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Direct Dynamics Study of Ultrafast Vibrational Energy Relaxation in Ice Ih

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Car−Parrinello molecular dynamics (CPMD) and a previously developed wave packet model are used to study ultrafast relaxation in water clusters. Water clusters of 15 water molecules are used to represent ice Ih. The relaxation is studied by exciting a symmetric or an asymmetric stretch mode of the central water molecule. The CPMD results suggest that relaxation occurs within 100 fs. This is in agreement with experimental work by Woutersen and Bakker and the earlier wave packet calculations. The CPMD results further indicate that the excitation energy is transferred both intramolecularly and intermolecularly on roughly the same time scale. The intramolecular energy transfer occurs predominantly between the symmetric and asymmetric modes while the bend mode is largely left unexcited on the short time scale studied here.

1. Introduction

Water is the most common solvent and understanding its behavior is of general interest. Despite the apparent simplicity of the water molecule, the complexity of the liquid makes water a challenging research area still not fully understood. Due to its capability to form a hydrogen-bonded network, water possess special and unique physical and chemical properties. The binding energy of hydrogen bonds is small enough that such bonds form and break rapidly. This fact together with the versatility of the hydrogen bonds between water molecules results in difficulty in modeling water and its properties.

Many vital chemical reactions occur in water. For the reactions to take place, the molecules involved have to accumulate sufficient energy to react. In a large molecular system, as when water is involved, there are many competing processes. Therefore, insight into how the energy flows between competing channels is of great interest. For example, if a vibrational mode in a water molecule is excited, the energy released when the mode relaxes may be intramolecularly transferred, dissipated into the heat bath, or alternatively resonantly transferred to an adjacent water molecule. The OH-stretch in water has been studied extensively[1−7] and for the HDO molecule diluted in heavy water it has been most popular to perform investigations.[8−21] Much of this work has recently been reviewed by Rey et al.[22]

The energy relaxation of an excited vibrational mode in a water molecule can occur by energy transfer to other vibrational modes or to rotational and/or translational degrees of freedom. The pathways may involve intramolecular energy transfer where for instance an excited asymmetric mode could transfer its energy to the symmetric mode within the molecule. The energy mismatch between the modes would be transferred to the solvent. Another pathway could be a resonant energy transfer from the excited mode to an accepting mode in an adjacent molecule. This is usually a slow process but recently Woutersen and Bakker[4] have found it to occur in water on a time scale less than 100 fs.

The mechanism of the resonant energy transfer in water has been investigated by Woutersen and Bakker.[4] Using femtosecond mid-infrared pump−probe spectroscopy, they studied the dynamics of pure liquid H_2O and of liquids with different concentrations of HDO in D_2O. They found that the rate of the intermolecular energy transfer increases with increasing concentration of HDO in D_2O. Woutersen and Bakker also found that in pure H_2O, the intermolecular energy transfer occurs faster than their time resolution of approximately 100 fs. They concluded that the Förster energy transfer mechanism, which assumes that dipole−dipole interactions dominate, was not sufficient to explain the rapid intermolecular energy transfer. This observation means that additional effects based on dipole−quadrupole, quadrupole−quadrupole, and higher order interactions should be considered. In a very recent experimental study, Amir et al. have found intermolecular energy transfer in liquid water to occur on a similar time scale as found by Woutersen and Bakker.[23]

In a recent study of Poulsen et al.,[24] the intermolecular energy relaxation was investigated in a wave packet study assuming a harmonic expansion for the interaction potential. The study included both liquid water at 300 K and ice Ih at 273 K. The results of Poulsen et al.[24] suggest that intermolecular resonant energy transfer can take place on a 100-fs time scale in both phases. The analysis of Woutersen and Bakker is not applied to ice. The wave packet study, however, suggests that the relaxation rate in ice is comparable to that found in liquid water. In the following it is therefore assumed that the present ice study is also relevant for relaxation in liquid water.

