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Ultrafast Energy Transfer from the Intramolecular Bending Vibration to Librations in Liquid Water

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A theoretical study of the water bend-to-libration energy transfer in liquid H_2O has been performed by means of nonequilibrium classical molecular dynamics computer simulations. Attention has been focused on the time scale and mechanism of the decay of the fundamental H_2O bend vibration and the related issue of the decay of water librational (hindered rotational) excitations, including the important role of that for the excited molecule itself. The time scales found are 270 fs for the decay of the average energy of an H_2O molecule excited to the $\nu = 1$ state of the bending oscillator and less than 100 fs for excess rotational (librational) kinetic energy, both consistent with recent ultrafast infrared experimental results. The energy flow to the excited molecule rotation and through the first several solvent shells around the excited water molecule is discussed in some detail.

1. Introduction

Advances in ultrafast spectroscopy have made it now possible to study vibrational energy transfer in neat liquid water.[1−8] Just as in earlier studies on isotopic variants such as HOD dilute in liquid D_2O,[5,10,11] rapid energy transfer for excited water stretch fundamentals is found, with the overtone of the bend being the major initial acceptor of the energy.[1−5] But, as has been emphasized,[4,5] there are, of course, important differences between water and its isotopic variants, notable vibrational differences being the strong coupling between the near-resonant (nominal) symmetric and antisymmetric stretches in H_2O and the ultrafast resonant transfer of OH stretch excitations between neighboring water molecules. There is also a difference in the extent of experimental information currently available for neat liquid water. In particular, two-color ultrafast infrared (IR) experiments[1−3] have provided considerable direct information on the relaxation/energy flow dynamics of the H_2O bend fundamental and the water librations.

After resonant excitation of the bend fundamental transition by a femtosecond infrared pulse,[1,2] both the transient absorption on the $\nu = 1$ to 2 transition and the bleaching of the fundamental transition display an initial exponential decay having a 170 fs relaxation time, corresponding to depopulation of the $\nu = 1$ state. (Other infrared experiments[6−8] give slightly longer times ranging up to 260 fs; a much longer time scale of 1.4 ps for bend relaxation was found after much stronger excitation by means of ultrafast infrared−Raman techniques.[4]) The OH bend vibration represents the intramolecular vibrational mode with the lowest frequency, and water librations (hindered rotations) were strongly implicated in this rapid energy transfer into the surrounding (unexcited) water shells.[1,2] Experiments involving direct excitation within the higher frequency portion of the water librational band[2,3] indicate a decay time of less than 100 fs.[9] The initial relaxation of both the OH bend vibration and librations is followed by subpicosecond processes of energy redistribution and delocalization into the bulk of the liquid. The experiments performed with excitation of approximately 1 percent of water molecules in the sample suggest the formation of a macroscopically heated liquid on a time scale of a few picoseconds, independent of the specific vibrational mode that was excited initially.[3]

In the present work, we undertake a classical molecular dynamics study of an excited water bend fundamental vibration in pure water in a first effort to comprehend molecular level aspects of its evidently very rapid energy transfer to the surrounding water molecules and the involvement of water librations therein.

Since the water librations have been implicated[1] in the bend energy transfer for H_2O (as well as in its isotopic variants[11]) and the decay of excited librations has itself been probed experimentally,[2,3] it would clearly be of interest to be able to characterize the water librational motions in terms of normal modes to simplify the description of the energy flow. In the simplest image, one could imagine that the energy transfer from an excited OH bend would involve a vibration-to-vibration (VV) transfer from the high frequency bend ($\sim$1600 cm^{-1}) to a combination or overtone of water librations. This route would necessarily involve relatively high frequency librations, and on the assumption that high frequency librations would be fairly localized (i.e., not involve many water molecules), it might be not difficult to find the accepting librational mode(s) initially involved in the VV transfer. In the following, we briefly discuss some aspects of the water librations in this perspective. Unfortunately, we will conclude that a normal mode perspective

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does not seem to be useful in the stated perspective. This conclusion motivates a different approach that we will follow.

Librational modes in water have been examined in several theoretical investigations, often in terms of “instantaneous normal modes” (INM) or “quenched normal modes”.[12−15] The most relevant conclusion for the present purposes is that[12] for either mode definition, librational motions appear to generally be quite collective in character, involving tens of water molecules (up to ∼100) over the majority of the librational spectrum. Although there is a diminution in the number of water molecules involved in the higher frequency range 800−1000 cm^{-1} region, the number drops below ∼10 molecules only in the highest frequency portion of that region, in a fashion which depends on the mode definition. Since the water bend frequency is ∼1600 cm^{-1}, these results indicate that in either of the scenarios of VV transfer to a librational overtone or combination band, the accepting librations cannot safely be regarded as localized. Thus, these results indicate that a librational normal mode perspective cannot be easily employed in an analysis of bend and librational energy flow. In the present work, we circumvent this limitation and employ instead the readily monitored rotational (librational) kinetic energy of water molecules to probe the librational motion of water molecules.

To this end, we have performed sets of nonequilibrium simulations in which a single water molecule is vibrationally excited along the bend coordinate at time $t = 0$. We have then followed the time evolution of its average bend energy and, to examine energy flow to and from the librations, the time evolution of the rotational kinetic energy of the molecule itself, its four nearest neighbors, and its farther 12 nearest neighbors, corresponding approximately to the first and second hydration shells, respectively, of the excited molecule. (A similar strategy has been previously applied in theoretical studies of vibrational energy transfer of various solutes in solution.[16−18]) To further characterize the water librational energy flow, we have also followed in separate simulations the average time evolution generated by exciting the rotations of a water molecule around each of its axes of inertia for both the excited molecule and its first two hydration shells. Our use throughout of classical, rather than quantum, simulations is justified a posteriori by the reasonable agreement with the experimental time scales. Further aspects of the experimental results are discussed in connection with the simulation results.

