J. Phys. Chem. A **2003,** *107,* 8420−8428

Wave Packet Study of Ultrafast Relaxation in Ice Ih and Liquid Water. Resonant Intermolecular Vibrational Energy Transfer

Jens Aage Poulsen,* Gunnar Nyman, and Sture Nordholm

Physical Chemistry, Göteborg University, S-412-96 Göteborg, Sweden

Received: December 6, 2002; In Final Form: June 4, 2003

By using quantum chemistry, the fundamental normal modes and the frequencies of ice Ih and room-temperature water clusters containing up to 15 water molecules are constructed. These normal modes are then used on the basis of assumed harmonic dynamics for analyzing the survival probability and energy decay of wave packets which reflect symmetric and asymmetric stretch excitations in single water molecules. Following symmetric stretch excitation, it is found that the wave packet survival probability and the OH stretch mode energy both decay on a sub-100-fs time scale in both phases. For asymmetric stretch excited states, the characteristic relaxation time is below 100 fs in ice Ih, but it is slower in liquid water. In both cases, it is found that the dynamics are truly many-body in character, since clusters of size ∼15 are required to converge the early time behavior of the OH mode relaxation processes. The results support the suggestion of Woutersen and Bakker (*Nature* **1999**, *402*, 507−509) that, in liquid water, intermolecular vibrational energy transfer occurs on a sub-100-fs time scale. The dynamics appear to be predominantly of harmonic character.

1. Introduction

Vibrational energy relaxation (VER) in the condensed phase remains a challenging and exciting subject in the field of physical chemistry due to the complexity and variety of such processes. For instance, the time scales spanned in VER range from slow millisecond multiphonon relaxation processes at cryogenic temperatures, for example, the relaxation of vibrationally excited O_2 in O_2(l) at 70 K,[1] to subpicosecond relaxation, exemplified by the VER of the OH stretch of HOD in D_2O(l), taking place with a time constant of 740 fs.[2] Another aspect of condensed phase VER showing tremendous variation is the nature of the VER process itself. Depending on the number and nature of intramolecular modes in the excited solute and the presence of proper accepting modes in the liquid, being vibrations, translations, or rotational degrees of freedom, the process can be split into three fundamentally different VER mechanisms: (i) The first is intramolecular vibrational relaxation (IVR), where a new solute mode becomes excited by accepting energy from the initially excited mode. An amount of energy corresponding to the energy mismatch between the two modes is deposited in the solvent.[3] Examples are CH_3Cl in CH_3Cl(l)[4] and OH stretch to bend transitions in HOD/D_2O mixtures, as observed by Deak and co-workers.[5] (ii) The second is pure energy relaxation, where the whole quantum of excitation is transferred to the liquid, ending up as solvent thermal energy. This is the only important pathway for a simple diatomic such as CN^-(aq).[6] (iii) The third is resonant energy transfer, where one quantum transfers between two identical molecules, leaving the system with the excitation in the same degree of freedom but transferred to another molecule. Examples are matrix isolated CH_3F[7] at 10−20 K and the mechanism put forth by Woutersen and Bakker[8] for describing ultrafast OH bond VER in liquid water; see below. For the majority of systems studied so far, mechanisms (i) and (ii) occur faster than the third one, except at low temperatures.[7,9] What makes VER even more challenging is the fact that the processes are expected to be quantum mechanical[10−13] and, in general, many-body in character,[14] which makes accurate treatments extremely difficult.

Pure water represents a solvent in which fast relaxation processes take place: Investigations of the subsequent dynamics of an initially excited OH bond in HDO/D_2O mixtures in the solid and liquid state have been carried out by Woutersen et al.,[2] showing the lifetime of an OH bond excitation in water to be 740 fs, which is short compared to the lifetimes of other excited aqueous solutes.[6,15,16] The lifetime in Ice Ih was found to be even shorter: 380 fs. The short lifetimes were ascribed to the effectiveness of the hydrogen bond network as an energy transmitter.[2] Also, Lock and co-workers have studied the equilibration dynamics of liquid water and alcohols, following a local deposition of energy in OH bonds.[17] It was found that water had the fastest equilibration time, 0.5−0.6 ps. Furthermore, the process determining the equilibration time for water was argued to be of IVR nature, where the energy initially localized in an OH bond transfers to the internal bending mode, as is also observed in gas-phase VER.[18] According to Lock et al., this intramolecular energy transfer occurs on an ultrafast time scale of ∼130 fs. The internal state subsequently relaxes on a time scale of 0.55 ps. Deak[5] and co-workers used IR−Raman techniques to obtain lifetimes for OH stretches in HDO and H_2O molecules dissolved in D_2O(l). The observed lifetime of ∼1 ps was in good agreement with the findings of Woutersen et al.[2] They further showed that in the VER of HOD in D_2O(l) intermolecular vibrational energy transfer occurs with a large quantum yield, meaning that a vibrational quantum in the OH bond of HOD can, by an IVR process, convert to an HOD OD mode quantum which then resonantly transfers energy to a band of OD modes in the D_2O liquid.[5]

Woutersen and Bakker[8] measured the rotational anisotropy of vibrationally excited OH groups in pure water and HDO/D_2O mixtures. (Here, the rotational anisotropy provides a measure of how fast initially excited and aligned dipole vectors reorientate and consequently loose their alignment.) In these mixtures, they found that, by increasing the OH concentration,

10.1021/jp0225469 CCC: $25.00

the rotational anisotropy decreased on a faster time scale. This was explained by proposing an ultrafast intermolecular energy transfer mechanism between adjacent OH groups in the liquid. In pure water, where the OH group concentration is largest, the decay of the anisotropy was observed to take place on a sub-100-fs time scale.[8] That intermolecular resonant energy transfer between adjacent OH groups in water should take place on a sub-100-fs time scale and thereby beat the fast 740-fs time scale for OH mode population decay came as a real surprise.[9] The possibility that adjacent OH oscillators can exchange energy is not surprising, since we imagine it to be made possible by the three-dimensional hydrogen bond network in water. What *is* surprising is the reported sub-100-fs time scale, which is the fastest time scale observed for any VER process in liquids.[9] Hence, in short, we think we know the nature of the process but we are surprised at its efficiency. It is the goal of this paper to model the intermolecular OH energy transfer using simple harmonic theory for the dynamics and to extract a time scale for this process. We consider water both in its liquid form at room temperature and in its natural solid state, ice Ih.

