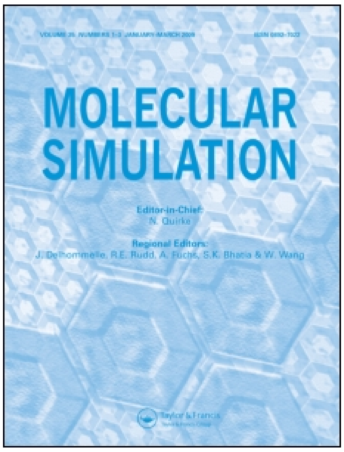

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Vibrational Relaxation Time of CN^- Ion in Water Studied by Mixed Quantum-classical Molecular Dynamics: Comparison with Fermi's Golden Rule and Influence Functional Theory

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Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water. The calculated relaxation time was compared with those based upon Fermi's golden rule with classical interaction and influence functional theory with classical bath. They are in good agreement with each other. Flexible water model adopted here enhanced the relaxation rate by a factor of about 5 compared with the rigid rotor model. This supports our previous result of path integral influence functional theory that intramolecular bending of water plays an essential role in the relaxation.

Keywords: Vibrational relaxation; Molecular dynamics; Mixed quantum-classical approximation; Flexible water model

INTRODUCTION

In the last decade, computational studies for vibrational energy relaxation of solute in solvent have actively been carried out, developing new theoretical methods [1–11]. Recently, in the same direction, we proposed [2] a method based upon mixed quantum-classical molecular dynamics and applied it to the relaxation of cyanide ion in the aqueous solution. However, the method inevitably includes particular approximations, as is the case for the other methods proposed so far, since rigorous quantum dynamics calculation for the condensed phase is actually impossible even by current high performance supercomputers or parallel computers. Then, test of validity of the theory becomes very important.

The validity of the calculation may be demonstrated by comparing the resultant relaxation time with experiment. However, in this case, the calculation includes two factors to be tested. The first one is the method itself and the other is potential model. These two are independent of each other such that they must be investigated separately. In the present study, in order to test our method, i.e. mixed quantum-classical molecular dynamics with mean field approximation, the calculated relaxation time has been compared with those evaluated by Fermi's golden rule with classical force and path integral influence functional theory with classical bath.

The system is a cyanide ion in water for which we have already reported detailed analysis based upon both path integral influence functional theory and, as stated above, mixed quantum-classical molecular dynamics. In the former case, a flexible water model was used. However, in the latter case, a rigid rotor model was adopted for water in spite of the fact that the bending motion of water plays an essential role in the relaxation process. Thus, in the present study, a flexible water model is newly adopted in order to include the very important relaxation mechanism and to keep the calculation consistent with the previous calculation based upon influence functional theory.

METHOD

Time-dependent Schrödinger equation for the wave function $\psi(x,t)$

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t)$$
$$= [H_0 + V_{\mathrm{I}}(\mathbf{R}^N(t),x)]\psi(x,t) \qquad (1)$$

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may be solved for vibrational degree of freedom x of a solute molecule of interest, which is coupled to classical equation of motion

$$\mathbf{M}\frac{\mathrm{d}^2\mathbf{R}^N(t)}{\mathrm{d}t^2} = -\frac{\mathrm{d}V_\mathrm{C}(\mathbf{R}^N(t))}{\mathrm{d}\mathbf{R}^N(t)} + \mathbf{F}_Q(\mathbf{R}^N(t)) \qquad (2)$$

for all other solvent degrees of freedom $\mathbf{R}^N(t)$ [2]. The solvent degrees of freedom include bending and stretching of the solvent as well as translation and rotation of the solute and solvent. Here, H, H_0, V_I and V_C are the Hamiltonian of x in the solution, Hamiltonian of x in vacuum, interaction between the solute and solvent, and potential energy for the solvent, respectively. The $\hbar$ and $\mathbf{M}$ are Planck constant and mass matrix, respectively.

