

## Temperature dependent spectral densities and quantum activated rate theory

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# Temperature dependent spectral densities and quantum activated rate theory

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The variability with temperature of spectral densities and rates calculated with quantum activated rate theory is investigated. Classical spectral densities at two temperatures are computed via molecular dynamics for a model of proton transfer in methyl chloride. In addition, quantum dynamics is computed for spectral densities which artificially boost variability at low frequency. We find significant variation in computed spectral densities at moderate frequency. These variations, however, have little effect on overall computed quantum dynamics. In contradistinction, artificial variation in spectral densities at the lowest frequencies can generate fairly significant effects on quantum dynamics. Detailed flux correlation function calculations are presented which illustrate this phenomenon. © 1998 American Institute of Physics. [S0021-9606(98)51237-8]

## I. INTRODUCTION

The theoretical study of reaction rates in solution has undergone an explosion of activity recently. Broadly, these investigations may be classified into two main approaches. First, those that rely on classical or quantum simulation of many-body intermolecular potentials<sup>1,2</sup> and second, approaches which transform the effect of the condensed phase environment to a spectral density.<sup>3–7</sup> The motivation behind this transformation is that after it is accomplished, semi-analytic approaches may be derived which allow the computation of condensed phase dynamics in a small fraction of the time required for a full simulation. The justification for such a transformation relies on an observation of Zwanzig<sup>8</sup> that if one assumes that the many-body Hamiltonian representing the reaction in the fluid is well approximated by a system in a bilinearly coupled harmonic bath,

$$H = \frac{P_s^2}{2m_s} + V(s) + \sum_k \left[ \frac{P_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 \left( q_k - \frac{c_k s}{m_k \omega_k^2} \right)^2 \right], \quad (1.1)$$

then, classically, this Hamiltonian may be rigorously integrated in the bath coordinates to produce a generalized Langevin equation in which the time dependent friction may be obtained from a cosine transformation of the discrete spectral density,

$$J(\omega) = \frac{\pi}{2} \sum_k \frac{c_k^2}{m_k \omega_k} \delta(\omega - \omega_k). \quad (1.2)$$

It must be emphasized that these harmonic modes need bear no relation to actual motions of the fluid system. They may only model a “basis set” for the actual motions in the system. Even with this caveat, however, it is not guaranteed that in a realistic system treating the solvent harmonically will produce accurate results. A diagnostic of the suitability of a

harmonic model is found in the temperature dependence of the spectral density. In a system well represented by the Hamiltonian of Eq. (1.1), the spectral density will be independent of temperature. This paper presents a numerical investigation of the temperature dependence of spectral densities in models of condensed phase reaction dynamics, and of how temperature dependent spectral densities might affect the calculation of quantum rates in solution. It is motivated by recent experimental observations of the Fleming group.<sup>9</sup> In three pulse photon echo experiments they found that the spectral density for solvation of a dye molecule in ethylene glycol is dependent on temperature—in particular at very low frequencies. This temperature dependence is a manifestation of the anharmonic nature of the true solvent.

The generalized Langevin equation with the appropriate friction (and random force related by the fluctuation-dissipation theorem) is known in many cases to accurately reproduce the exact dynamics. One of the most popular approaches to the classical problem of activated rate theories has been the Grote-Hynes<sup>3</sup> approach. This result may be found as an approximation to the generalized Langevin equation, or as has recently been emphasized by Pollak,<sup>4</sup> it may be derived directly from the application of transition state theory to the microscopic Hamiltonian given by Eq. (1.1). In fact a detailed numerical study of the  $S_N2$  displacement of chloride in methyl chloride solvated in water<sup>7</sup> showed that Grote-Hynes theory was quite accurate over a wide range of parameters. The Zwanzig Hamiltonian has recently received extensive attention as a basis for quantum theories of rates in condensed phases. The Pollak<sup>10</sup> group has produced a quantum turnover theory, Makri has performed numerical experiments using the quasi-adiabatic propagator algorithm developed in her group,<sup>11</sup> Miller, Chandler and Voth<sup>12</sup> and the Voth group have applied quantum centroid methods<sup>13</sup> and

our group has developed evolution operator methods<sup>14,15</sup> to accurately calculate rates in condensed phase assuming the starting point is the Zwanzig Hamiltonian. These numerous approaches are beginning to prove practical enough that one may envision the calculation of rates in solution will become as routine as such calculations in the gas phase. For example, we have recently studied the effects of promoting vibrations and rapid tunneling of protons in organic acid crystals using such methods.<sup>16</sup> In that study, the fitting of quantum chemical parameters was possible because the rate of proton transfer in the crystal could be calculated very quickly using our quantum activated rate approach.