The remainder of this paper is organized as follows. Various methodological aspects are presented in Section 2. Simulation results for both bend and librational energy transfer, as well as discussion of the energy flow pathways involved, follow in Section 3; and Section 4 offers some concluding remarks, including some comments on recent related theoretical work.[19,20]

2. Methodology

The classical molecular dynamics computer simulations were performed using a modified version of DL_POLY_2.[21] All simulations were run in the microcanonical ensemble at an average temperature $T = 300$ K, and 200 water molecules were placed in a cubic simulation box, of length 18.15 Å, chosen to reproduce the experimental density, with periodic boundary conditions. All water molecules except the one selected for excitation were treated as rigid bodies, and the integrations of the rigid body rotational equations of motion were performed using the Fincham Implicit Quaternion Algorithm.[22] The Verlet algorithm[23] was used to integrate the translational part.

The SPC/E water model[24] was used in the simulations, with a modification now described, to take into account the bend motion. We ignore all stretching molecular vibrations of the water molecules,[25] and for most of the calculations, we allow only a single water to have a bending vibration. For the single (nonrigid) water molecule selected for bend excitation, a harmonic intramolecular bend potential was applied,

$$V(\theta) = \frac{1}{2}k'(\theta - \theta_{eq})^2 \tag{1}$$

where θ is the instantaneous bend angle and θ_{eq} is the corresponding value for the SPC/E geometry. The OH bond lengths for this molecule were kept fixed at the value corresponding to the SPC/E geometry by using the SHAKE algorithm.[26] The time step used was 1 fs, and the system was equilibrated for 500 ps. We fit the value of the force constant k' in eq 1 to correctly reproduce the experimental bend frequency. We found that the value of $k' = 90.45$ kcal/mol results in a bending frequency of 1660 cm^{-1}, very similar to the experimental value of 1650 cm^{-1}.[3] This frequency was evaluated by calculating the Fourier transform of the hydrogen velocity autocorrelation function for the bending molecule in an equilibrium run of 1000 ps. The water librational band position at 510 cm^{-1} was calculated from a separate equilibrium simulation of 200 SPC/E water molecules using the same method.[27]

From a long equilibrium run, we saved snapshots of the entire system every 3 ps. Each saved configuration was used as the starting configuration for a nonequilibrium run, in which the nonrigid water molecule was (classically) given energy equivalent to a single quantum of vibrational energy in the bending mode. This means that at $t = 0$ of each nonequilibrium trajectory, the kinetic energy of the bend normal mode of such a molecule was modified by adjusting its velocity[16] in a way such that the total change of kinetic energy was equal to the bend excitation energy (ΔE about 5 kcal/mol, ∼1700 cm^{-1}). The velocities of the other modes and of all other molecules were assigned according to a Boltzmann distribution at 300 K. Normal mode analysis was performed on the excited H_2O molecule at each time step of the nonequilibrium simulations; the bend normal mode was obtained as the eigenvector of the mass-weighted Hessian matrix formed by the second derivatives of the intramolecular potential with respect to the Cartesian displacements (in our model, the bend is the only intramolecular vibrational motion). A similar procedure was applied for higher energy excitations (15 kcal/mol, ∼5200 cm^{-1}) of the H_2O bend.

For each set of calculations within, there were a total number of 1000 nonequilibrium trajectories, and results from each simulation were averaged over this total number of trajectories. No temperature control was introduced during these several-ps-long nonequilibrium runs. An estimate of the error associated with the simulation was made by dividing the full set of trajectories into 10 blocks and by calculating the mean square displacement of the result obtained in each block with respect to the overall average value.

Librational excitations were separately studied by running three sets of nonequilibrium trajectories in which we excited the hindered rotation of a water molecule around its three inertial axes. In each set, extra kinetic energy was given for the rotational motion of the excited molecule around one of the axes by adjusting its initial angular velocity. The three different sets were run separately, and the results for the average decay of the total rotational kinetic energy were combined by averaging them.

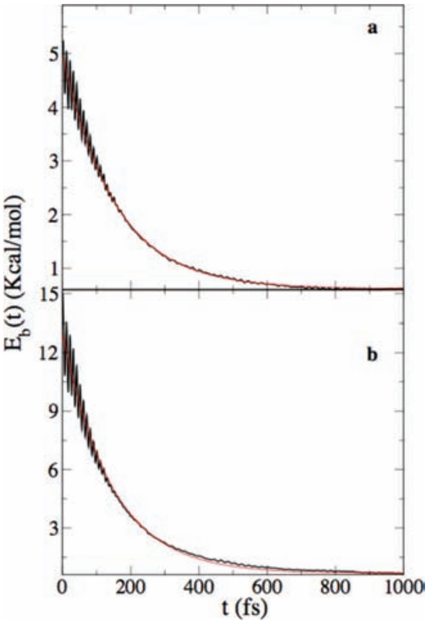

Figure 1. Simulations of the average H_2O bend energy relaxation after excitation of one water molecule, in the case that all molecules are allowed to bend (stretches frozen). a: Initial 5 kcal/mol bend excitation. b: Initial 15 kcal/mol bend excitation. In each panel, the red, dashed line is an exponential fit, with relaxation times of 150 fs (a) and 140 fs (b).

Finally, several equilibrium time correlation simulations have been carried out to provide a comparison with the nonequilibrium studies. An equilibrium simulation of SPC/E water (200 molecules) was performed to calculate the time correlation functions of the angular momentum, of the squared angular momentum, and of the fluctuations of the total rotational kinetic energy. Equilibrium simulations of 200 water molecules were also run with a model that represents the extension of the partially flexible model described above. In such an extension, all water molecules are free to bend with the same potential as in eq 1 and the same force constant. The validity of the model was tested by calculating some standard structural and dynamical properties, as well as the infrared spectrum. The equilibrium trajectory was used to calculate the autocorrelation function of the bend energy.