With respect to the classical system, mean field approximation was assumed for the force $\mathbf{F}_Q(\mathbf{R}^N(t))$ from the quantum system [2] such that

$$F_Q(\mathbf{R}^N(t)) = -\int_{-\infty}^{\infty}\mathrm{d}x\psi^*(x,t)\frac{\partial V_\mathrm{I}(\mathbf{R}^N(t),x)}{\partial\mathbf{R}^N(t)}\psi(x,t). \qquad (3)$$

Now, the force $\mathbf{F}_Q$ is so called the Hellmann-Feynman force. When these coupled equations of motion are solved simultaneously, the interaction V_I, is a function of time through the solvent motion $\mathbf{R}^N(t)$. This time-dependent potential causes non-adiabatic transition to the solute. Then, total energy of the total system is conserved along the trajectory. A Morse oscillator was assumed for the solute intramolecular degree of freedom. The wave function $\psi(x,t)$ was expanded by the eigen functions of Morse oscillator in vacuum such that dynamics of the solute vibration is described by time evolution of expansion coefficient $c_i(t)$ with respect to the eigen functions of H_0. In order to calculate vibrational relaxation time, expansion coefficient $c'_i(t)$ with respect to the eigen function of H in the solution was evaluated by converting $c_i(t)$. Then, $|c'_i|^2$ represents the probability that the system is found in the ith vibrational state. Details are described, elsewhere [2].

CALCULATIONS

The calculation was almost the same as that reported previously [2] except for the potential function for water. In the present study, SPC/E based fully flexible model by Parker and Heyes [12] was adopted in order to take account of the contribution of bending motion of water to the relaxation as stated above. Totally, 123 MD runs were executed starting from statistically independent initial conditions. In order to obtain them, preliminary MD calculations were carried out for each of the 123 runs starting from randomly generated configurations and velocities. After 20 ps equilibration run, during which the temperature was controlled at 300 K by the Nosé thermostat, we reset the time to be $t = 0$ and set the c_i values such that $|c'_1(0)|^2 = 1$ and $|c'_i(0)|^2 = 0$ for $i \neq 1$, assuming the first excited state for the system at $t = 0$. Trajectory of each run was traced for further 50 ps in order to observe the vibrational relaxation.

RESULTS AND DISCUSSION

In Fig. 1, the survival probability $|c'_i|^2$ averaged over 123 different initial configurations is presented. This corresponds to the ensemble average, which may be observed experimentally. The almost linear line found in this semilogarithmic plot is likely to show an exponential decay of the survival probability of the first excited state. A solid linear line in the figure is a line fitted to the probability, from which the relaxation time was estimated to be 24 ps.

Validity of the present method may be tested by comparing it with Fermi's golden rule where the classical approximation is applied to the solvent. According to the Fermi's golden rule [13], the relaxation rate from the first excited state to the ground state is presented by

$$\tau_{01}^{-1} = \frac{2\hbar^{-2}}{1+e^{-\beta\hbar\omega_{01}}}\int_{-\infty}^{\infty}\mathrm{d}t e^{i\omega_{01}t}\langle[\tfrac{1}{2}V_{01}(t)V_{10}(0)]_+\rangle \qquad (4)$$

where $\langle[\frac{1}{2}V_{01}(t)V_{10}(0)]_+\rangle$ is quantum symmetrized correlation function of the interaction $V_{01} = \langle 0|V_\mathrm{I}|1\rangle$. In the classical solvent approximation, the quantum correlation function is just replaced by the classical autocorrelation function $\langle V_{01}(t)V_{01}(0)\rangle$. This is in the same class of the approximation as the present study, i.e. mixed quantum-classical approximation. Here, quantum correction factor [9,14,15] was not applied since we are going to directly compare the present calculation with the Fermi's golden rule with the classical interaction. The classical correlation function

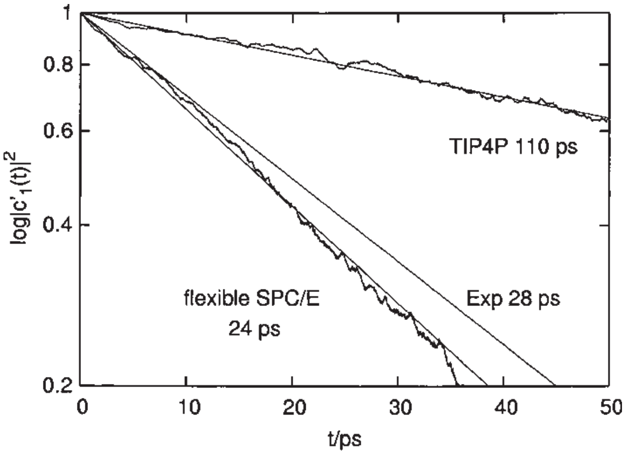

FIGURE 1 Semilogarithmic plot of the averaged survival probability $|c'_1(t)|^2$ for the first excited state of the solute.

