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Vibrational relaxation in the condensed phase

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A modified Landau-Teller equation for vibrational relaxation in the condensed phase is proposed. This equation differs from previous approaches by accounting for the fluctuations of the energies of the vibrational levels that result from the interactions with the surroundings (bath). In the conventional approach the effects of the bath are only included in the coupling between the relaxing and accepting vibrational modes. It is shown that the additional inclusion of the fluctuations of the energy levels can lead to a dramatic change of the vibrational relaxation rate. © 2004 American Institute of Physics. [DOI: 10.1063/1.1808116]

I. INTRODUCTION

In vibrational relaxation the energy of an excited vibration is transferred to a combination of lower-frequency vibrations and/or other degrees of freedom. In polyatomic atomic molecules, these lower energy degrees of freedom are often formed by a few strongly coupled, lower-frequency intramolecular vibrational modes.^{1–3} The sum of the frequencies of these strongly coupled intramolecular modes is in general not exactly equal to the frequency of the relaxing mode. This energy difference has to be compensated, because vibrational relaxation can only take place if the energy is conserved. Hence, in general the relaxation process also involves the excitation or deexcitation of additional low-frequency intermolecular modes that are often denoted as bath modes. These bath modes thus play an essential role in the vibrational relaxation, although the energy accepted or provided by these modes is in general very small compared to the energy of the relaxing vibration. In the condensed phase, there are many different types of low-frequency intermolecular modes that can assist in the vibrational relaxation process. Clearly, in the gas phase most of these modes will be missing, which explains why for small molecules vibrational relaxation in the gas phase is orders of magnitude slower than in the condensed phase.

The rate of bath-assisted vibrational relaxation can be calculated in a perturbative approach using a Landau-Teller formulation of Fermi's Golden Rule.⁴ In this description, the relaxation rate is proportional to the time-correlation function of the fluctuating coupling between the relaxing and accepting vibrational modes. The energy mismatch between these modes is then compensated by the appropriate frequency of the coupling. The fluctuations follow from the dependence of the coupling on particular bath modes. For instance, they can result from changes in the solvation structure or in the molecular conformation.⁵ As a result, the rate of vibrational energy transfer can give information on conformational molecular dynamics.

The interactions with the bath not only affect the coupling between the relaxing and the accepting modes, they also lead to fluctuations of the energies of these modes and thereby to pure dephasing of the vibrational transitions.

These fluctuations can assist in vibrational relaxation by decreasing the energy difference between the interacting levels. Recently, the effects of the fluctuations of the energy levels have been calculated for the CH stretch vibration of liquid chloroform⁶ and the OH stretch vibration of liquid methanol.⁷ In these studies, the relaxation rate was calculated in a nonperturbative approach by numerical integration of the time-dependent Schrödinger equation. In this paper, we propose to describe the effects of energy fluctuations on vibrational relaxation with a modified expression of the Landau-Teller equation. To this extent, we derive an alternative form of this equation that contains terms representing the energy fluctuations of the interacting levels.

II. THEORETICAL MODEL

A. General description of vibrational relaxation

For a molecule in the condensed phase the Hamiltonian is given by

$$H = H_S + H_B + V_{SA} + V_{SB}, \quad (1)$$

with H_S the vibrational Hamiltonian of the molecule, H_B the Hamiltonian of the bath, V_{SA} the anharmonic coupling of the molecular vibrations, and V_{SB} the coupling between the molecular vibrations and the bath. The coupling V_{SB} depends on both the vibrational and the bath coordinates. The couplings V_{SA} and V_{SB} can lead to vibrational energy relaxation.

In the treatments of Lawrence and Skinner^{8–10} and Rey and Hynes,^{11,12} the vibrational states are anharmonic eigenstates, which implies that these states include the effect of the anharmonic coupling V_{SA} . This approach has as an important consequence that vibrational relaxation can result from an interaction V_{SB} that is only of first or second order in the vibrational normal mode coordinates. In the treatment of Lawrence and Skinner, the Hamiltonian of the system includes the average effect of the condensed phase environment on the energies of the vibrational eigenstates of H_S . Hence, the states $|\phi_i\rangle$ and $|\phi_f\rangle$ are eigenstates of the Hamiltonian $H_0 = H_S + V_{SA} + \langle\langle V_{SB} \rangle\rangle_b$, where $\langle\langle V_{SB} \rangle\rangle_b$ denotes a bath average of V_{SB} . In addition, Lawrence and Skinner account for the average effect of V_{SB} in the Hamiltonian of the bath, by including V_{SB} at the mean values of the coordinates

$\{q\}$ of the molecular vibrations. Hence, in this treatment $V_{SB}(\{q_{nn}\})$, with $q_{nn} = \langle \phi_n | q | \phi_n \rangle$, is added to the bath Hamiltonian. If the vibrational system is anharmonic, the mean vibrational coordinates $\{q_{nn}\}$ and the bath Hamiltonian will be dependent on the occupied vibrational state $|\phi_n\rangle$. The vibrational states thus depend on the bath, because they are eigenfunctions of $H_0 = H_S + V_{SA} + \langle\langle V_{SB} \rangle\rangle_b$, and the bath in turn depends on the occupied vibrational state because the bath Hamiltonian depends on the values of $\{q_{nn}\}$. Therefore, given the nature of the vibrational state $|\phi_i\rangle$, H_0 and H_B are to be determined in an iterative manner.^{8,9} In the present treatment, we will follow Lawrence and Skinner in including the bath average of V_{SB} in the system Hamiltonian, but we will not include $V_{SB}(\{q_{nn}\})$ in the Hamiltonian of the bath. The effect of the character of the vibrational state on the bath states and energies will be discussed in detail in Sec. II C.

