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Quantum Dynamical Simulation of the Energy Relaxation Rate of the CN^- Ion in Water

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The energy relaxation rate of a CN^- ion in water at 300 K has been calculated using the centroid molecular dynamics (CMD) simulation method. The simulation consisted of 107 water molecules and a single CN^- ion. An independently parameterized three site CN^- model was employed along with an ab initio potential for the CN^- bond coordinate. A flexible water model designed for quantized bulk water simulations was employed for the solvent. The equilibrium simulation results are seen to give a reasonable structure of the CN^- ion and its solvation in water. The calculated relaxation behavior is found to be biexponential with a fastest time scale of about 15 ps, which is comparable to the experimentally observed value.

Introduction

The vibrational energy relaxation of a solute in a solvent environment gives important information on the dynamical nature of the solute−solvent interactions.[1] The particular case of the vibrational relaxation of a solute ion in a polar solvent is interesting, since such systems exhibit a strong coupling between the solute and solvent molecules. Thus, numerous experimental studies have measured the relaxation rates of various systems of interest.[2−10]

On the theoretical side, many classical molecular dynamics-(MD) simulations have also been performed,[2,4,11,12] using the Landau−Teller formula,[13−15] (for a diatomic solute), which relates the relaxation rate to the solvent friction for energy dissipation problems, or by direct energy dissipation calculations. This classical approach should be effective in the systems in which the vibrational frequency of the solute is in the range of k_BT or less. However, it is expected to yield relatively less accurate results in cases that the vibrational frequency of the solute is larger than k_BT. In such cases, the quantum nature of the dynamics should play an important role in the relaxation phenomena.

The CN^- ion in water is both an interesting and relatively simple example, since direct information on the vibrational coupling between solute and solvent can be obtained due to the absence of intramolecular vibration transfer. As was shown by the experimental studies of Heilweil et al.[8] and Hamm et al.,[16] the relaxation rate for the system is 28 ± 7 ps in the dilute ion limit. Recently, Rey and Hynes[17] performed a classical MD simulations using the TIP4P water model and found the rate to be ∼58 ps. In their analysis, they used the Landau−Teller formula to estimate the vibrational relaxation rate. The relaxation rate of the same system has been predicted to be 8 ps by Shiga and Okazaki,[18] using the quantum mechanical Fermi-Golden rule, thus suggesting the importance of quantum effects in the system. They estimated the relaxation time by combining normal-mode analysis with Feynman path integral influence functional theory. The normal modes were prepared from 30 quenched structures from a series of classical MD simulations. These researchers again used the TIP4P water model in their simulations. The survival probability calculated by the same authors[19] shows that there is noticeable difference between a classical and quantum treatment of the system.

In related theoretical work, Bader and Berne[20] have studied quantum vibrational energy relaxation in the framework of harmonic bath models. One important conclusion from their study is that mixed quantum-classical approaches can be seriously in error and that one may be better off using a consistent treatment of all degrees of freedom of the condensed phase system. Recently, Skinner and co-workers[21,22] have incorporated quantum effects into their vibrational relaxation rate calculations of liquid oxygen by obtaining approximate quantum force−force time correlation functions from classical results, further highlighting the potential pitfalls of mixed treatments.

For the purpose of incorporating quantum effects into condensed matter simulations, the centroid molecular dynamics (CMD) simulation method,[23−26] which has recently been more rigorously formulated,[27] can provide a consistent simulation strategy. This may be particularly true in the case of vibrational energy relaxation in the spirit of the Bader and Berne's conclusions. In this paper, we therefore calculate the relaxation rate of a CN^{-1} molecule in water by the CMD method. One key aspect of the present work is that the models for both CN^- and water have been independently parametrized to fit unrelated data, and the internal vibrational potential of CN^- is taken from an ab initio calculation. Thus, the vibrational energy relaxation rate is obtained in the CMD simulation without any additional parameter fitting.

The outline of this paper is as follows: In section II, a brief description of the CMD method and simulation model used in this study will be given, while the simulation results are presented in section III. The simulation results are divided into two subsections: equilibrium results and dynamical results. Finally, concluding remarks appear in section IV.