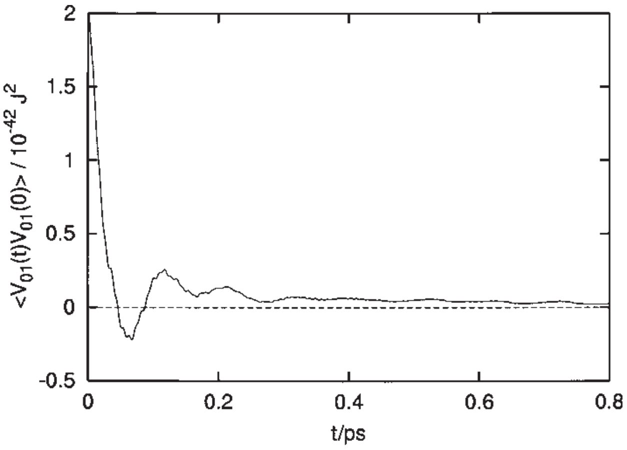

FIGURE 2 Calculated classical autocorrelation function of interaction $\langle V_{01}(t)V_{01}(0)\rangle$.

is easily obtained from the trajectory of the present calculation. The result is presented in Fig. 2. A number of papers reported that the force correlation function is composed of fast decay with a time constant of about 0.1 ps as well as slow decay of about 1 ps [16–19]. This is the case for the present correlation function in Fig. 2, too. The latter is often called a long time tail. Although the long time behavior is not given in the figure, the function converges to zero in about 2 ps. Although its molecular origin of the long time tail has not been discussed in detail in the above papers, the time constant may closely be related to the structural relaxation time of the solution since the force on the solute and the interaction with the solvent must be a function of solution structure. In fact, for example, the structural relaxation time of liquid water is about 2 ps [20], the order of magnitude being the same as the slow decay found in the correlation functions of force and interaction. Fourier transformation, or power spectrum, of this function is also presented in Fig. 3. Although no modes are found in the instantaneous normal mode density of state at frequency higher than about 1000 cm^{-1} except for bending and stretching as shown in our previous analysis [8], the interaction spectrum shows small but nonnegligible intensity for this frequency region. This clearly comes from nonlinear interactions between the solute vibration and the solvent. Following Eq. (4), intensity of the power spectrum at $\omega_{01} = 2080\,\text{cm}^{-1}$ presents the relaxation time of 30 ps. This is in good agreement with that obtained by the present method, 24 ps.

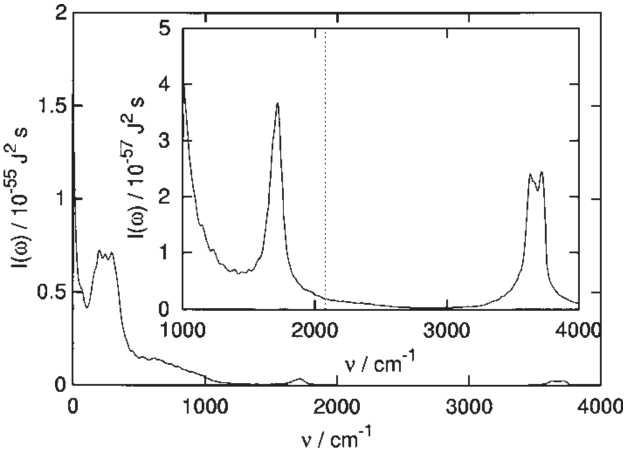

FIGURE 3 Power spectrum of the classical autocorrelation function of interaction $\langle V_{01}(t)V_{01}(0)\rangle$. The dotted line represents the averaged transition frequency of CN$^-$ in solution. The inset shows an expanded power spectrum for ν from 1000 to 4000 cm^{-1}.