The computational approach to the relaxation of the OH bond excitations in water can be carried out in various ways depending on the options selected in the following aspects of the problem: (a) potential model—ab initio or generic (effective pair potentials etc.)? (b) dynamics—classical or quantum? Exact or approximate? We may select one of the many intermolecular water potentials and add a simplified intramolecular water potential to model a solute water molecule in a water cluster in a generic manner, that is, in a qualitative way. The alternative, which we shall prefer in this case, is to turn to high level quantum chemistry for a description of the inter- and intramolecular interactions. In this way we can produce a more reliable potential, albeit at some cost in computational effort and loss of simplicity of form. With respect to the dynamics, we must decide to what degree we shall include quantum effects and whether we shall seek a numerically exact solution or be satisfied with a simplified and approximate form of dynamics. In this study we shall adopt a greatly simplified form of dynamics based on the harmonic approximation; that is, we shall expand the potential around the minimum and retain only terms up to second order in the deviations from equilibrium. The nuclear dynamics are then expressed in normal modes which are separable, and the dynamics are easily obtained on any time scale. This type of dynamics is often assumed in the study of phonons in solids and vibrational dynamics of molecules, for example, in the Slater theory of reaction rates.[19] Also, harmonic dynamics have been applied to describe processes occurring on short time scales in liquids, thereby providing an analytic short-time formalism referred to as instantaneous normal mode theory.[20] We are well aware that anharmonic couplings are present and likely to affect the intermolecular motions strongly. There are, however, many significant advantages in the harmonic approximation: (a) It can be obtained for large clusters by use of ab initio methods. (b) Quantum and classical dynamics are both readily accessible. (c) It is likely to provide a good estimate of fast relaxation times and a lower bound on the rate of relaxation. In this case we have experimental evidence of fast relaxation of OH stretch excitations and hope to show that the high rates are to a good extent already captured by adopting a harmonic model of water clusters.

This paper is structured as follows: In section 2, the Ice Ih and water models are presented. Section 3 contains a summary of the computational details of the model together with basic wave packet theory. In section 4, the results are presented and discussed. Finally, we conclude in section 5.

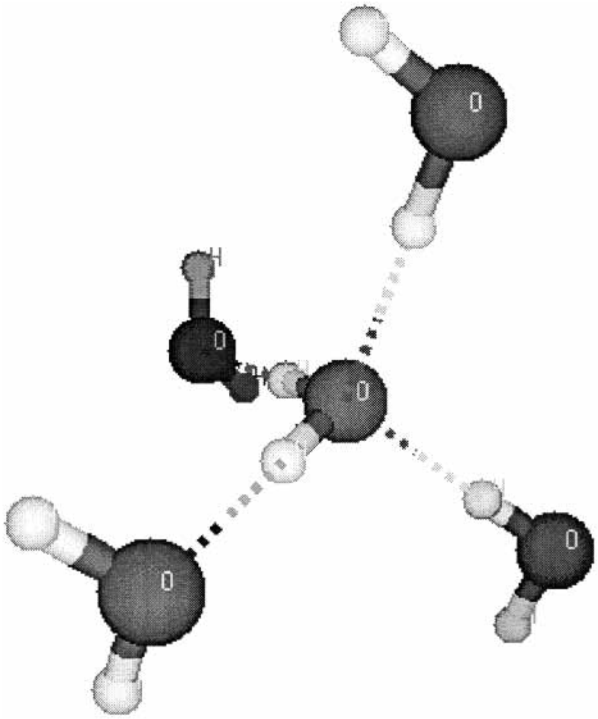

Figure 1. Characteristic structure of a tetrahedrally coordinated water molecule.

2. Ice Ih and Water Model

To directly simulate the time-dependent rotational anisotropy following excitations of OH stretches in water is a daunting task. First, we would need to know the precise nature of the excited wave packets. Clearly, this is an extremely difficult task. A further complication is that the rate of decay of the rotational anisotropy also contains contributions from IVR and rotational relaxation.[8]

Instead of mimicking the time-dependent anisotropy, we can formulate other projects which will give insight into the intermolecular energy transfer occurring in water: Let us consider the resonant energy transfer and survival probability of wave packets initially representing symmetric or asymmetric stretch excitations of water monomers in water clusters. (One could also consider the golden rule approach,[21] which has been used extensively in modeling VER in the condensed phase.[3,4,6,15,16,] It has however recently been shown by Herman and coworkers[22,23] that this approach is not suited for describing resonant $V \rightarrow V$ transfer, due to a long-time coherence between the energy exchanging resonant states. This phenomenon shows up as a probability, $P(t)$, varying nonlinearly as a function of time, for energy relaxation, which makes the extraction of a rate constant meaningless.) In the following, such excited states will be loosely referred to as OH stretch excited states. The survival probability or energy of such initial states should decay fast, on a 100-fs time scale or faster, if the mechanism proposed by Woutersen et al. is correct. For such excited states, we have the following picture of the OH stretch intermolecular energy transfer process: A wave packet corresponding to an excited OH stretch mode in one water molecule is initiated. In liquid water, a tetrahedral four-neighbor structure is dominating[24,25] (see Figure 1), which means that on average almost four hydrogen bonds connect to each water molecule. The hydrogen bonding is strong: For the water dimer the energy is about 2.6

kcal/mol,[26] indicating a strong coupling between atoms in neighboring water molecules. We imagine this coupling to facilitate the resonant energy transfer. In ice Ih, that is, ordinary ice, the same tetrahedral structure around each water molecule is present but now it is almost optimal, in the sense of perfect hydrogen bonding,[25] which makes us expect that the ice Ih hydrogen bond network will actually be a more effective mediator of OH mode resonant energy transfer than the network in liquid water.

2.1. Choosing a Correct Potential and Dynamics Method. From a conceptual point of view, ice Ih is easier to simulate than liquid water, since, in crystals, an approximate harmonic phonon description of the vibrational motion of the atoms is permissible.[27] This is because no unstable modes, with imaginary frequencies, are present in solids as opposed to liquids.[20] However, Stratt and co-workers[20,28,29] have shown that the dynamics even of a liquid, on a short time scale of typically 50−100 fs, can be accurately modeled by phonon dynamics, since, on such a time scale, the low frequency, slow motions along unstable directions are not yet significant. This approach is referred to as instantaneous normal mode dynamics.[20] Hence, following Stratt,[20] a harmonic description of a liquid is valid on a sufficiently short time scale. Two arguments further support using instantaneous normal mode dynamics for our particular problem. First, in water at room temperature, only 6% of all modes are unstable,[20] which makes water "solidlike" as compared to other liquids.[20] Second, we are interested in particularly fast processes occurring on a sub-100-fs time scale. Below we will give further arguments for using a simple harmonic model in our study.