In this paper, we compare results obtained by the wave packet approach by Poulsen et al.[24] for ice Ih with results from Car−Parrinello Molecular Dynamics[25,26](CPMD) simulations. The vibrational energy transfer in ice is thus investigated by a quantum dynamics approach and a classical dynamics approach. The wave packet study only considered the rate of resonant intermolecular energy transfer. In CPMD, however, also intramolecular energy transfer and nonresonant intermolecular energy transfer is included. Further, the CPMD approach includes anharmonic effects, albeit the dynamics are classical. This thus allows us to estimate the relative importance of inter- and intramolecular energy transfer and to what extent the symmetric, asymmetric, and bending modes within a molecule are involved.

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The purpose of this paper is not to mimic the experiments of Woutersen and Bakker or Amir et al., but to investigate the time scales in the ultrafast intermolecular resonant energy transfer mechanism proposed by these authors.

This paper is organized such that in Section 2, the methods used are briefly reviewed before the results are presented and discussed in Section 3. Finally in Section 4 the conclusions are summarized.

2. Methods

The general idea here is to study energy relaxation in a cluster of water molecules by vibrationally exciting primarily the central water molecule. In an earlier wave packet study Poulsen et al.[24] found that within their model 15 water molecules were sufficient to study the initial stage of the relaxation in liquid water and ice. It is assumed that clusters of 15 water molecules are large enough also in the present study. The excitation is done such that either mainly the symmetric normal mode or alternatively the asymmetric normal mode of the central water molecule is given approximately one quantum of vibrational energy. The symmetric stretch excitation is achieved by moving each of the H atoms along the relevant OH internuclear axis and then finally moving the O atom so that the center of mass is left unchanged. A similar procedure is used for the asymmetric stretch vibration excitation.

In the present work ice Ih at 273 K is studied. The initial geometry is the same as the one in the study by Poulsen et al.,[24] which means that it corresponds to an equilibrium structure for ice at normal pressure and temperature.

2.1. Wave Packet Dynamics Approach. The quantum dynamics model used here is the one adopted by Poulsen et al.[24] In this model a molecule or a cluster of molecules are treated by an analytic wave packet propagation. This is made possible by obtaining the potential energy and the second derivatives at the equilibrium geometry and assuming a Taylor expansion to second order to be valid. For this to be reasonable, only geometries quite close to equilibrium should be important. This is assumed to be the case for ice Ih at 273 K when studied on a femtosecond time scale. The potential energy was calculated with the Gaussian 98 electronic structure program package,[27] using DFT employing the hybrid B3LYP exchange-correlation functional together with a 6-31G** basis set.[28]

In the work by Poulsen et al.,[24] the central water molecule is excited in the same way as described above by displacing the atoms from equlibrium such that the symmetric or asymmetric stretch mode is excited. The intermolecular energy transfer is followed by monitoring the survival probability of the analytically propagated wave packet in the excited vibrational state as a function of time. This survival probability is given by[24]

$$|\langle\Psi(0)\,|\Psi(t)\rangle|^2 = \sum_{i,j=M+1}^{N} c_i^{\,2} c_j^{\,2} \cos((\omega_i - \omega_j)t)$$

where the sum is over normal modes which contribute significantly to the central water molecule excitation. ω_i is the frequency of mode i and c_i^2 is the probability of mode i being excited. The c_i coefficients are obtained by expressing the excitation of the central water molecule in the cluster normal modes.[24]

Monitoring the wave packet survival probability is essentially equivalent to monitoring the averaged potential energy of the OH bonds in the central water molecule. The potential energy of the central water molecule was for this purpose obtained in a local mode approximation. The fraction potential energy remaining in the central water molecule after some time t, $f_{\text{exc}}(t)$, was obtained by normalizing with the initial potential energy in the central water molecule. This gives

$$f_{\text{exc}}(t) = \frac{(\Delta r)^2_{\text{OH(1)}}(t) + (\Delta r)^2_{\text{OH(2)}}(t)}{(\Delta r)^2_{\text{OH(1)}}(t{=}0) + (\Delta r)^2_{\text{OH(2)}}(t{=}0)}, \qquad (1)$$

where Δ signifies deviation from equilibrium (and bending motion does not need to be considered). As mentioned above, in the wave packet model nonresonant intermolecular and all intramolecular energy transfer, in a normal mode basis, are neglected. Hence the wave packet model describes neither the energy transfer within a water molecule nor thermalization by the bath.

