Molecular Dynamics Study of the Solvation Structure of Aqueous NaCn Solution: Instantaneous and Quenched Solvation Structures

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MOLECULAR DYNAMICS STUDY OF THE SOLVATION STRUCTURE OF AQUEOUS NaCN SOLUTION: INSTANTANEOUS AND QUENCHED SOLVATION STRUCTURES

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Hydration structures of aqueous cyanide ion at room temperature and that quenched to local potential minima have been investigated by molecular dynamics calculations. Atomic distribution functions around the ion showed that a strong linear bonds are formed between the ion and water molecules in two regions, *i.e.*, in the C and N atom regions. This is clearly found for the quenched structure, whereas it is ambiguous for the instantaneous structure due to the thermal motion. Time evolution of equilibrium bond length and instantaneous transition frequency of C—N vibrational stretching mode were obtained along the constant-temperature trajectory from the local field on the C and N atoms by the solvent water molecules. The C—N vibrational frequency and the equilibrium bond length were evaluated at each quenched structures, too. These calculations are compared with the infrared and Raman spectroscopic measurements.

I. INTRODUCTION

Molecules in the solution have a variety of physical properties than in the isolated state. In this sense, it is interesting to investigate the solvation effect on the dynamics of the molecules in terms of the interaction between the solute and its surrounding molecules. Along with this, the hydration of CN⁻ ion, for example, has been actively studied both by experiments and molecular dynamics (MD) simulations in order to clarify molecular

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vibration in the condensed phase [1 – 5]. The purpose of the present study is to find stable solvation structures hidden in the thermal motion of the molecules and to analyze the vibrational dynamics of the ion. Here, two different simulations have been performed for aqueous cyanide ion. One is the ordinary MD calculation at 300 K, and the other is the calculation finding the potential local minimum configuration, i.e., quenching. The former solvation structures, which hereafter we designate as the 'instantaneous structures', are produced by Nosé-Hoover's constant-temperature and constant-volume technique. The latter, the 'quenched structures' are searched by setting the thermostat parameter to be 0 K [6].

   Time evolution of the first and second derivatives with respect to the vibrational degree of freedom of the intramolecular vibrational potential of the ion were calculated for the instantaneous structure taking account of the interaction with the solvent water molecules, from which the time evolution of equilibrium bond length and instantaneous transition frequency of the C—N vibration may be evaluated [7]. We also show that the radial distribution function for the quenched configuration are more highly ordered than that for the instantaneous structure. In the quenched configuration, H and O atoms of water molecules alternately surrounded the CN^- ion. The solvation effect on the vibration of the hydrated CN^- ion was found to be the blue shift relative to the isolated CN^-.

II. CALCULATION

The molecular dynamics calculation has been performed for the system composed of 254 H_2O molecules, one Na^+ ion, and one CN^- ion. Total of 256 molecules was accommodated in a cubic cell with a side length of 19.8 Å, which corresponds to 1 g/cm^3. The molecules were modeled as rigid rotors. TIP4P potential model by Jorgensen et al. [8] has been adopted for H_2O and the ionic model by Ferrario et al. [9] for Na^+ and CN^- ions. Lorentz – Berthelot combination rule has been assumed for different kinds of Lennard-Jones potential sites. The interaction has been truncated for sites beyond the distance of a half of the cell length applying the periodic boundary condition. The temperature was controlled using the Nosé – Hoover thermostat. The production run was executed for total of 1,000,000 steps with the time step of $\Delta t = 0.5$ fs. A hundred initial configurations were chosen every 10,000 step of the production run for quenching, i.e., every 5 ps. The quenching was performed setting the thermostat to be 0 K. The first 50,000 steps with $\Delta t = 0.5$ fs was followed by 10,000 steps run with the

time step of 0.1 fs to freeze the molecular motion down; the temperature was less than 10^{-3} K. During these procedures, the potential was smoothly cut off through 8.9 – 9.9 Å using a ordinary switching function [10] to obtain the potential minimum structures. The integration of the equation of motion was done by the predictor – corrector method.