2.2. Why a Harmonic Model Should Work. The nature of resonant energy transfer, a type (iii) process, contains a simplifying feature. As we will argue below, a simple harmonic normal mode (NM) description of the dynamics allows for the modeling of the energy transfer. This is opposed to intramolecular energy transfer, a type (ii) process, where delicate higher order anharmonic couplings in the intramolecular potential are required for driving the process; see, for example, the recent VER study of CH_3Cl in $CH_3Cl(l)$.[4] To see that simple harmonic dynamics accounts for resonant energy transfer, let us consider the water dimer (which consists of two hydrogenbonded water molecules) in its equilibrium geometry. We consider the intermolecular potential as a perturbation added to the zeroth-order Hamiltonian, which is the sum of two harmonic vibrational water monomer Hamiltonians. The zeroth-order eigenstates are hence direct products of vibrational eigenstates for the two isolated molecules. As coordinates for the dimer we first select the three NMs in each molecule. We label these $\{q_i\}_{i=1}^{6}$ in the following sequence: symmetric stretch (water one), asymmetric stretch (water one), bending (water one), and then the three NMs for water number two in a similar sequence. The remaining coordinates, $\{q_i\}_{i=7}^{18}$, are the standard center of mass coordinates and Euler angles for each molecule. The values of all 18 coordinates are chosen so as to reproduce the dimer equilibrium geometry. This fully determines their value, up to an irrelevant value of the whole dimer center of mass coordinates and Euler angles. Afterward, the coordinates $\{q_i\}_{i=7}^{18}$ are frozen at their specific values, to make things simple, not because it is essential for the argument. The dimer intermolecular potential energy can now be Taylor-expanded in the six vibrational NMs around the minimum geometry of the dimer

$$V_{\text{int}} = \sum_{i=1,6} \alpha_i q_i + \sum_{i,j=1,6;i<j} \alpha_{i,j} q_i q_j + ... \qquad (1)$$

The lowest order term in this expansion, which induces an annihilation of one quantum of, say, symmetric stretch in water one (deactivating state $|1\rangle \equiv |100000\rangle$) and creates a corresponding quantum in water two (activating state $|2\rangle \equiv |000100\rangle$), is clearly the quadratic term $V' \equiv \alpha_{1,4} q_1 q_4$, since in terms of boson creation and annihilation operators this term equals

$$V' = \frac{\hbar}{2m\omega(\text{sym})} \alpha_{1,4} (b_1^\dagger b_4^\dagger + b_1 b_4 + b_1^\dagger b_4 + b_1 b_4^\dagger)$$

(ref 30), where ω(sym) and m equal the monomer water symmetric stretch frequency and reduced mass, respectively. Also, $b_1^\dagger$ is the creation operator for the symmetric stretch of molecule one and so forth. Using the method of variation of constants,[31] it is now straightforward to find an expression for the probability of symmetric stretch resonant energy transfer from water one to water two:

$$P(t) = \left| \frac{1}{i\hbar} \int_0^t \mathrm{d}s\, V'_{12} \exp(i\omega_{12} s) \right|^2 = \frac{t^2}{\hbar^2} |V'_{12}|^2 \qquad (2)$$

with

$$V'_{12} = \langle 1|V'|2\rangle = \frac{\hbar}{2m\omega(\text{sym})} \alpha_{1,4}$$

and where we have used $\omega_{12} \equiv E_1 - E_2 = 0$ for the two degenerate zero-order states $|1\rangle$ and $|2\rangle$. Equation 2 is nothing but the first term in a Taylor expansion of the Rabi formula.[31] Hence, already at the harmonic level of interaction, resonant vibrational energy transfer is allowed. Also, we see that, by making the harmonic truncation in eq 1, terms coupling, for instance, the symmetric stretch in water one with the bending mode 2-fold excited in number two are not accounted for, since such transitions require retaining the cubic terms or extending the variation of constant method to higher order couplings in V_{int}. Hence, such processes are not included in our simple harmonic model. We further note that the first term beyond the harmonic truncation in eq 1, which again couples $|1\rangle$ and $|2\rangle$, is a quartic term. Hence, within first-order perturbation theory, our harmonic approximation is exact to third order in the Taylor expansion of the intermolecular interaction.

2.3. Further Arguments for a Harmonic Model. Since resonant energy transfer between neighboring OH groups is included in a harmonic phonon treatment, the simplest possible analysis would proceed as follows: Construct the NMs of the water cluster, from some yet unspecified potential. Then perform wave packet dynamics for locally excited OH stretch modes and monitor their survival probability and energy relaxation. This can be done analytically, which greatly simplifies matters. A further argument for this method is that, by limiting the potential to harmonic order, the NMs can then be derived from ab initio electronic structure theory, ensuring high quality harmonic couplings in eq 1. On the other hand, more advanced dynamical approaches, but utilizing more approximate analytical potentials, could retain the anharmonicity of the water cluster potential. For example, effective time-dependent self-consistent field (TDSCF) approaches, specifically designed for propagating vibrational wave packets in anharmonic clusters, have been developed.[32,33] However, these approaches require the existence of high quality flexible water potentials, which faithfully describe vibration−vibration coupling between modes in adjacent water molecules. Moreover, it has been suggested that, due to the proximity of adjacent OH bonds in water, high order multipole couplings are important,[9] meaning that not only dipole−dipole but also higher order multipole couplings should be accurately modeled by the potential. The requirement that the water molecules be flexible rules out sophisticated rigid body ab initio water pair potentials such as NEMO[34] and SAP-5s[35] which rigorously include dispersion and induction effects. The simple point charge (SPC) models for water,[36,37] which allow for flexibility, are not suited for our purpose, since they represent effective potentials with many-body interactions represented as two-body interactions. Clearly, such potentials are, by construction, not expected to predict precise harmonic couplings between atoms in adjacent water molecules. Another potential, namely the water pair potential of Reimers, Watts, and Klein (RWK2),[38] which also includes an intramolecular potential, should be considered. This combined inter- and intramolecular potential has been improved by Coker and co-workers[39] to better fit the infrared dimer absorption spectrum, which means that the above-mentioned vibration−vibration coupling indeed is taken into account. However, a serious shortcoming of the RWK2 potential is its use of fixed point charges, which ideally should depend also on the geometry of the water molecule. It has been shown by Morita and co-workers[16] that the inclusion of the latter dependence can be crucial for accurately describing VER in the condensed phase. Another problem with the RWK2 potential is its inability to describe induction effects.[40] Hence, these considerations lead us to choose between (i) a model which is dynamically primitive, since it neglects anharmonic effects but on the other hand has a good description of the fundamental harmonic couplings from which it derives its dynamics, and (ii) a dynamically higher level theory, for example, the TDSCF approach, including the anharmonicity of the water cluster, but at the expense of not knowing the accuracy of even the harmonic part of the water potential. We have chosen the former, also more simple, approach as our starting point for investigations, which should later consider anharmonicity.

