Dynamics of Resonant Energy Transfer in OH Vibrations of Liquid Water[†]

Mino Yang

Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea
E-mail: MinoYang@chungbuk.ac.kr

Energy transfer dynamics of excited vibrational energy of OH stretching bonds in liquid water is theoretically studied. With time-dependent vibrational Hamiltonian obtained from a mixed quantum/classical calculation, we construct a master equation describing the energy transfer dynamics. Survival probability predicted by the master equation is compared with numerically exact one and we found that incoherent picture of energy transfer is reasonably valid for long-time population dynamics. Within the incoherent picture, we assess the validity of independent pair approximation (IPA) often introduced in the theoretical models utilized in the analysis of experimental data. Our results support that the IPA is almost perfectly valid as applied for the vibrational energy transfer in liquid water. However, proper incorporation of radial and orientational correlations between two OH bonds is found to be critical for a theory to be quantitatively valid. Consequently, it is suggested that the Förster model should be generalized by including the effects of the pair correlations in order to be applied for vibrational energy transfer in liquid water.

Key Words : Water, Master equation, Energy transfer, OH stretching, Förster

Introduction

Vibrational spectroscopies are useful techniques to study the structure and dynamics of liquid water.[1] Probing OH stretching vibration of a water molecule is particularly informative since the frequency of the vibration is sensitive to its local environment such as hydrogen bonding. Isotope-substituted samples (for example HOD in D_2O solvent) have been studied by many researchers to understand the static and dynamic properties of local environment of an OH bond.[2-11] In such systems, the OH bond is safely assumed to be decoupled from all the other OD bonds in the system and the local structure and dynamics around the OH bond can be studied in the absence of any complication arising from molecular couplings.

However, in neat water, every OH bond is coupled to other OH bonds in the liquid to a certain extent. Due to the couplings, when an OH bond is excited, the excited energy is transferred to nearby OH bonds which are resonant with the excited OH bond. The energy transfer process is manifested in spectroscopic data such as IR and Raman line shapes,[7,12-16] vibrational pump-probe anisotropy,[14,17-19] and two-dimensional surface vibrational spectroscopy.[20] The manifestation of energy transfer hinders one extracting the information about local spectral dynamics directly from the analysis of experimental results. Therefore it may need to characterize the energy transfer process in prior to performing experimental studies to unravel the structure and dynamics of water.

Modeling the dynamics of energy transfer occurring over

many OH bonds in water is an elaborate task. First issue arises from the mechanism of molecular coupling. Recent studies introduced and calculated the potential and momentum couplings between two intramolecular OH bonds in a water molecule using a quantum chemical method.[16,21] The most reasonable approximation for the couplings between two intermolecular OH bonds might be based on the dipole-dipole coupling.[13,21] Since the intermolecular distance between two water molecules is, however, comparable with the molecular size, the validity of dipole-dipole coupling may be limited. Nonetheless, such mechanisms of molecular couplings have been shown to be successful in reasonably reproducing experimental absorption and Raman line shapes[13,16,21] and nonlinear vibrational spectroscopies such as pump-probe anisotropy decay and 2DIR line shapes.[19]

With the given mechanisms of molecular couplings, it still needs to be clarified whether the mechanism of vibrational energy transfer is coherent or incoherent. In the coherent mechanism, the population of excited vibrational energy is rapidly transferred before vibrational dephasing is completed while in the incoherent mechanism it is done only after vibrational dephasing time. From our previous studies using a mixed quantum/classical method for absorption and Raman line shapes[16] and anisotropy decay of pump-probe experiment,[22] it was discussed that coherent mechanism prevails in the time scale relevant to the line shapes while the incoherent mechanism is reasonably valid for the description of long-time population dynamics.

Another crucial issue in the theoretical modeling of energy transfer dynamics arises from many-body dynamics. As an OH bond called donor (D) is excited, nearby OH bonds called acceptors (A's) are competing to accept the energy. Furthermore, once one of them accepts the energy, the A

may return it back to the D or transfer it to another A. As such, excited vibrational energy evolves *via* various pathways and it is a very complicated problem to describe the time-dependence of the population of excited vibrational energy. The ensemble-averaged behavior of the population dynamics may be described by a master equation. Solving the master equation, one may find the average probability of excited energy remaining on the donor (survival probability) at a later time *t*, which conveniently represents the complicated dynamics of excited population undergoing the various pathways.

If (1) an initially excited molecule (D) were static, (2) the excited energy were transferred irreversibly from the D to A's, and (3) A's were statistically independent of each other, instead of solving the master equation, we could find the survival probability to be given by a much simpler way as a product of pair survival probabilities.[22-24] The pair survival probability for a particular pair of D and A reflects the dynamics of the pair only in the absence of all the other A's and can be easily obtained in appropriate forms. This generic approach has been popularly employed in the studies of diffusion-influenced reaction kinetics as in Smoluchowski equation approach.[24] The famous Förster model for energy transfer problem is also based on such assumptions and has been utilized to analyze many experimental data.[25] Therefore, if one wants to employ the pair-wise approaches, the three key assumptions validating the pair-wise approaches for the survival probability should be verified for the specific system of interest, neat water in the present paper.