Methods

A. Centroid Molecular Dynamics (CMD). In CMD,[23−27] dynamical properties are calculated by classical-like equations of motion for the system Feynman path centroids, i.e.,

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$$m\frac{\mathrm{d}^2\mathbf{q}_\mathrm{c}}{\mathrm{d}t^2} = -\nabla V_\mathrm{c}[\mathbf{q}_\mathrm{c}(t)] \tag{1}$$

where $\mathbf{q}_\mathrm{c}(t)$ is the centroid coordinates of the system. The centroid potential of mean force (CPMF) $V_\mathrm{c}(\mathbf{q}_\mathrm{c})$ is given by

$$V_\mathrm{c}(\mathbf{q}_\mathrm{c}) = -(1/\beta)\ln\left[\frac{\rho_\mathrm{c}(\mathbf{q}_\mathrm{c})}{\rho_\mathrm{c}^0(\mathbf{q}_\mathrm{c})}\right] \tag{2}$$

where $\rho_\mathrm{c}{}^0(\mathbf{q}_\mathrm{c})$ is the free particle centroid density, and $\rho_\mathrm{c}(\mathbf{q}_\mathrm{c})$ is the centroid density for a given potential. The centroid density $\rho_\mathrm{c}(\mathbf{q}_\mathrm{c})$ is given by

$$\rho_\mathrm{c}(\mathbf{q}_\mathrm{c}) = \int\cdots\int D\mathbf{q}(\tau)\delta(\mathbf{q}_\mathrm{c} - \mathbf{q}_0)\exp\{-S[\mathbf{q}_i(\tau)]/\hbar\} \tag{3}$$

with

$$S[\mathbf{q}(\tau)] = \int_0^{\beta\hbar}\mathrm{d}\tau\left\{\frac{m}{2}\dot{\mathbf{q}}(\tau)^2 + V[\mathbf{q}(\tau)]\right\} \tag{4}$$

and the particle centroid variable is defined as follows:

$$\mathbf{q}_0 = \frac{1}{\hbar\beta}\int_0^{\hbar\beta}\mathrm{d}\tau\mathbf{q}(\tau) \tag{5}$$

A CMD simulation requires the "on the fly" calculation of centroid mean force, which can be shown to be equal to the classical force averaged over the constrained path configurations generated according to the integrand of eq 3. One of several algorithms can be used for this purpose.[26]

It should also be noted that for the case of general operators such as the bond energy as in the present study, there may be two levels of approximation involved in a CMD simulation. The first is in the underlying dynamical CMD propagation scheme,[23−25,27] while the other is in the representation of the operators. In the case of operators linear in position or velocity, the second approximation is not necessary. In the present work, however, the solute bond energy function is used, which is a nonlinear function of position and momentum. The resulting approximation implemented in this work (i.e., the operator approximation mentioned earlier) is to treat the bond energy function classically, but to propagate the underlying dynamics using CMD.[24,25] The main effect of such an approximation is that the initial time value of correlation functions are not properly estimated due to the classical treatment of the zero-time quantum mean-squared fluctuation. However, in this paper we are only interested in the time dependence of the relaxation function in order to extract the energy decay rate (i.e., the decay function is normalized to unity).

B. Simulation Models for *CN*$^-$ and Water. The intermolecular potential energy functions for CN$^-$ for the purposes of MD simulation have been investigated in detail by Klein and McDonald,[28] Bounds et al.,[29] and Ferrario et al.,[30] based on that derived for solid KCN. Using this three-site model, Eaton et al.[31] and Ferrario et al.[32] predicted the equilibrium structure of in water with a fixed CN$^-$ distance, while Shiga and Okazaki[18] predicted the relaxation time of CN$^-$ as stated earlier. All of these simulations have been carried out using the TIP4P water model for the solvent.

In the current investigation, we have also used the three site model of Ferrario et al. (model E) for CN$^-$ without further modification, which contains $-0.8e$ point charge at the N atomic site, $-1.0e$ charge at 0.862 Å to the carbon side from the center of mass, and 0.8e charge at 0.526 Å to the carbon side from the center of mass.