3. Energy Transfer: Results and Discussion

3.1. Energy Transfer from the H_2O Bending Mode with All Molecules Capable of Bending. We begin by examining the decay of the H_2O bend energy after excitation of one water molecule at an energy of 5 kcal/mol, corresponding to one H_2O bend quantum and, for comparison, an initial excitation of 15 kcal/mol, corresponding to approximately three bend quanta. In this calculation, all the water molecules in the sample are capable of bending (but not stretching). Figure 1 shows an exponential envelope that decays with a relaxation time of 150 fs (5 kcal/mol excitation) and 140 fs (15 kcal/mol excitation). Thus, the relaxation time shows negligible dependence on the bend excitation amount. This time is quite close to the 170 fs decay determined in the ultrafast IR experiments,[2,3] a point to which we return below.

The observed lack of dependence of the bend energy relaxation time on the excitation energy would also follow from a standard first-order perturbational ("linear response") approach to the nonequilibrium problem,[28] in which the time dependence in each case would be governed by the equilibrium time correlation function (tcf) of the fluctuating bend energy. That tcf is shown in Figure 2, and indeed, the envelope decay time is again 140 fs.

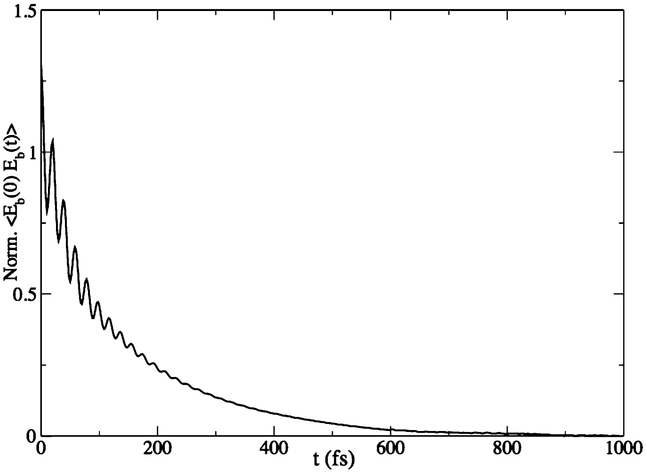

Figure 2. Total bend energy autocorrelation function (normalized) in the simulation where all water molecules are allowed to bend (stretches frozen). Normalization was carried out by (1) subtracting the equilibrium value and (2) dividing by the initial value. We note that such a value was determined by considering the envelope of the decay, to avoid the effect due to the oscillation at small values of t.

Despite these encouraging results, considerable caution needs to be exercised for several reasons. First, the experiment is *not* sensitive to bend-to-bend intermolecular VV transfer, since it is the sample population of an excited bend state that is monitored;[1,2] by contrast, the present simulations follow the bend energy of a single molecule. Further, polarization-resolved experiments[1] indicate a constant pump−probe anisotropy during the bend lifetime, ruling out any important contribution from the intermolecular VV transfer route. Actually, assuming for purposes of estimation that intermolecular dipole−dipole interaction is the dominant coupling in the bend to bend intermolecular VV transfer[29] and scaling the 100 fs VV transfer of the OH stretch[30] with the ratio of the bend to stretch transition dipole squared, we estimate a VV transfer time of the bend much longer than 150 fs. Second, any such VV transfer should properly be treated quantum mechanically,[31] whereas the present treatment is purely classical, so that the accuracy of the calculated transfer could be questioned. Accordingly, we examine the bend energy relaxation in a different manner, now described.

3.2. Energy Transfer from the H_2O Bending Mode with Only the Excited Molecule Capable of Bending. For the reasons just discussed, we now turn to the discussion of the bend energy relaxation obtained by examining the decay of the H_2O bend energy after excitation of one water molecule at an energy corresponding to one quantum of the bend, but now all molecules except the excited one are rigid. Intermolecular bend-to-bend VV transfer[6,20] is accordingly not possible. Figure 3a displays the result for the average bend energy obtained from the nonequilibrium simulations, with an error of ±0.05 kcal/mol.

An exponential fit of the average bend energy decay in Figure 3a yields a relaxation time equal to 270 fs. This is comparable to, although longer than, the experimental value of 170 fs,[1,2] but not with a 1.4 ps time scale found via ultrafast infrared-Raman techniques.[4] We note for later reference that the same 270 fs relaxation time is found for an initial bend excitation of 15 kcal/mol (Figure 3b).

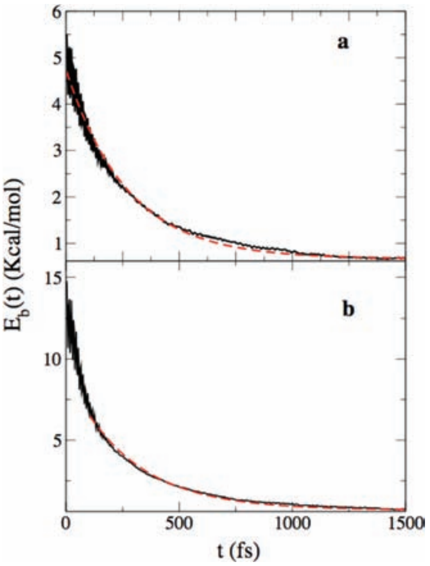

Figure 3. Simulations of the average H_2O bend energy relaxation after excitation of one water molecule, immersed in rigid, SPC/E water. a: Initial 5 kcal/mol bend excitation. b: Initial 15 kcal/mol bend excitation. In each panel, the red, dashed line is a fit with an exponential having a relaxation time of 270 fs.