III. RESULTS AND DISCUSSION

Atom-atom partial distribution functions are shown in Figure 1. First, we discuss on the hydration structure of CN^- ion based upon g_{HC} and g_{HN}. Peaks of the g_{HC} and g_{HN} are found to be much sharper for the quenched configuration than for the instantaneous configuration. The first peaks in g_{HC} and g_{HN}, which represent direct bondings of the hydrogen atom to the ion are higher than those found in g_{HO}, g_{HNa} and g_{HH}. This indicates strong interactions between the ion and the H atom in the first solvation shell. However, the most striking is that four peaks are clearly found in g_{HN} and three in g_{HC} for the quenched structure which is in contrast to the case of the instantaneous structure where these are merged into two broad peaks. Since the distance between the first peak of g_{HN} and g_{ON} and between those of g_{HC} and g_{OC}, 0.9 Å and 1.0 Å, respectively, are almost the same as the inter-molecular O—H bond length of 0.9 Å, it is clear that the water molecule forms a bond with the ion such that N—H—O and C—H—O are on the straight lines, $i.e.$, linear bonding. In fact, the distribution functions of H—N—O and H—C—O angles, presented in Figure 2, show sharp peaks at $\theta = 0$ for the quenched structure. The distributions for the instantaneous structure at the room temperature are broader due to the thermal motion than those for the quenched structure in this case, too. In order to investigate fine structure of the hydration in the quenched structure, two-dimensional distribution of H and O atoms around CN^- is plotted in Figure 3. The plot is presented separately for two kinds of the H atoms according to the distance from the ion. Here, H(1) represents the hydrogen atom that is closer to the center of mass of cyanide ion than its partner hydrogen in the same water molecule, H(2). Now, it is interesting to find that H and O atoms are alternately located around the ion. Stripes are observed when the figures are put upon each other. Further, we can see that there are two regions from which the water molecules make bonds with the ion. One is the hydration around C atom and the other is that around N atom. This clearly shows that four peaks found in g_{HN} come from two different hydrated water molecules. All peaks may easily be assigned as
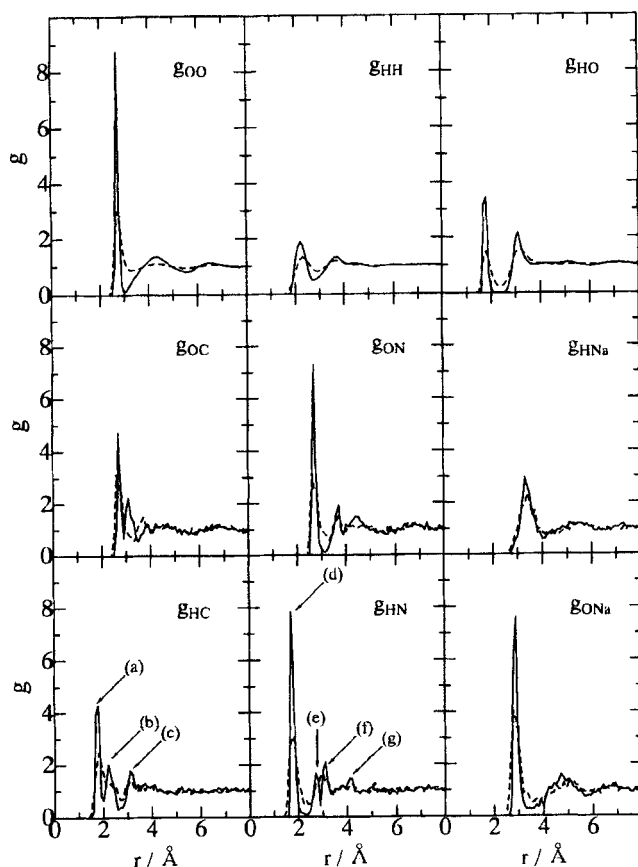
FIGURE 1   Radial distribution functions of the instantaneous structure (dashed line) and the quenched structure (solid line). The peaks of g_{HC} are assigned to (a) H(1) directly bonded to C, (b) H(2) indirectly bonded to C, and (c) H(1) directly bonded to N, respectively, and the peaks of g_{HN} are assigned to (d) H(1) directly bonded to N, (e) H(2) indirectly bonded to N, (f) H(1) directly bonded to C, and (g) H(2) indirectly bonded to C, respectively. For definition of H(1) and H(2), see the text.