The relaxation of an excited vibration $|\phi_i\rangle$ can be described with Fermi's Golden Rule that is derived from first-order time-dependent perturbation theory. If $|\phi_i\rangle$ and $|\phi_f\rangle$ are eigenstates of the Hamiltonian H_0 , vibrational relaxation results from the coupling $V'_{SB} = V_{SB} - \langle\langle V_{SB} \rangle\rangle_b$. Using Fermi's Golden Rule, the rate of transfer from the initial level $|\phi_i\rangle$ to other vibrational states $|\phi_f\rangle$ is given by

$$T_1^{-1} = \frac{2\pi}{\hbar} \sum_{b, f \neq i, c} \frac{e^{-E_b/kT}}{Z_B} |\langle \phi_i | \langle \phi_{ib} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle|^2 \times \delta(E_{ib} - E_{fc}), \quad (2)$$

with ϕ_{ib} and ϕ_{fc} denoting bath states, Z_B the reservoir partition function, and E_{ib} and E_{fc} the initial and final state energies, corresponding to the states $|\phi_i\rangle|\phi_{ib}\rangle$ and $|\phi_f\rangle|\phi_{fc}\rangle$, respectively. The delta function in Eq. (2) can be Fourier transformed giving

$$T_1^{-1} = \frac{1}{\hbar^2 Z_B} \int_{-\infty}^{\infty} dt \sum_{b, f \neq i, c} e^{-E_b/kT} e^{i(E_{ib} - E_{fc})t/\hbar} \times |\langle \phi_i | \langle \phi_{ib} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle|^2. \quad (3)$$

B. Conventional approach to the influence of the bath

The energies E_{ib} and E_{fc} can be written as $E_{ib} = E_{i0} + E_b$, and $E_{fc} = E_{f0} + E_c$, with the energies E_{i0} and E_{f0} eigenenergies of $H_S + V_{SA} + \langle\langle V_{SB} \rangle\rangle_b$, and the energies E_b and E_c eigenenergies of H_B . If we define $\hbar\Delta\omega_{if} = E_{i0} - E_{f0}$, and rewrite Eq. (3) in the Heisenberg representation we obtain

$$T_1^{-1} = \frac{1}{\hbar^2 Z_B} \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \times \sum_b \langle \phi_i | \langle \phi_{ib} | e^{-H_B/kT} e^{iH_B t/\hbar} V'_{SB} | \phi_f \rangle \times \langle \phi_f | e^{-iH_B t/\hbar} V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle. \quad (4)$$

The equality of Eqs. (3) and (4) can easily be seen by inserting a closure $\sum |\phi_{fc}\rangle\langle\phi_{fc}|$ between $|\phi_f\rangle$ and $\langle\phi_f|$ and using $\langle\phi_{fc}| e^{-iH_B t/\hbar} = \langle\phi_{fc}| e^{-iE_c t/\hbar}$. The operator $e^{iH_B t/\hbar}$ describes the time evolution of the occupied bath states: $\sum_b \langle\phi_{ib}| e^{iH_B t/\hbar} = \sum_b \langle\phi_{ib}| e^{iE_b t/\hbar}$.

Equation (4) can be written as

$$T_1^{-1} = \frac{1}{\hbar^2 Z_B} \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \times \sum_b \langle \phi_{ib} | e^{-H_B/kT} e^{iH_B t/\hbar} V'_{SB,if} e^{-iH_B t/\hbar} V'_{SB,fi} | \phi_{ib} \rangle = \frac{1}{\hbar^2} \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \langle\langle V'_{SB,if}(t) V'_{SB,fi}(0) \rangle\rangle_b \quad (5)$$

with $V'_{SB,if}(t) = e^{iH_B t/\hbar} \langle\phi_i| V'_{SB} | \phi_f \rangle e^{-iH_B t/\hbar}$ and $\langle\langle A \rangle\rangle_b = (1/Z_B) \text{Tr}\{e^{-H_B/kT} A\}$, with the trace taken over the bath states. Equation (5) is often referred to as the Landau-Teller formula. This formulation of Fermi's Golden Rule in terms of a Fourier transform of a fluctuating coupling represents a very general approach to the description of the effect of the bath on vibrational relaxation.

C. Extended description of the influence of the bath

The Golden Rule expression of Eq. (2) and the subsequent equations are derived under the assumption that the coupling V'_{SB} does not have diagonal matrix elements, i.e., $\langle\phi_i| \langle\phi_{ib}| V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle$ and $\langle\phi_f| \langle\phi_{fc}| V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle$ are assumed to be zero. Clearly, this assumption is not always valid. For instance, in molecular collisions¹³ and non-adiabatic electronic transitions¹⁴ the diagonal terms can play an important role and the diagonal matrix elements have to be retained in the theoretical description. In the condensed phase, the system-bath coupling is known to lead to pure dephasing, which implies that the coupling V'_{SB} has nonzero diagonal matrix elements that lead to fluctuations in the energies of the vibrational states. In the following, we will show that these fluctuations can play an important role in vibrational relaxation, and we derive a modified Golden Rule expression and Landau-Teller equation in which the effects of the energy fluctuations of the vibrational levels are included.

Starting point of the derivation is the time-dependent Schrödinger equation $i\hbar\partial\Psi(t)/\partial t = H\Psi(t)$, with $\Psi(t) = \sum_{i,b} c_{ib} \phi_i \phi_{ib}$. Following the renormalized treatment of Lawrence and Skinner, the ϕ_i states are the eigenfunctions of the Hamiltonian $H_0 = H_S + V_{SA} + \langle\langle V_{SB} \rangle\rangle_b$, with eigenenergies E_{i0} . This implies that the perturbation mixing the states is $V'_{SB} = V_{SB} - \langle\langle V_{SB} \rangle\rangle_b$. Substitution of the wave function $\Psi(t)$ in the Schrödinger equation, and multiplication from the left with $\langle\phi_f| \langle\phi_{fc}|$ gives

$$i\hbar \frac{\partial c_{fc}(t)}{\partial t} = \sum_{i \neq f, b} \langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle c_{ib}(t) + \langle \phi_f | \langle \phi_{fc} | H | \phi_f \rangle | \phi_{fc} \rangle c_{fc}(t). \quad (6)$$

Substitution of $c_{fc}(t) = b_{fc}(t) e^{-iE_{fc}t/\hbar}$ and multiplication of both sides with $e^{iE_{fc}t/\hbar}$ gives

$$i\hbar \frac{\partial b_{fc}(t)}{\partial t} = \sum_{i \neq f, b} \langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle \times b_{ib}(t) e^{i(E_{fc} - E_{ib})t/\hbar} + \langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle b_{fc}(t). \quad (7)$$