As important as spectral density approaches to condensed phase dynamics have been and will continue to be, it is important to remember the basic assumptions inherent in their application to the condensed phase problem. The first assumption is that bath modes are bilinearly coupled to the reaction coordinate. In the Langevin picture, this translates into a friction which is independent of coordinate. Practically, when friction correlation functions are calculated via molecular dynamics, the independence of coordinate is used to evaluate a friction on a reaction coordinate particle fixed at the top of the free energy barrier to reaction.<sup>17</sup> As described above, Hynes *et al.*<sup>7</sup> did not find this to be a difficulty in the reaction they studied; following Berne,<sup>6</sup> Voth and co-workers<sup>2</sup> in extensive classical numerical simulations, they found that nonlinear couplings which result in spatially dependent frictions can have significant effects on reaction rates and produce significant deviations from Grote-Hynes predictions.

The second assumption inherent in the spectral density approach is that the bath is accurately modeled by a collection of harmonic oscillators. An anharmonic bath will result in a temperature dependent spectral density. If one wants to simulate a quantum reaction in solution via a quantum activated rate approach, the assumption of a harmonic bath allows one to calculate a friction correlation function, and so a spectral density at high temperatures using classical mechanics. If the spectral density is independent of temperature, then it should be rigorously correct to use this function in the calculation of a quantum rate at any temperature. The Fleming group's<sup>9</sup> recent experimental results suggest that variations of the spectral density with temperature could be significant. The question we address in this paper is how significant are these variations in spectral density likely to be, when computing rates from a rigorous quantum approach based on the Zwanzig Hamiltonian; and additionally, how sensitive to temperature variations are numerically computed spectral densities. This investigation is made possible by our recently developed interaction representation form for quantum evolution operators as applied to the Zwanzig Hamiltonian Eq. (1.1), which allows rapid computations of the exact quantum rate for a variety of spectral densities.

The structure of this paper is as follows. The next section describes the calculation of quantum rates for a double well potential in a bath for a variety of spectral densities. The range of spectral densities is chosen to represent the kind of variability observed in the Fleming experiments. Interestingly enough, moderate changes in the overall spectral den-

sity, for example changes large enough to alter the reorganization energy of the solvent (the integral of the spectral density over the frequency) by 15% have very little effect on the rate as long as the low frequency modes are left relatively unchanged. Rather significant effects are found when the spectral density for the lowest frequency modes are altered with the overall reorganization energy of the solvent kept constant. This has significant implication for the use of spectral densities calculated from classical molecular dynamics simulations, and so in the next section of the paper we report the calculation of spectral densities for the transfer of a proton from phenol to an amine in methyl chloride. This reaction has been the subject of various approximate simulations which have predicted different rates.<sup>18,19</sup> The many-body intermolecular potential that the previous studies and the current work utilize is manifestly anharmonic, and the computation of the spectral density at two different temperatures will indicate how important the anharmonic nature of the bath may be in determining the dynamics of the reaction. The paper closes with conclusions which discuss the implications of the reported results for the use of spectral densities in the calculation of quantum activated rates, and the use of purely harmonic descriptions for condensed phase reaction dynamics.

## II. QUANTUM ACTIVATED RATES WITH VARIABLE SPECTRAL DENSITIES

The Fleming group<sup>9</sup> measured spectral densities for the solvation of the dye labeled IR144 in ethylene glycol at 297 and 397 °K. Their results showed significant variation at low frequencies (i.e., less than 3 cm<sup>-1</sup>). In fact, they also showed fairly significant variation at higher frequencies, but they felt<sup>20</sup> that it was less clear whether this resulted from complex inverse fittings or was an actual observation. In order to test the effect of such variability we constructed a number of spectral densities for use in rate calculations. First, we wished to include exaggerated low frequency components as found in the experimental results. It is well known that superohmic spectral densities have rather different dynamic behavior<sup>21</sup> and so we constructed the spectral densities from sums of ohmic densities with exponential cutoffs. In particular, we employed

$$J(\omega) = \eta\omega[e^{-\omega/\omega_c} + fe^{-\omega/\omega_{c1}}]. \quad (2.1)$$