To investigate the mechanism of such a rapid energy redistribution, we first focus on the excited H_2O molecule and on the water molecules in the hydration shell formed by its closest neighbors. We select the four molecules which were found to be the closest, on the basis of the distance between centers of mass, to the excited H_2O at the beginning of the simulation. With the anticipation that the H_2O's bend energy is primarily transferred to water librations, we monitor for all of these molecules the time evolution of the molecular rotational kinetic energy, which as described in the Introduction is the most accessible probe of the librations. This kinetic energy (averaged over the different nonequilibrium runs) is calculated via the definition

$$K^{\mathrm{rot}}(t) = \frac{1}{2}\sum_{i=1}^{3} I_i \omega_i^2 \qquad (2)$$

where i labels the three inertia axes, I_i are the eigenvalues of the instantaneous inertia tensor, and ω_i are the projections of the angular velocity, $\boldsymbol{\omega}$, along these inertia axes. The rotational kinetic energy results when the central water has an initial 5 kcal/mol bend excitation are reported as the black lines in Figure 4.

Evidently, the energy transfer from the bend of the excited H_2O to its water neighbors occurs on a very fast time scale and quickly propagates to outer hydration shells. Except for a slight but notable initial rotational kinetic energy increase and subsequent decay for the excited H_2O shown in Figure 4, there is no significant variation in the kinetic rotational energy and in the translational energy (results not shown) in the average over the nonequilibrium trajectories; only small fluctuations around the thermal equilibrium values are observed. However, the energy given to the H_2O bend is about 5 kcal/mol, and if this energy is rapidly transferred to the excited and several neighboring water molecule librations, significant changes in the average properties would not be expected.

We attempt to make the energy flow pattern from an excited H_2O bend visible by increasing the initial energy in that bend.

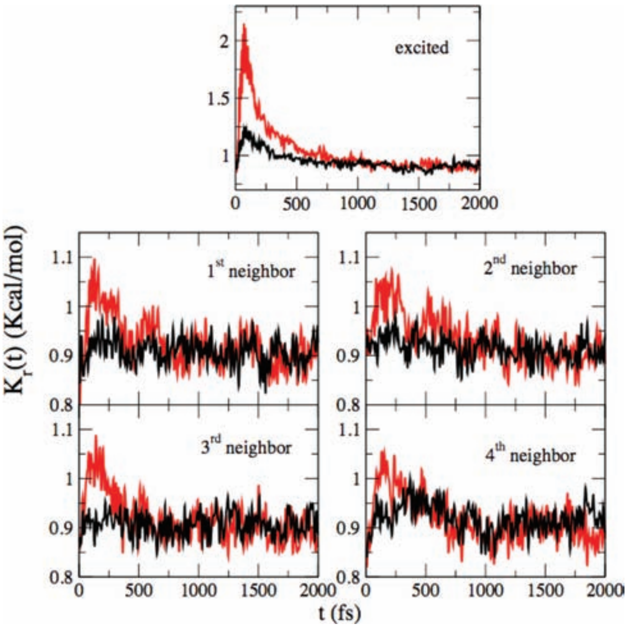

Figure 4. Simulations of rigid bulk water with a partially flexible (stretches frozen) vibrationally excited water: average variation in time of the rotational kinetic energy. In the top panel, we show the results obtained for the molecule that is vibrationally excited. The other panels show the rotational kinetic energy for each of the closest neighbors of the excited molecule, as indicated by the corresponding labels. The black line refers to an excitation of the bend of the central molecule with 5 kcal/mol; the red one, to an excitation corresponding to 15 kcal/mol.

Thus, we performed a different set of nonequilibrium simulations in which we excited the bend with an amount of kinetic energy, ~15 kcal/mol, which is 3 times larger than used in the initial calculations. The corresponding bend energy decay is shown in Figure 3b. The best single exponential fit for t larger than the experimental resolution ($t > 100$ fs^2) gives again 270 fs, as for the lower bend excitation case.[32] (In contrast to the 5 kcal/mol bend excitation case, we cannot provide the equilibrium time correlation function comparison due to the insufficient statistics associated with a single bending water molecule.) This identical time scale for the two bend excitation energies indicates that we can use the higher 15 kcal/mol bend excitation results as representative and to elucidate the energy flow mechanism applying at lower energies.

As is seen in Figure 4 (red curves for 15 kcal/mol bend excitation), the evolution of the kinetic rotational energies of the excited molecule and of its neighbors is much more evident than in the lower initial bend excitation case. The rise of the librational kinetic energy of the excited molecule is the largest in amplitude and the most rapid, as is its decay, indicating that this motion is quite important in the energy flow mechanism. In comparison, for the four water neighbors, the corresponding energy rise and amplitude is smaller and slightly slower, respectively, with the decays also slightly slower. The statistics are insufficient to make any reliable distinction between the behavior of these four waters so that henceforth, we will treat the first hydration shell as a unit. In addition, it is important to note that even though the energy flow is more visible with this higher bend excitation simulation, the amount of energy in any librational motion at any time (including that of the excited molecule) is still significantly less than the initial bend energy. This seems consistent only with a rapid energy flow both from the excited molecule to the first shell waters and from these

