].

nitrogen does not completely satisfy all the assumptions required for the IOSA/EFCSA, it has been chosen as a reference system since a variety of accurate spectroscopic and kinetic data are available for it.

The proposed general $\Gamma(r,\omega)$ matrix is thus five-parametric (depending upon $A,\alpha,\gamma,\chi,\omega_0$). The value of γ has been fixed ($\gamma=1.5$) as recommended by the theory of collision-induced spectral line shapes [23]: variations around $\gamma=1.5$ have little effect on the calculated characteristics. Translational-shape calculations [23] give $\omega_0=a/R_0\sqrt{m\beta}$, where m is the collisional reduced mass, while $a\approx 1.5$ is a dimensionless coefficient; in this way, χ and ω_0 are correlated. From the sophisticated N_2-N_2 potential [25] one can infer that $R_0\approx 0.3$-0.4 Å. Using $\sigma=3.73$ Å [25], one may exploit $\chi\approx 0.01$ and $\omega_0\approx 100\ \mathrm{cm}^{-1}$ as reasonable estimates. The set ($\alpha=2$, $\gamma=1.5$, $\chi=0.01$, $\omega_0=100\ \mathrm{cm}^{-1}$) provides a reasonable fit of the measured isotropic $Q_1(J)$ line-broadening coefficients (see Fig. 2). The value $A=13.1$ mK/amagat was found by equating the calculated and measured [26] broadening coefficients at $J=8$; the specified parameter set leads to reasonable absolute values of the measured basic rates (see Fig. 1). The EFCSA predictions are also consistent with other available transition rates [24] from excited J states, as exemplified by the $J=6$ case (see Fig. 3).

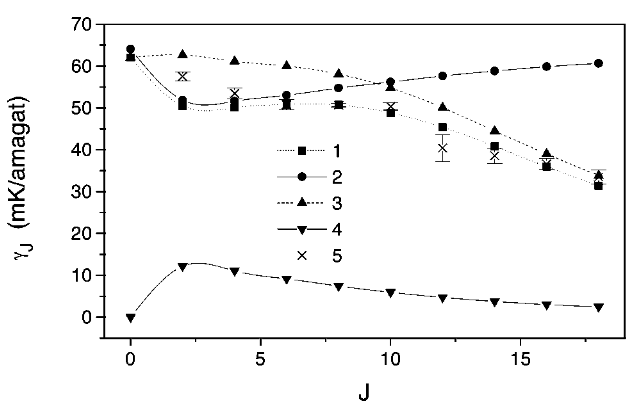

FIG. 2. Isotropic ($r=0$) and anisotropic ($r=2$) $Q(J)$ line-broadening coefficients of nitrogen ($T=293$ K): 1—EFCSA, $r=0$; 2—IOSA, $r=0$ (this paper); 3—EFCSA ($r=2$); 4—EFCSA adiabatic term ($r=2$); 5—experiment ($r=0$) [26].

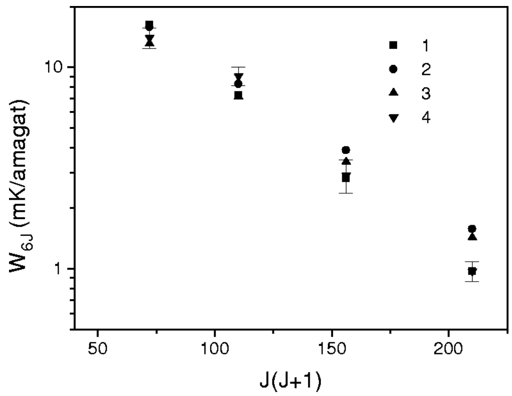

FIG. 3. Collisional $6\to J$ transition rates in nitrogen ($T=298$ K): 1—EFCSA, 2—IOSA (this work), 3—exponential energy-gap model [28], and 4—measurements [24].

On the contrary, the IOSA (with the same parameters, except for $\omega_0\to\infty$) is incompatible with the experimental widths for $J\geqslant 6$ (see Fig. 2); similar patterns have been obtained for $r=0$ by direct IOSA calculations [4,27]. One sees from Fig. 3 that the IOSA gives a weaker rate decrease on $|J-J'|$ than the EFCSA does.