The intramolecular CN$^-$ potential employed in the present work is given by a fit to gas phase ab initio data[33] such that

$$V(Q) = 0.52414Q^2 - 0.63439Q^3 + 0.45656Q^4 - 0.26260Q^5 + 0.1287Q^6 - 0.06029Q^7 + 0.02183Q^8 \tag{6}$$

where $Q = r - r_0$ with $r_0 = 1.17682$ Å. The energy units here are in atomic units. The flexible SPC/F$_2$ model for water[34] was used which was independently parametrized for use in quantizied water simulations. Site−site interactions between the CN$^-$ and water molecules were used, and the Coulombic terms were handled by the Ewald summation method. The Lennard-Jones potentials for the CN$^-$/water interaction were formed with Lorentz−Berthelot rules with the Lennard-Jones parameters[32] $\epsilon_\mathrm{CC} = 51.6$ K, $\epsilon_\mathrm{NN} = 42.7$ K, $\sigma_\mathrm{CC} = 3.43$ Å, and $\sigma_\mathrm{NN} = 3.32$ Å.

C. Calculations. The simulation box consisted of 107 water molecules and a single CN$^-$ ion. The water (both hydrogen and oxygen) and CN$^-$ ion were quantized by assigning 24 quasi-particles to each nucleus ($p = 24$). Initially 108 water molecules (SPC/F$_2$) were prepared with a density 0.996 g/cm^3. Then, a normal mode path integral molecular dynamics (PIMD) simulation[35] was performed to reach an equilibrium state at 300 K. The total PIMD simulation time was 20 ps with a time step 0.36 fs. At the equilibrated structure one of the water molecules was then replaced by the CN$^-$ ion. A further PIMD simulation was performed for another period of 20 ps to establish equilibrium in the presence of the solute. Starting from this structure, eleven equilibrium configurations were obtained from the PIMD simulation by taking the configurations at intervals of 5 ps. A Nosé−Hoover thermostat[36−40] of chain length 2 was attached to each degree of freedom to ensure canonical sampling.

From each initial equilibrated structure, CMD simulations were performed beginning with an initial CN$^-$ excitation of 2080 cm^{-1} achieved through an internal potential energy boost. The vibrational relaxation rate in other studies has been found to be insensitive to the form of the initially excited energy, i.e., kinetic or potential energy.[4] Also, since the potential energy surface of CN$^-$ around this region is fairly close to harmonic, the vibrational relaxation rate is further expected to be insensitive to the excited energy.[4,12]

The adiabatic CMD simulation[26] was carried out with a time step 0.012 fs with the fictitious mass of the higher order normal modes set to 0.005 au. It should be noted that the vibrational relaxation in the current CMD run is a nonequilibrium process, even though CMD was originally intended for equilibrium dynamics simulation. However, given that CMD provides an accurate description of equilibrium time correlation functions, the present application is consistent with the spirit of the Onsager regression hypothesis.

Results and Discussion

A. Equilibrium Structure. There are at least two criteria to determine the solvation number of a solute,[32,41,42] i.e., based on energy and structure. We have calculated the solvation number of a *quantum* CN$^-$ ion in SPC/F$_2$ water through a PIMD simulation in these two ways. First, the CN$^-$/H$_2$O the pair distribution functions were calculated. Figures 1 and 2 show the calculated pair distribution function, $g_\mathrm{CO}(r)$ and $g_\mathrm{NO}(r)$, respectively. It is seen that the nitrogen side has more solvation than the carbon one, which is consistent with the other classical equilibrium simulations and experiments.[17,31,32,43] The water coordination number is calculated by integration of $g(r)$. But since some of the oxygens/hydrogens are double counted