shown in the figure. This is the same as the case of g_{HC} although the fourth peak is not clear. These two kinds of water molecules must make hydrogen bondings with each other to form a stable hydration shell. Location of the peak which appears in the radial distribution function for Na^+ in the quenched structure is similar to that in the instantaneous structure. Radial distribution function of g_{OO}, g_{HH}, and g_{HO} are also in correspondence with the previous work in pure water [6], and aqueous rare gas solutions [11].
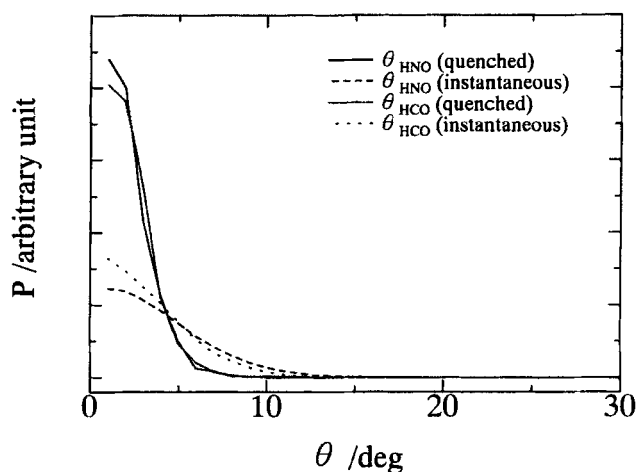
FIGURE 2   Distribution of H—N—O and H—C—O angle θ for water molecule in the first solvation shell of the CN⁻ ion for the instantaneous structure (dashed line) and the quenched structure (solid line). The first solvation shell was defined by the water molecules whose H(1) atoms are located within 2.6 Å from the center of mass of the cyanide ion. For definition of H(1), see the text.
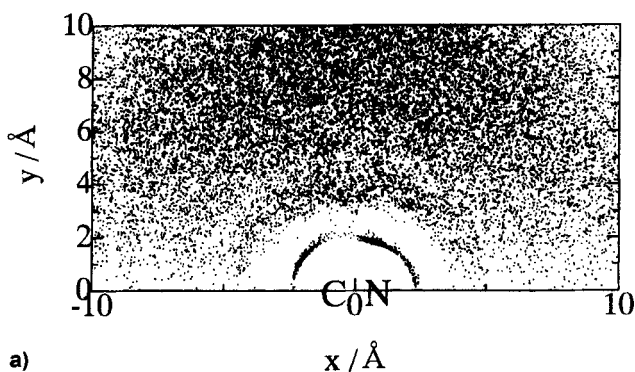

a)

FIGURE 3   Two-dimensional distribution of (a) H(1), (b) O, and (c) H(2) atoms around the CN⁻ ion. For definition of H(1) and H(2), see the text.

Instantaneous transition frequency ω and the equilibrium bond length x_e of C—N stretching local mode may be evaluated by the first and second derivatives of the total potential function with respect to the intramolecular vibrational degree of freedom x of the CN⁻ ion. If we describe the total potential function by