Figure 1 shows four spectral densities chosen to mimic the temperature variations found in Fig. 6 of Ref. 9. The first peak in the spectral density was chosen to be at 2 cm<sup>-1</sup>, with the four separate values given for the height of the low frequency peak. The main peak is at 500 cm<sup>-1</sup>. The overall effect on the integral of the spectral density over frequency (the reorganization energy) is moderate, with, respectively, 2%, 4%, and 8% increases in apparent reorganization energy as compared to the single ohmic with exponential cutoff. Quantum transmission coefficients for proton transfer in a double well of barrier height 0.0095 a.u. (2085 cm<sup>-1</sup>), and well frequency 0.0032 a.u. (707 cm<sup>-1</sup>) were calculated. This is a "quantum like" double well with the splitting in the ground state doublet equal to about 5×10<sup>-9</sup> atomic units. (This is the DW1 set of parameters that Makri<sup>11</sup> first em-

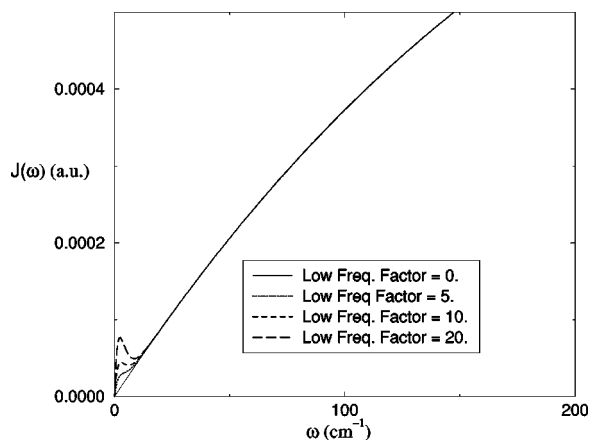


FIG. 1. Spectral densities with enhanced low frequency components. The form for these curves is given in Eq. (2.2), with the low frequency factor equal to  $f$ . The low frequency peak is at 2 while the cutoff is at  $500 \text{ cm}^{-1}$  as in Ref. 14.

ployed in her numerical study of the double well coupled to a harmonic bath, and our group subsequently reproduced with analytic evolution operator methods.) The spectral densities enter activated rate calculations in our interaction representation<sup>22</sup> formulation in two ways. First, as a linear coefficient in an adiabatic term, and second in a modified barrier frequency in a nonadiabatic correction,

$$\omega'_s = \sqrt{\omega_s^2 + \frac{2\eta\omega_c}{m_s\pi}}. \quad (2.2)$$

Throughout this paper we will be calculating the transmission coefficient  $\Gamma$  defined as the ratio  $\Gamma = k/k_{\text{TST}}$  of the quantum rate over the *multidimensional* transition state theory (TST) result. As is well known, this is equal to

$$k_{\text{TST}} = \frac{Q^\ddagger}{Q^r} \frac{k_B T}{2\pi} e^{-\beta V_0}, \quad (2.3)$$

where  $V_0$  is the barrier height,  $Q^\ddagger$  is the partition function of the transition state and  $Q^r$  is the partition function in the reactant well. We now briefly show that the conclusions we shall draw for the transmission coefficient hold without modification for the quantum rate as well.

For simplicity, we shall illustrate our point for a high value of friction, i.e., after the Kramers turnover. Pollak has shown<sup>4</sup> that

$$\frac{Q^\ddagger}{Q^r} = \frac{\lambda_0}{\omega_b} \frac{\omega_0}{k_B T}, \quad (2.4)$$

where  $\omega_0$ ,  $\omega_b$  are the reactant well and barrier frequencies, respectively, and  $\lambda_0$  is the unstable normal mode frequency at the saddle point. The ratio  $\lambda_0/\omega_b$  is of course the Grote-Hynes factor, calculated as the solution of the integral equation