In many cases, the last term is assumed to be zero, and the replacement of the coefficients $b_{ib}(t)$ by the amplitudes of the occupied vibrational/bath states eventually leads to the Fermi's Golden Rule expression of Eq. (2). Here we will retain the matrix element $\langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle$ in deriving a modified version of Fermi's Golden Rule (FGR) using first-order perturbation theory. We define $b_{fc}(t) = a_{fc}(t) e^{-i \langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle t / \hbar}$ and $b_{ib}(t) = a_{ib}^0 e^{-i \langle \phi_i | \langle \phi_{ib} | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle t / \hbar}$, where a_{ib}^0 represents the amplitude of an occupied vibrational/bath states. Substitution of these expressions and multiplication of both sides with $e^{i \langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle t / \hbar}$ gives

$$i\hbar \frac{\partial a_{fc}(t)}{\partial t} = \sum_{i \neq f, b} \langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle \times a_{ib}^0 e^{i(E_{fc} - E_{ib})t/\hbar + \delta\omega_{fc}t - \delta\omega_{ib}t}, \quad (8)$$

with $\hbar \delta\omega_{fc} = \langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle$ and $\hbar \delta\omega_{ib} = \langle \phi_i | \langle \phi_{ib} | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle$. If we integrate over t , multiply $a_{fc}(t)$ with its complex conjugate, and neglect all cross terms of different states $|\phi_{ib}\rangle$, we obtain

$$|a_{fc}(t)|^2 = \frac{1}{\hbar^2} \sum_{i \neq f, b} |\langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle|^2 |a_{ib}^0|^2 \times \frac{|1 - e^{i(\Delta\omega_{fc,ib} + \delta\omega_{fc} - \delta\omega_{ib})t}|^2}{(\Delta\omega_{fc,ib} + \delta\omega_{fc} - \delta\omega_{ib})^2} = \frac{1}{\hbar^2} \sum_{i \neq f, b} |\langle \phi_f | \langle \phi_{fc} | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle|^2 |a_{ib}^0|^2 \times F(t, \Delta\omega_{ib,fc} + \delta\omega_{ib} - \delta\omega_{fc}), \quad (9)$$

with $\Delta\omega_{fc,ib} = (E_{fc} - E_{ib})/\hbar$ and $F(t, \omega) = \sin^2(-\omega t/2)/(-\omega/2)^2$. The long time limit of the function F is a δ function:¹⁵ $\lim_{t \rightarrow \infty} F(t, \omega) = 2\pi\hbar t \delta(\hbar\omega)$. If we consider only one occupied initial vibrational state, replace the function F by the δ function and $|a_{ib}^0|^2$ by $e^{-E_b/kT}/Z_b$, and if we sum over all possible final states ϕ_f , we obtain

$$T_1^{-1} = \sum_{f,c} \frac{\partial |a_{fc}(t)|^2}{\partial t} = \frac{2\pi}{\hbar} \sum_{b,f \neq i,c} \frac{e^{-E_b/kT}}{Z_B} |\langle \phi_i | \langle \phi_{ib} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle|^2 \times \delta(E_{ib} - E_{fc} + \hbar \delta\omega_{ib} - \hbar \delta\omega_{fc}). \quad (10)$$

This equation is similar to the Golden Rule expression of Eq. (2), but differs in the energies contained in the δ function. The δ function now contains additional energy terms $\hbar \delta\omega_{fc}$ and $\hbar \delta\omega_{ib}$ that were absent before.

Equation (10), can be Fourier transformed giving

$$T_1^{-1} = \frac{1}{\hbar^2 Z_B} \int_{-\infty}^{\infty} dt \times \sum_{b,f \neq i,c} e^{-E_b/kT} e^{i(E_{ib} - E_{fc} + \hbar \delta\omega_{ib} - \hbar \delta\omega_{fc})t/\hbar} \times |\langle \phi_i | \langle \phi_{ib} | V'_{SB} | \phi_f \rangle | \phi_{fc} \rangle|^2. \quad (11)$$

If we now use that $E_{ib} = E_{i0} + E_b$ and $E_{fc} = E_{f0} + E_c$, and that $\langle \phi_i | \langle \phi_{ib} | e^{i(E_{ib} + \hbar \delta\omega_{ib})t/\hbar} = \langle \phi_i | \langle \phi_{ib} | e^{i(E_{i0} + H_B + \langle \phi_i | V'_{SB} | \phi_i \rangle)t/\hbar}$, we can write Eq. (11) as

$$T_1^{-1} = \frac{1}{\hbar^2 Z_B} \int_{-\infty}^{\infty} dt \sum_b e^{-E_b/kT} e^{i\Delta\omega_{if}t} \times \langle \phi_i | \langle \phi_{ib} | e^{i(H_B + \langle \phi_i | V'_{SB} | \phi_i \rangle)t/\hbar} V'_{SB} \times \sum_{f \neq i,c} |\phi_f\rangle \langle \phi_{fc} | \langle \phi_{fc} | \langle \phi_f | e^{-i(H_B + \langle \phi_f | V'_{SB} | \phi_f \rangle)t/\hbar} \times V'_{SB} | \phi_{ib} \rangle \phi_i \rangle. \quad (12)$$

The functions $\langle \phi_i | V'_{SB} | \phi_i \rangle$ and $\langle \phi_f | V'_{SB} | \phi_f \rangle$ represent potential energy terms in the bath coordinates. In an adiabatic picture, the energies of the states $|\phi_i\rangle$ and $|\phi_f\rangle$ depend parametrically on the bath coordinates, thus determining the dependence of $\langle \phi_i | V'_{SB} | \phi_i \rangle$ and $\langle \phi_f | V'_{SB} | \phi_f \rangle$ on the bath. It should be noted that these terms represent a different contribution to the bath Hamiltonian than the interaction V_{SB} evaluated at the mean value of the vibrational coordinates that was included in the renormalized bath Hamiltonian in the treatment of Lawrence and Skinner.^{8,9} For instance, if the states $|\phi_i\rangle$ and $|\phi_f\rangle$ would be harmonic, the terms $V_{SB}(\{\langle \phi_i | q | \phi_i \rangle\})$ and $V_{SB}(\{\langle \phi_f | q | \phi_f \rangle\})$ would be the same, while the terms $\langle \phi_i | V'_{SB} | \phi_i \rangle$ and $\langle \phi_f | V'_{SB} | \phi_f \rangle$ can still have a strongly different dependence on the bath coordinates.

