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Fluctuating Energy Level Landau−Teller Theory: Application to the Vibrational Energy Relaxation of Liquid Methanol

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State-to-state vibrational energy relaxation (VER) rates of the OH-stretch fundamental to select vibrational modes of liquid methanol are presented. The rates are calculated via a modified, fluctuating Landau−Teller (FLT) theory approach, which allow for dynamical vibrational energy level shifts. These rates are then compared to previously published results from Gulmen and Sibert [*J. Phys. Chem. A* **2004**, *108*, 2389] for the traditional Landau−Teller (LT) method as well as results calculated through time-dependent perturbation theory (TD), which naturally allow for the fluctuation. For the first time, this method is applied to a polyatomic molecular system, and the FLT theory greatly reduces the discrepancy between the LT and TD results or, at a minimum, is comparable to the LT approach with very little additional computational cost.

I. Introduction

Nothing is more fundamental to the study of chemistry than understanding how molecules interact with each other and learning to manipulate reactions. Both of these topics are interrogated in vibrational energy relaxation (VER) studies in the condensed phase. Since VER rates are affected by the solvent, we are given clues as to the nature of these interactions.[1] Likewise, it is possible to prepare a nonequilibrium distribution of vibrational energy to promote a specific reaction pathway,[2] which is limited by the rate of relaxation.

There are several methods by which one can calculate VER rates: instantaneous normal mode theory,[3] centroid molecular dynamics,[4,5] and Landau−Teller (LT) theory.[6,7] All of these methods have been successfully utilized in VER studies and each have their advantages. Instantaneous normal mode theory is particularly adept at allowing for an investigation of solute−solvent interactions which aid the relaxation process; centroid molecular dynamics allows for the inclusion of quantum mechanical effects in time correlation functions (TCF). However, LT theory has been the predominant method to calculate VER rates. This is due to the simplicity of the implementation of the method while still possessing a good description of VER phenomena for a variety of polyatomic molecular systems.[8−13] A limitation of the LT method is the requirement that the vibrational energy levels do not vary in time.

While fixed energy levels are a qualitatively good approximation for a weakly interacting liquid like neat chloroform[11] this approximation is more problematic for strongly interacting hydrogen bonded liquids such as liquid methanol[13] or HOD in D_2O.[10,12] In the case of $CHCl_3$ the relaxing ν(CH) fundamental is red-shifted tens of wavenumbers from the gas-phase value with a comparable spectral width, while the ν(OH) fundamental in these hydrogen bonded liquids red-shift hundreds of wavenumbers with a breadth to match. This implies the distribution of molecular environments the chromophore experiences is quite broad, and for HOD/D_2O the ν(OH) frequency shift has a characteristic 170 fs time scale associated with the movement of a few molecules and a slower 1.2 ps time scale for collective

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movement.[14] Both of these time scales for frequency shifts are important in VER of HOD/D_2O, since they occur on a similar 0.7−0.9 ps T_1 lifetime.[15,16] MeOH, by nature of also having an isolated ν(OH) involved in hydrogen bonding, has a similar VER lifetime[17] and should have similar frequency fluctuation dynamics.

Energy level separation has been shown to effect the VER rate of MeOH[13] and HOD/D_2O[18] via time-dependent perturbation theory (TD) calculations. Comparison of the LT rates with ones obtained through TD, which naturally incorporates the fluctuations in the energy levels, shows occasional disagreement and sometimes complete disagreement. In the case of the relaxation rate of the ν(OH) fundamental of MeOH to the nearly degenerate δ(OH) 2ν(CO) combination band, the LT and TD rates disagree by 3 orders of magnitude.[13] The disagreement is due entirely to the dynamical energy level fluctuations, and quantitative agreement can be realized for the LT and TD rate constants when the energy levels are held fixed in the TD calculation.[13]

While the TD method is quite useful, it is a more costly calculation because one has to solve the time-dependent Schödinger equation. Also the TD method does not lend itself to the use of a quantum correction factor (QCF) to help bridge the difference between the classical and quantum TCF.[19] Therefore, we will take advantage of the fluctuating Landau−Teller (FLT) method of Bakker[20] and apply that to the calculation of VER rates of liquid MeOH and show, for the first time, that this method ameliorates the previous discrepancies between the LT and TD results. In particular, the 3 order of magnitude difference between the δ(OH) 2ν(CO) combination band is reduced to less than a factor of 2.

