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On the Importance of the Classically Forbidden Region in Calculations of the Relaxation Rate for High-Frequency Vibrations: A Model Calculation[†]

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The quantum mechanical relaxation rate for a high-frequency vibrational mode is evaluated for a one-dimensional model system having two diatomic molecules involved in a collinear collision. The thermally averaged rate is obtained as an integral over energies for the relative translation of the two molecules. These calculations show that energies several times K_BT make the largest contributions to the rate. Several orders of magnitude of cancellation due to phase interference is found in the evaluation of the coupling matrix elements between the initial and final states, and this is one of the main factors leading to the very small value for the relaxation rate. The region near the classical turning point in the relative translational motion of the colliding molecules dominates the calculation of the contribution to the rate at each energy. Calculations using low-order expansions of the translational potential energy and the interstate coupling about this turning point provide good approximations to the exact quantum mechanical rate. This suggests a possible method for performing calculations of the rate by means of realistic simulations of liquid systems.

I. Introduction

Vibrational relaxation plays an important role in the energy flow and dissipation in many physical processes. The accurate evaluation of the energy relaxation rate for high-frequency vibrational modes in liquids has proven to be a difficult problem. Early efforts on this problem were motivated by work in solids or gases. One approach treated the relaxation as due to the interaction between the relaxing vibrational mode and a phonon bath.[1−10] Another approach considered the relaxation as being the result of independent binary collisions between molecules, in which the transition probability per collision is obtained from calculations or experimental data, and a collision frequency is estimated from kinetic or hydrodynamic considerations.[11−16] Hydrodynamic models[17,18] and classical simulations with the vibration coupled to a stochastic bath[29−21] have also been employed in calculations of vibrational relaxation rates. More recent work has employed the time domain form of Fermi's golden rule, expressing the relaxation rate as the Fourier transform of the autocorrelation function of the force on the vibrational coordinates due to interactions with the other particles in the liquid.[22−25] In that work, the Fourier transform of the classical autocorrelation function is multiplied by a factor that approximately corrects for the quantum nature of the problem, increasing the relaxation rate over that obtained using just the classical autocorrelation function.[26−30] Other approaches have used semiclassical formalisms[31,32] to evaluate the autocorrelation function form of the vibrational relaxation rate expression[33−37] or expressions related to this.[38,39]

The relaxation rates for high-frequency vibrations are very small. For instance, the experimentally measured rate for the vibrational relaxation of O_2 in the liquid is 4×10^{-10} ps^{-1} at 80 K.[40] This very slow rate results numerically, at least in part, from the large amount of phase cancellation in the integrations involved in the rate expression. This is evident, for instance, in the evaluation of the Fourier transform in the time dependent autocorrelation function formulation of the problem.[22−25] In order to better understand the nature of the phase cancellation and gain insight into methods for organizing the calculation of the rate constant in a manner that accurately accounts for this important aspect of the problem, a one-dimensional model for the vibrational relaxation in a collinear collision of two identical diatomic molecules is studied. The use of a one-dimensional model allows for the exact evaluation of the quantum mechanical thermally averaged rate expression for this system. The results obtained show that the phase cancellation reduces the interaction integral by over 5 orders of magnitude compared with the maximum value of the integrand. Since the rate expression contains the square of the interaction integral, the rate for this model system is reduced by many orders of magnitude by phase interference. This phase cancellation is entirely accounted for in the evaluation of the contribution from each energy to the thermally averaged rate, and the resulting energy dependent contribution is a smoothly varying, nonoscillatory function of energy. The thermally averaged rate is found to be dominated by energies several times K_BT. Thus, the Boltzmann factor at these energies contributes to the smallness of the rate as well.

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It is found in these fully quantum calculations that the magnitude of the contribution from each energy to the thermally averaged rate expression is largely determined by the behavior of the interaction between the molecules in the region around the classical turning point in the translational motion of the colliding partners. This feature of the problem suggests a possible way to organize realistic Monte Carlo simulations of the relaxation rate in liquids.