An important characteristic of Eq. (12) is that the bath Hamiltonians contained in the exponential factors $e^{i(H_B + \langle \phi_i | V'_{SB} | \phi_i \rangle)t/\hbar}$ and $e^{-i(H_B + \langle \phi_f | V'_{SB} | \phi_f \rangle)t/\hbar}$ differ, whereas in all previous treatments these bath Hamiltonians are the same [see Eq. (5)]. We will show that the difference between the bath Hamiltonians contained in the exponential factors of Eq. (12) can have a strong effect on the vibrational relaxation rate.

Dropping the closure $\sum_c |\phi_{fc}\rangle \langle \phi_{fc}|$ in Eq. (12) gives

$$T_1^{-1} = \frac{1}{\hbar^2 Z_B} \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \sum_b e^{-E_b/kT} \times \langle \phi_{ib} | e^{i(H_B + \langle \phi_i | V'_{SB} | \phi_i \rangle)t/\hbar} \langle \phi_i | V'_{SB} | \phi_f \rangle \times e^{-i(H_B + \langle \phi_f | V'_{SB} | \phi_f \rangle)t/\hbar} \langle \phi_f | V'_{SB} | \phi_i \rangle | \phi_{ib} \rangle. \quad (13)$$

Equation (13) can be written as

$$T_1^{-1} = \frac{1}{\hbar^2} \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \langle \langle e^{i(H_B + \langle \phi_i | V'_{SB} | \phi_i \rangle)t/\hbar} \times \langle \phi_i | V'_{SB} | \phi_f \rangle e^{-i(H_B + \langle \phi_f | V'_{SB} | \phi_f \rangle)t/\hbar} \langle \phi_f | V'_{SB} | \phi_i \rangle \rangle \rangle_b, \quad (14)$$

with $\langle\langle A \rangle\rangle_b = (1/Z_B) \text{Tr}\{e^{-H_B/kT} A\}$, with the trace taken over the bath states.

Using the relation,^{16,17}

$$e^{-i(H_0+V)t/\hbar} = e^{-iH_0t/\hbar} e^{-i\int_0^t dt' e^{iH_0t'/\hbar} V e^{-iH_0t'/\hbar}}, \quad (15)$$

we can transform Eq. (14) into

$$T_1^{-1} = \frac{1}{\hbar^2} \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \langle\langle e^{i\int_0^t dt' V'_{SB,ii}(t')/\hbar} \times V'_{SB,if}(t) e^{-i\int_0^t dt' V'_{SB,ff}(t')/\hbar} V'_{SB,fi}(0) \rangle\rangle_b, \quad (16)$$

where $V'_{SB,mn}(t) = e^{iH_B t/\hbar} \langle\phi_m|V'_{SB}|\phi_n\rangle e^{-iH_B t/\hbar}$ and e_0 denotes a time-ordered exponential.

D. Interpretation

In Eq. (16) the two different fluctuations induced by the bath can easily be recognized. In the first place, the interactions with the bath lead to fluctuations of the anharmonic coupling characterized by the correlation function $V'_{SB,if}(t)V'_{SB,fi}(0)$. This term represents the usual approach to the description of bath mediated vibrational relaxation. Second, the interactions with the bath lead to fluctuations of the energies of the vibrational levels, expressed by the terms $V'_{SB,ii}(t')$ and $V'_{SB,ff}(t')$.

The fluctuations of the energy levels and the fluctuations of the coupling $\langle\phi_i|V'_{SB}|\phi_f\rangle$ represent different matrix elements of the coupling V'_{SB} . The fluctuations of the coupling are the result of matrix elements $\langle\phi_i|\langle\phi_{ib}|V'_{SB}|\phi_f\rangle|\phi_{fc}\rangle$, with $b \neq c$ and $i \neq f$. This implies that the transition between the states $|\phi_i\rangle$ and $|\phi_f\rangle$ is accompanied by the excitation or deexcitation of quanta in the bath modes. This excitation or deexcitation can lead to a compensation of the energy mismatch between $|\phi_i\rangle$ and $|\phi_f\rangle$ that enables the transition.

The fluctuations of the energy levels follow from the dependence of the potential energy terms $\langle\phi_i|V'_{SB}|\phi_i\rangle$ and $\langle\phi_f|V'_{SB}|\phi_f\rangle$ on the bath coordinates. If the addition of these potential energy terms to the bath Hamiltonian H_B would not lead to a change of the wave functions of the bath, these potential energy terms would commute with H_B and the only effect of these terms is a time-independent change of the energies of the states $|\phi_{ib}\rangle|\phi_i\rangle$ and $|\phi_{fc}\rangle|\phi_f\rangle$. These time-independent changes of the energy can help in making the energy transfer resonant, but it clearly does not represent energy matching via fluctuations. However, if the matrix elements $\langle\phi_n|\langle\phi_c|V'_{SB}|\phi_n\rangle|\phi_b\rangle$ (with $b \neq c$ and $n=i$ or $n=f$), where $|\phi_b\rangle$ and $|\phi_c\rangle$ are eigenstates of H_B , are nonzero, the functions $V_{SB,ii}(t) = e^{iH_B t/\hbar} V_{SB,ii} e^{-iH_B t/\hbar}$ and $V_{SB,ff}(t) = e^{iH_B t/\hbar} V_{SB,ff} e^{-iH_B t/\hbar}$ are time dependent. If the time dependence of $V_{SB,ii}(t)$ and $V_{SB,ff}(t)$ differs, the fluctuations of these functions can lead to a cancellation of the energy mismatch $\hbar\Delta\omega_{if}$, and thus enable the relaxation. An equivalent way of describing this effect is as follows. Due to the presence of the terms $\langle\phi_i|V'_{SB}|\phi_i\rangle$ and $\langle\phi_f|V'_{SB}|\phi_f\rangle$, the sets of bath states $\{|\phi_{ib}\rangle\}$ and $\{|\phi_{fc}\rangle\}$ will differ. As a result, the states $|\phi_{fc}\rangle$ and $|\phi_{ib}\rangle$ can have nonzero overlap while their average kinetic energies differ. Nonzero overlap, namely, only requires that the kinetic energies of $|\phi_{fc}\rangle$ and

$|\phi_{ib}\rangle$ are the same at particular values of the bath coordinates. The difference in average kinetic energy serves to compensate the energy mismatch $\hbar\Delta\omega_{if}$.