The energy flow pathways and time scales described in our previous study of the vibrational energy relaxation of the ν(OH) fundamental[13] are not altered appreciably by the new FLT results presented here. Since that study allowed for a qualitatively good description of the experimental results of Iwaki and Dlott,[17] the focus of this paper is on the significant discrepancies that we found between the LT and TD results for several state-to-state rates where energy fluctuations were seen to play a critical role. The purpose of this paper is to show that the theory of Bakker,[20] for including the energy fluctuations in LT, is easy to implement for realistic systems and provides good results.

In the remainder of this article we will explain how the fluctuations are introduced into the LT calculation and how they are applied to the OH stretch relaxation of liquid MeOH. Finally, we will discuss the results of the FLT method.

II. Method

The traditional LT method has been in the literature for over two decades,[6] and the FLT of Bakker,[20] while much younger, is also available in the literature. For the sake of brevity in this paper, we will not rederive the methods; we refer the reader to the work of Oxtoby[6] and Bakker[20] for details. The TD and LT calculations for MeOH relaxation have already been presented, so the authors refer the reader to Gulmen and Sibert[13] for the molecular specifics of this system.

To begin with, LT theory is based on perturbation theory, and the Hamiltonian

$$H = H_s + H_b + V \tag{1}$$

is separated into the relaxing solute vibrational Hamiltonian, the solvent bath and slow nuclear motion Hamiltonian, and the interaction between the solute and solvent, respectively. Essentially, the method allows one to calculate the rate of relaxation between a set of solute vibrational eigenstates $\{i\}$ driven by the interaction V which evolves under the time evolution of the solvent Hamiltonian H_b with eigenstates $\{\alpha\}$.

The rate expression for transition

$$k_{ij} = \frac{2\pi}{\hbar^2}\sum_{\alpha,\beta} P_\alpha |V_{i\alpha,j\beta}|^2 \delta(E_{i\alpha} - E_{j\beta}) \tag{2}$$

between states i and j from Fermi's Golden Rule can be manipulated to the more useful, Fourier transformed, spectral density equation

$$\hat{C}(\omega) = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{i\omega t}\langle V_{ij}(t)V_{ji}(0)\rangle_b \tag{3}$$

where $V_{ij}(t) = \exp[iH_bt/\hbar]V_{ij}\exp[-iH_bt/\hbar]$. The rate constant is equal to the spectral density evaluated at the average energy difference $k_{ij} = \hat{C}(\omega_{ij})$. Thus, the rate depends on the frequency difference between the two vibrational states ω_{ij} and the interaction TCF traced over the bath states. However, this expression assumes that the effect of the dynamical solvent induced vibrational energy level shifts of the relaxing solute molecule may be neglected.

To include the change in energy of the vibrational state over time, we follow the prescription of Bakker[20] and incorporate the diagonal interaction term in the energy expression $E_{i\alpha} = E_i + E_\alpha + V_{i\alpha,i\alpha}$. Inclusion of the diagonal interaction term leads to the FLT equation

$$k_{ij} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{i\omega_{ij}t}\langle \mathrm{e}^{i(H_b+V_{ii})t/\hbar}V_{ij}\mathrm{e}^{-i(H_b+V_{jj})t/\hbar}V_{ji}\rangle_b \tag{4}$$

Now, the diagonal elements of V are included in the evolution operator; however, we no longer have the same evolution operators acting on the off-diagonal interaction terms.