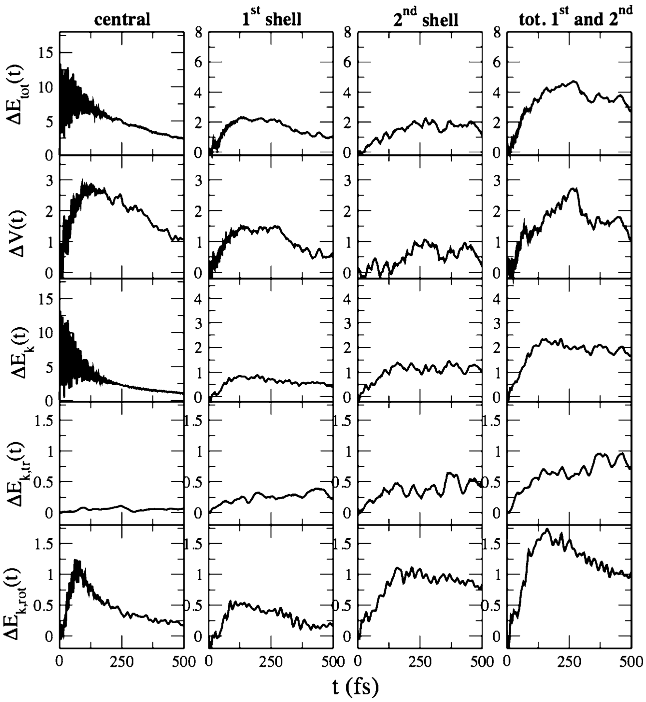

Figure 5. Bend excitation (only one molecule allowed to bend), energy decomposition with respect to equilibrium values for the excited molecule, the first shell molecules, the second shell molecules, and the first two shell molecules (columns from left to right). From top to bottom: total energy, potential energy (see text), kinetic energy, translational kinetic energy, and rotational kinetic energy.

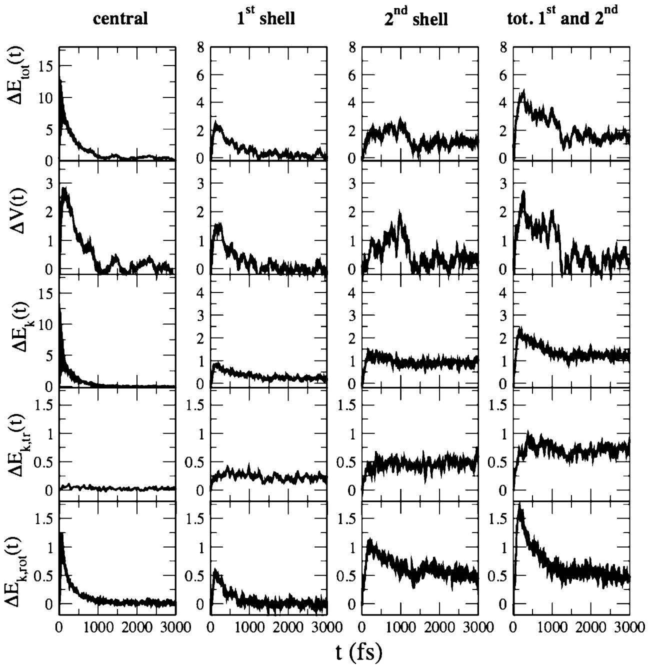

Figure 6. Same as in Figure 5, in a wider time interval.

first neighbors to the remaining water molecules outside of the hydration shell of the initially excited water molecule.

Accordingly, we now pursue a detailed analysis of the 15 kcal/mol bend excitation case, following the energy flow for both the excited molecule and its first hydration shell of four water neighbors, to which we add the second hydration shell, determined from equilibrium radial distribution results (not shown) to comprise 12 further water neighbors. In this analysis, we monitor, in addition to the central water molecule's bend energy, its total internal potential energy (associated with the bend) and the kinetic energy, including its rotational and translational contributions. We also monitor the potential energy of interaction with the remaining water molecules. For the first and second hydration shells of the central excited water molecule, we monitor the total energy, the potential energy, and the kinetic energy with its rotational components. All these energies are measured with respect to their equilibrium average values.

It proves convenient to present these results on both shorter (0−500 fs, Figure 5) and longer time scales (0−3000 fs, Figure 6). In the first column of these figures, for the excited molecule, the total energy (first entry) is the sum of the kinetic energy (translational + rotational + bend) and of the potential energy (potential energy of the bend + intermolecular interaction energy—Coulomb and LJ—with all surrounding molecules). The second entry in this column is the potential energy of interaction of the excited molecule with the first and second shell neighbors. The third entry in the column is the total kinetic energy (bend plus translation and rotation) for the excited molecule, with the remaining two entries being the kinetic energies of translation and rotation for the excited molecule. For the next two columns, separately involving only the (rigid) water molecules in the first or second shell, the first entry is the total energy, potential plus kinetic, of the water molecules in the specified shell, with the second entry, the potential energy, calculated as the interaction energy within the shell. The remaining kinetic energy entries are self-explanatory, as is the final column.

Figure 5 reveals a number of results for the energy flow on the shorter 500 fs time scale. Concerning the initial flow of the energy out of the bend excitation, the librational motion of the bend-excited molecule is evidently an important energy acceptor, appearing on a ~30 fs time scale, with the librational excitation of the first hydration shell rapidly following on a ~60 fs time scale. Rapid transfer to the second hydration shell is exhibited by the rise in ~150 fs. That energy is being further transferred beyond these two shells into the surrounding "bulk" water is indicated by an accounting of the total energy: at ~100 fs, nearly all of the initial 15 kcal/mol excess energy can be accounted for; at ~200 fs, only ~9 kcal/mol can be accounted for; and at 500 fs, only ~5 kcal/mol can be accounted for; that is, ~10 kcal/mol has flowed into the bulk by this time. Concerning the potential energy, the second row in Figure 5 indicates that there is a certain amount of potential "strain" rapidly created for the excited water, which is followed somewhat later by such a strain within the first and second hydration shells.

We have stressed above the important energy accepting role of the bend-excited water molecule's rotational kinetic energy (KE) at the earliest times (up to ~70 fs). Figure 5 also shows that by ~125 fs, the total librational KE in the two hydration shells starts to exceed that of the excited molecule. The excited molecule's rotational KE dominates its translational KE, approaching the small value of the latter only at ~500 fs. Similarly, in the hydration shells, the librational, rather than translational, KE is the primary short time kinetic energy receptor of the bend energy (and of the excited molecule rotational KE). The rotation KE/translation KE ratio for the two shells in Figure 5 is ~2.5 at both 100 and 200 fs, becoming ~1 at ~500 fs.