The matrix $\Gamma_{JJ}^{J'J'}(0;0)$ defines the rotational-energy relaxation cross section σ_E via

$$n_L\bar{v}\sigma_E=\langle\Delta E^2\rangle \Bigg/ \sum_{JJ'} A_J A_{J'}\Delta E_J\Delta E_{J'}(\Gamma^{-1}(0;0))_{JJ}^{J'J'}, \tag{43}$$

where n_L is the Loschmidt number, $\bar{v}=\sqrt{8kT/\pi m}$, ΔE is the rotational energy fluctuation, and $\langle\Delta E^2\rangle$ stands for its mean-square value. Due to the energy weighting factors, σ_E is rather sensitive to the distribution of off-diagonal Γ-matrix elements at higher J values. For example, the energy-gap model [28], which accurately reproduces the isotropic linewidth distribution, gives $\sigma_E=15.8$ Å^2, which strongly disagrees with the experimental values [9(3) Å^2] collected in Ref. [29]. An even greater disagreement was found presently with the IOSA limit: $\sigma_E(\mathrm{IOSA})=20.3$ Å^2. On the contrary, the EFCSA result ($\sigma_E=9.7$ Å^2 at $T=298$ K) is in good accord with the experiment. Remarkably, an orthogonal transformation in the line space to the Laguerre polynomials $L_n(\varepsilon_J)$ of the discrete variable $\varepsilon_J=\beta E_J$ [13] practically diagonalizes the IOSA matrix. The Laguerre eigenbasis appears in the classical Keilson-Storer model [1], the relevant eigenvalues being given by $\gamma_n=\gamma(1-\lambda^{2n})$. This dependence is well reproduced in the IOSA limit with the collisional ''softness'' parameter $\lambda\approx0.80$.

One of the main advantages of the EFCSA approach over the conventional IOSA/ECSA approaches is its ability to produce all characteristics obtained by spectroscopies characterized by nonscalar photon-molecule coupling. The results for the anisotropic (with $r=2$) Raman $Q_0(J)$ and $S_0(J)$ line half widths are depicted in Figs. 2 and 4. The adiabatic contributions proportional to $\Phi_L'(0)$ amount to 20% for the first anisotropic $Q_0(J)$ lines, and are also shown there; due to this contribution, the anisotropic $Q_0(J)$ lines are always broader than the isotropic ones that are affected by inelastic collisions only. The EFCSA predicts a similar situation for the $S_0(J)$ lines, whose widths are equal to the half sum of the isotropic $Q(J)$ and $Q(J+2)$ line widths plus the adiabatic contribution (see Fig. 4). However, the latter is pronouncedly weaker in comparison with the anisotropic Q_0 lines (cf. Figs. 2 and 4). The calculated $S_0(J)$ half widths are somewhat higher (5–15 %) than the spontaneous Raman data [30,31], but are close to those obtained by Raman gain spectroscopy [32] (see Fig. 4).

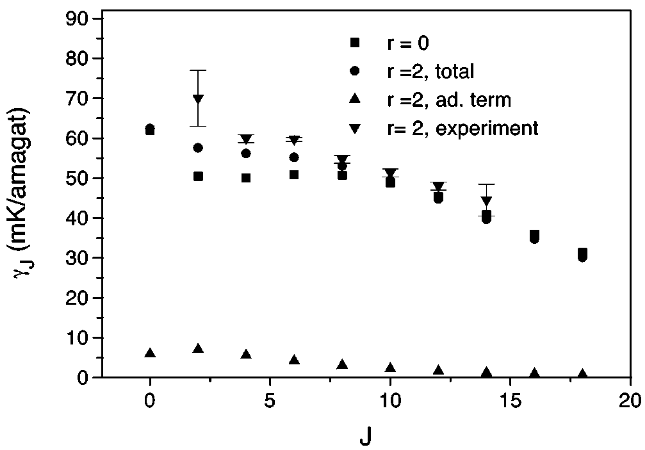

FIG. 4. EFCSA broadening coefficients of $Q_1(J)(r=0)$ and $S_0(J)(r=2)$ nitrogen lines ($T=293$ K). Adiabatic parts of $S_0(J)$ broadening coefficients and experimental data [32] are also shown.