With the use of time-dependent perturbation theory again, we factor the exponential operator

$$\mathrm{e}^{-i(H_b+V_{ii})t/\hbar} = \mathrm{e}^{-iH_bt/\hbar}\exp_o[-i(\int_0^t \mathrm{d}t'\, \mathrm{e}^{iH_bt'/\hbar}V_{ii}\mathrm{e}^{-iH_bt'/\hbar})/\hbar] \tag{5}$$

where $\exp_o[\cdots]$ is the time-ordered exponential. While this result is formally exact, there is no guarantee of convergence. After retention of all terms in the expansion series, the rate of relaxation becomes

$$k_{ij} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{i\omega_{ij}t}\langle \mathrm{e}_o^{\,i\int_0^t \mathrm{d}t' V_{ii}(t')/\hbar}V_{ij}(t)\mathrm{e}_o^{\,-i\int_0^t \mathrm{d}t' V_{jj}(t')/\hbar}V_{ji}(0)\rangle_b \tag{6}$$

For a simpler notation, we define a modified interaction operator

$$V'_{ij}(t) = \mathrm{e}_o^{\,i\int_0^t \mathrm{d}t' V_{ii}(t')/\hbar}\,[e^{iH_bt/\hbar}V_{ij}e^{-iH_bt/\hbar}]e_o^{\,-i\int_0^t dt' V_{jj}(t')/\hbar} \tag{7}$$

so that we can recast the expression in the form of eq 3 where we replace V with V'. Time symmetrization of the TCF yields

$$\langle V'_{ij}(t)V'_{ji}(0)\rangle_b = \frac{2}{1 + \exp(-\beta\hbar\omega_{ij})}\left\langle\frac{1}{2}[V'_{ij}(t), V'_{ji}(0)]_+\right\rangle_b \tag{8}$$

to give the final FLT equation

$$k_{ij} = \frac{2}{\hbar^2(1 + \exp(-\beta\hbar\omega_{ij}))}\int_{-\infty}^{\infty} \mathrm{d}t\, e^{i\omega_{ij}t}\left\langle\frac{1}{2}[V'_{ij}(t), V'_{ji}(0)]_+\right\rangle_b \tag{9}$$

TABLE 1: Time Constants (in ps) Out of the ν(OH) State Are Presented for Several Methods: TD, LT without a QCF (LT_0), FLT without a QCF (FLT_0), LT with the Harmonic/Schofield QCF (LT_{HS}), FLT with the Standard QCF (FLT_S), and FLT with the Harmonic/Schofield QCF (FLT_{HS})[a]

	state	ω	TD	LT_0	FLT_0	LT_{HS}	FLT_S	FLT_{HS}
1	2ν(CO) $\rho(CH_3)$	249.4	9.4	30.3	15.1	17.2	9.8	8.5
2	2δ(OH)	665.3	13.9	29.8	11.8	7.4	6.1	2.9
3	δ(OH) ν(CO) $\rho(CH_3)$	−98.0	14.9	20.1	15.1	25.4	19.7	19.3
4	δ(OH) $2\rho(CH_3)$	−191.6	38.0	160	46.3	81.3	79.8	74.8
5	δ(OH) 2ν(CO)	−5.6	65.9	0.05	51.8	0.05	52.5	52.5
6	ν(CH)	566.3	156	616	441	184	235	131
7	δ_s(CH) δ_a(CH)	415.4	425	807	517	323	293	207
total			3.4	8.0[b]	3.8	4.1[b]	2.8	1.8

[a] The total VER time constant for these states is compared in the last row. The average energy ω separating the ν(OH) from the presented state is in wavenumbers. [b] Without the contribution from state δ(OH) 2ν(CO).

This expression is still completely quantum mechanical. To utilize a molecular dynamics simulation, we replace $\hat{C}(\omega)$ with its classical analogue $\hat{C}^{CL}(\omega)$. The time ordered exponential is replaced with an ordinary exponential, and one finds

$$\left\langle \frac{1}{2}[V'_{ij}(t), V'_{ji}(0)]_+ \right\rangle_b^{CL} = \langle [\cos \theta_{ij}(t)] V_{ij}(t) V_{ji}(0) \rangle_b^{CL} \quad (10)$$

where $\theta_{ij}(t) \equiv \int_0^t dt'[V_{ii}(t') - V_{jj}(t')]/\hbar$ is the additional quantity needed to perform an FLT calculation.