3. Computational Details

In this section we address the problem of choosing a suitable level of electronic structure theory, which enables us to compute reliable frequencies and NMs of water clusters. Also, we consider the definition of the initial vibrational nonstationary states and the basic wave packet theory needed to propagate these. Finally, the details of the ice Ih structure and water molecular dynamics simulation are presented.

3.1. Electronic Structure Method. To determine frequencies and NMs for clusters ranging from 5 to 15 water molecules, electronic structure calculations were performed using the Gaussian 98[41] electronic structure program package using DFT employing the hybrid B3LYP exchange-correlation functional together with a 6-31G** basis set.[42] To check the accuracy of B3LYP, we calculated symmetric stretch wave packet survival probabilities (WSPs) for a water pentamer structure, by utilizing the B3LYP functional and also by an ab initio second-order Møller−Plesset (MP2) calculation using the same basis set. Ab initio calculations based on an MP2 level of theory, which includes electron correlation, have been shown to accurately describe the structure of water clusters.[43] Figure 2 shows the WSP and that good agreement between the calculations is obtained. We have also applied B3LYP with a more complete basis set, that is, aug-cc-pVDZ. However, as Figure 2 shows, the basis set effect is small. Our interest is in finding the initial decay rate of the WSP, and for this purpose the agreement between the curves is excellent. Therefore, we base all calculations on the less-time-consuming B3LYP/6-31G** approach.

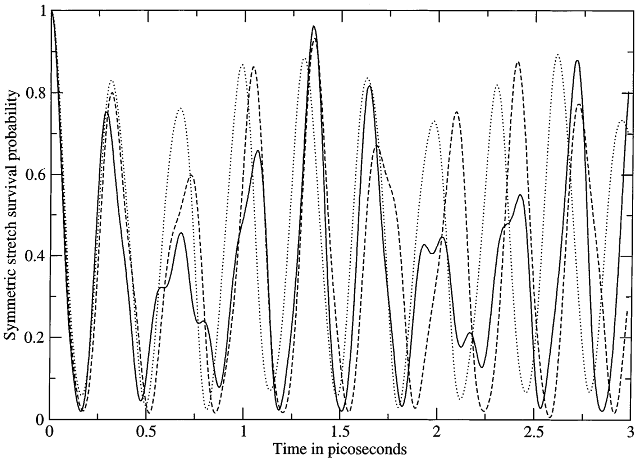

Figure 2. Level of agreement between MP2 and B3LYP. WSP for a symmetric stretch wave packet in the pentamer structure: solid line, MP2; dashed line, B3LYP; dotted line, B3LYP+AUGpVDZ.

3.2. Wave Packet Dynamics. Given a cluster geometry with water molecules derived from either ice Ih or liquid water, we need to perform dynamics of wave packets moving in the harmonic water cluster potential. When modeling our initial nonstationary OH stretch state, we shall need the relation between local Cartesian displacement coordinates on each atom and the NMs. The relation is[44]

$$\vec{X} = \mathbf{A}\vec{\tilde{Q}} \tag{3}$$

where $\vec{X}$ is the vector containing the actual physical displacements of the cluster atoms and $\vec{\tilde{Q}}$ represents the changes in mass weighted NMs. The matrix $\mathbf{A}$ is given by

$$\mathbf{A} = \mathbf{G}^{1/2}\mathbf{L} \tag{4}$$

where $\mathbf{G}^{1/2}$ is a diagonal matrix containing inverse square roots of atomic masses. $\mathbf{L}$ contains the orthonormal column vectors corresponding to a unitary transformation of mass weighted coordinates $\vec{Y}$:

$$\vec{Y} = \mathbf{G}^{-1/2}\mathbf{X} = \mathbf{L}\vec{\tilde{Q}} \tag{5}$$

The mass weighted NMs are related to dimensionless normal modes, $\vec{Q}$, (DNMs) by the linear transformation

$$\vec{Q} = \mathbf{\Lambda}\vec{\tilde{Q}} \tag{6}$$

where $\Lambda_{ij} = \delta_{ij}(\omega_i/\hbar)^{1/2}$. In the last equation, ω_i is the frequency of the ith NM and δ_{ij} is Kroneckers delta. To create an excitation of, for example, symmetric stretch nature, in the central water molecule of the cluster, we proceed as follows: Physical displacements of atoms in the central H_2O molecule are chosen by moving the hydrogens an amount toward the oxygen atom, along the bonds, and finally moving the oxygen so that the center of mass is conserved. The particular amount of displacement is of no significance, since our potential is harmonic. The above procedure is here referred to as a simple “geometric” symmetric stretch excitation. An asymmetric stretch excitation is defined in a similar manner. We then know $\vec{X}$ and we can calculate $\vec{Y}$. Equations 5 and 6 are then solved for $\vec{Q}$, which means that we have an excitation corresponding to a linear combination of DNMs

$$\varsigma = \sum_{i=1}^{N} c_i Q_i \tag{7}$$

where N is the total number of modes, ranging from 45 to 135.

Let us require normalization

$$\sum_{i=1}^{N} c_i^2 = 1 \tag{8}$$

We apply this excitation to an initial thermal state of our cluster which can have excitations in low frequency modes. For simplicity, we assume that the high frequency stretch and bending modes do not have any thermal excitations, which is reasonable at 273−298 K. Let our initial thermal vibrational state have the energy

$$E_0 = \sum_{i=1}^{N} \hbar\omega_i(\nu_i + {}^1/_2) \tag{9}$$

and wave function

$$|\Psi\rangle_0 = \prod_{i=1}^{N} H_{\nu_i}(Q_i)\exp\left(-\frac{1}{2}Q_i^2\right) \tag{10}$$

where we have introduced the Hermite polynomials, including normalization, for each NM. To excite this state, according to eq 7, we apply the excitation operator

$$\varsigma^{\dagger} = \sum_{i=1}^{N} c_i b_i^{\dagger} \tag{11}$$

where $b_i^{\dagger}$ is the standard boson creation operator,[30] creating a single quantum of excitation in the ith mode. The summation in eq 11 can be modified to only include the high-frequency stretch modes, since the expansion in eq 7, in practice, does not have any components representing the low frequency modes. Let us number the latter from 1 to M, $M < N$, so that the high frequency modes are numbered from $M + 1$ to N. Our new wave function and energy are then