2.2. Ab Initio Molecular Dynamics. To be able to use first principles obtained potential energy data we choose to employ ab initio molecular dynamics (AIMD). Well-known AIMD approaches are Ehrenfest molecular dynamics, Born−Oppenheimer molecular dynamics, and Car−Parrinello molecular dynamics (CPMD).[25,26] In Ehrenfest molecular dynamics the time-step must be small as it is dictated by the motion of the electrons, which is explicitly treated. This is not the case in Born−Oppenheimer molecular dynamics whereby the time-step can be much longer as it is determined by the nuclear motion. On the other hand, the electronic energy must be minimized in each time-step, which is not required in Ehrenfest molecular dynamics. In the CPMD approach a fictious mass is used for the electrons whereby a longer time-step can be used even though the electronic motion is dynamically treated. The fictious mass must be sufficiently smaller than the mass of the nuclei that their time-scales are different enough to keep energy from flowing between nuclear and electronic degrees of freedom. We have chosen to employ the CPMD method in this work.

In the CPMD approach density functional theory with a plane wave basis is used to find the potential energy, allowing for quite large systems to be studied and still including dipole−dipole, dipole−quadrupole, and higher order couplings. A general CPMD computer program has been developed.[29] This code could be directly applied in our study, with one simple modification as described below. Since CPMD has been extensively reviewed[25] we only discuss issues of specific interest to our application.

In CPMD the complete nuclear dynamics are included in the classical approximation. Therefore anharmonic effects and intramolecular and nonresonant energy flow is automatically included. This was not the case in the wave packet study of Poulsen et al.,[24] which only included resonant intermolecular energy transfer in the harmonic approximation.

2.2.1. Reference Potential. We wish to monitor how much potential energy is stored in the central water molecule. To do this we define an intramolecular reference potential for this molecule. The RWK2 potential of Reimers et al.[30] is used to construct the reference potential. The RWK2 potential includes intramolecular interactions as well as intermolecular interactions, and has been shown to be an accurate model for studying water clusters.[31] A reference potential corresponding to the harmonic part of the RWK2 potential is used, which gives the following equation in atomic units:

$$V_{\text{H}_2\text{O}} = 0.26543(\Delta S_1)^2 + 0.27219(\Delta S_2)^2 + 0.07798(\Delta S_3)^2 + V_{\text{o}} \qquad (2)$$

where V_0 is a constant and the displacements ΔS_1, ΔS_2, and ΔS_3 are given by

$$\Delta S_1 = \frac{\Delta R_{OH_1} + \Delta R_{OH_2}}{\sqrt{2}} \tag{3}$$

$$\Delta S_2 = \frac{\Delta R_{OH_1} - \Delta R_{OH_2}}{\sqrt{2}} \tag{4}$$

$$\Delta S_3 = \Delta\theta \tag{5}$$

with $\Delta R_{OH_i} = R_{OH_i} - R_0$; $i = 1, 2$, $R_0 = 1.0$ Å, $\Delta\theta = \theta_{HOH} - \theta_0$, and $\theta_0 = 109.5°$ obtained from the initial geometry of the ice cluster.

The reference potential was used to estimate how much the OH bond lengths on the central water molecule should be contracted/extended to approximately excite either the symmetric or asymmetric mode to an energy equivalent of the first excited quantum mechanical level. For the symmetric stretch both of the bond lengths were reduced by 0.095 Å, which corresponds to an increase of energy in the system of about 3210 cm^{-1}. We let this single wavenumber represent the whole distribution of wavenumbers in ice which largely correspond to symmetric stretches of a water molecule. The wavenumbers of the asymmetric stretch are slightly higher and we let them be represented by a value of about 3300 cm^{-1}. The asymmetric stretch was initiated by reducing one OH bond length by 0.10 Å and increasing the other one by the same amount.