The importance of including the fluctuations of the energies of the vibrational levels in vibrational relaxation can be illustrated in the following way. If there are only two eigenstates $|\phi_{i0}\rangle$ and $|\phi_{f0}\rangle$ of the vibrational Hamiltonian without anharmonic coupling, then $|\phi_i\rangle = |\phi_{i0}\rangle + a|\phi_{f0}\rangle$ and $|\phi_f\rangle = |\phi_{f0}\rangle - a|\phi_{i0}\rangle$, with $a = \langle\phi_{i0}|V_{SA}|\phi_{f0}\rangle/(E_{i0} - E_{f0})$. If the coupling V'_{SB} only has diagonal elements in the zero-order states $|\phi_{i0}\rangle$ and $|\phi_{f0}\rangle$, the coupling matrix element $V'_{SB,if}$ of Eqs. (5) and (16) takes the form

$$V'_{SB,if} = \langle\phi_{i0} + a\phi_{f0}|V'_{SB}|\phi_{f0} - a\phi_{i0}\rangle = \frac{\langle\phi_{i0}|V_{SA}|\phi_{f0}\rangle}{E_{i0} - E_{f0}} \times (\langle\phi_{f0}|V'_{SB}|\phi_{f0}\rangle - \langle\phi_{i0}|V'_{SB}|\phi_{i0}\rangle). \quad (17)$$

When the coupling V'_{SB} leads to a compensation of the energy difference $E_{i0} - E_{f0}$, then $\langle\phi_{f0}|V'_{SB}|\phi_{f0}\rangle - \langle\phi_{i0}|V'_{SB}|\phi_{i0}\rangle = E_{i0} - E_{f0}$, and $\langle\phi_i|V'_{SB,if}|\phi_f\rangle = \langle\phi_{i0}|V_{SA}|\phi_{f0}\rangle$. This implies that the coupling V'_{SB} has tuned the states ϕ_i and ϕ_f into resonance, thereby making the anharmonic interaction effective in making the transition. Hence, a large transition rate is expected. However, in the conventional formulation of Eq. (5), the relaxation rate will remain small, because this equation contains a factor $e^{i\Delta\omega_{if}t}$ representing the original energy difference between the two states in the absence of the coupling V'_{SB} . In contrast, the additional time-dependent exponential terms $e^{i\int_0^t dt' V'_{SB,ii}(t')/\hbar}$ and $e^{-i\int_0^t dt' V'_{SB,ff}(t')/\hbar}$ of Eq. (16) will largely compensate the term $e^{i\Delta\omega_{if}t}$ in case the shifts of the energy levels of ϕ_i and ϕ_f induced by V'_{SB} are sufficiently slow and long living. Therefore, Eq. (16) indeed accounts for the expected increase in relaxation rate when the levels ϕ_i and ϕ_f are tuned into resonance by V'_{SB} .

Often vibrational relaxation is described using states that are eigenstates of the system Hamiltonian without anharmonic coupling.¹⁸ Then the states ϕ_i and ϕ_f are product states of normal mode wave functions. In that case, the states can be coupled both by the anharmonic interaction and by the fluctuating part of the system-bath coupling. In the conventional description of Eq. (5), this means that the anharmonic coupling must be dependent on the bath coordinates to compensate for the energy mismatch $\hbar\Delta\omega_{if}$. Since the anharmonic coupling is an intramolecular interaction, its dependence on the bath coordinates is expected to be small. In Eq. (16) the energy mismatch $\hbar\Delta\omega_{if}$ can be compensated by the fluctuations of the energies of ϕ_i and ϕ_f , which implies that following this equation, vibrational relaxation can result from the relatively large time-independent part of the anharmonic coupling.

E. Calculation of the relaxation rate using molecular dynamics simulations

The vibrational relaxation rate T_1^{-1} is the sum of the rates k_{if} where f denotes all possible final states $|\phi_f\rangle$ to

which the initial state $|\phi_i\rangle$ can relax. In most molecular dynamics simulations, the rates k_{if} are calculated using a classical description of the bath. Hence, the quantum correlation functions of Eqs. (5) and (16) are to be replaced by classical correlation functions that can be evaluated with molecular dynamics simulations. However, a classical correlation function is a symmetric function in time, whereas the quantum correlation functions of Eqs. (5) and (16) are not symmetric. This has two important consequences. First, the relaxation rates no longer fulfill detailed balance: $k_{fi} = k_{if} e^{-\hbar\Delta\omega_{if}/kT}$. Second, the use of classical correlation functions in general leads to an underestimation of the relaxation rate, especially at high frequencies.¹⁹ Hence, the replacement of the quantum correlation function by a classical function should be accompanied by the addition of a so-called quantum correction factor (QCF), as a result of which the relaxation rate k_{if} fulfills detailed balance and acquires the correct value at high frequencies. The precise form of the QCF depends on the physics of the relaxation process.

Another consequence of the evaluation of the correlation functions with classical molecular dynamics simulations is that the time evolution of the bath states, as expressed by $e^{-iH_B t/\hbar}$, is assumed not to be affected by the terms $e^{i\int_0^t dt' V'_{SB,ii}(t')/\hbar}$ and $e^{-i\int_0^t dt' V'_{SB,ff}(t')/\hbar}$. This implies that these terms now commute with the correlation function of the coupling $V'_{SB,if}(t)V'_{SB,fi}(0)$. Moreover, since the fluctuations are assumed not to affect the time evolution of the bath states, the time-ordered exponential can be replaced by an ordinary exponential. By substituting the quantum correlation functions for classical functions and a QCF, and by writing the time-ordered exponential functions as one ordinary exponential, the following expression for the relaxation rate is obtained:

$$T_1^{-1} = \sum_{f \neq i} \frac{Q(\Delta\omega_{if})}{\hbar^2} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \times \langle \langle e^{i\int_0^t dt' [V'_{SB,ii}(t') - V'_{SB,ff}(t')]/\hbar} V'_{SB,if}(t) V'_{SB,fi}(0) \rangle \rangle. \quad (18)$$