$$|\Psi\rangle = \sum_{i=M+1}^{N} c_{\mathrm{i}} H_1(Q_{\mathrm{i}})\exp\left(-\frac{1}{2}Q_i^2\right)\prod_{j=1}^{M} H_{\nu_j}(Q_j) \exp\left(-\frac{1}{2}Q_j^2\right)\prod_{j=M+1, j\neq i}^{N} H_0(Q_j)\exp\left(-\frac{1}{2}Q_j^2\right) \tag{12}$$

$$E = \sum_{i=1}^{N} \hbar\omega_i(\nu_i + {}^1/_2) + \sum_{i=M+1}^{N} c_i^2\hbar\omega_i \tag{13}$$

yielding an excitation energy of

$$\Delta E = \sum_{i=M+1}^{N} c_i^2\hbar\omega_i \tag{14}$$

The wave packet in eq 12 is easily propagated:

$$|\Psi(t)\rangle = \sum_{i=M+1}^{N} c_i \exp(-i(\hbar\omega_i + E_0)t/\hbar)H_1(Q_i) \exp\left(-\frac{1}{2}Q_i^2\right)\left\{\prod_{j=1}^{M} H_{\nu_j}(Q_j)\exp\left(-\frac{1}{2}Q_j^2\right)\prod_{j=M+1, j\neq i}^{N} H_0(Q_j) \exp\left(-\frac{1}{2}Q_j^2\right)\right\} \tag{15}$$

We can now, finally, evaluate the wave packet autocorrelation function

$$\langle\Psi(0)|\Psi(t)\rangle = \sum_{i=M+1}^{N} c_i^2 \exp(-i(\hbar\omega_i + E_0)t/\hbar) \tag{16}$$

and consequently the survival probability

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

Other valuable information which can be extracted from the NM analysis is the rate of energy relaxation for an excited OH stretch mode. Since we have a mapping between NMs and Cartesian displacement coordinates through eq 3, we can readily evaluate an OH distance in the excited central water molecule. Within a local mode or valence bond description of the excited molecule,[38] the potential energy part of a water molecule is approximated as

$$V_{\mathrm{H_2O}} = \frac{1}{2}k_{\mathrm{OH}}\Delta r_{\mathrm{OH(1)}}^2 + \frac{1}{2}k_{\mathrm{OH}}\Delta r_{\mathrm{OH(2)}}^2 + \frac{1}{2}k_{\Theta}\Delta\Theta^2 \tag{17}$$

Hence, the potential energy in an OH bond is simply proportional to Δr_{OH}^2, which is readily obtainable from the NM analysis. In an important paper for the VER community, Bader and Berne[10] pointed out that classically determined energy relaxation rates for vibrationally excited modes are exact, provided that the underlying dynamics are harmonic. This means that the approximate local mode energy in eq 17 should give a reasonable description of the energy decay of excited OH bonds in the water cluster. We have calculated the decay of the total OH stretch energy function, being proportional to $\Delta r_{\mathrm{OH(1)}}^2 + \Delta r_{\mathrm{OH(2)}}^2$, and found it to be very similar to the WSP function in the solid and liquid phase for all considered excitations.

3.3. Ice Ih Crystal. We consider an ice Ih crystal at 0 degrees centigrade and 1 bar; see Figure 3. The crystal data are as follows: The cell is made up of SPC/E[37] water molecules, having an OH bond length of 1.00 Å and a HOH angle of 109.5°, which makes the water molecules fit perfectly into the ice Ih tetrahedral structure. In our crystal, each oxygen atom is tetrahedrally surrounded by four other oxygen atoms at a distance of 2.76 Å, which is in accord with experiments at this temperature and pressure.[45] The lattice constants a and c are 7.37 and 4.52 Å, respectively, also in agreement with measurements.[45] There is a great deal of flexibility with regard to positioning the hydrogen bonds in the crystal, allowing for six fundamental ways that the central water molecule can coordinate to its four neighbors,[46] thereby allowing for more or less ordered ice structures. We have chosen to study only one structure, since we feel that little variation, if any, is expected, since, in all possible structures, the number of hydrogen bonds and the interatomic distances remain the same.[46] We consider ice Ih clusters with 5 to 15 molecules. These structures are derived by cutting the central water molecule and its 4 to 14 closest neighbors out of the structure shown in Figure 3. In the central water molecule, OH stretch motions are then initiated. In Figure 4, the largest cluster with 15 water molecules is shown.

3.4. Molecular Dynamics of Liquid Water at 300 K. To simulate liquid water, we employed the MOSCITO molecular dynamics simulation package[47] using 108 SPC/E[37] molecules at a density of 1.0 g/cm^3. A cubic simulation box of length 14.79 Å together with periodic boundary conditions was employed. A potential cutoff equal to half the box length was adopted. The geometry of the water molecules was held rigid by applying the SHAKE algorithm of Ryckaert et al.[48] The simulation time step was 1 fs, and the Berendsen thermostat[49] was applied in