2.2.2. Computational Procedure. Ab initio molecular dynamics simulations based on DFT[32,33] were performed with versions 3.5.1 and 3.5.3 of a downloadable CPMD program.[29] These program versions were slightly modified to allow canonical sampling of different initial atomic velocities for the trajectories. For the exchange-correlation, a generalized gradient corrected functional of Perdew, Burke, and Ernzerhof (PBE)[34] was used, which has previously been adopted in water studies.[35,36] The core-valence interaction was described by a norm-conserving Trouiller–Martins pseudopotential,[37] which has been shown to provide a good description of water systems.[38]

The ice cluster investigated in this study consists of 15 water molecules with hexagonal symmetry (ice Ih). The water molecule in the center was surrounded tetrahedrally by four other water molecules, with a distance of 2.76 Å between oxygens, thus giving the same tetrahedral structure of the cluster as in the wave packet approach.

The system was treated as isolated where the wave functions were expanded in plane waves with an energy cutoff of 70 Rydberg using a box size of 12.56 Å. The simulations were performed with a time step of 3.0 au with a fictitious electron mass of 550 au. Output from the trajectories was recorded at every 10th time-step.

2.2.3. Initial Velocities. A vibrational mode on the central water molecule is excited by changing the OH bond lengths as described above. Presumably the main effect of the behavior of the vibrational energy relaxation is due to the excitation of the vibrational mode. Some effect of the thermal motion of the atoms in the cluster is also possible. Here we initiate all trajectories with the same geometry but allow for a thermal distribution of initial velocities. The 3.5.1 and 3.5.3 versions of the distributed CPMD code do not allow for a thermal distribution of the initial velocities to be sampled. Only a minor modification was required , however, to arrange for this. It was done by allowing the subroutine that generates thermal velocities in the CPMD code to be called with different random numbers rather than by using the same one each time as is the case in the distributed codes. In this way, 20 trajectories with different initial thermal velocities were ran at 273 K for the excitation of the symmetric mode and likewise for the excitation of the asymmetric mode. This gives us a statistical base for the conclusions. Having run n sample trajectories, each with an outcome x_i, the standard deviation (σ) is obtained by the formula

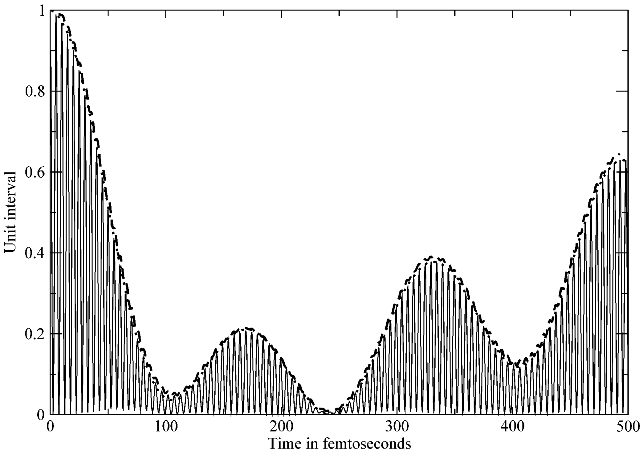

Figure 1. Potential energy of the central water molecule (arbitrary units) after symmetric stretch excitation, evaluated by using eq 1 (solid line) and the wave packet survival probability (dotted line). Also included is the potential energy of eq 1 but averaged over 10 fs and multiplied by a factor of 2 (dashed line).

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n - 1}} \tag{6}$$

where $\bar{x}$ is the mean of the n sample outcomes.

3. Results and Discussion

In this section, we first report some results for vibrational energy transfer in ice Ih using “the wave packet approach” of Poulsen et al.[24] Thereafter we report results from the CPMD approach. Finally, as a check of the consistency of the computational model used, one ice simulation was carrried out where the central H_2O water molecule is surrounded by 14 D_2O molecules.

3.1. The Wave Packet Approach. Figure 1 shows the potential energy (in arbitrary units) of the central water molecule after symmetric stretch excitation, evaluated by using the potential in eq 1 and the wave packet survival probability. The H_2O potential energy oscillates with the vibrational period but when it is averaged over a vibrational period, it essentially coincides with the wave packet survival probability. After about 50 fs the averaged potential energy of the central water molecule has been reduced to half of its initial value. As the wave packet model only describes intermolecular resonant energy transfer, it supports the experimental findings[4] that this process occurs on a time scale of less than 100 fs.