II. Theory

The one-dimensional model system considered in this work contains a homonuclear diatomic molecule in the first excited vibrational state undergoing a collinear collision with another molecule of the same type. If the magnitude of the asymptotic relative momentum of the two particles is p_i before the collision, the rate constant for relaxation from vibrational state i to vibrational state f is given by Fermi's golden rule[41] as

$$k_{i\to f} = \frac{2\pi}{\hbar}|V_{if}^{(b)}|^2\rho_f^{st} \tag{1}$$

where ρ_f^{st} is the density of final states at the energy corresponding to p_i and the superscript b indicates that the matrix elements are taken over quantum states for the translational motion using particle-in-the-box normalization. The density of states dn_f/dE is given by $\rho_f^{st} = dn_f/dE = (m/p_f)L/\pi\hbar)$ where m is the reduced mass for the relative motion of the two particles, L is the box length, and p_f is the asymptotic relative momentum of the two particles in the final state. If the box normalization factors are factored out of the interaction matrix elements, $V_{if}^{(b)} = (2/L)V_{if}$, eq 1 can be rewritten as

$$k_{i\to f} = \frac{8m}{p_f\hbar^2}|V_{if}|^2\rho \tag{2}$$

where a factor of $1/L$ has been replaced by the particle number density ρ. This replacement of $1/L$ from the single collision partner case with a particle density corresponds to treating the system as having ρL collision partners independently interacting with the vibrationally excited molecule. In the calculations below, this density is taken to be unity. Since the interaction between the particles is short ranged, the interaction integral

$$V_{if} = \int_0^\infty \Psi^*_f\,(R,r_a)V_{int}(R,r_a)\Psi_i(R,r_a)dRdr_a \tag{3}$$

is independent of the box length after the normalization factors of $(2/L)^{1/2}$ have been factored out. The rate expression, eq 2, is also independent of the box length. The calculations treat the box length as infinite. In eq 3, the coordinate R is the distance between the centers of mass of the colliding particles, and r_a is the bond length of the molecule undergoing the vibrational transition.

Equation 2 gives the rate when the system has a specific value for the relative momentum of the colliding molecules. The thermally averaged rate expression is given by

$$k_T = \rho Q_p^{-1}\int_0^\infty \frac{8m}{p_f\hbar^2}V_{if}^2e^{-\beta p_i^2/2m}dp_i \tag{4}$$

where p_i is the asymptotic relative momentum of the colliding particles before the collision, $p_f = (p_i^2 + 2m\Delta E)^{1/2}$, ΔE is the vibrational excitation energy, $\beta = 1/K_BT$, K_B is Boltzmann's constant, and $Q_p = \int_0^\infty \exp(-\beta p_i^2/2m)dp_i = {}^1/_2(2\pi mK_BT)^{1/2}$.

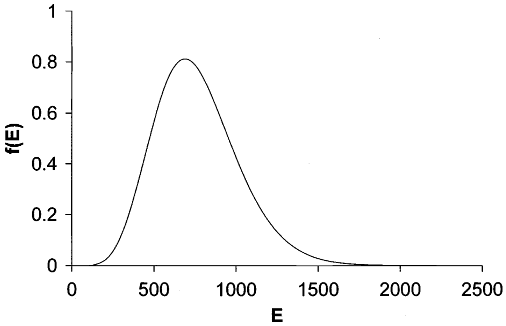

Figure 1. $(2m/\hbar^2)V_{if}^2e^{-\beta E}/p_f \times 10^{13}$ is plotted where E is the translational energy in Kelvin of the system before the collision and p_f is the asymptotic relative momentum of the particles in the final state (after the vibrational transition).

The interaction potential between the particles is taken to be

$$V(r) = 4\epsilon(\sigma/r)^{12} \tag{5}$$

in most calculations in this work, where r is the distance between the pair of atoms, one from each molecule, which are closest to each other. The parameters $\epsilon = 38$ K (degrees Kelvin) and $\sigma = 320$ pm, which are reasonable values for the repulsive interaction between O_2 molecules,[24] are employed in this work. The vibrational transition energy is taken to be $\Delta E = 2273.8$ K, and a reduced mass of $m = 16$ u is employed. The distance r is related to the distance between the centers of mass of the molecules by $R = r + r_a/2 + r_b/2$, where r_a and r_b are the bond lengths for the two molecules. In this work, molecule a is initially in the first excited vibrational state, and the rate at which this molecule relaxes to its vibrational ground state is calculated. Resonant transfer of the vibrational excitation energy to the other molecule is ignored, and the bond length of the second molecule, r_b, is held fixed at the equilibrium bond length r_e. The coordinates describing our system are the separation of the centers of mass, R, and the bond length, r_a. The first-order expansion of the potential in $q = r_a - r_e$