Different forms of the QCF have been discussed in Refs. 19 and 20. Oxtoby proposed that expressions such as Eqs. (5)

and (16) have to be rewritten in the form of a time-symmetrized anticommutator in order to connect it with a classical correlation function. This results in $Q_O(\omega) = 2(1 + e^{-\hbar\omega/kT})^{-1}$. A more detailed calculation assuming the bath to be harmonic yields a so-called harmonic QCF: $Q_H(\omega) = (\hbar\omega/kT)(1 - e^{-\hbar\omega/kT})^{-1}$. In case the bath frequencies are very low and many quanta are dissipated or absorbed from the bath, the QCF follows from the so-called Schofield approximation: $Q_S(\omega) = e^{\hbar\omega/2kT}$. In Ref. 16 a hybrid form of the harmonic and the Schofield QCF was proposed: $Q_{HS}(\omega) = e^{\hbar\omega/4kT}(\hbar\omega/kT)^{1/2}(1 - e^{-\hbar\omega/kT})^{-1/2}$. This QCF turns out to give a good description in the case where the fluctuation force depends exponentially on the coordinates of harmonic bath degrees of freedom. This QCF was used successfully to describe the vibrational relaxation of water.^{9,10}

III. DISCUSSION

The exponential functions representing the fluctuations of the energy levels will have no effect on the relaxation when the frequency fluctuations $V'_{SB,ii}(t')$ and $V'_{SB,ff}(t')$ would be completely correlated. Then, the term $e^{i\int_0^t dt' [V'_{SB,ii}(t') - V'_{SB,ff}(t')]/\hbar}$ vanishes and Eq. (16) reduces to Eq. (5). However, in general the frequency fluctuations of the vibrational levels will not be correlated and can even be anticorrelated. For instance, fluctuations in hydrogen-bond interaction strength have an opposite effect on stretching vibrations and bending vibrations. Hence if the state $|\phi_i\rangle$ represents the excited state of an O–H stretch vibration and $|\phi_f\rangle$ the overtone of a bending mode involving the same O–H group, fluctuations in the hydrogen bond interaction with the O–H group will have a very strong effect on the frequency difference $V'_{SB,ii}(t') - V'_{SB,ff}(t')$.

A comparison of the relative importance of the correlation function $\langle \langle V'_{SB,if}(t) V'_{SB,fi}(0) \rangle \rangle_b$ and the exponential term can be made by describing the time-dependent functions as independent Gaussian processes. This implies that the frequency fluctuations of the levels $|\phi_i\rangle$ and $|\phi_f\rangle$ are assumed to be uncorrelated. Using cumulant expansions²¹ we obtain

$$T_1^{-1} = \sum_{f \neq i} \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} \langle \langle e^{-\hbar^{-2} \int_0^t dt_1 \int_0^{t_1} dt_2 [\langle \langle V'_{SB,ii}(t_1) V'_{SB,ii}(t_2) \rangle \rangle_b + \langle \langle V'_{SB,ff}(t_1) V'_{SB,ff}(t_2) \rangle \rangle_b]} \langle \langle V'_{SB,if}(t) V'_{SB,fi}(0) \rangle \rangle_b \rangle. \quad (19)$$

Often it is assumed that the correlation function decays as

$$\frac{1}{\hbar^2} \langle \langle V_{SB,mn}(t_1) V_{SB,nm}(t_2) \rangle \rangle_b = D_{mn}^2 e^{-|t_1 - t_2|/\tau_{c,mn}}, \quad (20)$$

with $\tau_{c,mn}$ a correlation time constant expressing the time scale of the fluctuations. The parameter $\hbar\Delta_{mn}$ represents the range over which the energy is modulated. The use of Eq. (20) implies that there are no memory effects in the bath

correlation function: the correlation function of Eq. (20) only depends on the time difference $t_1 - t_2$, and not on the absolute values of t_1 and t_2 . It should be noted that this Markovian treatment can only be applied when the bath correlation time constant τ_c is shorter than T_1 . If the bath fluctuations would be extremely slow ($\tau_c > T_1$), the system is inhomogeneous on the time scale of the relaxation. This means that T_1 depends on the phase relation between the bath states $|\phi_{ib}\rangle$,

because this phase relation determines where the relaxing system resides in the inhomogeneous distribution at the moment of relaxation. Hence, for $\tau_c > T_1$, the cross terms of the bath states $|\phi_{ib}\rangle$ can no longer be neglected in Eq. (9) and T_1 will depend on bath correlation functions that have memory for the initial phase relation of the bath states. In

contrast, if $\tau_c < T_1$, the relaxing system samples all positions in the inhomogeneous distribution before relaxation occurs, with the result that the relaxation no longer depends on the initial phase relation of the bath states. Substitution of Eq. (20) in Eq. (19) and solving the integrals in the exponent gives

$$T_1^{-1} = \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} e^{-D_{ii}^2 \tau_c^2 [e^{-t/\tau_{c,ii}} + t/\tau_{c,ii} - 1]} e^{-D_{ff}^2 \tau_c^2 [e^{-t/\tau_{c,ff}} + t/\tau_{c,ff} - 1]} e^{-t/\tau_{c,if}} \quad (21)$$

It follows from Eq. (21) that the relative importance of the fluctuations in the energies and in the coupling will be determined by the relative magnitudes of the bath correlation time constants $\tau_{c,ii}$, $\tau_{c,ff}$, and $\tau_{c,if}$, the frequency ranges D_{ii} , D_{ff} , and D_{if} , and the detuning $\Delta\omega_{if}$. In Fig. 1, the relaxation rate is shown as a function of the detuning $\Delta\omega_{if}$ at four different values of the product $D\tau_c$, with $D_{ii} = D_{ff} = D_{if} = D$ and $\tau_{c,ii} = \tau_{c,ff} = \tau_{c,if} = \tau_c$ (solid curves), and $D_{if} = D$, $D_{ii} = D_{ff} = 0$, and $\tau_{c,ii} = \tau_{c,ff} = \tau_{c,if} = \tau_c$ (dashed curves). The dashed curves thus represent the conventional description of vibrational relaxation of Eq. (5), where the effect of the fluctuations of the energy levels is absent.

When $D\tau_c \ll 1$, the difference between the solid and the dashed curve vanishes [Fig. 1(a)]. In this limit, Eq. (21) simplifies to

$$T_1^{-1} = \sum_{f \neq i} \int_{-\infty}^{\infty} dt e^{i\Delta\omega_{if}t} e^{-t/T_{2,ii}} e^{-t/T_{2,ff}} e^{-t/\tau_{c,if}}, \quad (22)$$

with $T_{2,mm} = (\Delta_{mm}^2 \tau_{c,mm})^{-1}$. When $D\tau_c \ll 1$, the fluctuations of the energy levels are in the limit of motional narrowing.