Figure 2 corresponds to Figure 1 but for asymmetric stretch excitation. Here the potential energy has decayed to half of its initial value after about 80 fs. This is slower than for the symmetric excitation, but also in this case the process takes place on an ultrafast time scale in agreement with the experiments.[4]

We note the close agreement between the wave packet survival probability and the average H_2O potential energy of

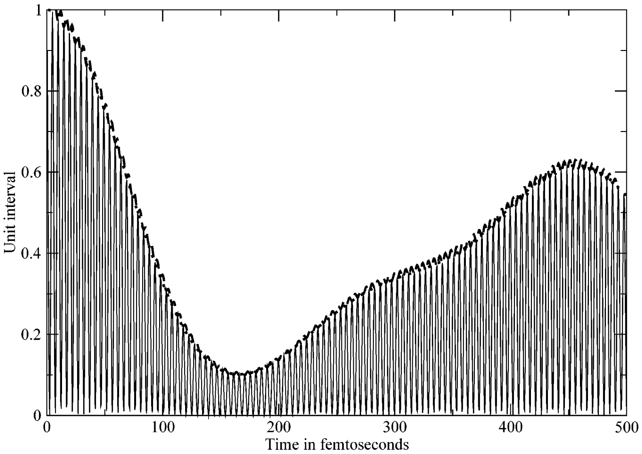

Figure 2. Potential energy of the central water molecule (arbitrary units) after asymmetric stretch excitation, evaluated using eq 1 (solid line) and the wave packet survival probability (dotted line). Also included is the potential energy of eq 1 but averaged over 10 fs and multiplied by a factor of 2 (dashed line).

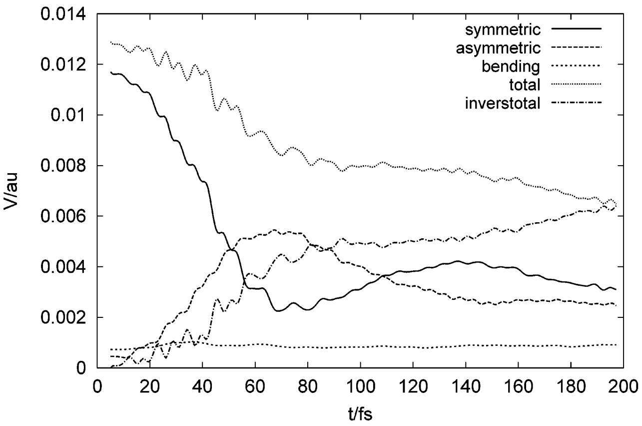

Figure 3. Potential energy in hartrees, averaged over 10 fs and 20 trajectories, of the central water molecule in various modes as indicated by the labeling, after symmetric stretch excitation. “total” means total potential energy in the central water molecule while “inverstotal” means total potential energy that has left the central water molecule.

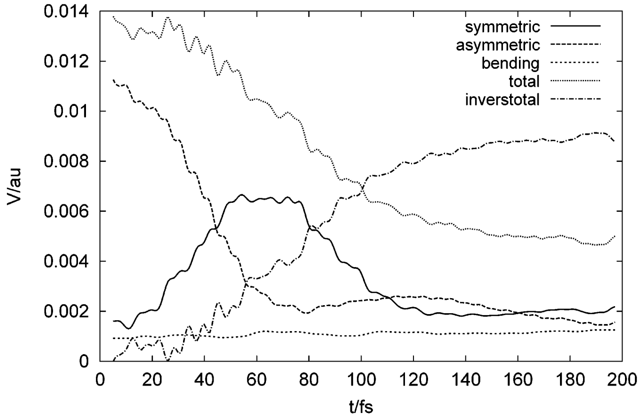

Figure 4. Potential energy in hartrees, averaged over 10 fs and 20 trajectories, of the central water molecule in various modes as indicated by the labeling, after asymmetric stretch excitation. “total” means total potential energy in the central water molecule while “inverstotal” means total potential energy that has left the central water molecule.