In neat water, however, the validities of those assumptions are questionable because every OH dipole keeps incessantly moving (and therefore the static assumption seems to be invalid) and is virtually resonant to each other so that the energy can transfer reversibly from one to another. Also, energy acceptors around a single donor are closely packed to form a very structured hydrogen bonding network and therefore they should be strongly correlated (and therefore the independent-pair assumption seems to be invalid). In this paper, we will examine the validities of the assumptions mentioned above when they are applied to liquid water.

Recently, Skinner group developed a mixed quantum-mechanics/classical-mechanics (QM/CM) theory for vibrational dynamics in liquid water and successfully applied to interpret several experimental observations.[4,26] Assuming that the theory reasonably well represents the structure and dynamics of liquid water, we calculate the survival probability using the theory and compare it with approximate ones obtained by employing the various levels of approximations. From the comparative study, we will assess the applicability of pair-wise approaches for the vibrational energy transfer phenomena in water.

Theory

Hamiltonian and Mixed QM/CM Calculations. We describe the dynamics of OH vibrations of water using a mixed QM/CM method. Two local OH stretching modes of a water molecule (system) are treated quantum mechanically and the bending mode is frozen to the average conformation of its ground state. The hindered translational and librational degrees of freedom of the water molecules called the bath are approximately described by classical mechanics.

The transition Hamiltonian of the quantum mechanical OH bonds with two states coupled to the fluctuating baths is written as

$$H(t)=\sum_{i=1}^{N}|i\rangle\langle i|\hbar\omega_i(t) + \sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}|i\rangle\langle j|\hbar\omega_{ij}(t) \qquad (1)$$

where $\omega_i(t)$ is the fluctuating transition frequency of an OH bond *i* and $\omega_{ij}(t)$ is the coupling frequency between the two OH bonds *i* and *j*. $|i\rangle$ is the excited vibration state where the bond *i* is in its first excited state and the other OH bonds are in their ground states. The dependence of the transition frequency $\omega_i(t)$ on the baths are mapped to a single collective variable, the electric field along the O-H bond *i* which are formed by point charges of surrounding water molecules.[4,21,27,28]

When the bonds *i* and *j* are within the same molecule, they are coupled to each other *via* the momentum and potential coupling mechanisms and $\omega_{ij}(t)$ is the intramolecular coupling frequency whose time-dependence is mapped to the time-dependence of the electric fields along the two bonds.[21] When the bonds *i* and *j* are on different water molecules, they are assumed to be coupled *via* the dipole-dipole coupling mechanism. Then, if the two bonds are separated by a distance r_{ij}, their coupling Hamiltonian is written by

$$\hbar\omega_{ij}=\frac{\kappa_{ij}}{r_{ij}^3}m_i m_j \qquad (2)$$

where m_i is the transition dipole of *i*. Here, κ_{ij} defined by

$$\kappa_{ij}=\hat{u}_i\cdot\hat{u}_j-(\hat{u}_i\cdot\hat{r}_{ij})(\hat{u}_j\cdot\hat{r}_{ij}) \qquad (3)$$

is dependent on the relative orientation Ω_{ij} of the transition dipoles of *i* and *j* where $\hat{u}_i$ is the unit dipole vector of *i* and $\hat{r}_{ij}$ is the unit vector of relative displacement of *i* and *j*. Therefore, the time dependence of the intermolecular coupling frequency $\omega_{ij}(t)$ reflects temporal fluctuations of the distance r_{ij}, relative orientation Ω_{ij}, and also the transition dipoles. The bath-dependence of the transition dipole (non-Condon effects) is mapped to the electric field along the dipole.[21,29]

Once an OH bond is excited, the excited energy can transfer to another OH bond *via* the two coupling mechanisms. This energy transfer process competes with vibrational energy relaxation process in which the excited OH bond decays to its ground state by dissipating the energy to other classical modes.[30-33] We assume that the latter process can be described phenomenologically by life time decay and that the two competing processes occur independently. So hereafter we ignore the vibrational relaxation process.

To implement the mixed QM/CM method, MD simulation of water molecules was performed on 128 SPC/E water molecules in the NVE ensemble at 298 K. The integration

time step of the simulation was 1 *fs* and at every 10 *fs* all atomic coordinates were saved to generate a 2 *ns* atomic trajectory. From the trajectory, we determined the electric field along every individual dipole and then, by using the mapping relations, the time-dependent Hamiltonian Eq. (1). One thousand starting points were selected at every 1 *ps* from the trajectory and they represents different initial configurations of the baths.

Exact Population Dynamics and Numerical Integration of Schrödinger Equation (NISE). For each initial configuration, we randomly select an OH bond, which is excited at time zero. With the time-dependent transition Hamiltonian determined by the mixed QM/CM method, we calculate the dynamics of excited population in an exact way (within numerical accuracy) by numerically integrating the Schrödinger equation for the probability amplitude $F_{jk}(t)$ that the excitation energy created on a dipole k at time zero is found on a dipole j at time t:

$$\frac{d}{dt}F_{jk}(t) = -i\omega_j(t)F_{jk}(t) - i\sum_{\substack{l=1 \\ l\neq j}}^{N}\omega_{jl}(t)F_{lk}(t) \qquad (4)$$

along with the initial condition $F_{jk}(t=0)=\delta_{jk}$. The survival probability that the excitation energy still remains on the initially excited dipole is defined by

$$S_{\text{NISE}}(t) \equiv \langle |F_{kk}(t)|^2 \rangle \qquad (5)$$

where $\langle \cdots \rangle$ denotes the average over the equilibrium ensemble.