$$\frac{\lambda_0}{\omega_b} = \frac{\omega_b}{\lambda_0 + \hat{\gamma}(\lambda_0)}, \quad (2.5)$$

where  $\hat{\gamma}(\lambda_0)$  is the Laplace transform

TABLE I. Values of the quantum transmission coefficient  $\Gamma = K_{\text{exact}}/k_{\text{TST}}$  for a double well coupled to a dissipative bath. The double well is described by the parameters given for Fig. 4. The coupling to the bath is described by the spectral densities shown in Fig. 1. Results are presented for four coupling strengths or reduced viscosities  $\eta = 0.2, 0.9, 1.5, 2.5$ . The first viscosity is before Kramers turnover, the second in the turnover regime, and the last two well after turnover.

$\eta$	$\Gamma(f=0)$	$\Gamma(f=5)$	$\Gamma(f=10)$	$\Gamma(f=20)$
0.2	2.23	2.22	2.20	2.16
0.9	3.52	3.42	3.33	3.17
1.5	2.95	2.87	2.79	2.64
2.5	2.28	2.20	2.13	1.99

$$\hat{\gamma}(\lambda_0) = \frac{2}{m_s \pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \frac{\lambda_0}{\omega^2 + \lambda_0^2}. \quad (2.6)$$

In this paper we will examine small changes of the spectral density  $J(\omega)$ ; using Eqs. (2.5) and (2.6) it is easy to show numerically that these changes have very little effect on the Grote-Hynes coefficient Eq. (2.4), therefore the classical recrossing corrections are not significantly affected by the modest modifications of the spectral density that we examine in this paper. In conclusion, the calculation of the transmission coefficient  $\Gamma$  shows whether these changes of the spectral density affect the *quantum* character of the reaction.

Flux correlation functions were calculated for the double well described after Eq. (2.1), coupled to baths described by the spectral densities shown in Fig. 1 for a variety of reduced viscosities  $\eta$ . We chose reduced viscosities of 0.2, 0.9, 1.5 and 2.5. The first low viscosity is before the Kramers turnover, 0.9 is just after or part of it, and 1.5 and 2.5 are both in the slow drop-off spatial diffusion region. The results of modifying the spectral density are shown in Table I. They were uniform and relatively modest. The largest modification in the spectral density always resulted in a decrease in the transmission coefficient by about 10%.

The results just described show that low frequency peaks in the spectral density can have a noticeable effect on calculated rates of chemical reactions in condensed phase. The

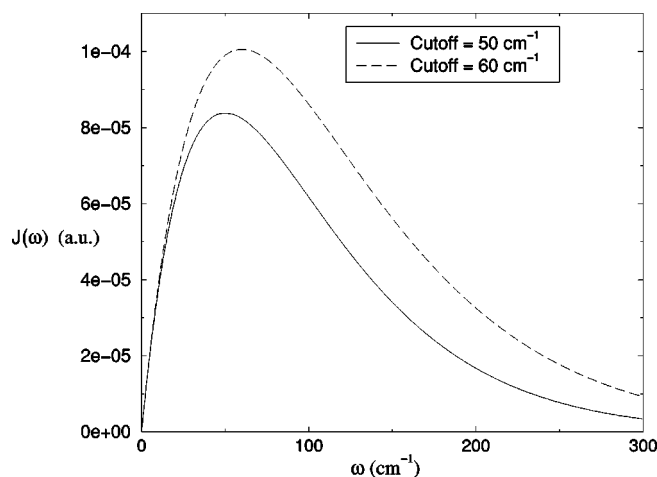


FIG. 2. Ohmic with exponential cutoff spectral densities with cutoffs at 50 and  $60 \text{ cm}^{-1}$ .