For this work we chose the standard approach of replacing the time symmetrized quantum TCF with the time symmetrized classical TCF by assuming that they are approximately equal. The factor that emerges from the symmetrization is often referred to as the standard quantum correction factor (QCF). While there is no exact means by which to replace the quantum TCF with a classical analogue, there are several suggestions for how to make the switch and many revolve around a multiplicative QCF $Q(\omega)$, where $\hat{C}(\omega) \approx Q(\omega)\hat{C}^{CL}(\omega)$.[19] Another useful QCF is the Harmonic/Schofield QCF $Q(\omega) = e^{\beta\hbar\omega/4}(\beta\hbar\omega/(1 - \exp(-\beta\hbar\omega)))^{1/2}$ because it was shown to be particularly effective for transitions that involve multiphonon relaxation.[19] The most fundamental property associated with any QCF is that it ensures that the detailed balance $k_{ij} = k_{ji}e^{-\beta\hbar\omega_{ji}}$ is satisfied.

Since the FLT expression is almost identical with the LT expression, the former expression is readily calculated with a marginal increase of computational effort due to the evaluation of the diagonal elements and storage of the integrals.

III. Results and Discussion

Despite the successes[8−13] of LT, our goal with this paper is to demonstrate that the FLT method reliably incorporates the effect of dynamical fluctuations, like the TD calculations, and avoids the pitfalls of LT theory. We have chosen to calculate the state-to-state VER time constants for several states using TD, LT, and FLT. To designate the different QCF's, we shall employ the convention of LT_0 for no QCF, LT_S for the standard QCF, and LT_{HS} for the Harmonic/Schofield QCF. The results are presented in Table 1 in ascending order of their TD VER lifetimes.

For the purposes of our discussion, since experimental state-to-state time constants are not available, the TD results will be our guide for evaluating the methods. The TD method naturally includes the dynamical energy fluctuations, and it portrays a qualitatively correct picture of the VER phenomenon being investigated.[13] Since the TD results do not satisfy detailed balance, the natural results to compare to are those of the LT_0 and FLT_0. On inspection, the FLT_0 results agree more closely with the TD results in all cases. These results are presented graphically in Figure 1 where the time constants have been normalized by the TD results.

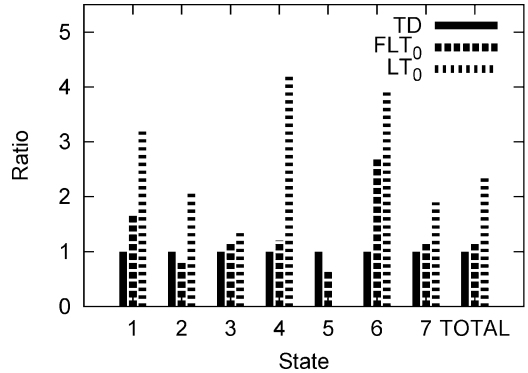

Figure 1. Comparison of the time constants for the TD, LT_0, and FLT_0 results for the seven states listed in Table 1, as well as the total time constant, normalized by the TD results. Refer to Table 1 for the state labels.

The experimental lifetime of the ν(OH) fundamental is about 1 ps,[17] yet the LT lifetime for this state was 2 orders of magnitude smaller because the δ(OH) 2ν(CO) state had a time constant of 0.05 ps. Use of the FLT_0 method has considerably lengthened the VER time constant of this transition to 51.8 ps and this compares well with the 65.9 ps TD time constant, especially considering that the LT_0 result differed by 3 orders of magnitude and is so small that it is not able to be seen in Figure 1. This is consistent with the idea that even though the average separation between the two states is -5.6 cm^{-1}, during the lifetime of the excited vibration these states move out of resonance and couple less strongly. Thus, the LT method that enforces the constant average energy difference ω_{ij} overestimates the rate, which can be seen for the LT_0 and FLT_0 spectral densities for this transition in the $\omega \approx 0$ region of Figure 2.

Another important state in the VER of MeOH is 2δ(OH). This state is theoretically found to be the predominant energy accepting mode in the HOD/D_2O system.[10,12] For strong hydrogen bonds the ν(OH) red shifts while the 2δ(OH) blue shifts.[18] This decrease of separation between the states results in faster relaxation.[13,18] Iwaki and Dlott[17] confirmed[13] via experiment and TD calculations that the excitation of different subensembles of the ν(OH) band lead to qualitatively different dynamics; when the red side of the band was excited, more of the vibrational energy was transferred to the 2δ(OH) state.