For comparative studies to be presented later, we also perform numerically exact calculations with a modified version of the Hamiltonian (NISE1). Here, for every initial configuration, the distance r_{ij} in the time-dependent *inter-molecular coupling frequency*, Eq. (2), is fixed to its initial value over the entire time propagation of the particular element of ensemble. Namely, in NISE1 the molecular distances in dipole-dipole coupling terms are assumed to be static while the other dynamical variables (rotations of dipoles and bath fluctuation inducing the non-Condon transition) are given the same as in NISE. Hereafter this will be referred to as "static approximation".

Incoherent Hopping Dynamics and Master Equation (ME). Dynamics of vibrational energy transfer is often understood in terms of incoherent hopping processes.[15,17] In hopping processes, excited vibrational energy of an OH bond (D) is transferred to another OH bond (A) after dephasing of the excited D is completed. In that case, the rate process between a particular pair of D and A is suitably described in terms of the rate constants associated with the pair.

In the same manner done for NISE, we randomly select an OH bond in a given configuration of water molecules generated by the MD simulation and the bond is excited at time zero. The other OH bonds in the equilibrium distribution can accept the excitation energy from the initially excited bond. Then, in the picture of hopping mechanism, we may construct a classical master equation along with

pair-wise rate constants, which are assumed to be time-independent within the time scale of energy transfer, is constructed as

$$\frac{d}{dt}P_{jk}(k) = -\sum_{\substack{l=1 \\ l\neq j}}^{N}k_{lj}P_{jk}(t) + \sum_{\substack{l=1 \\ l\neq j}}^{N}k_{jl}P_{lk}(t) \qquad (6)$$

where $P_{jk}(t=0)=\delta_{jk}$. Here $P_{jk}(t)$ is the conditional probability that the excitation energy created on an OH bond k at time zero is found on a bond j at time t and k_{lj} is the intramolecular (whose value is determined below) or intermolecular rate constant [Eq. (13)] depending on whether or not the bonds l and j are in the same molecule. The master equation is numerically solved for various initial configurations of molecular coordinates and the survival probability is obtained by the following average

$$S_{\text{NE}}(t) \equiv \langle P_{kk}(t) \rangle \qquad (7)$$

and its solution gives us the full information on the incoherent energy transfer dynamics.

The pair-wise rate constant for two OH bonds n and m are given by the perturbation theory as[34,35]

$$k_{nm} = 2\text{Re}\int_0^\infty dt \left\langle \omega_{nm}(t)\omega_{mn}e^{i\int_0^t(\omega_n(\tau)-\omega_m(\tau))d\tau} \right\rangle \qquad (8)$$

where the forward and backward rate constants are identical in the classical bath limit. For an intramolecular pair of D and A, the time-dependent transition and coupling frequencies are calculated, in the framework of the mixed QM/CM method, from the electric field generated by the MD simulation as discussed above and the resulting *intra*molecular rate constant obtained by taking the time-integration of Eq. (8) is obtained as $k_{\text{intra}}^{-1} = 0.48\, ps.$[22]

For an intermolecular pair of D and A, one may want to describe the intermolecular vibrational energy transfer in terms of the popular rate equation approach, Förster resonance energy transfer (FRET). Here we briefly review the model. The model assumes that the relative distance r and orientation Ω of two target chromophores are *static* over the dephasing time scale of excited chromophores. Then, inserting the dipole-dipole coupling Hamiltonian Eq. (2) into the expression of rate constant Eq. (8), we obtain the distance- and orientation-dependent rate constant as

$$k_{\text{inter}}(r,\Omega) = \frac{2\kappa^2}{\hbar^2 r^6}\text{Re}\int_0^\infty dt \left\langle m_D(t)m_A(t)m_D m_A e^{i\int_0^t(\omega_D(\tau)-\omega_A(\tau))d\tau} \right\rangle_{r,\Omega}, \qquad (9)$$

Usually the fluctuations in transition energy and transition dipole are assumed to be independent of chromophores. In that case, the rate constant simplifies to

$$k_{\text{inter}}(r,\Omega) = \frac{3}{2}\frac{\kappa^2}{\tau_0}\left(\frac{r_0}{r}\right)^6 \qquad (10)$$

where τ_0 is the natural lifetime of the excited state and r_0 is the so-called Förster radius which reflects the fluctuations in

transition energies and transition dipoles of the independent D and A:

$$r_0^6 \equiv \frac{4\tau_0}{3\hbar^2} \mathrm{Re} \int_0^\infty dt \left\langle m_D(t) m_D e^{i\int_0^t \omega_D(\tau) d\tau} \right\rangle \left\langle m_A(t) m_A e^{-i\int_0^t \omega_A(\tau) d\tau} \right\rangle. \quad (11)$$