$$V \approx V_e + (\partial V/\partial q)_e q \tag{6}$$

is used in the evaluation of the coupling between the initial and final vibrational states. V_e is taken to be the zeroth-order potential, and $(\partial V/\partial q)_e q$ is the perturbation, H_1, which provides the interstate coupling. The zeroth-order quantum states of the system, $\Psi_j(r_a,R)$, are taken to be products of harmonic oscillator vibrational wave functions, $\varphi_j(q)$, and translational wave functions, $\psi_j(R)$. The coupling matrix element $<\Psi_f\,|H_1|\Psi_i>$ is given by

$$V_{if} = \frac{\hbar}{(2\mu\Delta E)^{1/2}}\int_0^\infty \psi^*_f(R)(\partial V/\partial q)_e\psi_i(R)dR \tag{7}$$

where the harmonic oscillator result $\int\varphi_1(a)q\varphi_0(q)dq = \hbar/(2\mu\Delta E)^{1/2}$ has been employed, where μ is the reduced mass for the vibration.

III. Results

Initial and final quantum wave functions for the translational coordinate are calculated for the system described in the previous section. Calculations are performed with $T = 80$ K for values of the asymptotic kinetic energy for the initial state wave function between 0 and 2500 K. The integrand in eq 4 is plotted as a function of the asymptotic kinetic energy before transition in Figure 1. The maximum of this function occurs at an initial kinetic energy of slightly less than 700K. Higher energy

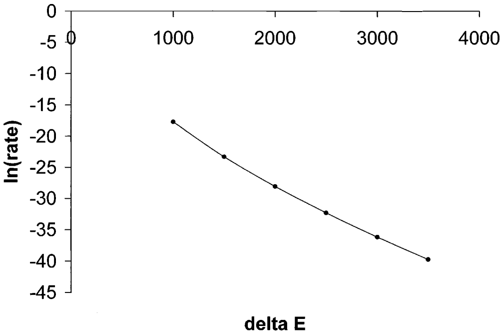

Figure 2. Log(rate) is plotted versus the vibrational excitation energy in Kelvin. The rate is given in ps^{-1}.

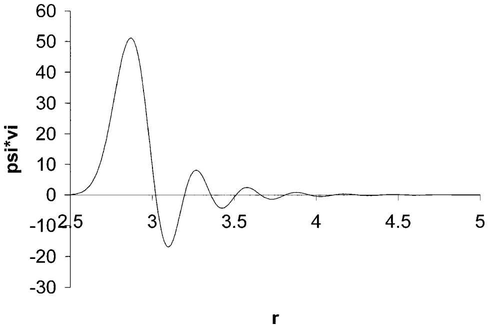

Figure 3. $(\partial V/\partial q)_e \psi_i \hbar/(2\mu\Delta E)^{1/2}$ is plotted versus $r = R - r_e$ for an initial kinetic energy of 700K with $\Delta E = 2273.8$ K. The distance is given in angstroms (10^{-10} m).

collisions are more likely to result in vibrational transitions (i.e., have larger values of $|V_{if}|$), while the Boltzmann factor accounts for the decreasing likelihood of collisions at higher energies. The rapid growth of V_{if} with increasing collision energy results in a maximum at an energy several times the thermal energy of 80 K. The calculated rate for this one-dimensional model system is 5.98×10^{-14} ps^{-1}. The rate, the logarithm of which is plotted as a function of ΔE in Figure 2, is a rapidly decreasing function of the vibration excitation energy.

Figure 3 is a plot of $(\partial V/\partial q)_e \psi_i \hbar/(2\mu\Delta E)^{1/2}$ versus $r = R -- r_e$ for an initial kinetic energy of 700K for the case with $\Delta E = 2273.8$ K. This quantity multiplied by the final state translational wave function, ψ_f, is the integrand for the calculation of V_{if}. The function has a maximum on the order of 50, while the value for V_{if} is 2.56×10^{-4}. The final state wave function, ψ_f, is a rapidly oscillating function with a magnitude on the order of one. The final state momentum near the classical turning point for the initial state is given by $p_f = (2m\Delta E)^{1/2}$, and the corresponding de Broglie wavelength is 0.02 Å. Phase cancellation due to the rapid oscillations of ψ_f results in more than 5 orders of magnitude decrease in the value of the integral compared with the maximum in the integrand. Small errors in the calculation of the initial and final state wave functions or in the evaluation of the integral can cause considerable errors in the result. The integrand for the energy integration, which is shown in Figure 1, is, on the other hand, a smooth, easily integrated function.

