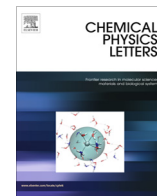




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Chemical Physics Letters

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Research paper

# Vibrational frequency fluctuations of ionic vibrational probe in water: Theoretical study with molecular dynamics simulation

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## ARTICLE INFO

## Article history:

Received 25 December 2016

In final form 4 March 2017

Available online xxxxx

## ABSTRACT

The vibrational dynamics of  $\text{SCN}^-$  in  $\text{H}_2\text{O}$  are theoretically investigated by molecular dynamics simulations. Based on the vibrational solvatochromism theory, we calculate the frequency–frequency time correlation function of the  $\text{SCN}^-$  anti-symmetric stretching mode, which is characterized by time constants of 0.13 and 1.41 ps. We find that the frequency fluctuation is almost determined by the electrostatic interaction from the water molecules in the first-hydration shell. The collective dynamics of the water molecules in the first-hydration shell is found to be similar to that of bulk water, though the hydrogen bond between the ion and water molecule is very strong.

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## 1. Introduction

In aqueous solutions, various dynamical properties of solute molecules are affected by surrounding water molecules through the hydrogen bond (HB) between solute and solvent molecules. Especially, transition energies of both the vibrational and electronic states and molecular structures of solutes fluctuate by thermal motions of water molecules, which eventually influence reactivities and pathways of chemical reactions in solutions and biological functions.

It has been well known that the vibrational frequency of a solute molecule is a good probe to investigate microscopic details of its surrounding environment. In aqueous solutions [1], structural changes of HB network cause the fluctuation in the vibrational frequency of a solute. Therefore, the vibrational frequency fluctuation of a solute provides insight into dynamics of solvents and solute–solvent interactions.

The vibrational frequency fluctuation of a solute is characterized by the frequency–frequency time correlation function (FFTCF;  $C_{\omega}(T)$ ) defined as:

$$C_{\omega}(T) \equiv \langle \Delta\omega(T)\Delta\omega(0) \rangle \quad (1)$$

where  $\Delta\omega(T)$  is the temporal frequency shift at time  $T$  and  $\langle \dots \rangle$  denotes the time average. Third-order nonlinear spectroscopy in

the infrared (IR) region such as three-pulse IR photon echo (IR3PE) and two-dimensional IR (2DIR) has been proven to be a powerful technique to quantify FFTCF in solution phases. So far, several groups including us have performed IR3PE and 2DIR measurements to investigate the vibrational frequency fluctuations of ionic probes such as  $\text{N}_3^-$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  in water [2–7]. In a series of the studies, we have found the following facts for FFTCF of ionic probe molecules in aqueous solutions. (i)  $C_{\omega}(T)$  can be expressed by a bi-exponential function with a constant term. The time constant of the fast decay component is shorter than 100 fs, falling into the fast modulation limit [8], and in the analysis of the 2DIR measurements we use a delta function for that component [9]. (ii) For the slow component, although the pre-exponential factor depends on the ionic probe molecule, the time constant is almost independent of the solute; the time constant is around 1.0 ps to 1.5 ps for any ionic vibrational probe. (iii) Fayer and Tokmakoff groups performed the 2DIR measurements for HOD diluted in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , respectively, and reported that these systems also show the vibrational frequency fluctuations on the time scale of about 1 ps [10,11]. In order to explain these observations we proposed that collective dynamics of the surrounding water molecules around the ion are important for the vibrational frequency fluctuations of the solute rather than the HB dynamics between the solute and solvent [2]. However, detailed mechanism for these observations has not been clarified yet at a molecular level.

Molecular dynamics (MD) simulation provides rich information on vibrational frequency fluctuation of a solute from the point of view of solvation dynamics and solute–solvent interactions. To date, theoretical calculations have been applied to estimate FFTCF for

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water [12] and simple ionic probe molecules in aqueous solutions [13–15]. In earlier theoretical work on  $\text{N}_3^-$  in  $\text{D}_2\text{O}$ , by using optimized quantum mechanical/molecular mechanical method, Li et al. successfully reproduced the long-time decay of FFTCF ( $T > 250$  fs) of the anti-symmetric stretching mode. They suggested that the slow decay component of FFTCF may result from collective dynamics of surrounding water molecules due to long range interactions because they found that the TCF of the HB number fluctuation decays slightly faster at long time than the FFTCF of  $\text{N}_3^-$  [13]. The slow decay component was originally interpreted as arising from the making and breaking of azide-water HBs [4]. In order to obtain more detailed understanding for the experimentally observed slow ( $\sim 1$  ps) frequency fluctuation of the ionic probe molecules in water, it is important to investigate the water dynamics around the solutes in detail.