Equation using the trajectory of the mixed QM/CM method yields $r_0 = 2.07$ Å when $\tau_0 = 0.74\ ps$.[22]

When the chromophores rotate more rapidly than energy transfer occurs, one can take the average of orientation factor κ^2 over a distribution of Ω. For a random distribution of relative orientations, it is equal to 2/3 and the orientation-averaged rate constant is

$$k_{\mathrm{inter}}(r) = \frac{1}{\tau_0} \left(\frac{r_0}{r}\right)^6. \quad (12)$$

However, we found that, from the mixed QM/CM calculation for liquid water, the orientation factor is strongly correlated with the separation distance r of two OH dipoles.[22] Therefore, the average of orientation factor should be defined to be r-dependent so that it needs to be taken over a subset of dipole pairs with the same separation distance. In this case, the distance-dependent rate constant becomes

$$k_{\mathrm{inter}}(r) = \frac{3}{2} \frac{\langle \kappa^2 \rangle_r}{\tau_0} \left(\frac{r_0}{r}\right)^6 \quad (13)$$

where $\langle \kappa^2 \rangle_r$ is the ensemble average of orientation factors of two intermolecular OH dipoles separated by a distance r.

Results and Discussion

Pair-Wise Dynamics (NISE *vs* ME). We consider the pair-wise energy transfer dynamics of two interacting OH bonds. In each starting point of the MD trajectory, we select two OH bonds. Their couplings to the other OH bonds are made to be turned off while the coupling between the two bonds remains on. One of them (D) is excited at time zero and then, as time goes on, the excited energy may remain on D or transfer to the other OH bond (A). The survival probability that the excited energy remains at time t on the initially excited D is calculated by NISE, Eq. (5), and is denoted by $S_{\mathrm{NISE}}^0(t)$. On the while, in the framework of ME, since the excited energy stays on either D or A, the survival probability denoted by $S_{\mathrm{ME}}^0(t)$ is given by

$$S_{\mathrm{ME}}^0(t) = \frac{1}{2}(1 + e^{-2kt}) \quad (14)$$

where k is, depending on the type of the selected OH bonds, either time-independent intramolecular $k_{\mathrm{intra}} = 1/(0.48\ ps)$ determined above or intermolecular rate constant with the static approximation. Here the superscript ^{0} denotes the pair-wise dynamics.

We first consider pair-wise intramolecular energy transfer and the accuracy of ME is assessed by comparing $S_{\mathrm{ME}}^0(t)$ with $S_{\mathrm{NISE}}^0(t)$ for the case. The two survival probabilities are displayed in Figure 1. The figure illustrates that the non-exponential behavior of the exact survival probability (NISE)
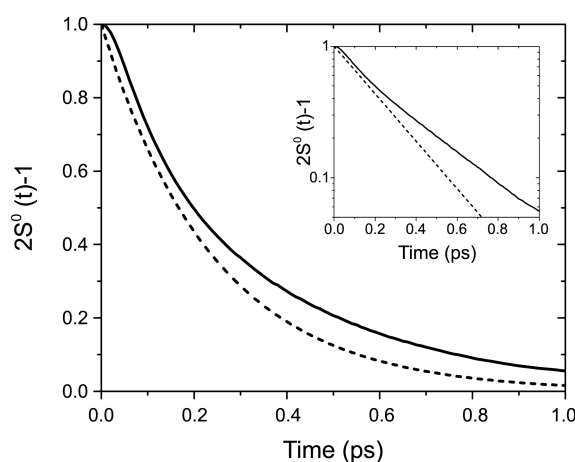
Figure 1. Survival probabilities of intramolecular pair predicted by NISE (solid) and ME (dashed). The time scale for ME is obtained as $k_{\mathrm{intra}}^{-1} = 0.48\ ps$ by the perturbation theory. The inset is the semi-log plot.

is apparent at very short times and the further decay prevailing after about 0.2 *ps* is slower than the prediction of ME. Even so, ME for the intramolecular energy transfer is reasonably good in reproducing the overall decay of the exact pair-wise survival probability but with lower amplitudes.

Similar approach is applied to examine the accuracy of ME for the dynamics of pair-wise intermolecular energy transfer. In ME for this case, the static approximation is invoked; the distance between two intermolecular dipoles is fixed to its initial value over the relaxation time of the survival probability. The survival probabilities of NISE, NISE1, and ME with the Förster intermolecular rate constant Eq. (13) are calculated for two cases of initial separation between the two intermolecular dipoles, $r = 2.4$ Å (the nearest neighbor) and $r = 3.2$ Å (the second nearest neighbor) in Figure 2. The pair-wise energy transfer between a target dipole and its nearest neighbor should be dominant in pure liquid water where the target dipole is coupled to every neighboring intermolecular dipole while that between a
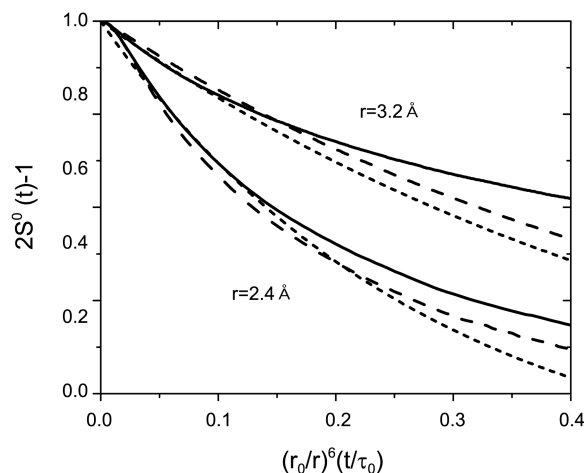
Figure 2. Survival probability of a pair of intermolecular OH dipoles. NISE (solid), NISE1(dashed) and ME (short-dashed).