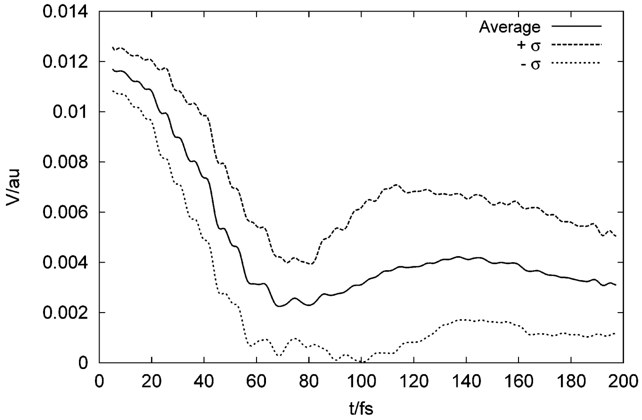

Figure 5. Potential energy in hartrees, averaged over 10 fs and 20 trajectories, of the central water molecule in the symmetric stretch mode after symmetric stretch excitation. Also shown is one standard deviation.

the central water molecule. This suggests that in the CPMD calculations we can monitor an averaged potential energy and compare the results with those previously obtained for the wave packet survival probability.

3.2. The CPMD Approach. *3.2.1. Pure H_2O.* The figures in this section all show potential energy in some form as a function of time. In all cases, each potential energy point represents an average over 10 fs, which approximately corresponds to a symmetric or asymmetric stretch vibrational period. The first point in each figure is thus shown at 5 fs and represents an average over the first 10 fs. Figure 3 shows the CPMD result after excitation of the symmetric stretch vibration of the central water molecule in the cluster. The potential energy of each mode of the central water molecule is shown as an average over 20 trajectories.

A number of observations can be made based on Figure 3. First, the energy relaxation from the symmetric mode is very fast, occurring with a halftime of about 40−50 fs. Most of the excitation energy has left the symmetric mode in less than 100 fs. A second observation is that when the energy of the symmetric mode decreases, the energy of the asymmetric mode increases by roughly half of that amount. The interpretation is that energy flows quickly from the symmetric to the asymmetric mode. The remaining energy flow out of the symmetric mode is almost exclusively intermolecular, which thus occurs with almost the same efficiency as the transfer to the asymmetric mode. Energy tranfer to the bending mode is very small on the time-scale studied here.

Figure 4 shows CPMD results after excitation of the asymmetric stretch vibration of the central water molecule in the cluster. The potential energy of each mode of the central water molecule is shown as an average over 20 trajectories. It is seen that about half of the excitation energy has left the excited mode in less than 50 fs, as was also observed for the symmetric excitation. Most of the excitation energy has left the asymmetric mode within 100 fs. The energy is initially transferred to the symmetric mode and intermolecularly in almost equal shares while there is hardly any energy transfer to the bending mode.

The experiment of Woutersen and Bakker[4] revealed the existence of a sub-100-fs resonant vibrational energy transfer process in agreement with the time scales found in Figures 3 and 4 and the less detailed results of the wave packet approach.

As mentioned the results shown in Figures 3 and 4 are averages over 20 trajectories where the inital atomic velocities have been thermally sampled. Figures 5 and 6 illustrates the spread of the results from the individual trajectories by showing the standard deviations. Figure 5 shows the potential energy in the symmetric stretch after its excitation. Figure 6 shows the potential energy in the asymmetric stretch after its excitation. There is certainly statistical uncertainty in the results but the mainly qualitative observations made above should be valid.

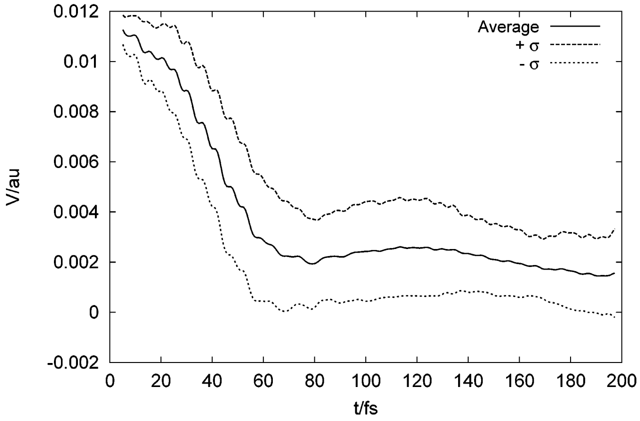

Figure 6. Potential energy in Hartree, averaged over 10 fs and 20 trajectories, of the central water molecule in the asymmetric stretch mode after asymmetric stretch excitation. Also shown is one standard deviation.