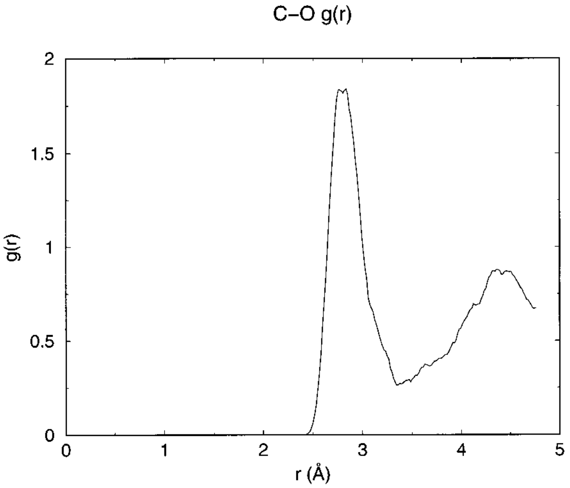

Figure 1. C-O pair distribution function.

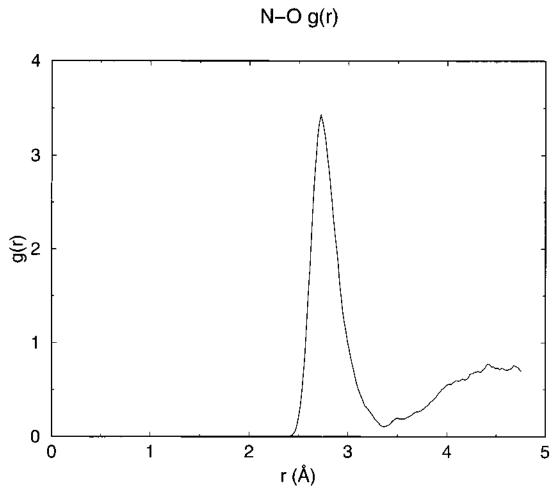

Figure 2. N-O pair distribution function.

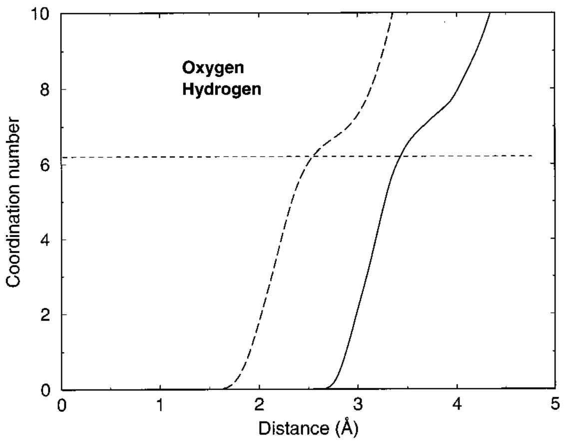

Figure 3. Number of solvent water molecules based on the CN⁻ $g(r)$ from the center of mass.

by $g_{CO}(r)/g_{NO}(r)$, we calculated $g(r)$ from the center of mass of CN⁻ instead of from the C or N sites. Figure 3 shows the integration of the calculated $g(r)$. As can be seen in this figure, the solvation number is about 6.

One can also estimate the solvation number based on the hydration energy. Figure 4 shows the energy distribution of the solute−solvent dimer. The energy distribution exhibits a well resolved bonded and nonbonded pair separation. If one considers a dimer which has less than −5.2 kcal/mol as hydrogen bonded, the solvation number is also estimated to be about 6 from Figure 5, which gives the number of dimer pairs by integration of Figure 4. The experimental solvation number is believed to be around five, and other simulations[17,31,32] give a slightly higher solvation number (5 or 6).

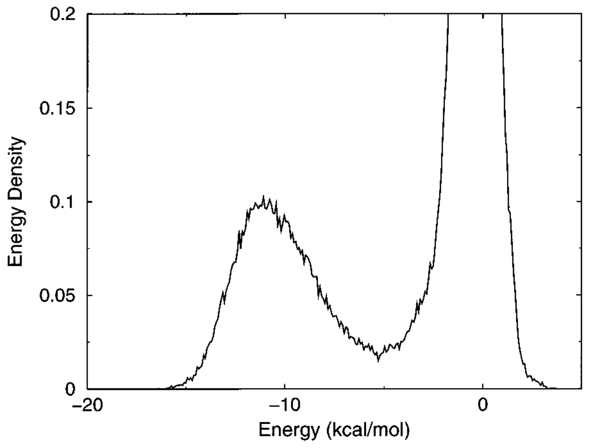

Figure 4. Energy distribution of CN⁻-water dimers.