target dipole and its second nearest neighbor may be responsible more for dilute mixture where the concentration of intermolecularly coupled OH dipoles is low.

We note the effect of water mobility revealed in difference between NISE and NISE1 displayed in Figure 2. The nearest neighbor around a target dipole diffuses away as time passes and, since the dipole-dipole interaction is highly dependent on separation distance, the rate of pair-wise energy transfer between them gets slow down with time. Therefore the static approximation employed in NISE1 and in ME should cause in this case the errors to make the pair survival probability of the target dipole decay faster. On the while, the second nearest neighbor transiently diffuses towards the target dipole and then eventually gets separated away. In this case, the pair-wise energy transfer between them is transiently assisted and then hindered by spatial diffusion. Therefore the static approximation in this case should erroneously result in the pair survival probability of the target dipole decaying transiently slower and then faster as displayed in Figure 2. Despite the small errors caused by the static approximation, the predictions of ME are reasonably good in early times of relaxation. Therefore one may be based on the incoherent picture to analyze the population decay of excited vibrations in water for short times (although its coherent nature is apparent).

Many-Body Dynamics (NISE *vs* ME). Finding ME to be reasonably valid for the description of short time dynamics of pair-wise intramolecular and intermolecular energy transfer in water, one may want to extend the approach to fully coupled OH bonds in liquid water. We consider two water liquids, a mixture of 15% H_2O in D_2O and pure H_2O liquid. For the mixture, 15% of the OH bonds of SPC/E water molecules were randomly selected and they were assigned as OH bonds and the rest as OD bonds. Then, the couplings between OH and OD bonds were turned off due to their large energy gap.

The survival probabilities for fully coupled OH bonds in the two water liquids are calculated by NISE and NISE1 [Eq. (5)] and ME [Eq. (7)] and they are presented in Figure 3. Comparing the predictions of NISE1 and NISE for the mixture, one can see that the static approximation is valid at short times but leads to slower decay of survival probability at long times; the excitation energies created on the OH bonds remote from other OH bonds survive there for longer times and their transfer to other OH bonds in equilibrium distribution are assisted by the molecular diffusion. Therefore this error should be amplified in dilute mixtures and the models developed upon the static approximation should overestimate vibrational couplings. In the pure liquid, the static approximation seems reasonable since energy transfer occurs more rapidly in non-exponential manner to the nearest neighbors of the excited bond than molecular diffusion occurs and the approximation is good enough over the entire time scale of relaxation in pure water.

The flaw of the static models, slow decay at long times, is also found in the prediction of ME for the dilute mixture as displayed in Figure 3. This implies that analyses of experi-
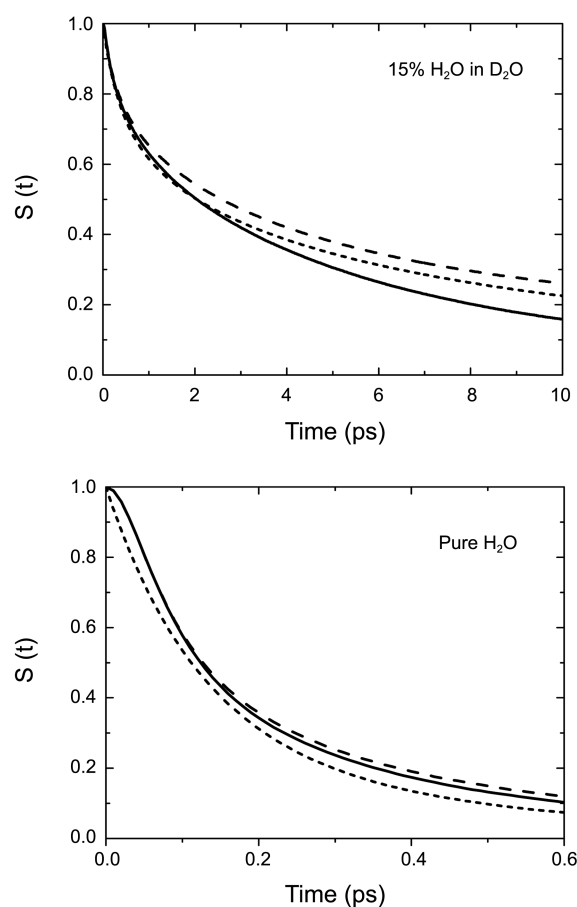
Figure 3. Comparison of survival probabilities calculated by NISE (solid), NISE1(dashed) and ME (short-dashed) for fully coupled OH dipoles in two concentrations of H_2O. In ME, the pair-wise rate constants were calculated under the static approximation for interchromophore distances as in Förster model [as mentioned in Eq. (9)].