The half width measurements of the isotropic $Q_1(J)$ lines are possible due to the vibration-rotation coupling that splits the branch. In the anisotropic Q_0 branch ($r=2$), the splitting is absent, and only integral broadening effects can be observed. Theory [13] gives an expression for the Fourier transform $C_Q(t)$ of the anisotropic Q_0-branch profile,

$$C_Q(t)=\exp(-\Gamma_Q t)[1+\alpha_Q(\Gamma_Q t)^2], \tag{44}$$

which fits the observed time dependence well [33] when $\alpha_Q=0.057(5)$. The corresponding experimental ($T=293$ K) cross-section σ_Q is 34.4(6) Å^2 [34]. Both characteristics can be calculated with the known Γ matrix: $\sigma_Q=31.1$ Å^2; $\alpha_Q=0.077$. Our IOSA results do not considerably deviate from these values: $\Gamma_Q(\mathrm{IOSA})=28.4$ Å^2, $\alpha_Q(\mathrm{IOSA})=0.088$. The reason is that the adiabatic effects, pronounced in the $r=2$ case, are insensitive to the increase in ω_0; besides, the energy weighting that influences the Γ_E value is absent for Γ_Q. The region adjacent to the main diagonal, i.e., characterized by moderate $|J-J'|$ values, contributes the most to Γ_Q; the matrix elements in this region are not much affected by variations of ω_0.

The accuracy of EFCSA is further supported by the calculation of the time correlation function $C_{\mathbf{J}}(t)$ of the angular momentum. The cross section ($\sigma_J=15.8$ Å^2) so obtained is close to that derived from NMR spectra (14.5 Å^2 [35]). As has been said above, the present IOSA formulation leads to a nonzero value for σ_J; its value (14.8 Å^2) almost coincides with the measured one. Strikingly, the associated Laguerre polynomials $L_n^{(1)}(\varepsilon_J)$ $(n=0,1,2\ldots)$ [13] practically diagonalize the IOSA $\Gamma(1,0)$ matrix, the eigenvalues closely following $\gamma_n^{(\mathbf{J})} \propto 1-\lambda_{\mathbf{J}}^{2n+1}$ with $\lambda_{\mathbf{J}} \approx 0.73$. The energy and angular-momentum ''softness'' parameters so obtained reasonably match one another showing that the N_2-N_2 impacts more likely fall into the soft-collision ($\lambda=1$) regime than they do the strong-collision ($\lambda=0$) regime.

Generally, a realistic behavior of the EFCSA matrix in the most physically important domains of frequency and rotational quantum numbers is supported by the results of this study. The simulated rates were found to be sensitive to variations of χ and ω_0; for example, an increase in the value of χ to 0.015 results in $\sigma_Q = 31.4$ Å^2, $\sigma_J = 14.8$ Å^2, and $\alpha = 0.067$, all of which are in better agreement with the experiment. Final conclusions on the usefulness of the proposed model may be drawn following a complete multiproperty optimization; further, direct calculation, or more accurate modeling, of the $F_L(t)$, is desirable. This topic will be the subject of future studies.

IV. SUMMARY

We briefly summarize the results obtained. Assuming the collisions to be rapid, corrections for both the electromagnetic field frequency and molecular rotation are rigorously introduced into the Zwanzig-Mori matrix $\Gamma(r,\omega)$ describing relaxation of an arbitrary rth rank tensor. The allowance is thus made for incomplete binary collisions (off-energy shell scattering) [10] as well as for a finite rotational Massey parameter. The fundamental properties of the derived ECFSA matrix have been demonstrated: (a) the symmetry relative to interchange of the line-space indices, (b) the positive definiteness, (c) the sum-rules relation, (d) the time-reversal symmetry, and (e) the dispersion relations. The matrix elements are expressed via the Fourier transforms of the bath time correlation functions $F_L(t)$ obtained at fixed molecular orientation. A bath-spectrum model consistent with the known N_2-N_2 potential gives encouraging results for a number of the rotational-relaxation characteristics measured in room-temperature nitrogen. In order to avoid direct dynamic calculations, a few leading moments can first be calculated and then employed to reconstruct the bath-spectral functions. The treatment can be extended to solve related problems (such as rotational relaxation of symmetric and spherical tops, spectroscopy of bending states of linear molecules, and collisional coherence of radiative transitions in different molecules).