Furthermore, although the potential model for water is a little bit different from the present one, calculated relaxation time based upon influence functional theory in the $\hbar \to 0$ limit with respect to the solvent degrees of freedom, i.e. classical bath, was 28 ps [9]. This is in good agreement with the present result of 24 ps, too. Thus, these three methods, i.e. the present method, Fermi's golden rule with classical correlation function, and path integral influence functional theory in the classical bath limit, are consistent with each other and expected to give a reasonable picture for the relaxation.

Here, the calculated relaxation times based upon these three methods are summarized in Table I together with the results based upon rigid rotor model for solvent water. Now, the effect of intramolecular modes of water in this system on the vibrational relaxation time can be discussed. The previously reported relaxation time based upon rigid rotor TIP4P solvent water was about 110 ps. Averaged time evolution of the survival probability is also presented for the system of TIP4P rigid rotor solvent and the relaxation rate for the present fully flexible SPC/E is several times faster than that for the rigid rotor TIP4P is shown in Fig. 1. Further, the calculation based on Fermi's Golden rule showed almost the same result, where the flexible model of water accelerates the relaxation time from 138 to 30 ps [1]. These clearly mean that the intramolecular degrees of freedom of the solvent water play a very important role in the relaxation. This is in good correspondence to the experimental analysis based upon pump-probe time-resolved spectroscopy by Hamm *et al.* [21], as well as our previous analysis based upon path integral influence functional theory

TABLE I Calculated relaxation times based on mixed quantum-classical molecular dynamics, Fermi's Golden rule, and influence functional theory for CN$^-$ ion in water

Method	*Flexible water (ps)*	*Rigid water (ps)*
Mixed quantum-classical molecular dynamics	24	110 [2]
Fermi's Golden rule with classical interaction	30	138 [1]
Influence functional theory with classical bath	28 [9]	200 [9]

[9], where bending mode of water was clarified to be essentially important among them.

On the other hand, the experimental relaxation time has been reported to be 28 ps by Hamm *et al*. [21]. Agreement between the present calculation and the experiment is apparently good, as shown in Fig. 1, too. However, we must evaluate this very carefully. According to our previous work [9], the calculated relaxation time was estimated to be about 3 ps based upon fully quantum mechanical path integral influence functional theory using the same potential model for CN^- ion. The overestimation of the relaxation rate may be caused by the overestimation of the interaction. Further, quantum effect of the solvent is significantly large [9] for the solute with transition frequency of $2080\,cm^{-1}$ such that the classical solvent gives the relaxation time nearly one order of magnitude greater than the quantum solvent. Furthermore, a broad combination ν_A band experimentally found at $2150\,cm^{-1}$ in IR spectrum [22] is neglected in the present potential model. Since IR spectrum may be related to the oscillation of dipole moment of the total system, the electric field on the solute must oscillate at the same frequency. That is, the band must accelerate the relaxation as discussed by Hamm *et al*. [21]. However, since our potential model does not include the nonlinear interaction with the bending mode of water in an explicit way, no peak is found around $2{,}150\,cm^{-1}$ in the interaction spectrum in Fig. 3. This neglect of the ν_A band in the model may result in a low relaxation rate. Since contribution of the ν_A band to the total intensity of IR spectrum is read from the experimentally observed spectrum [22] to be about the same as the other contributions, the calculated relaxation rate might be considerably underestimated.

In any case, considering these facts, the agreement between the present relaxation time and the experimental one may be a result of cancellation of the overestimation of interaction with the underestimation of relaxation rate caused by the classical solvent approximation and the neglect of the ν_A combination band.

CONCLUSION

Molecular dynamics calculations based upon mixed quantum-classical approximation have been executed for vibrational relaxation of CN^- in water. The calculated relaxation time showed good agreement with those obtained by Fermi's golden rule with classical force and path integral influence functional theory with classical bath. This clearly means that the methods give physically valid relaxation time within the used potential model. Apparent agreement with the experiment may be regarded as a result of cancellation of the overestimation of interaction with the underestimation of relaxation rate caused by the classical solvent approximation and the neglect of the ν_A combination band.

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