mental data by any model based on ME with the static approximation should be made with care for dilute mixtures. In the pure liquid, the non-exponential decay occurring at short times is not able to be reproduced by ME and consequently the overall amplitude of survival probability calculated by ME is lower than those of NISE and NISE1. In conclusion, (1) the static approximation invoked in NISE1 and Förster model substantially slows down the decay of survival probability of excited OH vibrations in dilute mixture of water but works well in dense concentration like pure water except at very short times. (2) If the molecular mobility is incorporated properly, ME with the pair-wise rate constants determined by the perturbation theory is good enough to describe exact energy transfer dynamics except for the short time behavior in a dense concentration.

Independent Pair Approximation (IPA). Instead of solving the master equation numerically, the survival probability within the hopping model can be derived to a simpler form, as discussed in Introduction, by considering the behavior of independent D-A pairs. Assuming that D is static and that the pair-wise survival probabilities of all D-A pairs decay independently of each other,[23,24] we may obtain

the survival probability by multiplying the pair-wise survival probabilities for all intramolecular and intermolecular D-A pairs:

$$S_{IP}(t)=\{\alpha S_{ME,intra}^0(t)+(1-\alpha)\} \times$$

$$\int_V \cdots \int_V S_{ME,inter}^0(r_1;t) \cdots S_{ME,inter}^0(r_N;t)W_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)d\mathbf{r}_1 \cdots d\mathbf{r}_N \quad (15)$$

where N is the number of A bonds in the system of volume V and $W_N(\mathbf{r}_1,..,\mathbf{r}_N)$ is the N-particle probability density of finding the intermolecular A bond 1 at $\mathbf{r}_1$, 2 at $\mathbf{r}_2$ and so on with the D bond placed at the origin of the coordinate system. The curly bracket term describes the decay pathway *via* intramolecular energy transfer and the multiple integration term is responsible for the decay pathway *via* intermolecular energy transfer. The first term in the curly bracket of Eq. (15) is of the case that the D bond sees another A bond on the same molecule (HOH) with the probability α (in pure water $\alpha = 1$ and in the isotope mixture $\alpha < 1$) and the second term is the survival probability of the D bond when the intramolecular energy transfer is not possible in HOD molecules.

The pair-wise survival probabilities $S_{ME,intra}^0(t)$ and $S_{ME,inter}^0(r;t)$ given by Eq. (14) in the hopping model are re-expressed, respectively, as

$$1-S_{ME,intra}^0(t)=\frac{1}{\lambda}(1-e^{-\lambda k_{intra}t}) \quad (16)$$

$$1-S_{ME,inter}^0(r;t)=\frac{1}{\lambda}(1-e^{-\lambda k_{inter}(r)t}) \quad (17)$$

where the intermolecular rate constants are assumed to be given by Eq. (13). Here we generalized both expressions to express the pair-wise survival probabilities for the case that the back transfer of the excited energy from A's to initially excited D is neglected (irreversible energy transfer from D to A's). In this case, $\lambda = 1$ and otherwise $\lambda = 2$.

Equation (15) should be exact within the framework of ME when the static D transfers its energy *irreversibly* to A and bath variables associated with different pairs of D and A are uncorrelated. When back transfer from A to D occurs, which is the case of OH bonds in liquid water, the approximation of independent relaxation of pair-wise survival probability should be no longer valid since the excited energy jumping around on a particular D-A pair can flow into another D-A pair and the energy transfer dynamics of the two pairs should be correlated. In order to check whether or not such a challenging many-particle effect caused by the back transfer refrains from separating the energy transfer dynamics into pair-wise dynamics, we will see the result of Eq. (15) in comparison with the result of the master equation (6) below. Equation (15) is evaluated by taking the average over the MD trajectory representing the equilibrium distribution.

In addition to the factorization with respect to the dynamical effects, the many-body equilibrium distribution function also may be factorized. If we assume that the N-particle probability density W_N is approximated as a product of N spherical symmetric two-particle probability density functions:

$$W_N(\mathbf{r}_1,..,\mathbf{r}_N) \approx \frac{g(r_1)}{V} \cdots \frac{g(r_N)}{V} \quad (18)$$

where $g(r)$ is the pair correlation function of intermolecular OH dipoles, we can simplify the part of intermolecular pathway of Eq. (15) in the thermodynamic limit where $N,V \rightarrow \infty$ and $N/V = \rho,$[22,23,25] and we get the survival probability within the IPA as

$$S_{IP}(t) \approx f(t)\exp\left[-\frac{4\pi\rho}{\lambda}\int_0^\infty \{1-e^{-\lambda k_{inter}(r)t}\}g(r)r^2dr\right] \quad (19)$$

where

$$f(t) \equiv 1-\frac{\alpha}{\lambda}(1-e^{-\lambda k_{intra}t}).$$

By the pair-wise approximation for the equilibrium distribution function, Eq. (18), the interactions between the intermolecular A dipoles are approximately taken into account only in the structure of pair correlation function between D and A. In the following, the effects of this equilibrium structure in pair correlation function are examined.