Figure 6 shows that the total kinetic energy of the first and second water shells reaches a constant value after approximately 1 ps. At this time, the excess energy originating from the initial bend excitation is essentially spread over the whole ensemble of water molecules, and a macroscopic temperature is established. For an amount of excess energy of 15 kcal/mol initially supplied to the central water molecule, we estimate, with the heat capacity of water, an increase in macroscopic temperature of 4 K for a 200 water molecule sample. Both the time scale on which the macroscopically heated ensemble is formed and the temperature increase are in good agreement with the experimental results of refs 2 and 3.

Before proceeding, we return to the issue of the important initial transfer from excited water molecule bend to that same molecule's rotational kinetic energy. Since no OH stretching is allowed (see Section 3.1), no Coriolis coupling is possible, and the energy transfer must arise from centrifugal coupling,[11a,c,33] a point to which we return in the Concluding Remarks.

3.3. Librational Kinetic Energy Decay. The bend energy flow results recounted above clearly indicate the key participation of the excited water molecule's librational motion as the dominant very initial receptor of the central water's bend excitation energy and the hydration shell waters' librational kinetic energy as a conduit for the energy flow through the first two hydration shells out into the bulk water. As noted in the Introduction, librational excitation experiments have indicated a rapid flow through the librational manifold on a sub-100 fs time scale.[2,3] We now turn our attention to direct water librational excitations, keeping all the water molecules in the sample rigid, to explore the librational energy flow.

We produce the librational excitation in nonequilibrium simulations in which we give 5 or 15 kcal/mol extra kinetic energy to the rotational motion of a single water molecule (around each one of the three inertia axes in separate calculations). We then follow the rotational kinetic energy as a function of time, then averaged over the nonequilibrium runs. Figure 7a,b displays the results for the decay of the rotational kinetic energy associated with rotations around the *x*, *y*, and *z* axes (see Figure 7 for axis identification.).[34] The order of the moments of inertia about these axes is $I_y > I_z > I_x$. In each panel, we report the total rotational kinetic energy obtained in each set of simulations, each corresponding to initial excitation of rotations around a different axis. The decay of the librational excitation is extremely rapid in all three cases, occurring within 100 fs, a result in agreement with the ultrafast IR findings.[3] Unfortunately, the statistics for the case of a single rotationally excited water are insufficient to detect any small amplitude longer time decay, such as those identified experimentally in librational excitation, and associated with hydrogen bond lifetimes[3] and sample heating.[2] We also remark that, although there are noticeable differences for the rotational KEs about the different axes, their global behavior is sufficiently similar that in the following, we will focus solely on the total rotational kinetic energy of the molecule (eq 2).

The 5 and 15 kcal/mol excitation results for the total rotational kinetic energy, averaged over the three different sets corresponding to excitations around *x*, *y*, and *z*, are displayed as Figure 7c. As was the case for the different axis components, the decay is complete within 100 fs, but a question immediately arises as to the interpretation of the "bump" in the energy decay. Conceivably, this could arise from a back-transfer of rotational kinetic energy to the rotationally excited water molecule. We now show that the origin is a different one.

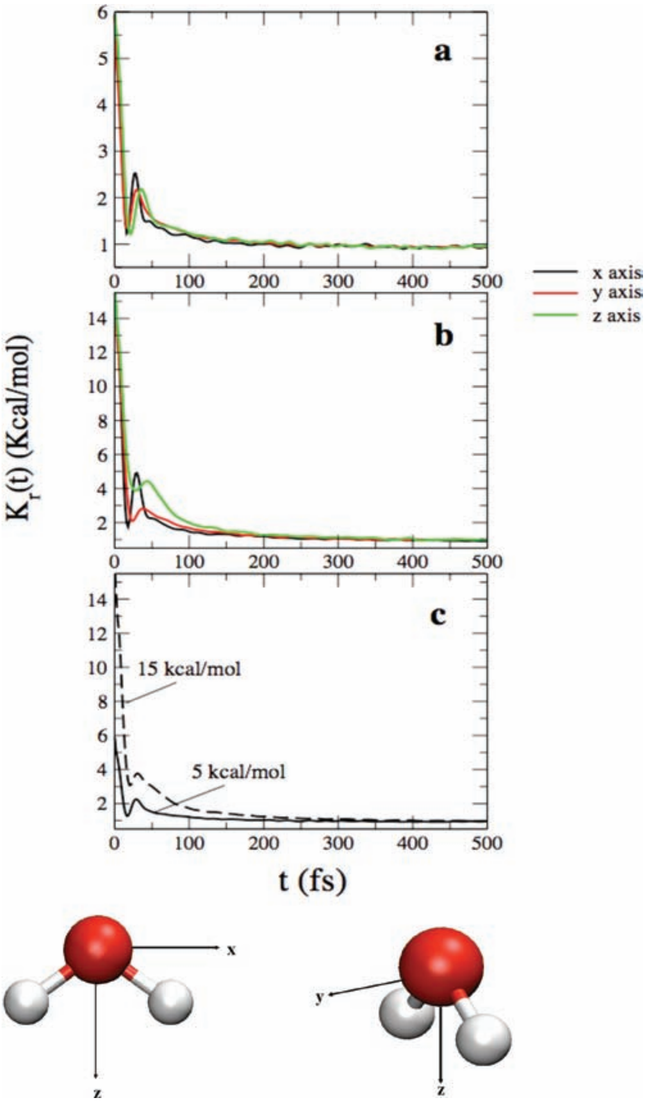

Figure 7. Average variation in time of the rotational kinetic energy for a water molecule that is given an excess kinetic energy (5 kcal/mol, a; 15 kcal/mol, b). Results for three sets of nonequilibrium simulations, corresponding to excitations around the *x*, *y*, and *z* inertial axis (shown at the bottom). The moment of inertia for the *y* axis is the largest, and that for the *x* axis is the smallest. The time evolution of the total rotational kinetic energy is shown for each set. In c, we show the total rotational kinetic energy, averaged over the three sets.