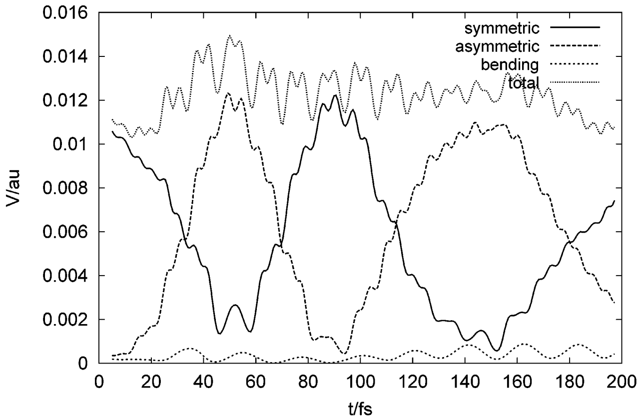

Figure 7. Potential energy in hartrees, averaged over 10 fs and 20 trajectories, of the central water molecule in various modes as indicated by the labeling, after symmetric stretch excitation. "total" means total potential energy in the central water molecule. The central water molecule is surrounded by 14 D_2O molecules.

3.2.2. H_2O in D_2O. Due to the frequency mismatch, intermolecular resonant energy transfer should not occur if the water molecules surrounding the central water molecule are replaced by D_2O molecules. This is tested in Figure 7 where the symmetric mode of the central water molecule is excited the same way as before but in a surrounding of 14 D_2O molecules. The pattern is totally different from the previous simulations. Since the frequencies of the vibrational modes in a D_2O molecule and in an H_2O molecule are not in resonance, the energy is now trapped within the central water molecule. The result shows that the excess energy in the initially excited symmetric mode oscillates to and from the asymmetric mode. The smaller oscillations seen in the total potential energy are related to the approximate way in which it is evaluated in eq 2. Thus Figure 7 suggests that there is no or only little intermolecular energy transfer. This in turn suggests that the intermolecular energy transfer in pure H_2O is mainly resonant energy transfer. We also note that there is no or only little involvement of the bending mode.

4. Conclusions

In this study we have used the CPMD approach to study ultrafast energy relaxation in ice Ih as modeled by a cluster of 15 water molecules. A symmetric or an asymmetric stretch mode localized on the central water molecule is initially excited and the potential energy of that motion is monitored. From the wave packet calculations using the approach of Poulsen et al.[24] we find that the potential energy averaged over a vibrational period agrees well with the wave packet survival probability in the excited state.

We observe efficient intramolecular energy transfer between the symmetric and asymmetric modes of the central water molecule. Intermolecular energy transfer occurs with roughly the same efficiency and is dominantly resonant energy transfer. Most of the initial excitation energy is transferred out of the excited mode in less than 100 fs. Energy transfer to the bending mode is not observed on the short time scale (<200fs) studied here. The results obtained in the CPMD calculations are consistent with the results of the wave packet approach. The wave packet results suggest that resonant vibrational energy relaxation in ice is at least as fast as that in liquid water. Therefore the present results are also consistent with the ultrafast resonant vibrational energy transfer process put forth by Woutersen and Bakker[4] from which it was concluded that resonant intermolecular energy transfer in liquid water occurs on a sub-100-fs time scale. The results are also consistent with the recent study of Amir et al.,[23] and further, we have seen an overall good agreement between harmonic wave packet calculations and classical CPMD results. This is in agreement with the picture that it is the *harmonic* part of the intermolecular potential which induces the resonant intermolecular energy transfer, since, for such a coupling-type, a classical and quantum description of the energy relaxation would give identical results. This is so far the fastest measured VER rate in the condensed phase. It has further been suggested that the fast intermolecular energy transfer within liquid water and ice means that the released energy will not be localized long enough to affect most chemical reactions.[39]

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