Förster Model. Equation (19) is further simplified if we completely ignore radial and orientation correlations between D and A dipoles in equilibrium. This limiting case corresponds to the well-known Förster model. In this case, the intermolecular rate constant given by Eq. (12) and the uniform pair correlation function $g(r)=1$ are placed in Eq. (19) and then we can reduce Eq. (19) along with Eqs. (16) and (17) to the analytic form:

$$S_F(t)=f(t)\exp\left(-\frac{4\pi r_0^3}{3}\rho\sqrt{\frac{\pi t}{\lambda \tau_0}}\right) \quad (20)$$

where the subscript F denotes Förster model.

Up to now, we presented three levels of IPA within the hopping model [Eqs. (15), (19), and (20)] and the validities of them are assessed by comparing their predictions of survival probability with that of "exact" ME, Eq. (7), calculated by solving the master equation, Eq. (6). Figure 4 illustrates that the IPA in both dynamical and static aspects, interestingly, works excellently for the description of OH vibration energy transfer in liquid water regardless of OH concentration. Both factorizations in dynamical and static many-body functions yield the survival probabilities almost indistinguishable to that of the "exact" master equation. Therefore we conclude that IPA itself is very successful at least for the description of OH vibration energy transfer in water if and only if the binary equilibrium structures in the pair correlation function and in the orientation factor of the intermolecular energy transfer rate constant are appropriately incorporated.

However, the final approximation (Förster model) ignoring any structure in the equilibrium pair distribution such as excluded volume of dipoles turns out to result in large errors in the survival probability. The error increases with OH concentration. In this approximation, D and A dipoles can
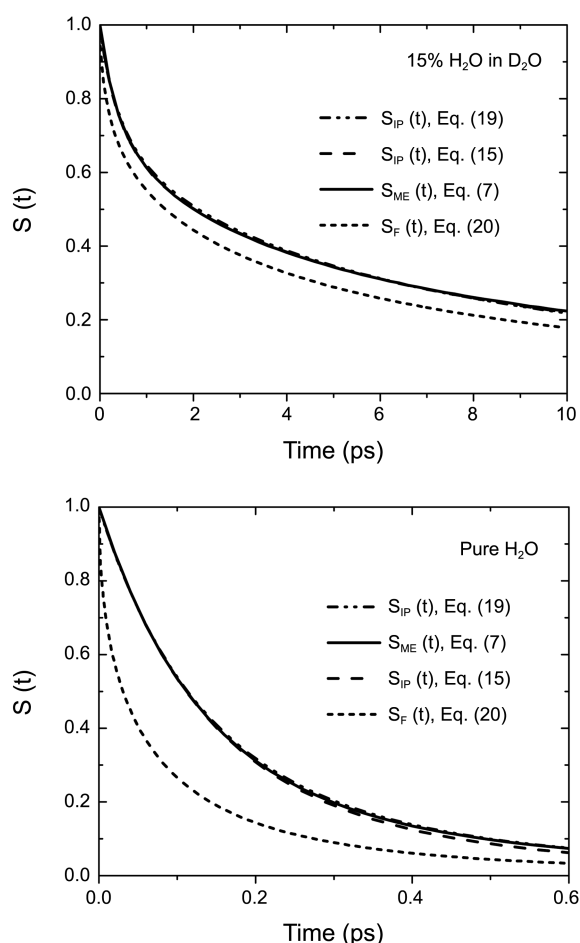
Figure 4. Comparison of three levels of independent pair approximation with the "exact" master equation. The predictions of the two of IPA's are almost superimposed with that of master equation.

approach up to very close distances going beyond the excluded volume of D-A pairs. The unphysical situation leads to very rapid decay of the survival probability at early times resulting from the energy transfer from D to A's which are located in the excluded volume and have unrealistically large pair-wise rate constants.

Conclusions

The dynamics of vibrational energy of OH bonds in liquid water has been characterized by using a mixed QM/CM calculation method. The survival probability calculated by a master equation with time-independent rate constants reasonably well coincides with that exactly calculated by solving the Schrödinger equation. Based on the observation, although coherent nature of energy transfer was shown to be manifested in absorption and Raman line shapes of liquid water,[16] it has been shown, in this paper, that incoherent picture can be reasonably correct for the description of the population dynamics of excited OH bonds except for very early time dynamics where non-exponential behavior prevails.

The static approximation in which the inter-chromophore distances in the molecular couplings are assumed to be fixed

is shown to be valid for short-time dynamics but as time goes on the mobility of molecules affects the long-time population dynamics. Therefore, the static approximation seems to be reasonably valid for pure water where the short-time dynamics of energy transfer is dominant while erroneously predicts slower decay in the survival probability of dilute mixtures where the long-time dynamics of energy transfer is dominant.