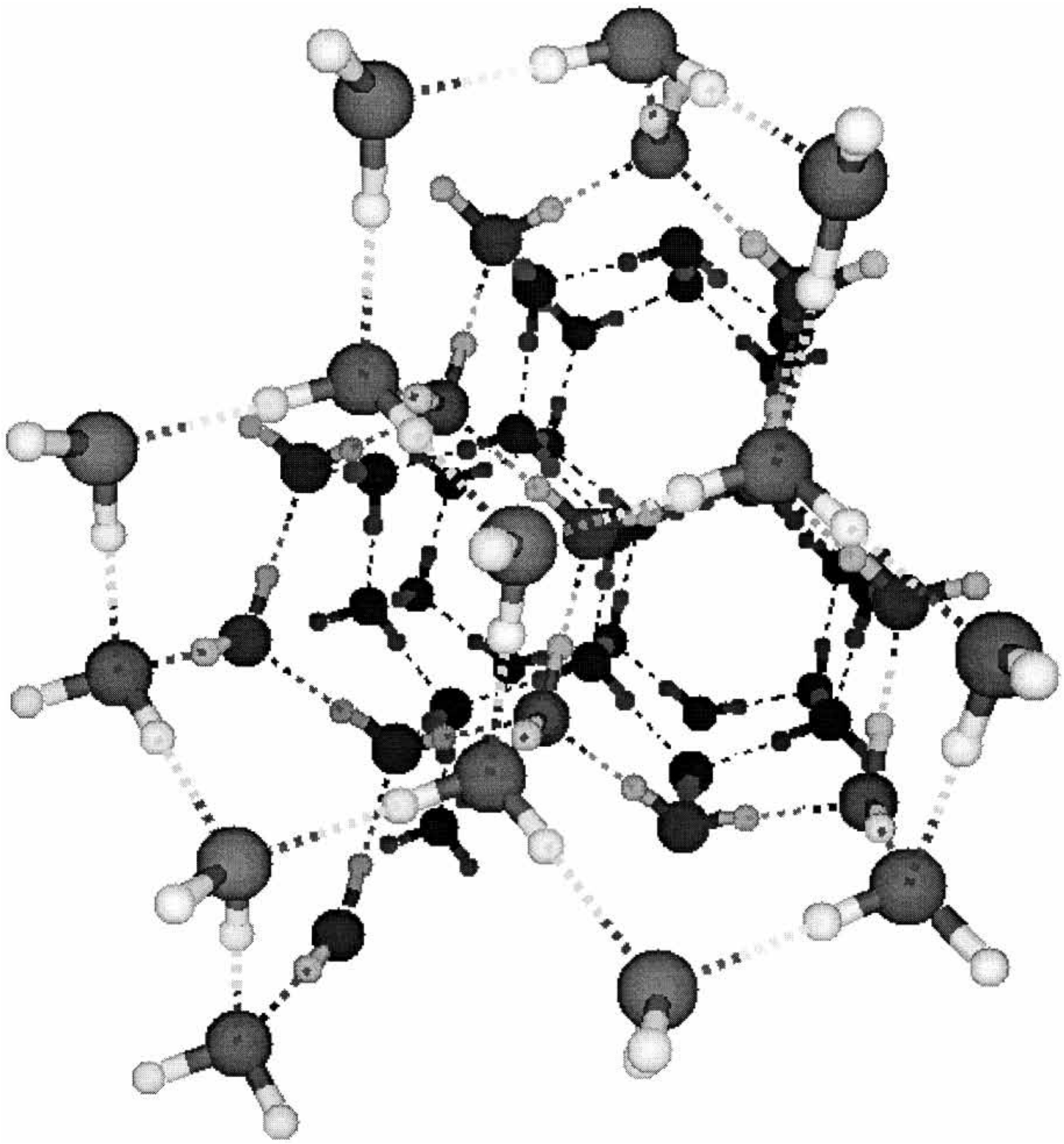

Figure 3. Ih structure of ice.

each time step in order to keep the temperature at 300 K. This was accomplished by using a coupling constant of 0.1 × 10^4 ps^{-1}. Long-range electrostatic interactions were handled by adopting the particle mesh Ewald (PME) summation method,[50] using a 16 × 16 × 16 grid for the Fourier representation of the charge density, and a spline interpolation of order 4. The Ewald convergence parameter α was assigned a value of 0.362 33 $Å^{-1}$ in accord with a suggested value of $5.37/2r_{cut}$,[51,52] where r_{cut} is the cutoff radius. After an equilibration time of 20 ps, 17 structures were sampled, one every 5 ps, and the data were saved for further analysis. For each of these structures, a cluster of 15 water molecules was derived by picking out the central water molecule and its 14 nearest neighbors.

4. Results

4.1. Ice Ih. In Figures 5 and 6, we show results for symmetric and asymmetric stretch wave packet survival probabilities, initiated in the central ice Ih water molecule, for clusters containing 5, 8, 12, and 15 water molecules. The wave packet excitation energies calculated according to eq 14 are, in order of increasing cluster size, 3278, 3282, 3279, and 3272 cm^{-1}. As Figure 5 shows, the symmetric stretch half-lives for the survival probability are 70, 67, 53, and 50 fs for clusters containing 5, 8, 12, and 15 water molecules, respectively. We note that the recurrences in the survival probability get quenched as the cluster size increases, which is also physically reasonable. In Figure 6 are shown similar results but now for initial asymmetric stretch excitations. The half-lives and excitation energies are now, in order of increasing cluster size, 243 fs (3346 cm^{-1}), 125 fs (3353 cm^{-1}), 87 fs (3344 cm^{-1}), and 79 fs (3333 cm^{-1}), showing that the relaxation is a bit slower and that the results are essentially converged with respect to cluster size. From these results, we see that the water molecules not only in the first solvation shell but also in the second shell contribute significantly to the wave packet decay process and indeed cannot be neglected. To check that convergence really is obtained for clusters with 15 molecules, we have performed similar calculations, employing clusters containing up to 32

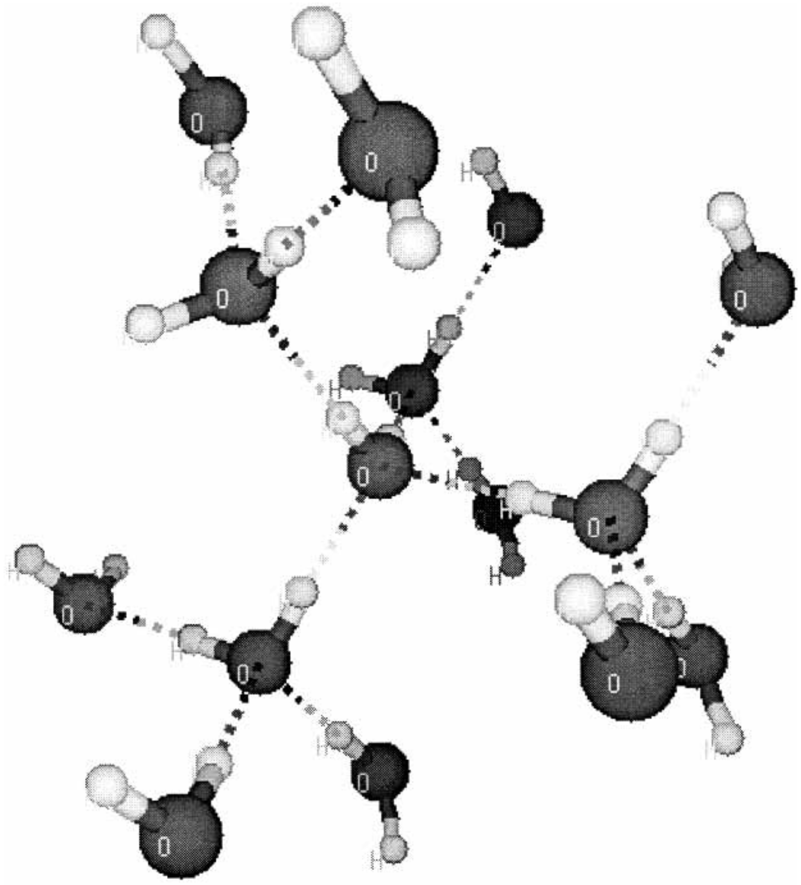

Figure 4. Ice Ih structure, 15 molecules.