As a result, the broadening induced by the fluctuations is negligible compared to the width of the Fourier transform of the correlation function. Hence, the fluctuations do not contribute to the vibrational relaxation rate, and the compensation of the detuning $\Delta\omega_{if}$ has to result from the correlation function $\langle\langle V'_{SB,if}(t) V'_{SB,fi}(0) \rangle\rangle_b$. For $D\tau_c \sim 1$ [Figs. 1(b) and 1(c)], there is a clear difference between the solid and the dashed curves. In this case, the broadening of the energies of the levels $|\phi_i\rangle$ and $|\phi_f\rangle$ due to the fluctuations is comparable to the spectral width of $\langle\langle V'_{SB,if}(t) V'_{SB,fi}(0) \rangle\rangle_b$. As a result, the broadening of the energy levels leads to a strong acceleration of the vibrational relaxation if the detuning is larger than the spectral width D . For detunings smaller than D , the broadening of the levels of energies has an adverse effect, since then the fluctuations rather lead to an increase of the average (absolute) detuning between $|\phi_i\rangle$ and $|\phi_f\rangle$, instead of a decrease. For $D\tau_c \gg 1$ [Fig. 1(d)], the solid and the dashed curve strongly differ at detunings $\Delta\omega_{if} < 10D$. At detunings $\Delta\omega_{if} \sim 3D$, the fluctuations of the energy levels lead to an increase of the relaxation rate by a factor of 10.

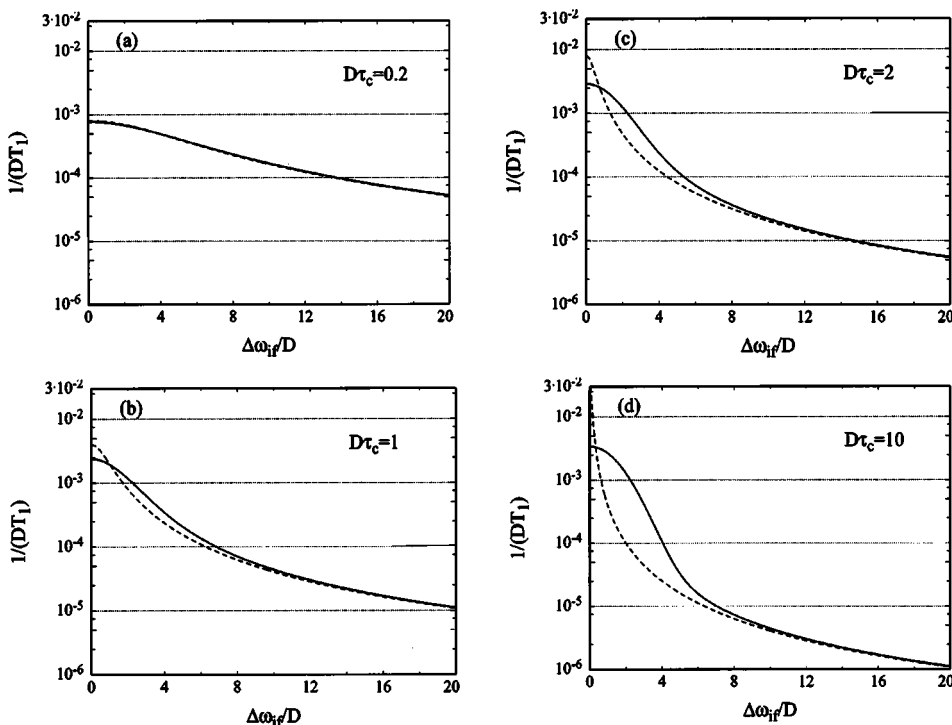


FIG. 1. Calculated vibrational relaxation rate as a function of the detuning $\Delta\omega_{if}$ between the initial state $|\phi_i\rangle$ and the final state $|\phi_f\rangle$ for four different characteristics of the fluctuations of the bath. The fluctuations are modeled as Gauss-Markov processes using a spectral width D and a bath correlation time τ_c . The solid curve is calculated using Eq. (21) including both the fluctuations of the coupling and the fluctuations of the energy levels [corresponding to Eq. (16)]. The dashed curve is calculated using Eq. (21), but without the fluctuations of the energy levels [corresponding to Eq. (5)].

Even for $D\tau_c \gg 1$ the difference between the dashed and the solid curves vanishes for $\Delta\omega_{if} \rightarrow \infty$. The origin of this effect is that for $D\tau_c \gg 1$ the spectral broadening of the energy levels has a Gaussian shape, whereas the spectrum of $\langle\langle V'_{SB,if}(t)V'_{SB,fi}(0) \rangle\rangle_b$ has a Lorentzian shape. Because a Gaussian decays much faster as a function of frequency than a Lorentzian, the spectral amplitude of the fluctuations of the energy levels is negligibly small for large $\Delta\omega_{if}$ compared to the spectral amplitude of $\langle\langle V'_{SB,if}(t)V'_{SB,fi}(0) \rangle\rangle_b$. Hence, very large detunings ($\Delta\omega_{if} > 10D$) can only be compensated by fluctuations of the coupling, and not by fluctuations of the energy levels. It should be noted, however, that this effect is a consequence of the description of the bath-induced fluctuations as Gaussian processes. If this description is not valid, the fluctuations of the energy levels may also affect the vibrational relaxation rate at large values of the detuning.

Figure 1 shows that the relaxation rate becomes large for $\Delta\omega_{if} \rightarrow 0$, especially for $D\tau_c \gg 1$ [Fig. 1(d)]. However, in the limit of small detuning, the perturbative approach that is used in deriving Eqs. (5) and (16) will be no longer valid. For small detuning, the relaxing and accepting vibrational states will become strongly mixed, and the relaxation process has to be calculated with a nonperturbative approach, for instance, by numerical integration of the time-dependent Schrödinger equation.^{6,7,9,10} Recently, this approach has been used to calculate the effects of energy-level fluctuations on the relaxation of the OH stretch vibration of liquid methanol⁷ and the CH stretch vibration of liquid chloroform.⁶ For liquid methanol, it was found that the energy-level fluctuations can indeed lead to strong mixing and avoided crossings of the interacting vibrational levels, thus leading to state-to-state relaxation rates that strongly differ from the rates predicted by the conventional Landau-Teller equation.⁷ Interestingly, for chloroform the energy-level fluctuations do not lead to a strong mixing of the CH stretch vibration and its accepting modes, because the fluctuations are strongly correlated.⁶ Hence, for this vibration the nonperturbative approach and the conventional Landau-Teller expression gave similar results. The method of numerically integrating the time-dependent Schrödinger equation has as a clear advantage over the perturbative Landau-Teller approach that it can describe vibrational relaxation in the limit that the interacting levels become strongly mixed. Disadvantages of this method are that the detailed balance is not conserved,^{6,9,10} that the quantum correction factor cannot be included, and that the (classical) bath cannot respond to a change in the vibrational state of the relaxing molecule.⁷

