Dynamical behavior of molecular partial charges implied by the far-infrared spectral profile of liquid water

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ABSTRACT

On the basis of the successful reproducibility of the band at $\sim$200 cm^{-1} (6 THz) in the far-infrared (terahertz) spectrum of liquid water by spectral simulations, and the intermolecular charge flux as the primary mechanism giving rise to the intensity of this band, the dynamical behavior of the molecular partial charges in liquid water implied by the presence of this band is examined theoretically. The molecular partial charges are typically within the range of ±0.03 e, with frequent short-time (<0.1 ps) excursions out of this range, and are rapidly modulated with a time constant of $\sim$0.12 ps. The long-time behavior of the time correlation function in the 0.3–10 ps region is related to the topological nature of the related molecular motions. The implication of the results on the use of time-domain terahertz spectroscopy to detect the properties of molecular motions in various environments is discussed.

1. Introduction

In our previous studies [1,2], theoretical simulations were carried out for the far-infrared (terahertz) spectrum of liquid water to clarify the main mechanism of the intensity generation. It was clarified that, for the intensity of the band at $\sim$200 cm^{-1} (6 THz), the intermolecular charge flux (modulation in the intermolecular transfer of electron density) induced by molecular translation motions plays a major role, and the intramolecular polarization effect contributes cooperatively to it. This intermolecular charge flux originates from the partial transfer of electron density from the hydrogen-bond acceptor to donor occurring upon hydrogen-bond formation [3–17]. Although its magnitude is not large ($\sim$0.01 e), it is rather long-ranged ($\sim$3 Å), so that it contributes significantly to the enhancement of the dipole moment induced by formation of an assembly of water molecules [7]. The extent of this intermolecular transfer of electron density depends rather strongly on the hydrogen-bond length, so that it gives rise to a significant modulation of the dipole moment (i.e., a dipole derivative) upon a molecular motion [1,2,18–25] that accompanies atomic displacements along hydrogen bonds.

The scheme of the relation among the directions of the molecular translations, intermolecular charge fluxes, and the dipole derivatives induced by them [25] are shown in Fig. 1. For example, upon the molecular translation along the *x* axis [which is the in-plane axis perpendicular to the C$_{2v}$ symmetry axis (*z*)] shown in Fig. 1(a), the hydrogen bond on the −*x* (left) side stretches, inducing a partial transfer of electron density from the hydrogen-bond donor to acceptor (i.e., a reduction of the extent of electron density transfer from the acceptor to donor), while the hydrogen bond on the +*x* (right) side shrinks, inducing a partial transfer of electron density from the hydrogen-bond acceptor to donor. As a result, these two charge fluxes contribute constructively to generate a large total dipole derivative in the +*x* direction. A similar explanation holds for the molecular translation along the *y* axis shown in Fig. 1(b).

What is particular to the molecular translation along the *z* axis is that, according to the scheme shown in Fig. 1(c), the dipole derivative induced on the +*z* and −*z* sides contribute destructively, but instead, a molecular partial charge is accumulated. Then, how large is the extent of this accumulation of molecular partial charge, and what is the time scale of its dynamical behavior? This type of accumulation of molecular partial charge is a marker of the asymmetry of the hydrogen-bond situations around tetrahedrally hydrogen-bonded water molecules, as well as the hydrogen-bond defect, and is discussed in relation to the structures of the interfaces of water with air or biomolecules [3,5]. Therefore, it is considered to be important to examine the magnitude and the time scale of the dynamical behavior of the molecular partial charges in liquid water implied by the appearance of the far-infrared (terahertz) band at $\sim$200 cm^{-1} (6 THz). The present study is devoted to this problem.

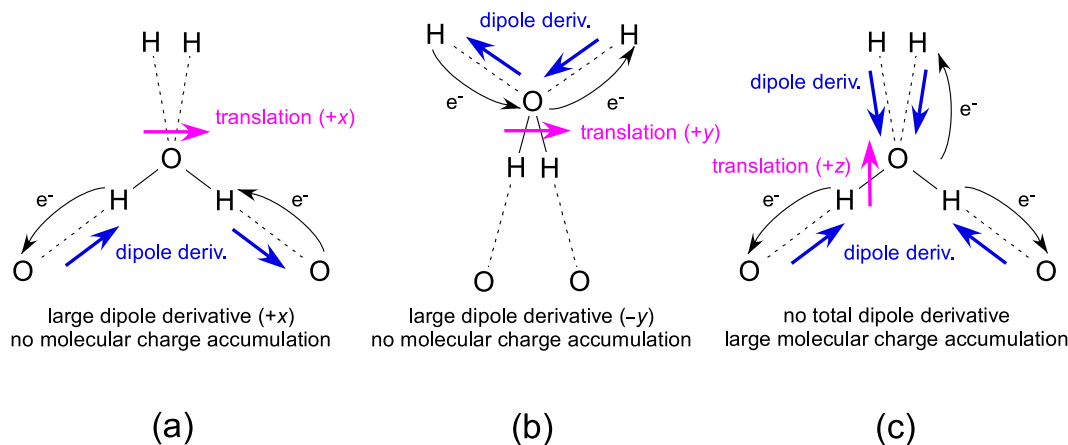*E-mail address:* torii.hajime@shizuoka.ac.jp

Fig. 1. Scheme of the intermolecular charge fluxes and the dipole derivatives induced by the molecular translations of hydrogen-bonded water molecules along the (a) x, (b) y, and (c) z molecular axes. (Adapted from Fig. 1 of Ref. [25].)