$$V = \frac{1}{2}\mu\omega_0^2 x^2 + \left.\frac{d(\Delta V)}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2(\Delta V)}{dx^2}\right|_{x=0} x^2, \qquad (1)$$
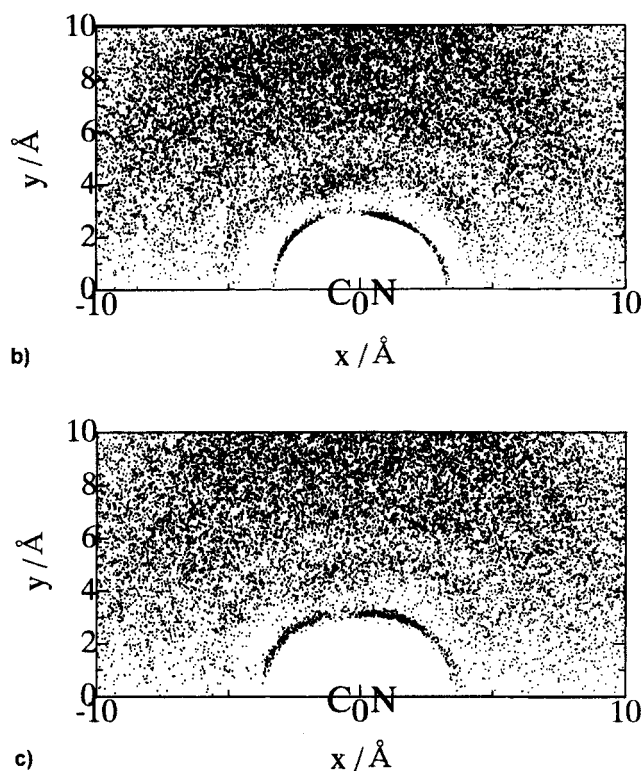
b)

c)

FIGURE 3   (Continued).

they may be expressed as

$$x_e = - \frac{d(\Delta V)/dx|_{x=0}}{\mu \omega_0^2 + d^2(\Delta V)/dx^2|_{x=0}} \tag{2}$$

and

$$\omega = \sqrt{\omega_0^2 + \frac{1}{\mu} \frac{d^2(\Delta V)}{dx^2}\bigg|_{x=0}} \tag{3}$$

where ΔV is the potential arising from the intermolecular solute–solvent interaction, μ is the reduced mass of CN^-, and ω_0 the vibrational frequency of the isolated CN^- determined by *ab-initio* calculation. The *ab-initio* calculation was done both for CN^- and CN^+ ions based upon B3LYP density functional theory using 6-31 + G^* basis set. Then calculated

frequency for CN^- was scaled by experimental frequency for CN^+ divided by the calculated value of CN^+ to give the frequency of the isolated CN^- $2067\,cm^{-1}$. Time evolution of ω and x_e are presented in Figures 4 and 5, respectively. The fluctuation is large. Further, the relaxation time is as short as about 50 fs. This may be caused by the rotational libration of hydrating water molecules. Distribution of ω and x_e are given in Figures 6 and 7, respectively, too. The width of the distribution of the bond length is
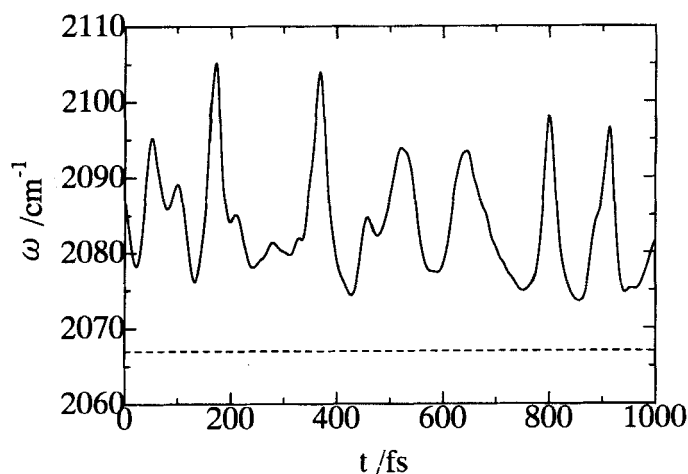