Semiclassical methods often ignore the classically forbidden regions. The classical turning point for the incoming particle is at about $r = 2.8$ Å. The large first peak in Figure 3 penetrates significantly into the classically forbidden zone, and the contribution from that region is important in canceling the contribution from the allowed region. Since ψ_f is a rapidly oscillating function, those regions in Figure 3 where the plotted function is changing most rapidly will provide the largest contributions to the integral. This function is rising relatively quickly in the region before the turning point, resulting in a relatively large contribution from this region. If the lower integration limit in eq 7 is changed to the classical turning point corresponding to relative momentum p_i for the colliding molecules, then the calculated rate is 1.02×10^{-5}, compared with the result 5.98×10^{-14} from the full calculation. In this case, neglecting the contribution from the classically forbidden regions results in a rate that is more than 8 orders of magnitude larger than the exact quantum calculations for this model system.

Since the evaluation of V_{if} involves several orders of magnitude of phase cancellation, the integration must be accurately performed out to a distance at which the interaction potential is small compared to the magnitude of the integral. It is of interest to discern what features of the system potential energy, $V_e(R)$, and the coupling between the vibrational states, $V_{int}(R)$, determine the value of this integral, where $V_{int}(R) = [\hbar/(2\mu\Delta E)^{1/2}](\partial V/\partial q)_e$. To this end, we expand $V_e(R)$ and $V_{int}(R)$ in the following form

$$F_n(R) = Ae^{-bx}(1 + \sum_{j=2}^{n} C_n x) \tag{8}$$

where $x = R - R_0$. Since the large first peak in Figure 3 is near the classical turning point for the incoming translational energy, the expansion point R_0 is taken to be the value of R at this turning point. The constants A, b, and C_n in eq 8 are chosen so that $F_n(R)$ and its first n derivatives agree with those of the function being expanded, $V_e(R)$ or $V_{int}(R)$. The form of the expansion presented in eq 8 is utilized in this work because it has the correct value at R_0, provides the correct first n derivatives, and decays exponentially to zero at large R. This last feature is important for the expansion of the coupling. If the expansion of the interstate coupling did not decay to zero, then the V_{if} integral, eq 7, would continue to oscillate rather than converge to a specific value.

Table 1 provides rate constants for various values of the order of the expansion of the potential, n_V, and the order of the expansion of the coupling, n_c, for the system with $\Delta E = 2273.8$ K. Fourth-order expansions for both $V_e(R)$ and $V_{int}(R)$ result in less than a 10% error. The rate calculated using second-order expansions differs from the exact result by only a factor of 2, which is generally considered a good level of accuracy for the calculation of a transition rate for a high-frequency vibration. These results suggest that even though the integrand in the V_{if} calculation continues to oscillate with a non-negligible magnitude out to a relatively large R, it is the behavior of $V_e(R)$ and $V_{int}(R)$ near the classical turning point for the initial state translational energy that largely determines the magnitude of the contribution to the rate constant from that energy.

Table 2 compares the exact quantum rate with values obtained using the expansion of the $V_e(R)$ and $V_{int}(R)$ for various values of ΔE. The results show that the errors resulting from the low-order expansions become more significant as ΔE increases. There is only about a 12% error when quadratic expansions are employed when $\Delta E = 1000$ K, and the quartic expansions yield results with less than 1% error. When $\Delta E = 3500$ K, the rate calculated using quadratic expansions is only about 1/3 of the exact value. This error is reduced to about 21% when quartic expansions are used, and it is less that 4% if sixth-order expansions are used.