ACKNOWLEDGMENTS

The author thanks Dr. J. V. Buldyreva for providing data on the Laguerre polynomials of a discrete variable. Financial support of the Russian Foundation for Basic Research (Project No.97-03-33655a) is gratefully acknowledged.

APPENDIX

Using the explicit forms of the operators $u^{(L)}$ and $v^{(L)}$ [Eqs. (14) and (15)], one obtains from Eq. (18):

$$\begin{aligned} F_L(t) &= (4\pi)^{-1}\sum_M \mathrm{Tr}_B\langle 00|W\exp(iH'_B t/\hbar)|LM\rangle \\ &\quad\times\langle LM|W\exp(-iH'_B t/\hbar)\rho'_B|00\rangle \\ &= (4\pi)^{-1}\sum_{M\alpha\beta}\langle 00\alpha|W\exp(iH'_B t/\hbar)|\beta LM\rangle \\ &\quad\times\langle LM\beta|W\exp(-iH'_B t/\hbar)\rho'_B|\alpha 00\rangle, \end{aligned} \tag{A1}$$

which, upon going to the eigenbasis of $H'_B(\Omega_a)$, becomes

$$\begin{aligned} F_L(t) &= (4\pi)^{-1}\sum_{M\alpha\beta}\rho'_B(\varepsilon_\alpha)\exp[i(\varepsilon_\beta-\varepsilon_\alpha)t/\hbar] \\ &\quad\times\langle 00|W_{\alpha\beta}|LM\rangle\langle LM|W_{\beta\alpha}|00\rangle. \end{aligned} \tag{A2}$$

The unitary transformation to the real tesseral harmonics $|L\tilde{M}\rangle$ [18] leaves the projector unchanged: $\Sigma_M|LM\rangle\langle LM| = \Sigma_M|L\tilde{M}\rangle\langle L\tilde{M}|$, and we have

$$\begin{aligned} \langle 00|W_{\alpha\beta}|L\tilde{M}\rangle &= \langle L\tilde{M}|W_{\beta\alpha}|00\rangle^* \\ &= \langle L\tilde{M}|W_{\alpha\beta}|00\rangle = \langle 00|W_{\beta\alpha}|L\tilde{M}\rangle^*. \end{aligned} \tag{A3}$$

Since the two matrix elements of W entering Eq. (A2) are complex conjugates, and the real eigenvalues ε_α are independent of Ω_a, one gets

$$F_L^*(t) = F_L(-t). \tag{A4}$$

Taking the Fourier transform $\Phi'_L(\omega)$ [see Eq. (24)] leads to

$$\begin{aligned} \Phi'_L(\omega) &= \frac{1}{4}\sum_{M\alpha\beta}\rho_B(\varepsilon_\alpha)\,\delta(\omega-\omega_{\beta\alpha})\langle 00|W_{\alpha\beta}|LM\rangle \\ &\quad\times\langle LM|W_{\beta\alpha}|00\rangle, \end{aligned} \tag{A5}$$

which can be directly shown to satisfy

$$\Phi'_L(-\omega) = \exp(-\hbar\omega/kT)\,\Phi'_L(\omega). \tag{A6}$$

This generalizes the well-known Boltzmann relation to the EFCSA case. Equation (A1) can be straightforwardly reduced to the perturbation-theory expression [13] by neglecting the anisotropy of H'_B in the exponential operators. In this case, the latter do not act on the rotational wave functions, and the perturbation theory expression readily follows, namely,

$$F_L(t) = \Pi_L^{-2}\,\mathrm{Tr}_B\,\rho_B(W^{(L)}(0), W^{(L)}(t)), \tag{A7}$$

in which the bath motion assumedly occurs in the isotropic intermolecular potential.

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