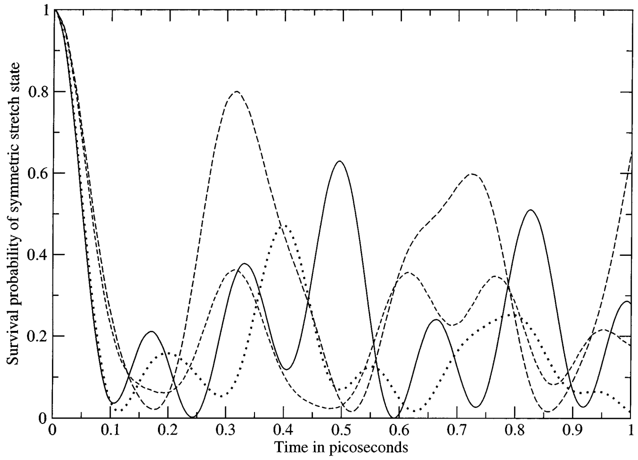

Figure 5. Survival probability of the symmetric stretch excitation for clusters of size 5, 8, 12, and 15 molecules: solid line, 15; dotted line, 12; dashed line, 8; long-dashed line, 5.

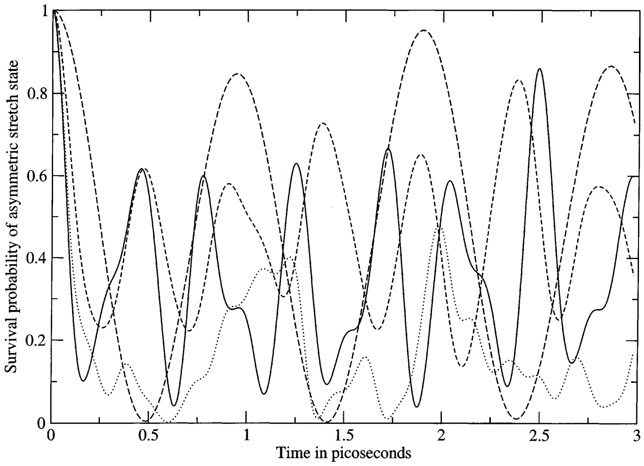

Figure 6. Survival probability for the asymmetric stretch excitation for clusters of size 5, 8, 12, and 15 molecules: solid line, 15; dotted line, 12; dashed line, 8; long-dashed line, 5.

molecules, using a semiempirical PM3 approach,[53] which indeed confirmed that this is the case. As a check of the consistency of the wave packet approach, we also investigated the effect of replacing the four neighbors in the pentamer cluster by D_2O. In Figure 7 it is seen that the initiated symmetric stretch excitation is now trapped in the central water molecule, since the OD stretches are not in resonance with the excited OH stretch motion in the central water molecule. We conclude that the excited geometric symmetric stretch state is close to the symmetric stretch eigenstate of the central water molecule. To describe the VER of an OH mode in a D_2O environment, higher order multiphonon processes should be included in the model. However, given our harmonic Hamiltonian, we cannot describe such processes.

4.2. Liquid Water Results. In Figure 8 is shown the symmetric stretch excited WSP derived from averaging over 10, 14, and 17 liquid water configurations. For 17 configurations, the half-life of the decay is 83 fs. The mean excitation energy is 3307 cm^{-1}. In Figure 9, similar results are shown, now for asymmetric stretch excitations. The mean excitation energy is 3401 cm^{-1}. We note that the asymmetric stretch WSP decays markedly slower than that in ice Ih. The half-life in liquid water is about 250 fs. Also, we see that the probability never drops below 30%. This is also seen when doing the same wave packet

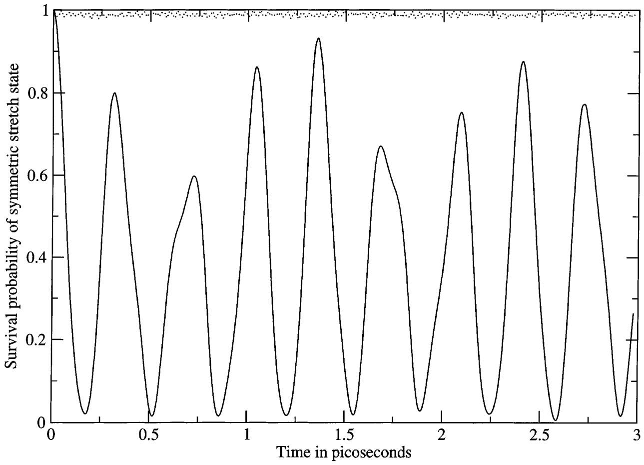

Figure 7. Survival probability for the symmetric stretch excitation for one H_2O molecule surrounded by four H_2O or four D_2O molecules: solid line, four H_2O molecules; dotted line, four D_2O molecules.

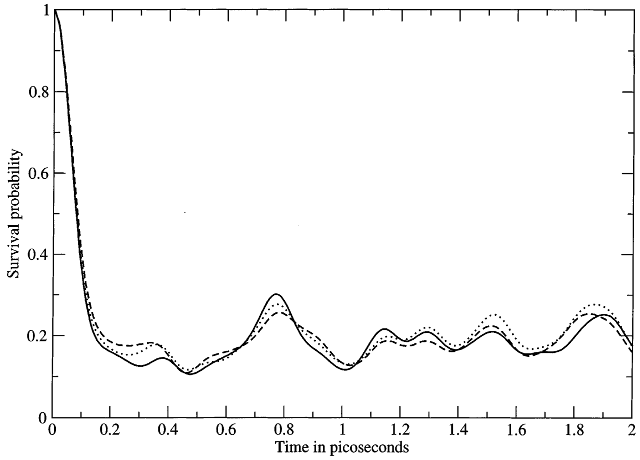

Figure 8. Decay of the symmetric stretch WSP for liquid water at 300 K. Results are for clusters of 15 molecules. The ensembles of initial conditions contain 10 (solid line), 14 (dotted line), and 17 (dashed line) entries.