In pursuing this issue, we first note that the kinetic energy behavior in Figure 7c is quite similar to that of the equilibrium time correlation function of the rotational kinetic energy of an HOD molecule in liquid H_2O.[11a] This motivates a comparison of the equilibrium tcf of the water rotational KE with the nonequilibrium decays, shown in Figure 8. Although the tcf bump is somewhat more pronounced than those for the nonequilibrium decays, the similarity is sufficient to use this tcf to explore the bump's origin. Just as in ref 11a, we consider the Gaussian approximation for the KE tcf, in terms of which this tcf is proportional to the square of the tcf of the rotational angular momentum, **J**, of the water molecule. Figure 8 shows that this approximation is satisfactory over the short time period including the bump. The angular momentum tcf itself exhibits classical and very pronounced "caging" behavior, in which the sign of the angular momentum is reversed due to the interaction with the surrounding water molecules. Accordingly, the rotational KE tcf reflects this time reversal (as do the nonequilibrium decays), indicating the bump feature is primarily a phase effect rather than an energy transfer effect.[35] In this perspective, an appropriate measure of the rotational energy relaxation time can be extracted from an exponential fit to the envelope of the average energy decays. This gives 25 fs for the 5 kcal/mol and a biexponential behavior (relaxation times of 15 and 100 fs, with weights of 0.87 and 0.13) for the 15 kcal/mol librational excitations, respectively (a fit to a single exponential gives a

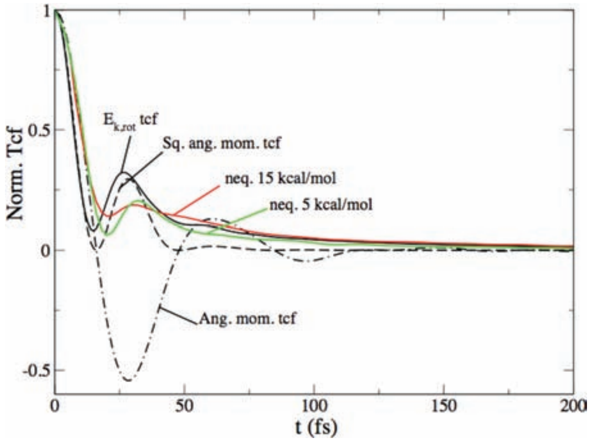

Figure 8. Comparison between equilibrium and nonequilibrium results for SPC/E water molecules. We show the normalized time correlation functions of the fluctuations of the rotational kinetic energy (full line), of the squared angular momentum (dashed line) and of the angular momentum (dashed-and-dotted line) and compare them to the normalized nonequilibrium results for the evolution of the total rotational kinetic energy after rotational excitation with 5 kcal/mol (in green) and 15 kcal/mol (in red).

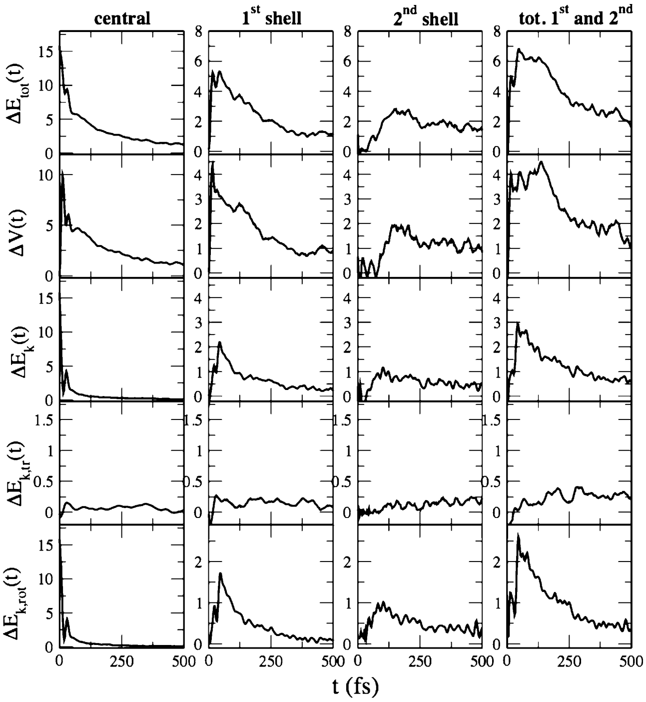

Figure 9. Rotational excitation (all molecules rigid), energy decomposition with respect to equilibrium values for the excited molecule, the first shell molecules, the second shell molecules, and the first two shell molecules (columns from left to right). From top to bottom: total energy, potential energy (see text), kinetic energy, translational kinetic energy, and rotational kinetic energy.