The importance of high-energy collisions in the results obtained here suggests that the major contributions to the relaxation in liquids might also come from regions well up on the repulsive wall of the molecule−molecule potential. If this

TABLE 1: Transition Rate (in ps^{-1}) for a One-Dimensional Model System with $\Delta E = 2273.8$ K for Various Values of n_V and n_c[a]

$n_c =$	$n_V = 2$	$n_V = 4$	$n_V = 6$	$n_V = 8$	$n_V = 10$
2	3.24×10^{-14}	4.08×10^{-14}	4.19×10^{-14}	4.20×10^{-14}	4.20×10^{-14}
4	4.35×10^{-14}	5.45×10^{-14}	5.59×10^{-14}	5.61×10^{-14}	5.61×10^{-14}
6	4.61×10^{-14}	5.77×10^{-14}	5.92×10^{-14}	5.94×10^{-14}	5.94×10^{-14}
8	4.64×10^{-14}	5.80×10^{-14}	5.96×10^{-14}	5.97×10^{-14}	5.97×10^{-14}
10	4.64×10^{-14}	5.80×10^{-14}	5.96×10^{-14}	5.98×10^{-14}	5.98×10^{-14}

[a] The value using the exact $V_e(R)$ and $V_{int}(R)$ is 5.98×10^{-14} ps^{-2}.

TABLE 2: Transition Rate (in ps^{-1}) for a One-Dimensional Model System with Various Values of ΔE, n_v, and n_c[a]

ΔE	$n_v = n_c = \infty$	$n_v = n_c = 2$	$n_v = n_c = 4$	$n_v = n_c = 6$
1000	2.01×10^{-8}	1.76×10^{-8}	2.00×10^{-8}	2.01×10^{-8}
1500	7.65×10^{-11}	5.64×10^{-11}	7.43×10^{-11}	7.64×10^{-11}
2000	6.45×10^{-13}	3.91×10^{-13}	6.03×10^{-13}	6.41×10^{-13}
2500	9.26×10^{-15}	4.56×10^{-15}	8.25×10^{-15}	9.14×10^{-15}
3000	1.96×10^{-16}	7.79×10^{-17}	1.65×10^{-16}	1.92×10^{-16}
3500	5.63×10^{-18}	1.80×10^{-18}	4.45×10^{-18}	5.43×10^{-18}
2273.8[b]	4.19×10^{-14}	2.52×10^{-14}	3.93×10^{-14}	4.16×10^{-14}

[a] The case with $n_v = n_c = \infty$ is the exact quantum calculation. [b] The potential energy $V(r) = 4\epsilon(\sigma/r)^{-12} + V_{ex}\exp(-r/r_v)$ is employed in the calculations at this ΔE.

is the case, then the use of low-order expansions of the potential and the coupling combined with quantum calculations of the initial and final translational states and of V_{if} may provide an avenue for accurate and computationally feasible calculations of vibrational relaxation rates in liquids. The potential employed in this work is a simple r^{-12} repulsion. This can be expected to provide a reasonable model for the interaction high on the repulsive wall in liquids. The question of whether the low-order expansion method continues to work in regions where the liquid-phase potential energy is more slowly varying is of interest. In order to address this question within the context of the model used here, the additional potential $V_{ex}\exp(-r/r_v)$ is added to the r^{-12} potential. The values $V_{ex} = 50$ K and $r_v = 5$ Å are employed. This additional potential adds a relatively slowly varying term to the short ranged, highly repulsive wall. Relaxation rates evaluated using this modified potential with $\Delta E = 2273.8$ K are presented in Table 2. The additional potential results in a slightly lower relaxation rate of 4.19×10^{-14}, compared with 5.98×10^{-14} when this added potential is not included in the calculation. The calculations using low-order expansions of V_e and V_{int} continue to provide good approximations[42] to the exact relaxation rate with this augmented potential.

IV. Discussion and Conclusions

The results for the one-dimensional model considered in this work provide several insights concerning the calculation of vibrational relaxation rates. First, the relaxation rate for this system is dominated by contributions from energies that are many times thermal energies. The fixed energy golden rule rate is an increasing function of energy. This increase is faster than the decrease in the Boltzmann factor at thermal energies, and it is only at the significantly higher energies that the decrease in the Boltzmann factor with increasing energy eventually results in the decay of the energy dependent contribution to the thermally averaged rate.