Independent-pair approximation in the hopping model turns out to be surprisingly accurate even for liquid water where the chromophores are not static, energy transfer occurs reversibly, and the equilibrium distribution of chromophores is highly structured. Therefore, one may safely employ any binary models if and only if the equilibrium binary distributions of molecules are properly incorporated in it. However, the most serious error is brought when one ignores the equilibrium structure of pair correlation function, particularly the excluded volume of two adjacent OH dipoles. Therefore, we suggest that the Förster model should be generalized to incorporate the influences of excluded volume.

References

1. Bakker, H. J.; Skinner, J. L. *Chem. Rev.* **2010**, *110*(3), 1498.
2. Moller, K. B.; Rey, R.; Hynes, J. T. *J. Phys. Chem. A* **2004**, *108*(7), 1275.
3. Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2002**, *117*(19), 8847.
4. Auer, B.; Kumar, R.; Schmidt, J. R.; Skinner, J. L. *P. Natl. Acad. Sci. USA* **2007**, *104*, 14215.
5. Auer, B. M.; Skinner, J. L. *J. Chem. Phys.* **2008**, *129*, 214705.
6. Auer, B. M.; Skinner, J. L. *Chem. Phys. Lett.* **2009**, *470*, 13.
7. Smith, J. D.; Cappa, C. D.; Wilson, K. R.; Cohen, R. C.; Geissler, P. L.; Saykally, R. J. *P. Natl. Acad. Sci. USA* **2005**, *102*, 14171.
8. Fecko, C. J.; Eaves, J. D.; Loparo, J. J.; Tokmakoff, A.; Geissler, P. L. *Science* **2003**, *301*(5640), 1698.
9. Asbury, J. B.; Steinel, T.; Stromberg, C.; Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L.; Fayer, M. D. *J. Phys. Chem. A* **2004**, *108*(7), 1107.
10. Asbury, J. B.; Steinel, T.; Kwak, K.; Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L.; Fayer, M. D. *J. Chem. Phys.* **2004**, *121*(24), 12431.
11. Fecko, C. J.; Loparo, J. J.; Roberts, S. T.; Tokmakoff, A. *J. Chem. Phys.* **2005**, *122*, 054506.
12. Loparo, J. J.; Roberts, S. T.; Nicodemus, R. A.; Tokmakoff, A. *Chem. Phys.* **2007**, *341*(1-3), 218.
13. Torii, H. *J. Phys. Chem. A* **2006**, *110*, 9469.
14. Paarmann, A.; Hayashi, T.; Mukamel, S.; Miller, R. J. D. *J. Chem. Phys.* **2008**, *128*, 191103.
15. Piatkowski, L.; Eisenthal, K. B.; Bakker, H. J. *Phys. Chem. Chem.*

Phys. **2009**, *11*, 9033.

16. Yang, M.; Skinner, J. L. *Phys. Chem. Chem. Phys.* **2010**, *12*(4), 982.
17. Woutersen, S.; Bakker, H. J. *Nature* **1999**, *402*, 507.
18. Kraemer, D.; Cowan, M. L.; Paarmann, A.; Huse, N.; Nibbering, E. T. J.; Elsaesser, T.; Miller, R. J. D. *P. Natl. Acad. Sci. USA* **2008**, *105*, 437.
19. Jansen, T. L. C.; Auer, B. M.; Yang, M.; Skinner, J. L. *J. Chem. Phys.* **2010**, *132*(22), 224503.
20. Zhang, Z.; Piatkowski, L.; Bakker, H. J.; Bonn, M. *Nat Chem* **2011**, *3*(11), 888.
21. Auer, B. M.; Skinner, J. L. *J. Chem. Phys.* **2008**, *128*, 224511.
22. Yang, M.; Li, F.; Skinner, J. L. *J. Chem. Phys.* **2011**, *135*(16), 164505.
23. Tachiya, M. *Radiation Physics and Chemistry* **1983**, *21*, 167.
24. Szabo, A. *J. Phys. Chem.* **1989**, *93*, 6929.
25. Baumann, J.; Fayer, M. D. *J. Chem. Phys.* **1986**, *85*, 4087.

26. Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2004**, *120*, 8107.
27. Skinner, J. L.; Auer, B.; Lin, Y. S. *Adv. Chem. Phys.* **2009**, *142*, 59.
28. Lin, Y. S.; Auer, B.; Skinner, J. L. *J. Chem. Phys.* **2009**, *131*, 144511.
29. Schmidt, J. R.; Corcelli, S. A.; Skinner, J. L. *J. Chem. Phys.* **2005**, *123*(4), 044513.
30. Nienhuys, H.-K.; Woutersen, S.; Santen, R. A. V.; Bakker, H. J. *J. Chem. Phys.* **1999**, *111*(4), 1494.
31. Deàk, J. C.; Rhea, S. T.; Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **2000**, *104*(21), 4866.
32. Lock, A. J.; Bakker, H. J. *J. Chem. Phys.* **2002**, *117*(4), 1708.
33. Lindner, J.; Vöhringer, P.; Pshenichnikov, M. S.; Cringus, D.; Wiersma, D. A.; Mostovoy, M. *Chem. Phys. Lett.* **2006**, *421*(4-6), 329.
34. Yang, M.; Fleming, G. R. *Chem. Phys.* **2002**, *282*, 163.
35. Jang, S. *J. Chem. Phys.* **2007**, *127*(17), 174710.