In this work, we aim to establish a microscopic picture on the vibrational frequency fluctuation of ionic probe molecules in  $\text{H}_2\text{O}$  by classical MD simulations. One of the final goals is to explain why the picosecond component is insensitive to the ionic probe molecule. Especially, we theoretically investigate on the vibrational frequency fluctuations of  $\text{SCN}^-$  in  $\text{H}_2\text{O}$ , which we recently reported the 2DIR experiment [9]. Furthermore, to examine the water dynamics in the hydration shell of  $\text{SCN}^-$ , we evaluate the single and collective rotational dynamics and HB dynamics of the water molecules.

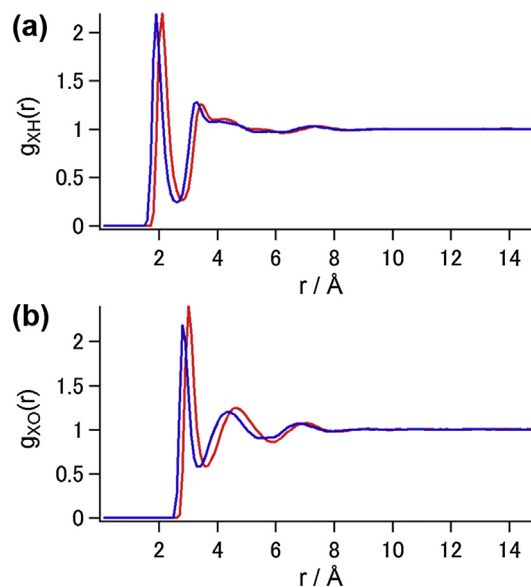
## 2. Computational details

Lee et al. developed the theoretical framework to calculate the SCN vibrational frequency shift of  $\text{SCN}^-$  induced by surrounding water molecules based on the vibrational solvatochromism theory [16]. We employed their method to calculate FFTCF in this work. In order to investigate the relationship between the SCN anti-symmetric stretching mode of the solutes and the local hydration environment, we optimized the geometry of the  $\text{SCN}^-$  molecule in gas phase and calculated normal mode at the B3LYP/6-311++G(3df,2pd) level by using the Gaussian 09 program [17]. Normal mode frequencies were scaled by multiplying a scaling factor of 0.9614 [18].

We performed classical MD simulations by using the PMEMD module of the AMBER 12 program [19]. The Lennard-Jones parameters and partial charges of  $\text{SCN}^-$  were determined by the ANTECHAMBER module and the RESP method [20] at the B3LYP/6-311++G(3df,2pd) level, respectively. The obtained partial charges of  $\text{SCN}^-$  are summarized in Table S1.  $\text{SCN}^-$  was solvated by 1387 TIP4P water molecules in a cubic box with the periodic boundary condition. The geometries of the solutes were spatially fixed at the coordinates optimized by B3LYP/6-311++G(3df,2pd) in the gas phase. For the neutralization, we added one  $\text{Na}^+$  cation [21] to the systems. Moreover, for comparison, we also conducted the MD simulations for pure  $\text{H}_2\text{O}$  system composed of 1118 TIP4P water molecules. The particle-mesh Ewald method was used for the long-range electrostatic interactions [22]. First, to determine the density of the system, an MD simulation was carried out for 500 ps with a time step of 0.5 fs under the  $NPT$  condition (1 atm, 293 K) with the Berendsen thermostat and barostat [23]. Next, to achieve the thermal equilibrium of the system, an additional constant temperature MD simulation was performed for 1 ns with a time step of 1 fs under the  $NVT$  condition (293 K,  $1.0 \text{ g/cm}^3$ ). Finally, a sampling MD simulation was performed for 6 ns, and all the MD trajectory data were used for further analyses.