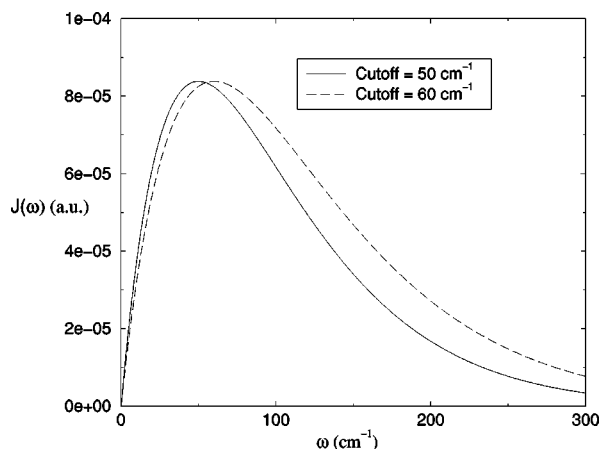


FIG. 3. Similar spectral densities to those shown in Fig. 2, but with the integrals of the spectral density normalized.

results in this case are, however, small. In order to understand the possible magnitude of the contribution of low frequency solvent motions to reactions, we studied the spectral densities given in Figs. 2 and 3. In Fig. 2 we show two spectral densities which are both ohmic with exponential cutoff. The only difference in the two cases is that the cutoff for the first case, given by the solid line, is at  $50\text{ cm}^{-1}$ , while that for the dashed line is at  $60\text{ cm}^{-1}$ . The reorganization energy in the two cases [given by the integral of  $J(\omega)/\omega$ ] is different by about 15%. In a standard Marcus<sup>23</sup> picture, this 15% change in activation barrier would be expected to yield a rather different rate, but in fact quantum rate calculations like those performed above show that the transmission coefficients for the two spectral densities are almost indistinguishable at a variety of reduced viscosities. The results are shown below in Table II. In this case we have included a calculation of the transmission coefficient at very high reduced viscosity in order to determine if the variation in spectral density becomes more apparent at the higher coupling strength.

In Fig. 3 we show the same two spectral densities with the only difference being that now the higher cutoff case has been normalized so that the reorganization energies are equal. Now the results shown in Table III are strikingly different.

The highest effect is seen at the highest coupling strength, and Fig. 4 presents the calculated flux autocorrelation functions<sup>24</sup> at a reduced viscosity of 4.5 for the three spectral densities presented in Figs. 2 and 3. The basic structure of the correlation functions seems always to be the same with the low frequency variation enhancing the features present in the other two cases. Again, note that without

TABLE II. Exact quantum transmission coefficients for the double well described by the parameters of Fig. 4, with the coupling to the dissipative environment given by the spectral densities shown in Fig. 2.

	$\eta=0.9$	$\eta=1.5$	$\eta=2.5$	$\eta=4.5$
$\omega_c = 50$	3.52	2.95	2.28	1.37
$\omega_c = 60$	3.43	2.88	2.20	1.34

TABLE III. Exact quantum transmission coefficients for the double well described by the parameters of Fig. 4, with the coupling to the dissipative environment given by the spectral densities shown in Fig. 3.

	$\eta=0.9$	$\eta=1.5$	$\eta=2.5$	$\eta=4.5$
$\omega_c = 50$	3.52	2.95	2.28	1.37
$\omega_c = 60$	3.71	3.35	2.60	1.70

renormalization the 50 and  $60\text{ cm}^{-1}$  results at low frequencies lie almost on top of each other. Because the high frequency variation in the spectral density given in Fig. 2 seems to have essentially no effect on the promotion of rate over the transition state result, it is clear that the variations presented in Table III are entirely due to the low frequency variation (i.e., less than  $5\text{ cm}^{-1}$ .) This is critical for two reasons when considering the recent Fleming group results. First, they were not able to measure the high frequency components of the spectral density with definitive accuracy. Our results show that this does not matter. Second, they find some level of variation at low frequencies. Our results show that this might matter. The low frequency “blips” they see and we model in Fig. 1 have limited effect, but the low frequency shift modeled in Fig. 3 does have a large effect. In order to see what types of temperature variations in spectral density might be found in a reasonable model of a chemical reaction in solution, the next section of this paper presents calculations at two temperatures of exact spectral densities for a model of a proton transfer reaction in polar solution, and then shows the effects of variations on quantum activated rate calculations.