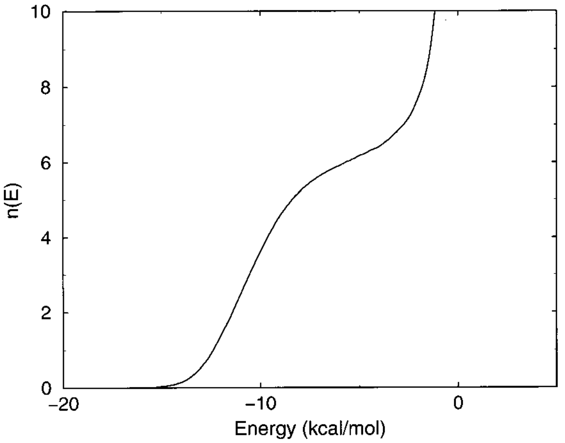

Figure 5. The solvation number estimated by integraton of Figure 4.

B. Dynamical Properties and Vibrational Energy Relaxation Time. The vibrational frequency of CN⁻ in SPC/F$_2$ water was first calculated by CMD. The vibrational frequency can be determined by calculating the C−N centroid distance-distance time correlation function $\langle d^{c}_{CN}(0)d^{c}_{CN}(t)\rangle$. In the CMD formalism, one then needs to use a Fourier relation to estimate the quantum correlation function, i.e.,

$$I(\omega) = (\hbar\beta\omega/2)\,(\coth(\hbar\beta\omega/2) + 1)Ic(\omega) \tag{7}$$

where $I^{c}(\omega)$ is Fourier transform of the centroid correlation function.

The calculated Fourier transform of the CN⁻ bond frequency is shown in Figure 6. The correlation function was calculated by running an equilibrium CMD simulation up to 2 ps with a single trajectory. Since this calculation was based on a single CN⁻ molecule, the statistical convergence is problematical, especially considering the short CMD run time due to its computation cost. Nevertheless, the experimental vibrational frequency is 2079 cm^{-1}, while the calculated frequency is about 2080 cm^{-1}. The calculated line width is about 50 cm^{-1}, while

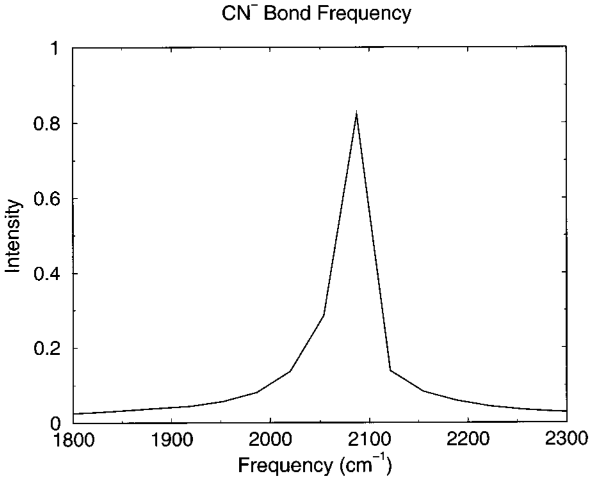

Figure 6. The Fourier transform of the CN^- vibration obtained by CMD simulation.