Moreover, the calculations illustrate that there are several orders of magnitude of phase cancellation in the evaluation of the transition matrix element V_{if} for a given energy. For the $\Delta E = 2273.8$ K calculation, it is found that this cancellation reduces the transition matrix element by a factor of over 10^{-5} compared with the maximum value of its integrand at $E = 700$K. Since the contribution to the rate at each energy is proportional to V_{if}^2, the effect of this cancellation on the rate is the square of the effect on V_{if} averaged over all energies. In the time dependent autocorrelation function approach, the rate expression is proportional to the Fourier transform at frequency $\omega = \Delta E/\hbar$ of the force autocorrelation function. In the harmonic oscillator approximation, this autocorrelation function is proportional to related quantity containing *two* factors of V_{int}, so the impact of the phase cancellation should be much greater on the autorcorrelation function than on V_{if}. This suggests that there may be numerical advantages to a method that accounts for the phase cancellation by numerically evaluating V_{ij} and then squaring it, as opposed to one that numerically evaluates a single quantity, the Fourier transform of the autocorrelation function, which incorporates the effect of all the phase cancellation. A similar result is reported by Rostkier-Edelstein, Graf, and Nitzan[25] in their analysis of numerical methods for evaluating the Fourier transform of the classical force−force autocorrelation function. This Fourier transform can be expressed in terms of the square of Fourier transform of the time dependent force on the relaxing mode using the Wiener-Khinchin theorem, and the authors find that the results based on this latter form are more reliable.

The contribution from the classically forbidden region to the integration required for the evaluation of V_{if} is very significant and must be accurately included in the calculation of this quantity. Neglect of this classical forbidden contribution results in a rate that is roughly 8 orders of magnitude too large compared with the full quantum calculation for the model system studied in this work. One would expect that the accurate inclusion of the classically forbidden contributions to the phase cancellation in the calculation of the time dependent autocorrelation function is similarly important when the rate is being evaluated as the Fourier transform of this quantity. The good results obtained using the linearized semiclassical method of Geva and co-workers[33−37] would indicate that the quantum phase cancellation is accurately accounted for in their implementation of the local harmonic approximation in the calculation of the Wigner transform of the force on the relaxing mode.

The results presented demonstrate that the behavior of the translational potential energy, V_e, and the interstate coupling, V_{int}, near the turning point in the classical translational motion at the energy of the initial state largely determines the magnitude of the contribution to the rate at that energy. Calculations using low-order expansions of V_e and V_{int} are able to provide values of the rate in good agreement with the exact calculations for this model. The use of fourth-order expansions results in only about a 10% error in the rate for the case with a vibrational excitation energy corresponding to O_2. If second-order expansions are employed for the simple model considered, then the rate obtained is still within a factor of 2 of the rate from the full calculation in this case. These results suggest that it may be possible to accurately simulate relaxation rates for high-frequency vibrations by using low-order expansions for the potential and coupling at classical turning points. The quantum wave function and coupling matrix elements, V_{if}, can then be obtained using these expansions. This computational procedure can be easily parallelized making simulations numerically feasible. The important aspect of this method is that the significant phase cancellation is accurately accounted for in the evaluation of V_{if}. Since the method focuses on the turning point in the classical motion, the Monte Carlo average over configurations in the simulation of a liquid system corresponds to the integration over the value of the initial asymptotic momentum in the rate expression employed in this work. The corresponding integrand for the one-dimensional model employed in this work, which is shown in Figure 1, is well suited for a Monte Carlo integration. The testing of this methodology on many dimensional models and its application to realistic simulation systems are topics for future work.

The application of the approach considered in this work to more realistic condensed phase systems would require expanding the many-particle potential at appropriate "turning points" in the classical motion. Since the potential would include the interaction with many particles, an independent binary collision model between pairs of particles is not assumed here. The direction of many-particle force on the vibrational degree of freedom is an obvious first choice for the collective degree of freedom. In addition, the expansion of the potential could include several collective degrees of freedom and low-order couplings between these, reminiscent of the instantaneous normal mode approach.[43,44] The work of Deng, Ladanyi, and Stratt[45] on contributions to the Fourier transform of the force−force autocorrection function indicates that a single collective mode provides an accurate description of Fourier transform at high frequencies in many cases, although they find the influence of rotations on the vibrational relaxation must also be accounted for in the case of a triatomic with a heavier center atom and much lighter end atoms. They also find that the high-frequency Fourier transform in dominated by short-range interactions and that long-range dipole−dipole interactions do not significantly contribute to it. This is similar to our numerical result that the addition of the long-range potential does not change the relaxation rate very much for our simple model.

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