### III. PROTON TRANSFER IN METHYL CHLORIDE

Proton transfer in solution is a prototypical example of a condensed phase quantum mechanical reaction. The influence of a polar solvent environment stabilizes the charge separation, making this reaction, which is very slow in the gas phase, proceed extremely rapidly in solution. A model of

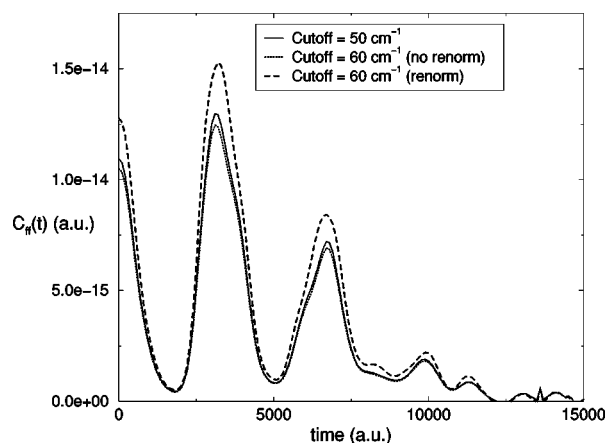


FIG. 4. Flux autocorrelation functions for proton transfer in a double well coupled to a dissipative bath. The baths and coupling are described by the spectral densities shown in Figs. 2 and 3, while the reduced viscosity is  $\eta = 4.5$ . The double well, as in Ref. 14, is described by a potential with height 2085, a barrier frequency of 500 and a frequency of oscillation in each well of  $707\text{ cm}^{-1}$ .

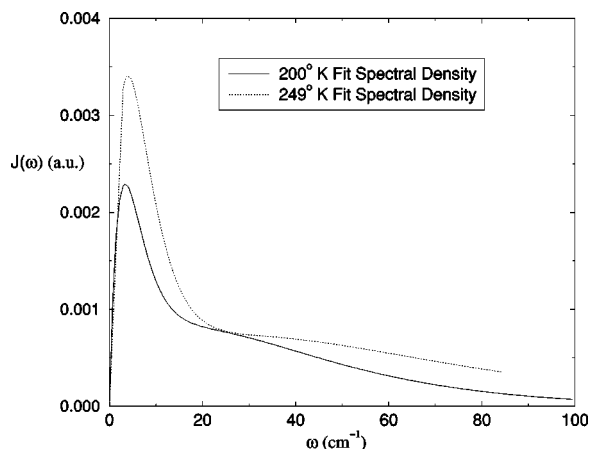


FIG. 5. A molecular dynamics calculated spectral density for the transfer of a proton from phenol to amine in methyl chloride solvent calculated at 200 and 249 °K. The potential for this system is taken from Ref. 18.

the transfer of a proton from phenol to amine in methyl chloride has been studied by Azzouzz and Borgis<sup>18</sup> and by Tully and Hammes-Schiffer.<sup>19</sup> Recently, we have undertaken a detailed study of this reaction using quantum activated rate theory. Details of this calculation will be presented later, but this provides a realistic model system on which theoretical spectral densities may be calculated. The process proceeds through a calculation of the force autocorrelation function with the proton fixed at the top of the reaction barrier. This corresponds to the Hamiltonian described by Eq. (1.1)—a harmonic bath bilinearly coupled to the reaction coordinate. Anharmonicities in the bath will appear eventually as temperature dependence in the spectral density. The potential surface for this reaction, described in Ref. 18, is manifestly anharmonic—the question to be answered is how closely does the harmonic bath model this system and if there are anharmonic effects present in spectral density calculations, how do these effects manifest themselves in eventual calculations of the rate?

Force autocorrelation functions were calculated at two temperatures: 200 and 249 °K. Details of the molecular dynamics calculations will be described elsewhere, but briefly, at each temperature the system was first equilibrated for 6 psec and then a molecular dynamics run was carried out for another 14 psec. A long run was necessary to insure complete decay of the force autocorrelation function. A cosine Fourier transform then yields the spectral density. Figure 5 presents the results for the spectral density calculated at 200 and 249 °K. In both cases (200 and 249 °K) we found a single exponential with ohmic form would not fit the data, while two linear with exponential cutoff forms fit the data extremely well. There is some slight variation at the very lowest frequencies, but the largest variation is found in the vastly different peak heights and the slower decay of the higher temperature spectral density. In any case, we will determine the effect of the variation on a rate calculation.