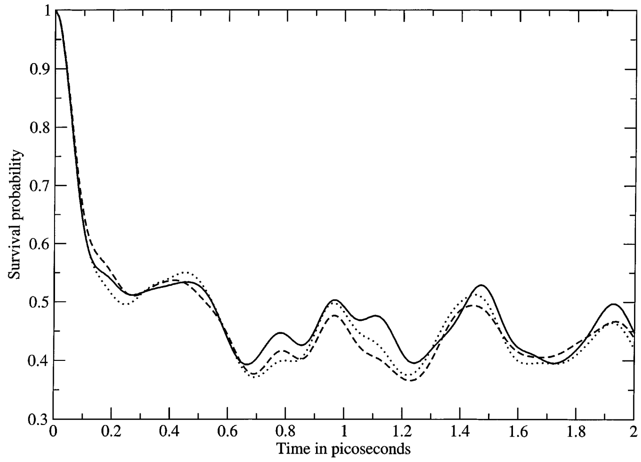

Figure 9. Decay of the asymmetric stretch WSP for liquid water at 300 K. Results are for clusters of 15 molecules. The ensembles of initial conditions contain 10 (solid line), 14 (dotted line), and 17 (dashed line) entries.

calculations on the 17 configurations, but now including 32 water molecules, using the more approximate PM3 semiempirical approach. Hence, the fact that the probability never drops below 30% is probably not due to effects pertaining to cluster size.

5. Conclusion and Discussion

We have calculated characteristic decay half-lives for symmetric and asymmetric stretch excited states in ice Ih and room-temperature liquid water. The wave packet lifetimes for symmetric stretch excitations were found to be ~50 and ~83 fs for ice Ih and liquid water, respectively. For asymmetric stretch excitations, the corresponding numbers were ~79 and ~250 fs, respectively. To a very good approximation, it was found that the same four half-lives also reflect the total OH mode energy decay in both phases. We have shown that, by adopting the simplest possible model, that is, by employing instantaneous normal mode theory, we are able to account for a resonant energy transfer mechanism which occurs on a sub-100-fs time scale. Hence, the findings in this paper support the proposal of Woutersen and Bakker,[8] that intermolecular resonant energy transfer occurs on an ultrafast time scale. We further find that the intermolecular energy transfer occurs most rapidly in ice Ih. The results of this paper add to our understanding of what happens after generation of an OH stretch excited state in liquid water. Depending on the amounts of symmetric and asymmetric stretch excited states in the wave packet, intermolecular resonant energy transfer takes place on a ~100−300 fs time scale. As suggested by Lock and co-workers,[17] a possible competing process, occurring on the same fast time scale, is the intramolecular energy transfer to the bending mode degree of freedom.

It is interesting that, in both phases, the symmetric stretch mode relaxes faster than asymmetric stretch, especially in liquid water. To understand this, we have counted the number of harmonic modes which participate in the relaxation dynamics by requiring that their expansion coefficient be larger than 50% of the coefficient of the major harmonic mode. In ice Ih, a total of three modes participate in the dynamics for both symmetric and asymmetric stretches. In liquid water, averaging over 17 configurations yields four and two modes for symmetric and asymmetric stretches, respectively. Hence, apparently, the number of energy acceptors for the asymmetric stretch goes down when going from ice to liquid water. This could also explain why the predicted asymmetric stretch WSP never drops below 30%: The excitation is simply spread out on too few a number of modes to become delocalized.

We finally emphasize again that our simple model is not capable of describing VER processes which are driven by anharmonic effects. This means that intramolecular relaxation, exemplified by energy transfer between symmetric and asymmetric stretch states in the same water molecule, is not included in our model. Inclusion of such effects could, for instance, make the asymmetric stretch WSP drop below 30% in our liquid water model. However, the observed almost identical decay of the OH mode classical energy and the OH WSP points in the direction of improvement of our model. This observation shows that roughly the same rates of decay can be found in classical MD simulations, monitoring the energy decay, and quantum calculations which provide decay rates of the WSP. An obvious extension of the model would then be to perform ab initio molecular dynamics, for example, Car−Parrinello molecular dynamics, and monitor the classical OH mode excess energy, following OH stretch excitations. This would allow for the inclusion of anharmonic effects but still retain a first-principles description of the molecular interactions. Also, such an approach would allow the study of intramolecular relaxation.

Acknowledgment. Support from the Swedish and Danish Research Councils is gratefully acknowledged.

References and Notes

(1) Everitt, K. F.; Egorov, S. A.; Skinner, J. L. *Chem. Phys.* **1998**, *235*, 115−122.

(2) Woutersen, S.; Emmerichs, U.; Nienhuys, H.-K.; Bakker, H. J. *Phys. Rev. Lett.* **1998**, *81*, 1106−1109.

(3) Rey, R.; Hynes, J. T. *J. Chem. Phys.* **1996**, *104*, 2356−2368.

(4) III, E. L. S.; Rey, R. *J. Chem. Phys.* **2002**, *116*, 237−257.

(5) Deak, J. C.; Rhea, S. T.; Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **2000**, *104*, 4866−4875.

(6) Rey, R.; Hynes, J. T. *J. Chem. Phys.* **1998**, *108*, 142−153.

(7) Apkarian, V. A.; Wiedeman, L.; Janiesch, W.; Weitz, E. *J. Chem. Phys.* **1986**, *85*, 5593−5610.

(8) Woutersen, S.; Bakker, H. J. *Nature* **1999**, *402*, 507−509.

(9) Nitzan, A. *Nature* **1999**, *402*, 472−475.

(10) Bader, J. S.; Berne, B. J. *J. Chem. Phys.* **1994**, *100*, 8359−8366.

(11) Egorov, S. A.; Skinner, J. L. *Chem. Phys. Lett.* **1998**, *293*, 469−476.

(12) Everitt, K. F.; Skinner, J. L.; Ladanyi, B. M. *J. Chem. Phys.* **2002**, *116*, 179−183.

(13) Poulsen, J. A.; Rossky, P. J. *J. Chem. Phys.* **2001**, *115*, 8024−8031.

(14) Whitnell, R. M.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.* **1992**, *96*, 5354.

(15) Poulsen, J. A.; Nymand, T. M.; Keiding, S. R. *Chem. Phys. Lett.* **2001**, *343*, 581−587.

(16) Morita, A.; Kato, S. *J. Chem. Phys.* **1998**, *109*, 1998.

(17) Lock, A. J.; Woutersen, S.; Bakker, H. J. *J. Phys. Chem. A* **2001**, *105*, 1238−1243.

(18) Finzi, J.; Hovis, F. E.; Panfilov, V. N.; Hess, P.; Moore, C. B. *J. Chem. Phys.* **1977**, *67*, 4053−4061.

(19) Nordholm, S.; Bäck, A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2289−2295.

(20) Stratt, R. M. *Acc. Chem. Res.* **1995**, *28*, 201−207.

(21) Oxtoby, D. W. *Adv. Chem. Phys.* **1981**, *47*, 487−519.

(22) Herman, M. F. *J. