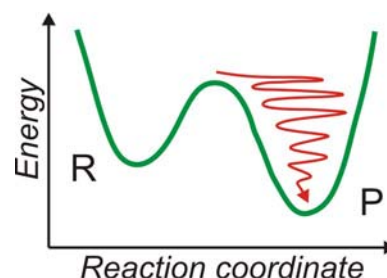


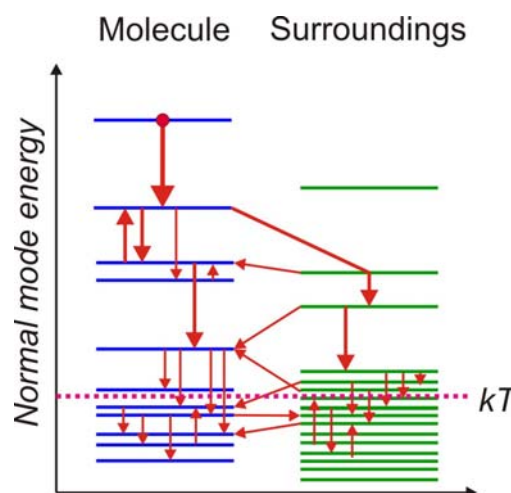
10.1 VIBRATIONAL RELAXATION*

Here we want to address how a quantum mechanical vibration undergoes irreversible energy dissipation as a result of interactions with other intra- and intermolecular degrees of freedom. Why is this process important? It is the fundamental process by which non-equilibrium states thermalize. As chemists, this plays a particularly important role in chemical reactions, where efficient vibrational relaxation of an activated species is important to stabilizing the product and not allowing it to recross to the reactant well. We will be looking specifically at vibrational couplings and relaxation, but the principles are the same for spin-lattice relaxation and electronic population relaxation through electron-phonon coupling.



For an isolated molecule with few vibrational coordinates, an excited vibrational state must relax by interacting with the remaining internal vibrations or the rotational and translational degrees of freedom. If a lot of energy must be dissipated, radiative relaxation may be more likely. In the condensed phase, relaxation is usually mediated by the interactions with the environment, for instance, the solvent or lattice. The solvent or lattice forms a continuum of intermolecular motions that can absorb the energy of the vibrational relaxation. Quantum mechanically this means that vibrational relaxation (the annihilation of a vibrational quantum) leads to excitation of solvent or lattice motion (creation of an intermolecular vibration that increases the occupation of higher lying states).

For polyatomic molecules it is common to think of energy relaxation from high lying vibrational states ($kT \ll \hbar\omega_0$) in terms of cascaded redistribution of energy through coupled modes of the molecule and its surroundings leading finally to thermal equilibrium. We seek ways of describing these highly non-equilibrium relaxation processes in quantum systems.



Classically vibrational relaxation reflects the surroundings exerting a friction on the vibrational coordinate which damps its amplitude and heats the sample. We have seen that a Langevin equation for an oscillator experiencing a fluctuating force $f(t)$ describes such a process:

$$\ddot{Q}(t) + \omega_0^2 Q^2 - \gamma \dot{Q} = f(t)/m \quad (10.1)$$

This equation ascribes a phenomenological damping rate γ to the vibrational relaxation; however, we also know in the long time limit, the system must thermalize and the dissipation of energy is related to the fluctuations of the environment through the classical fluctuation-dissipation relationship:

$$\langle f(t)f(0) \rangle = 2m\gamma kT \delta(t) \quad (10.2)$$

We would also like to understand the correspondence between these classical pictures and quantum relaxation.

Let's treat the problem of a vibrational system H_s that relaxes through weak coupling V to a continuum of bath states H_b using perturbation theory. The eigenstates of H_s are $|a\rangle$ and those of H_b are $|\alpha\rangle$. Although our earlier perturbative treatment didn't satisfy energy conservation, here we can take care of it by explicitly treating the bath states.

$$H = H_0 + V \quad (10.3)$$

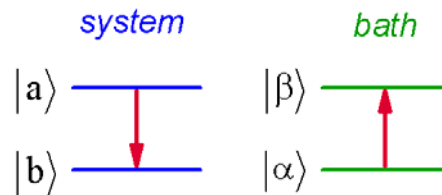
$$H_0 = H_s + H_b \quad (10.4)$$

$$H_s = |a\rangle E_a \langle a| + |b\rangle E_b \langle b| \quad (10.5)$$

$$H_b = \sum_{\alpha} |\alpha\rangle E_{\alpha} \langle \alpha| \quad (10.6)$$

$$H_0 |a\alpha\rangle = (E_a + E_{\alpha}) |a\alpha\rangle \quad (10.7)$$

We will describe transitions from an initial state $|i\rangle = |a\alpha\rangle$ with energy $E_a + E_{\alpha}$ to a final state $|f\rangle = |b\beta\rangle$ with energy $E_b + E_{\beta}$. Since we expect energy conservation to hold, this undoubtedly requires that a change in the system states will require an equal and opposite change of energy in the bath. Initially, we take $p_a = 1$ $p_b = 0$. If the interaction potential is V , Fermi's Golden Rule says the transition from $|i\rangle$ to $|f\rangle$ is given by



$$k_{fi} = \frac{2\pi}{\hbar} \sum_{i,f} p_i \left| \langle i | V | f \rangle \right|^2 \delta(E_f - E_i) \quad (10.8)$$

$$= \frac{2\pi}{\hbar} \sum_{a,\alpha,b,\beta} p_{a,\alpha} \left| \langle a\alpha | V | b\beta \rangle \right|^2 \delta((E_b + E_\beta) - (E_a + E_\alpha)) \quad (10.9)$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \sum_{a,\alpha,b,\beta} p_{a,\alpha} \langle a\alpha | V | b\beta \rangle \langle b\beta | V | a\alpha \rangle e^{-i((E_b - E_a) + (E_\beta - E_\alpha))t/\hbar} \quad (10.10)$$

Equation (10.10) is just a restatement of the time domain version of (10.8)

$$k_{fi} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V(t) V(0) \rangle \quad (10.11)$$

$$V(t) = e^{iH_0 t} V e^{-iH_0 t} \quad (10.12)$$

Now, the matrix element involves both evaluation in both the system and bath states, but if we write this in terms of a matrix element in the system coordinate $V_{ab} = \langle a | V | b \rangle$:

$$\langle a\alpha | V | b\beta \rangle = \langle \alpha | V_{ab} | \beta \rangle \quad (10.13)$$

Then we can write the rate as

$$k_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \sum_{\alpha,\beta} p_\alpha \langle \alpha | e^{+iE_\alpha t} V_{ab} e^{-iE_\beta t} | \beta \rangle \langle \beta | V_{ba} | \alpha \rangle e^{-i\omega_{ba} t} \quad (10.14)$$

$$k_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_{ab}(t) V_{ba}(0) \rangle_B e^{-i\omega_{ba} t} \quad (10.15)$$

$$V_{ab}(t) = e^{iH_B t} V_{ab} e^{-iH_B t} \quad (10.16)$$

Equation (10.15) says that the relaxation rate is determined by a correlation function

$$C_{ba}(t) = \langle V_{ab}(t) V_{ba}(0) \rangle \quad (10.17)$$

which describes the time-dependent changes to the coupling between b and a . The time-dependence of the interaction arises from the interaction with the bath; hence its time-evolution under H_B . The subscript $\langle \dots \rangle_B$ means an equilibrium thermal average over the bath states

$$\langle \dots \rangle_B = \sum_\alpha p_\alpha \langle \alpha | \dots | \alpha \rangle. \quad (10.18)$$

Note also that eq. (10.15) is similar but not quite a Fourier transform. This expression says that the relaxation rate is given by the Fourier transform of the correlation function for the fluctuating coupling evaluated at the energy gap between the initial and final state states.

Alternatively we could think of the rate in terms of a vibrational coupling spectral density, and the rate is given by its magnitude at the system energy gap ω_{ba} .

$$k_{ba} = \frac{1}{\hbar^2} \tilde{C}_{ba}(\omega_{ab}). \quad (10.19)$$

where the spectral representation $\tilde{C}_{ba}(\omega_{ab})$ is defined as the Fourier transform of $C_{ba}(t)$.

Vibration coupled to a harmonic bath

To evaluate these expressions, let's begin by consider the specific case of a system vibration coupled to a harmonic bath, which we will describe by a spectral density. Imagine that we prepare the system in an excited vibrational state in $v=|1\rangle$ and we want to describe relaxation to $v=|0\rangle$.¹

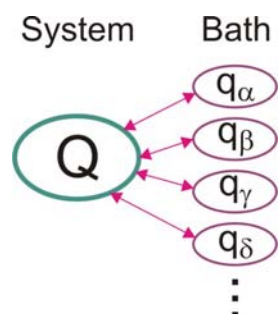
$$H_S = \hbar\omega_0 (\tilde{P}_\alpha^2 + \tilde{Q}^2) \quad (10.20)$$

$$H_B = \sum_\alpha \hbar\omega_\alpha (\tilde{p}_\alpha^2 + \tilde{q}_\alpha^2) = \sum_\alpha \hbar\omega_\alpha (a_\alpha^\dagger a_\alpha + \frac{1}{2}) \quad (10.21)$$

We will take the system-bath interaction to be linear in the system and bath coordinates:

$$V = H_{SB} = \sum_\alpha \xi_\alpha \tilde{q}_\alpha \tilde{Q}. \quad (10.22)$$

Here ξ is a coupling constant that describes the strength of the interaction between system and bath mode α . Note, that this bilinear coupling form suggests that the system vibration is a local mode interacting with a set of normal vibrations of the bath. In principle, this form of the coupling can be diagonalized to obtain a complete set of normal modes in which the system vibration is mixed slightly into each of the bath modes.



For the case of single quantum relaxation from $|a\rangle=|1\rangle$ to $b=|0\rangle$, we can write the coupling matrix element as

$$V_{ba} = \sum_\alpha \xi_\alpha (a_\alpha^\dagger + a_\alpha) \quad (10.23)$$

Evaluating eq. (10.17) is now much the same as problems we've had previously:

$$\begin{aligned}
 \langle V_{ab}(t) V_{ba}(0) \rangle_B &= \langle e^{iH_B t} V_{ab} e^{-iH_B t} V_{ba} \rangle_B \\
 &= \sum_{\alpha} \xi_{\alpha}^2 \left[(\bar{n}_{\alpha} + 1) e^{-i\omega_{\alpha} t} + \bar{n}_{\alpha} e^{+i\omega_{\alpha} t} \right]
 \end{aligned}
 \quad (10.24)$$

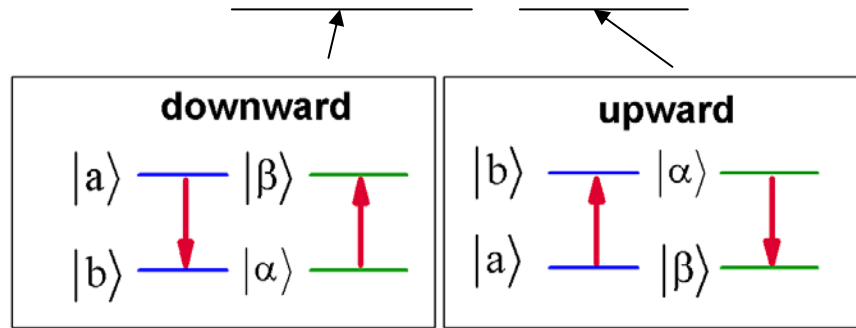
here $\bar{n}_{\alpha} = (e^{\beta \hbar \omega_{\alpha}} - 1)^{-1}$ is the thermally averaged occupation number of the bath mode at ω_{α} . In evaluating this we take advantage of relationships we have used before

$$\begin{aligned}
 e^{iH_B t} a_{\alpha} e^{-iH_B t} &= a_{\alpha} e^{-i\omega_{\alpha} t} \\
 e^{iH_B t} a_{\alpha}^{\dagger} e^{-iH_B t} &= a_{\alpha}^{\dagger} e^{+i\omega_{\alpha} t}
 \end{aligned}
 \quad (10.25)$$

$$\begin{aligned}
 \langle a_{\alpha} a_{\alpha}^{\dagger} \rangle &= \bar{n}_{\alpha} + 1 \\
 \langle a_{\alpha}^{\dagger} a_{\alpha} \rangle &= \bar{n}_{\alpha}
 \end{aligned}
 \quad (10.26)$$

So, now by Fourier transforming (10.24) we have the rate as

$$k_{ba} = \frac{1}{\hbar^2} \sum_{\alpha} [\xi_{\alpha}]_{ab}^2 \left[(\bar{n}_{\alpha} + 1) \delta(\omega_{ba} + \omega_{\alpha}) + \bar{n}_{\alpha} \delta(\omega_{ba} - \omega_{\alpha}) \right] \quad (10.27)$$



This expression describes two relaxation processes which depend on temperature. The first is allowed at $T = 0$ K and obeys $-\omega_{ba} = \omega_{\alpha}$. This implies that $E_a > E_b$, and that a loss of energy in the system is balanced by an equal rise in energy of the bath. The second term is only allowed for elevated temperatures. It describes relaxation of the system by transfer to a higher energy state $E_b > E_a$, with a concerted decrease of the energy of the bath. Naturally, this process vanishes if there is no thermal energy in the bath.²

To more accurately model the relaxation due to a continuum of modes, we can replace the explicit sum over bath states with an integral over a density of bath states W

$$k_{ba} = \frac{1}{\hbar^2} \int d\omega_{\alpha} W(\omega_{\alpha}) \xi_{ba}^2(\omega_{\alpha}) \left[(\bar{n}(\omega_{\alpha}) + 1) \delta(\omega_{ba} + \omega_{\alpha}) + \bar{n}(\omega_{\alpha}) \delta(\omega_{ba} - \omega_{\alpha}) \right] \quad (10.28)$$

We can also define a spectral density, which is the vibrational coupling-weighted density of states:

$$\rho(\omega_\alpha) \equiv W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \quad (10.29)$$

Then the relaxation rate is:

$$\begin{aligned} k_{ba} &= \frac{1}{\hbar^2} \int d\omega_\alpha W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \left[(\bar{n}(\omega_\alpha) + 1) \delta(\omega_{ba} + \omega_\alpha) + \bar{n}(\omega_\alpha) \delta(\omega_{ba} - \omega_\alpha) \right] \\ &= \frac{1}{\hbar^2} \left[(\bar{n}(\omega_{ba}) + 1) \rho_{ba}(\omega_{ab}) + \bar{n}(\omega_{ba}) \rho_{ba}(-\omega_{ab}) \right] \end{aligned} \quad (10.30)$$

We see that the Fourier transform of the fluctuating coupling correlation function, is equivalent to the coupling-weighted density of states, which we evaluate at ω_{ba} or $-\omega_{ba}$ depending on whether we are looking at upward or downward transitions. This is a full quantum expression, and obeys detailed balance between the upward and downward rates of transition between two states:

$$k_{ba} = \exp(-\beta \hbar \omega_{ab}) k_{ab}. \quad (10.31)$$

From our description of the two level system in a harmonic bath, we see that high frequency relaxation ($kT \ll \hbar \omega_0$) only proceeds with energy from the system going into a mode of the bath at the same frequency, but at lower frequencies ($kT \approx \hbar \omega_0$) that energy can flow both into the bath and from the bath back into the system. When the vibration has energies that are thermally populated in the bath, we return to the classical picture of a vibration in a fluctuating environment that can dissipate energy from the vibration as well as giving kicks that increase the energy of the vibration. Note that in a cascaded relaxation scheme, as one approaches kT , the fraction of transitions that increase the system energy increase. Also, note that the bi-linear coupling in eq. (10.22) and used in our treatment of quantum fluctuations can be associated with fluctuations of the bath that induce changes in energy (relaxation) and shifts of frequency (dephasing).

Multiquantum relaxation of polyatomic molecules³

Vibrational relaxation of polyatomic molecules in solids or in solution involves anharmonic coupling of energy between internal vibrations of the molecule, also called IVR (internal vibrational energy redistribution). Mechanical interactions between multiple modes of vibration of the molecule act to rapidly scramble energy deposited into one vibrational coordinate and lead to cascaded energy flow toward equilibrium.

For this problem the bilinear coupling above doesn't capture the proper relaxation process. Instead we can express the molecular potential energy in terms of well defined normal modes of vibration for the system and the bath, and these interact weakly through small anharmonic terms in the potential. Then we can extend the perturbative approach above to include the effect of multiple accepting vibrations of the system or bath. For a set of system and bath coordinates, the potential energy for the system and system-bath interaction can be expanded as

$$V_S + V_{SB} = \frac{1}{2} \sum_a \frac{\partial^2 V}{\partial Q_a^2} Q_a^2 + \frac{1}{6} \sum_{a,\alpha,\beta} \frac{\partial^3 V}{\partial Q_a \partial q_\alpha \partial q_\beta} Q_a q_\alpha q_\beta + \frac{1}{6} \sum_{a,b,\alpha} \frac{\partial^3 V}{\partial Q_a \partial Q_b \partial q_\alpha} Q_a Q_b q_\alpha \cdots \quad (10.32)$$

Focussing explicitly on the first cubic expansion term, for one system oscillator:

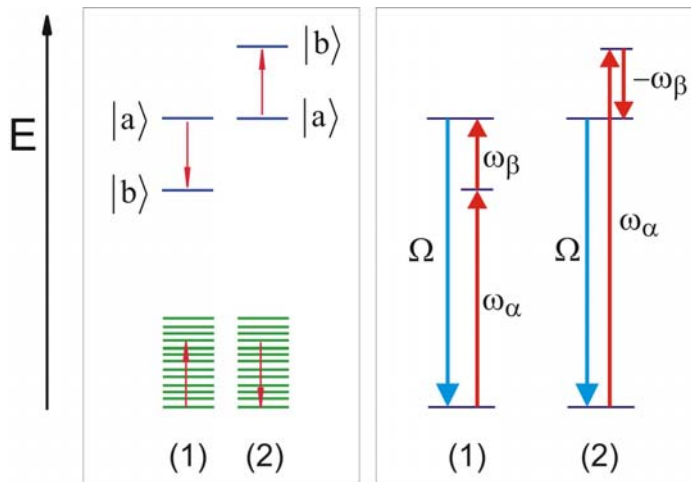
$$V_S + V_{SB} = \frac{1}{2} m \Omega^2 Q^2 + V^{(3)} Q q_\alpha q_\beta \quad (10.33)$$

Here, the system-bath interaction potential describes the case for a cubic anharmonic coupling that involves one vibration of the system Q interacting weakly with two vibrations of the bath q_α and q_β , so that $\hbar\Omega \gg V^{(3)}$. Energy deposited in the system vibration will dissipate to the two vibrations of the bath, a three quantum process. Higher-order expansion terms would describe interactions involving four or more quanta.

Working specifically with the cubic example, we can use the harmonic bath model to calculate the rate of energy relaxation. This picture is applicable if a vibrational mode of frequency Ω relaxes by transferring its energy to another vibration nearby in energy (ω_α), and the energy difference ω_β being accounted for by a continuum of intermolecular motions. For this case one can show

$$k_{ba} = \frac{1}{\hbar^2} \left[\left(\bar{n}(\omega_\alpha) + 1 \right) \left(\bar{n}(\omega_\beta) + 1 \right) \rho_{ba}(\omega_{ab}) + \left(\bar{n}(\omega_\alpha) + 1 \right) \bar{n}(\omega_\beta) \rho_{ba}(\omega_{ab}) \right] \quad (10.34)$$

where $\rho(\omega) \equiv W(\omega) \left(V^{(3)}(\omega) \right)^2$. Here we have taken $\Omega, \omega_\alpha \gg \omega_\beta$. These two terms describe two possible relaxation pathways, the first in which annihilation of a quantum of Ω leads to a creation of one quantum each of ω_α and ω_β . The second term describes the dissipation of energy by coupling to a higher energy vibration, with the excess energy being absorbed from the bath. Annihilation of a quantum of Ω leads to a creation of one quantum of ω_α and the annihilation of one quantum of ω_β . Naturally this latter term is only allowed when there is adequate thermal energy present in the bath.



Rate calculations using classical vibrational relaxation

In general, we would like a practical way to calculate relaxation rates, and calculating quantum correlation functions isn't practical. How do we use classical calculations for the bath, for instance drawing on a classical molecular dynamics simulation? Is there a way to get a quantum mechanical rate?

The first problem is that the quantum correlation function is complex $C_{ab}^*(t) = C_{ab}(-t)$ and the classical correlation function is real and even $C_{cl}(t) = C_{cl}(-t)$. In order to connect these two correlation functions, one can derive a quantum correction factor that allows one to predict the quantum correlation function on the basis of the classical one. This is based on the assumption that at high temperature it should be possible to substitute the classical correlation function with the real part of the quantum correlation function

$$C_{cl}(t) \Rightarrow C'_{ba}(t) \quad (10.35)$$

To make this adjustment we start with the frequency domain expression derived from the detailed balance expression $\tilde{C}(-\omega) = e^{-\beta\hbar\omega} \tilde{C}(\omega)$

$$\tilde{C}(\omega) = \frac{2}{1 + \exp(-\beta\hbar\omega)} \tilde{C}'(\omega) \quad (10.36)$$

Here $\tilde{C}'(\omega)$ is defined as the Fourier transform of the real part of the quantum correlation function. So the vibrational relaxation rate is

$$k_{ba} = \frac{4}{\hbar^2 (1 + \exp(-\hbar\omega_{ba}/kT))} \int_0^\infty dt e^{-i\omega_{ba}t} \text{Re}[\langle V_{ab}(t) V_{ba}(0) \rangle] \quad (10.37)$$

Now we will assume that one can replace a classical calculation of the correlation function here as in eq. (10.35). The leading term out front can be considered a “quantum correction factor” that accounts for the detailed balance of rates encoded in the quantum spectral density.

In practice such a calculation might be done with molecular dynamics simulations. Here one has an explicit characterization of the intermolecular forces that would act to damp the excited vibrational mode. One can calculate the system-bath interactions by expanding the vibrational potential of the system in the bath coordinates

$$\begin{aligned} V_s + V_{SB} &= V_0 + \sum_\alpha \frac{\partial V^\alpha}{\partial Q} Q + \sum_\alpha \frac{\partial^2 V^\alpha}{\partial Q^2} Q^2 + \dots \\ &= V_0 + FQ + GQ^2 + \dots \end{aligned} \quad (10.38)$$

Here V^α represents the potential of an interaction of one solvent coordinate acting on the excited vibrational system coordinate Q . The second term in this expansion FQ depends linearly on the system Q and bath α coordinates, and we can use variation in this parameter to calculate the correlation function for the fluctuating interaction potential. Note that F is the *force* that molecules exert on Q ! Thus the relevant classical correlation function for vibrational relaxation is a force correlation function

$$C_{Cl}(t) = \langle F(t) F(0) \rangle \quad (10.39)$$

$$k_{Cl} = \frac{1}{kT} \int_0^\infty dt \cos \omega_{ba}t \langle F(t) F(0) \rangle. \quad (10.40)$$

Readings and Notes

- * Oxtoby, D. W. Vibrational population relaxation in liquids. *Adv. Chem. Phys.* **47**, 487 (1981); Skinner, J. L. Semiclassical approximations to golden rule rate constants. *J. Chem. Phys.* **107**, 8717 (1997); Egorov, S. A., Rabani, E. & Berne, B. J. Nonradiative relaxation processes in condensed phases: Quantum versus classical baths. *J. Chem. Phys.* **110**, 5238 (1999).
- ¹ Note that we are using an equilibrium property, the coupling correlation function, to describe a non-equilibrium process, the relaxation of an excited state. Underlying the validity of the expressions are the principles of linear response. In practice this also implies a time-scale separation between the equilibration of the bath and the relaxation of the system state: The bath correlation function should work fine if it has rapidly equilibrated, even though the system may not have. An instance where this would work well is electronic spectroscopy, where relaxation and thermalization in the excited state occurs on picosecond time scales, whereas the electronic population relaxation is on nanosecond time scales.
- ² There is an exact analogy between this problem and the interaction of matter with a quantum radiation field. The interaction potential is instead a quantum vector potential and the bath is the photon field of different electromagnetic modes. Equation (10.27) describes has two terms that describe emission and absorption processes. The leading term describes the possibility of spontaneous emission, where a material system can relax in the absence of light by emitting a photon at the same frequency.
- ³ V. M. Kenkre, A. Tokmakoff and M. D. Fayer, "Theory of vibrational relaxation of polyatomic molecules in liquids," *J. Chem. Phys.*, **101**, 10618 (1994).