## 3. Results and discussion

We first discuss the hydration structure around  $\text{SCN}^-$ . Fig. 1 displays the pair radial distribution functions (RDFs) between X atom



**Fig. 1.** Pair radial distribution functions between  $\text{SCN}^-$  terminal atoms and  $\text{H}_2\text{O}$  (a) hydrogen and (b) oxygen atoms. Red and blue lines are the results for the sulfur and nitrogen atoms of  $\text{SCN}^-$ , respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of  $\text{SCN}^-$  ( $X = \text{S}$  or  $\text{N}$ ) and the H and O atoms of  $\text{H}_2\text{O}$  (denoted as  $g_{\text{XH}}(r)$  and  $g_{\text{XO}}(r)$ , respectively). The first minimum and maximum are summarized in Table 1. As presented in Fig. 1(a),  $g_{\text{SH}}(r)$  and  $g_{\text{NH}}(r)$  show sharp first peaks at  $\sim 2.0$  Å, arising from the HBs between  $\text{SCN}^-$  and water molecules. To define HBs between the sulfur and nitrogen atoms of  $\text{SCN}^-$  and a water molecule (denoted as  $\text{H}_2\text{O} \cdots \text{SCN}^-$  and  $\text{SCN}^- \cdots \text{H}_2\text{O}$ , respectively), we adopted geometrical criteria with respect to the length  $r_{\text{X} \cdots \text{H}}$  and the angle  $\theta_{\text{X-OH}}$  of a HB. Based on the angle-resolved RDFs as a function of these coordinates (see Supplemental Information), we defined the precise HB criteria as follows:  $r_{\text{S} \cdots \text{H}} \leq 2.8$  Å and  $\theta_{\text{S-OH}} \leq 30^\circ$  for  $\text{H}_2\text{O} \cdots \text{SCN}^-$  and  $r_{\text{N} \cdots \text{H}} \leq 2.6$  Å and  $\theta_{\text{N-OH}} \leq 30^\circ$  for  $\text{SCN}^- \cdots \text{H}_2\text{O}$ .

Next, in order to investigate HB dynamics between  $\text{SCN}^-$  and surrounding water molecules, we calculated the HB correlation functions (HBCFs) for  $\text{H}_2\text{O} \cdots \text{SCN}^-$  and  $\text{SCN}^- \cdots \text{H}_2\text{O}$ . Here, the HBCF was defined as [24]:

$$C_{\text{HB}}(T) \equiv \frac{\langle H(T)H(0) \rangle}{\langle H(0)H(0) \rangle} \quad (2)$$

where  $H(T) = 1$  if a specific HB is formed at time  $T$ , and  $H(T) = 0$  otherwise. Moreover, regarding to a water-water HB (denoted as  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ ), we used the geometrical definition given by Luzar and Chandler [24]. Fig. 2 displays HBCFs for  $\text{SCN}^- \cdots \text{H}_2\text{O}$  and  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$  (see HBCF for  $\text{H}_2\text{O} \cdots \text{SCN}^-$  in Fig. S5). The HBCFs are expressed by a triple-exponential function and the corresponding time constants are listed in Table 1. In the present work, we characterize the HB lifetime by a single time constant  $\tau_{1/e}$  defined as:  $C_{\text{HB}}(\tau_{1/e}) = e^{-1} C_{\text{HB}}(0)$ . The time constants  $\tau_{1/e}$  of  $\text{H}_2\text{O} \cdots \text{SCN}^-$  and  $\text{SCN}^- \cdots \text{H}_2\text{O}$  are 7.71 ps and 8.39 ps, respectively, which are consistent with the previous results for the HB dynamics between  $\text{SCN}^-$  and a  $\text{D}_2\text{O}$  molecule reported by Czurluk et al. [25]. Moreover, the value of  $\tau_{1/e}$  of  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ , corresponding to the HB dynamics of bulk water, is 2.81 ps, which is also consistent with the previous result from the classical MD simulation for the TIP4P water system [26]. The fact that the time constants  $\tau_{1/e}$  for the  $\text{SCN}^-/\text{water}$  system are longer than that of the bulk water shows that the HB between  $\text{SCN}^-$  and a water molecule is stronger than that between water molecules. Here, it should be noted that HB dynamics depends on the polarizability of water molecules. Previously, by performing

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