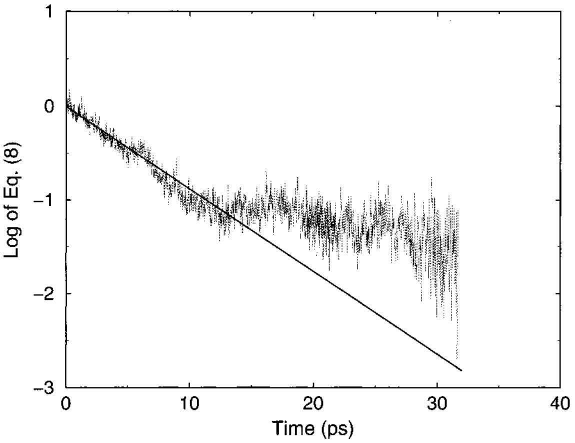

Figure 7. The energy dissipation of the CN^- ion as a function of time.

the experimental line result is about 18 cm^{-1}. This difference is likely to be primarily due to the limited run time of the CMD simulation.

From the CMD simulations with an initially excited CN^- stretch, one can estimate the vibrational relaxation rate from a decay law, i.e.,

$$\frac{\langle E_v(t)\rangle - \langle E_v(\infty)\rangle}{\langle E_v(0)\rangle - \langle E_v(\infty)\rangle} = \exp(-t/\tau_v) \qquad (8)$$

where the bracket denotes an average over the initial nonequilibrium distribution, and τ_v is the relaxation time.[12,44] Figure 7 is a semilog plot of eq 8, which shows the CN^- energy dissipation averaged over eleven independent CMD trajectories as a function of time. Even though there is significant statistical noise in the calculation due to the limited number of trajectories, one can see a general biexponential energy decay pattern. The largest relaxation time from this graph is about 15 ps, in reasonable agreement with the experimental result of 28 ± 7 ps.[8,16] Considering the degree to which reparametrization of the model has been avoided in this work, this level of agreement is quite encouraging.

There have been several studies regarding the possible relaxation mechanism for a polar solute (or ionic solute) in a polar solvent.[4,12,17,45,46] A recent analysis of Ladanyi and Stratt[45] has emphasized the importance of the initial solute−solvent configuration.[45] They suggested the possibility of an indirect role for electrostatic forces and the importance of short-range Lennard-Jones forces in the relaxation process. To gain some insight on the energy dissipation pathway into the solvent, we calculated the kinetic energy of the hydrogen atoms of the surrounding water molecules as a function of their distance from the CN^- ion for various time segments. The results are shown in Figure 8. Again, there is some statistical noise but one can recognize that the energy transferred to the water hydrogens next to CN^- is then rapidly transferred to the next solvation shell of water hydrogens within a short time. This result may suggest that the energy transfer at the early time controls the overall energy transfer rate, so that the initial configuration of the solute−solvent complex is indeed important, consistent with Ladanyi and Stratt's analysis.

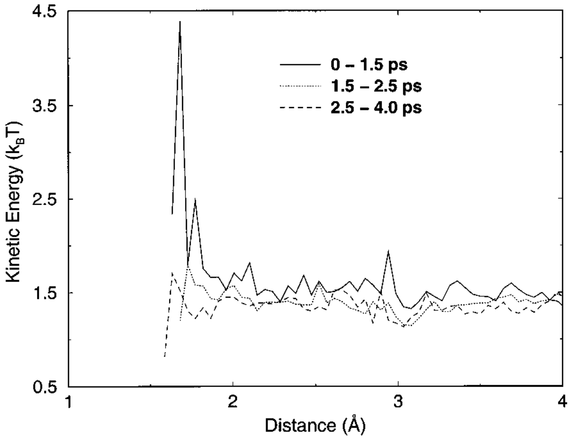

Figure 8. The kinetic energy of solvent water hydrogens as a function of distance between the CN^- ion and water for different time intervals. The distance is measured from the center of mass of the CN^- ion.

Concluding Remarks

In the paper, a CMD study of the virbrational energy relaxation rate of a CN^- ion in water has been carried out and found to give reasonable agreement with experiment. While vibrational relaxation is certainly sensitive to the simulation model, the present simulation was based on independently parametrized models to the maximum extent possible. One may seek to improve the model in the future by using condensed phase ab initio calculations to better characterize the CN^- intramolecular vibration and by considering other dynamical features such as vibrational dephasing. The detailed elaboration of the relaxation mechanism clearly require more extensive computational studies, and these will be the topic of future research.

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