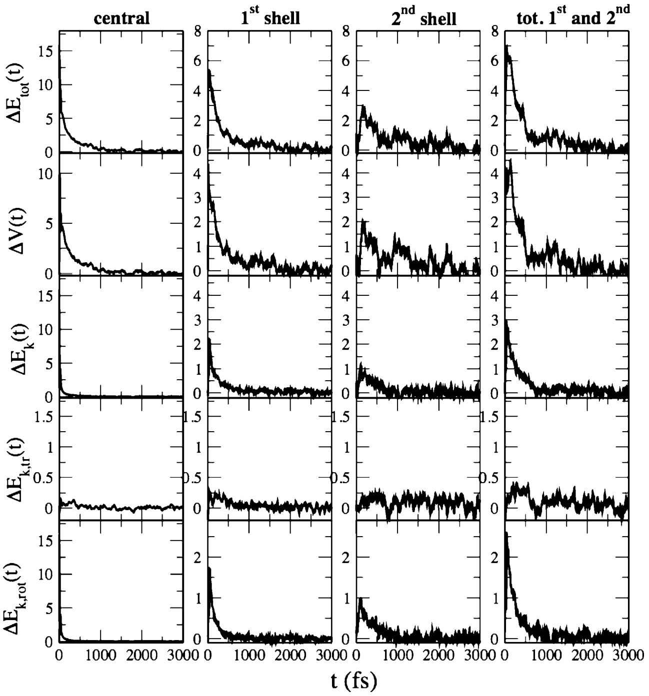

Figure 10. Same as in Figure 9, in a wider time interval.

relaxation time of 20 fs), consistent with the experimental conclusion of a sub-100 fs time scale.[2,3]

With this background, we turn to the details of the energy flow from the initially rotationally excited ("central") water molecule through its hydration shells and into the bulk. To this end, Figures 9 and 10 display—for the first 500 fs and for the longer time interval of 3000 fs respectively—the total, potential, and various kinetic energies for the central molecule and the first two hydration shells, always referenced to their equilibrium values. (Since all the water molecules are rigid here, there are obviously no internal bend potential and kinetic energy contributions.) The potential energy (PE) is calculated on the basis of the intermolecular potential terms (Coulombic and Lennard-Jones), with the parameters of the SPC/E model. For the central molecule, the PE corresponds to the interaction with all surrounding molecules. In the first shell, the PE is given by the interaction energy of those water molecules that are within the shell and similarly for the second solvation shell. The kinetic energy entries are self-explanatory.

Focusing first on the bottom three horizontal KE panels in Figure 9, it is seen that the rapid few tens of femtoseconds decay of the excited water librational KE has a rapid, successive response in the first and second hydration shell rotational KEs. This librational response dominates that of the translational KE. For example, the librational and translational KES in the two shells become comparable only at the end of the 500 fs period. Focusing now on the top three horizontal panels in Figure 9, it is seen first that the potential energy (PE) assigned to the central molecule rises very rapidly—considerable "strain" is created—decays somewhat more slowly, and remains larger than the central water's KE in the 500 fs time interval. These same features are seen in the first hydration shell response and in a muted and delayed form in the second shell response. Figure 10 gives a broader time scale perspective on the energy flow and indicates that the system has come very close to being in equilibrium by ~1 ps, and equilibrium has been reached in all displayed energies in ~2 ps. All these features are consistent with those presented in Figures 5 and 6 and discussed in Section 3.2.

4. Concluding Remarks

We have presented here classical molecular dynamics simulations for the energy relaxation of an excited bending vibration of a single water molecule in liquid water. The energy flow pathway has been probed by monitoring the rotational energy of the bend-excited water and its four closest neighbors. Similar simulations have been separately performed for a rotationally excited water molecule to specifically address the energy decay time scale and association energy flow pathway. The resulting time scales for the H_2O bend energy and rotational kinetic energy are, respectively, 270 and ~30 fs, in reasonable agreement with the experimental results discussed in the Introduction.

The key overall characteristics of the energy flow pathways found (described in detail in Section 3) are as follows: For the excited water bend (whose relaxation time is ~270 fs), there is an important initial energy flow to the librational motion of the bend-excited water. This librational energy and the (predominantly first hydration shell) librational energy received directly from the excited bend flows very rapidly through the bend-excited water's first two hydration shells and on into the remaining "bulk" of the water solvent. These shells have essentially returned to (a slightly higher temperature) equilibrium situation by about 1 ps. The energy flow pathway for a directly rotationally excited water molecule (whose relaxation time is ~30 fs) involves rapid flow through the molecule's first two hydration shells, consistent with the flow characteristics for the excited water bend case.

To the best of our knowledge, previous theoretical studies[20] of water bend relaxation have not addressed energy flow between the excited water molecule bend to the libration of that molecule nor followed the energy flow through the excited molecule's hydration shells. Concerning water librational energy flow itself, in a recent theoretical study of the two-dimensional IR spectrum of water,[19] it was inferred that librational energy motion relaxes on a time scale of ~180 fs, markedly longer than in the present work and the experimental upper bound.[2,3] This 180 fs time scale approximately triples if the water translations are suppressed, indicating a significant coupling between librations and hindered translations.[19,36] The consequences of such coupling is to a degree evident in our results, with the translational kinetic energy in the librationally excited water's two hydration shells becoming comparable to the rotational kinetic energy at ~500 fs; a similar phenomenon was found for the bend vibrationally excited water case.

The importance of the initial transfer of the water bend energy to the rotational, librational motion of the excited water found within clearly requires further elucidation; a separate study[37] indicating the key character of this pathway and which has informed the present interpretation, is presented elsewhere. From the point of view of the librational spectrum of water, the centrifugal coupling[11a,c,33,38] that we have invoked for this transfer has a 2-to-1 resonance character,[32,39] which with a water bend frequency of ~1600 cm^{-1} would implicate librational modes in the neighborhood of 800 cm^{-1}, which as discussed in the Introduction may or may not have a localized character.[12] In any event, this vibration−rotation intramolecular energy flow and the intermolecular flows involved in the water bend relaxation can be usefully studied via examinations of the power (work done by water molecules on a vibration (or rotation) and its spatial distribution,[37] along the lines introduced in ref 16a (see also ref 18). Generalized Landau−Teller approaches (see especially refs 11a and 11c and also ref 31) could also shed some light here. Similar remarks apply to Coriolis coupling.[11a] The approximation of classical mechanics to this problem also warrants investigation.[40] Studies of these issues are underway.

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