FIGURE 4   Time evolution of instantaneous transition frequency ω. Dashed line represents ω for the isolated ion, *i.e.*, ω_0.
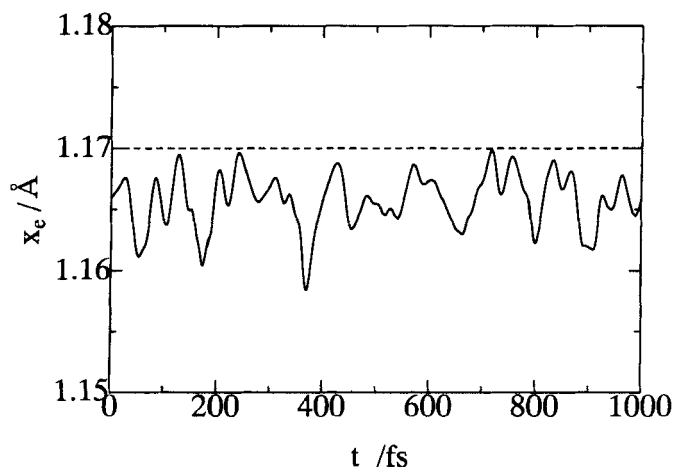

FIGURE 5   Time evolution of instantaneous equilibrium bond length x_e. Dashed line represents x_e for the isolated ion.
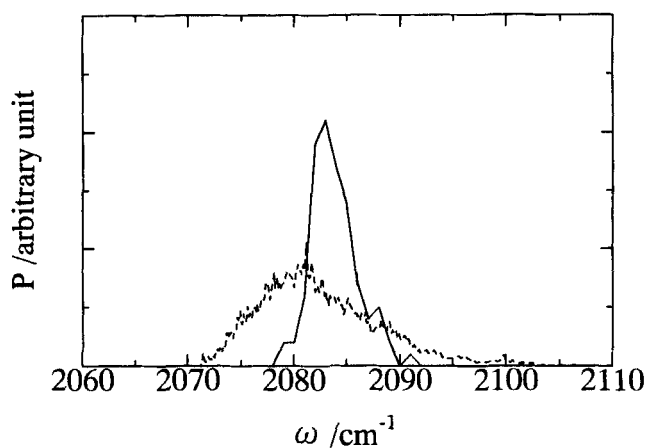
FIGURE 6   Distribution of instantaneous transition frequency for the instantaneous structure (dashed line) and the quenched structure (solid line).
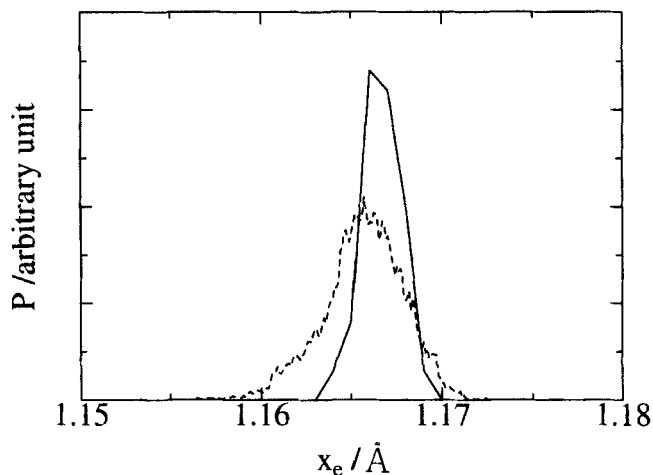

FIGURE 7   Distribution of equilibrium bond length x_e for the instantaneous structure (dashed line) and the quenched structure (solid line).

about $1/100$ Å, which is less than the dispersion of zero-point vibration of CN^-, $\sigma = 0.07$ Å. In the figure, a blue shift of about $15\,cm^{-1}$ relative to the isolated gas phase CN^-, $2067\,cm^{-1}$, is clearly found both for the instantaneous and quenched structure. With respect to the line width, Figure 6 represents the static limit of the inhomogeneous broadening in the vibrational spectrum, although the calculated width may be overestimated to some extent since the relaxation time of ω is short enough to cause a

motional narrowing. Standard deviation of the instantaneous frequency for the room temperature liquid is about $13\,\mathrm{cm}^{-1}$. This is about $6\,\mathrm{cm}^{-1}$ for the quenched structure. These are in moderate agreement with that obtained from infrared and Raman spectra, $9\,\mathrm{cm}^{-1}$ [1].

Acknowledgments

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