These two spectral densities were then used in a calculation of transmission coefficient for the same double well potential as employed in the last section. Flux autocorrelation functions were again calculated (at 200 °K, for both the

spectral densities shown in Fig. 5) using our exponential resummation methodology, and the result was plotted and integrated to yield the transmission coefficient. The two spectral densities pictured in Fig. 5 yielded similar transmission coefficients different by only 5%. Obviously, even the relatively large differences in spectral density shown in Fig. 5 do not greatly impact final rate calculations.

#### IV. CONCLUSIONS

The results of this study present a mixed set of warnings regarding the use of quantum activated rate theory in the calculation of rates of reactions in solution. We recall the motivation was to understand what kinds of variations in spectral densities will actually change the results of rate calculations. The results of the Fleming group<sup>9</sup> show small but real variations at the lowest frequencies in their particular case of solvation of a dye molecule in ethylene glycol. Our results in the last two sections show that variations in spectral densities at moderate to high frequencies do not affect final rate calculations. Thus, the calculation of rates (at least for the potential we have examined) seems relatively insensitive to anharmonic bath effects in this region of the spectrum. In addition, counterintuitively, the rate seems relatively insensitive to the integral of the spectral density over the frequency—the reorganization energy. The rate does, however, seem to depend crucially on the very low frequency modes of the solvent—less than 5 cm<sup>-1</sup>. This presents an immediate difficulty to the theorist, because it is exactly these modes which are the most difficult to accurately model—because of their low frequency, extremely long molecular dynamics runs are needed to calculate low frequency effects; and in this case error begins to overwhelm actual data. The strong dependence of the rate on the low frequency behavior of the environment and its coupling to the reaction coordinate is at first glance extraordinary. The system is too complex for purely analytic solution, but a reasonable understanding of this phenomenon may be found by examining earlier work on the spin-boson problem and general activated rate theory. First, Leggett's seminal work on the spin-boson problem,<sup>21</sup> while not directly addressing this issue, did find remarkable differences in the behavior of the two-level system coupled to an ohmic with exponential cutoff bath and a superohmic with exponential cutoff environment. At low temperatures, when one progresses to just slightly superohmic (say,  $\omega^{1.1}$  rather than  $\omega^1$ ), then the dynamics of the system abruptly changes from localization to underdamped oscillation. If one plots the two spectral densities described above, then one obtains a picture very much like that shown in Fig. 3. Second, one expects that effects on rates will be most pronounced when the environment couples strongly when a wavepacket is in the barrier region. Here, one expects quantum states to be closely spaced, and high-frequency environment modes will have sufficient frequency mismatch that energy transfer will be unfavorable. On the other hand, low frequency modes will act almost as a continuum and efficiently couple to reaction. The encouraging result of the calculations we present in the last section, however, are that when relatively long time molecular dynamics calculations are run, at least for a single model, while overall spectral

densities do vary, they do so in a fashion that seems to have relatively little impact on the final calculation of an observable. The message would seem to be that quantum activated rate theory with the use of a harmonic bath is a reasonable thing to do, but care must be taken for individual situations to insure that the very low frequency components of the spectrum do not vary greatly.

These results present a final challenge to theorists involved in the study of fluid structure. The results clearly show the relative insensitivity of reaction to high-frequency modes but the crucial role played by low frequencies. Recently there has been significant effort expended in the development of harmonic models of fluids—the instantaneous normal mode picture.<sup>25</sup> While some of the calculational approaches for such quantities as diffusion constants have recently been questioned,<sup>26</sup> the picture has provided an excellent visualization of the actual physics of solvation. Much of this work, of necessity, has concentrated on high-frequency modes of motion in the solution. It would seem that in order to understand the microscopic dynamics of reaction in solution, a significant challenge remains in elucidating the nature of low frequency coupling to the reaction coordinate. One possibility resides in calculating the modes in some optimal fashion.<sup>27</sup> Even if this is done, however, a method of identifying and following the time evolution of the low frequency modes will be needed. As yet, only high-frequency modes which retain their identity have proven amenable to such analysis.

We finally note that the use of classical spectral densities might be inappropriate for quantum activated rate calculations. Definition of a quantum spectral density is difficult, but a possible approach through a maximum free energy has recently been described by Pollak.<sup>28</sup> Further investigation of the variability of spectral densities generated by various approaches is clearly needed. In addition, it will always be important to determine if any variations actually manifest themselves in variations in observables such as computed rates.

## ACKNOWLEDGMENTS

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