It follows from Fig. 1 that energy-level fluctuations can affect vibrational relaxation over a wide range of detunings: the effects remain significant up to ten times the spectral range of the fluctuations. Especially for hydrogen-bonded systems the spectral range of the fluctuations can be quite large. For instance, for H₂O and HDO:D₂O, the fluctuations in the hydrogen-bond length lead to a spectral range of the OH-stretch vibration of ~ 200 cm⁻¹ and a frequency correlation function with a dominant time constant of ~ 500 fs.^{22,23} This implies that $D\tau_c \gg 1$, so that the energy fluctuations are expected to play an important role for relaxation channels of the OH stretch vibration with energy gaps up to

~ 2000 cm⁻¹. The effect of the energy fluctuations on the relaxation rate can be estimated for these systems, assuming that the fluctuations of the coupling have a similar spectral range and correlation time constant. For the relaxation of the OH stretch vibration of HDO:D₂O to the overtone of the OH bending mode (energy gap ~ 600 cm⁻¹), the fluctuations of the OH stretch vibrational frequency are thus expected to lead to an increase of the relaxation rate by a factor of 10. For the relaxation of the OH stretch vibration of HDO:D₂O to the OD stretch vibration (energy gap ~ 900 cm⁻¹), an increase by a factor of 3 is expected.

IV. CONCLUSIONS

Vibrational relaxation strongly depends on the presence of interactions between the relaxing molecule and its surroundings, because these interactions lead to fluctuations that compensate the energy mismatch between the interacting vibrational states. In the conventional description of vibrational relaxation, the fluctuations enter via the time dependence of the coupling connecting the relaxing and accepting vibrational states. Here we propose an extension of the influence of the interactions with the bath by incorporating also the fluctuations of the energy levels of the vibrational states. This results in the modified Landau-Teller expression shown in Eq. (16). The fluctuations of the energy levels can lead to a strong increase of the relaxation rate by tuning the relaxing level in resonance with the accepting level.

The Landau-Teller equation (16) contains both the fluctuating coupling and terms representing the fluctuations of the energies of the initial and the final states of the relaxation process. This equation can be transformed into Eq. (18) that contains classical correlation functions and can be evaluated using molecular dynamics simulations.

The relative importance of the fluctuations of the energy levels and the coupling strongly depend on the time scale and amplitude of the fluctuations. If the fluctuations are fast, which implies that the correlation time of the bath is short, the fluctuations of the energy levels are in the motional narrowing limit and the effect of these fluctuations on the relaxation becomes negligible. If the fluctuations are slow, they have a strong effect on the relaxation rate, leading to a decrease of this rate if the detuning is smaller than the spectral range of the fluctuations, and an increase of the vibrational relaxation rate if the detuning is larger than this range. We find that the fluctuations of the energy levels can lead to a tenfold increase of the vibrational relaxation rate, if the fluctuations of the coupling and the energy levels are Gauss-Markov processes with the same spectral width and correlation time.

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- ¹A. L. Harris, L. Rothberg, L. H. Dubois, N. J. Levinos, and L. Dhar, *Phys. Rev. Lett.* **64**, 2086 (1990).
- ²H. J. Bakker, P. C. M. Planken, and A. Lagendijk, *Nature (London)* **347**, 745 (1990).
- ³H. Graener and G. Seifert, *J. Chem. Phys.* **98**, 36 (1993).
- ⁴D. W. Oxtoby, *Adv. Chem. Phys.* **47**, 487 (1981).
- ⁵S. Woutersen, Y. Mu, G. Stock, and P. Hamm, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 11254 (2001).
- ⁶E. L. Sibert III and R. Rey, *J. Chem. Phys.* **116**, 237 (2002).
- ⁷T. S. Gulmen and E. L. Sibert III, *J. Phys. Chem. A* **108**, 2389 (2004).
- ⁸C. P. Lawrence and J. L. Skinner, *J. Chem. Phys.* **117**, 5827 (2002).
- ⁹C. P. Lawrence and J. L. Skinner, *J. Chem. Phys.* **119**, 1623 (2003).
- ¹⁰C. P. Lawrence and J. L. Skinner, *J. Chem. Phys.* **119**, 3840 (2003).
- ¹¹R. Rey and J. T. Hynes, *J. Chem. Phys.* **104**, 2356 (1996).
- ¹²R. Rey and J. T. Hynes, *J. Chem. Phys.* **108**, 142 (1998).
- ¹³M. S. Child, *Molecular Collision Theory* (Academic, London, 1974).
- ¹⁴A. Staib and D. Borgis, *J. Chem. Phys.* **103**, 2642 (1995).
- ¹⁵C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics* (Hermann, Paris, 1973).
- ¹⁶P. C. M. van Woerkom, J. de Bleyser, and J. C. Leyte, *Chem. Phys. Lett.* **20**, 592 (1974).
- ¹⁷D. W. Oxtoby, *Adv. Chem. Phys.* **40**, 1 (1979).
- ¹⁸V. M. Kenkre, A. Tokmakoff, and M. D. Fayer, *J. Chem. Phys.* **101**, 10618 (1994).
- ¹⁹S. A. Egorov, K. F. Everitt, and J. L. Skinner, *J. Phys. Chem. A* **103**, 9494 (1999).
- ²⁰J. L. Skinner and K. Park, *J. Phys. Chem. B* **105**, 6716 (2001).
- ²¹R. Kubo, *Statistical Physics II* (Springer, Berlin, 1995).
- ²²G. M. Gale, G. Gallot, F. Hache, N. Lascoux, S. Bratos, and J.-C. Leicknam, *Phys. Rev. Lett.* **82**, 1068 (1999).
- ²³S. Woutersen and H. J. Bakker, *Phys. Rev. Lett.* **83**, 2077 (1999).