2. Computational procedure

The far-infrared spectrum of liquid water (extending partly to the mid-infrared region) was calculated in the same way as in the previous study [2], i.e., by combining the trajectories of water molecules obtained by classical molecular dynamics (MD) and the separately considered intensity generation mechanisms (explained below) to derive the total dipole moment $\mathbf{M}(t)$ of the system at time t, and by taking the Fourier transform of its time correlation function $C_M(t)$, expressed as [26]

$$C_M(t) = \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle \tag{1}$$

$$\alpha_{IR}(\omega) = \frac{4\pi\omega \tanh(\beta\hbar\omega/2)}{3\hbar n(\omega)cV} \int_{-\infty}^{\infty} dt \exp(i\omega t) C_M(t) \tag{2}$$

where $n(\omega)$ is the frequency dependent refractive index (but the frequency dependence was neglected in the present study), V is the volume of the system, and $\beta = 1/k_B T$ at temperature T. The classical MD simulation was carried out for the liquid system of 1024 molecules in a cubic cell by using the TIP4Q potential function [27] at 265 K (which is 25 K above the melting point of TIP4Q water [27]). The volume of the cubic cell was fixed by referring to the experimental density of liquid water at 298.15 K. The time step was set to 1 fs. The system was equilibrated for about 0.4 ns, and then the spectrum was calculated from the trajectories during 14 ns. The duration of the integration for the Fourier transform in Eq. (2) was set to 65.5 ps [65536 (=2^{16}) steps of 1 fs] to secure the frequency resolution of 0.5 cm^{-1}.

With regard to the intensity generation mechanisms, the following three mechanisms were taken into account: (i) simple rotations (librations) of molecular permanent dipoles (of 2.44 D, incorporated in the TIP4Q potential [27]), (ii) intermolecular charge fluxes, and (iii) intramolecular polarizations. As explained in Section 1, the intermolecular charge flux through each hydrogen bond (mechanism ii) originates from the partial transfer of electron population from the hydrogen-bond acceptor to donor ($\rho_{D\leftarrow A}$) occurring upon hydrogen-bond formation, the extent of which is dependent on the hydrogen-bond length ($r_{O\cdots H}$), expressed as [2]

$$\rho_{D\leftarrow A} = \frac{b_{icf}}{2}(r_{O\cdots H} - r_{thrsh})^2 \qquad (r_{O\cdots H} \leqslant r_{thrsh}) \tag{3}$$

where r_{thrsh} is the threshold hydrogen-bond length, and b_{icf} is the coefficient of this dependence. As a result of this partial transfer of electron population, a bond dipole is generated on each hydrogen bond, which was evaluated by placing the molecular partial charges derived from Eq. (3) on the oxygen atoms of the hydrogen-bonded

molecules [2]. The sum of the dipoles generated in this way constitute the contribution of the intermolecular charge fluxes to $\mathbf{M}(t)$. The values of the parameters b_{icf} (=0.0884 Å^{-2}) and r_{thrsh} (=2.374 Å) were adopted from the previous study [2], where the values of these parameters were obtained from the linear regression of the dependence of the electron population derivative (the effect of basis set superposition error being removed) on the hydrogen-bond distance. The contribution of the intramolecular polarizations induced by intermolecular electrostatic interactions (mechanism iii) was evaluated by placing the molecular polarizability tensor [of 1.16 Å^3, assumed isotropic [2], obtained at B3LYP/6-31+G(2df,p)] at the molecular center of mass of each molecule and by calculating the electric field from the partial charges of the interaction sites (incorporated in the TIP4Q potential [27]) of the surrounding molecules. No iterative evaluation procedure was adopted in the present study.

The calculations described above (both the classical MD simulation and the spectral calculation) were carried out with our original programs on Dell PowerEdge T620 (with Intel Xeon E5-2650v2) and other servers in our laboratory. The computation time needed to calculate the spectrum was equivalent to about 430 h of a single CPU core of E5-2650v2.

3. Results and discussion

The calculated spectrum in the 0–1200 cm^{-1} region and the contributions to it of the individual intensity generation mechanisms are shown in Fig. 2. It is seen that a strong band and a shoulder band appear at ~800 cm^{-1} and ~200 cm^{-1}, respectively, in reasonable agreement with the observed spectrum [28,29]. This agreement (to the same extent as the previous ab initio MD calculations [18–20]) underpins the reliability of the analyses of the molecular partial charges and other quantities described below. The intensity of the ~800 cm^{-1} band is dominated by the molecular libration term (mechanism i), and is partially canceled by the libration–polarization cross term (i.e., the cross term between mechanisms i and iii), while a significant part of the intensity of the ~200 cm^{-1} band originates from the intermolecular charge flux term (mechanism ii) and the related cross terms, and the intramolecular polarization term (mechanism iii) contributes constructively to it. Compared with the spectra calculated at the melting point +25 K with various potential functions [2], it is noticed that the spectrum calculated in the present study with the TIP4Q potential is similar to those calculated with the TIP4P [30] and related potential functions (TIP4P/Ice [31], TIP4P/2005 [32], and TIP4P/Ew [33]). This result supports the idea [34,35] that the