The TD and FLT_0 results are in good agreement for this state. LT_0, on the other hand, has a time constant that is more than double the previous results. Though Figure 2 contains the spectral density for the δ(OH) 2ν(CO) transition, the main features of the difference between the LT_0 and FLT_0 method hold. Figure 2 shows that not only do you get a suppression of

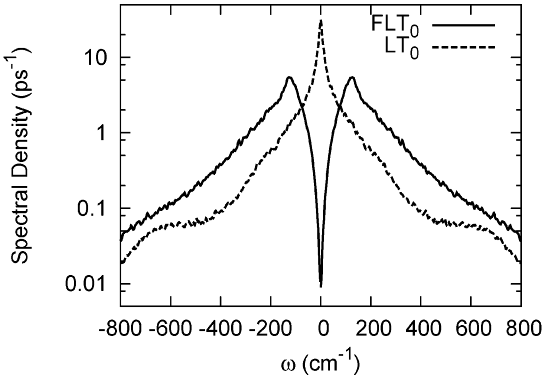

Figure 2. The spectral density for the δ(OH) 2ν(CO) state calculated through the use of Landau−Teller (LT$_0$) theory and the fluctuating Landau−Teller (FLT$_0$) theory are presented in units of the rate constant (ps^{-1}) versus frequency difference (cm^{-1}).

the rate around $\omega \approx 0$, but there is also an enhancement when $|\omega| > 100$ cm^{-1}. Bakker[20] observed similar differences in test calculations where the fluctuations were modeled as independent Gaussian processes, moreover he was able to modulate the magnitude of the suppression, enhancement, and crossover point by altering the spectral width and bath correlation time.

In summary, the TD and FLT$_0$ methods yield similar results for the ν(OH) relaxation. The biggest improvement of FLT$_0$ over LT$_0$ occurs for the δ(OH) 2ν(CO) mode; the FLT$_0$ method was able to reliably handle the erroneously fast relaxation seen with LT. Since there is only a marginal increase in the computational demand, this method holds promise for treating systems where the dynamical fluctuations have an important role to play in the relaxation dynamics.

The utilization of a QCF is an attempt to reproduce quantum mechanical effects while only calculating the classical TCF. While there is not a single QCF that approximates all physical situations with equal accuracy, Skinner and Park[19] indicate that the Harmonic/Schofield QCF is effective for multiphonon relaxation processes, which we suspect is the most important mechanism for VER of the MeOH ν(OH). However, the VER time scales calculated are only modestly sensitive to the use of a QCF since the relaxation tends to be dominated by intramolecular transitions that release a few hundred wavenumbers of energy into the bath. At room temperature for the 665.3 cm^{-1} transition from ν(OH) to 2δ(OH), the Harmonic/Schofield QCF is roughly twice as large as the standard QCF. In comparison, the ratio of the Harmonic/Schofield to standard QCF in liquid O_2 at 70 K is larger than 8000 to 1 at the only downward transition frequency of 1552.5 cm^{-1}.[21] When all of the states of MeOH are included in the calculation, the total relaxation time constant from FLT$_S$ is 1.6 ps and that drops to 1.0 ps for FLT$_{HS}$. These numbers differ from the total relaxation lifetimes of Table 1 since those values only include contributions from the select states shown. Both are in good agreement with the experimental lifetime of approximately 1 ps.[17]

While QCF's become increasingly important when the VER dynamics is more quantum mechanical (large transition energy and low temperature), the effect of fluctuations tends to be equally important for near resonant energy transfer. This is seen for the relaxation of the ν(OH) to the δ(OH) 2ν(CO) state, since the LT$_0$ time constant was 3 orders of magnitude smaller than that of the TD or FLT$_0$.

The FLT method displays the advantages of both the LT and TD methods; FLT is able to describe polyatomic relaxation processes for realistic systems using classical TCF's that can be improved upon with QCF's and the method also allows for dynamic energy level shifts which play an important role in the dynamics.

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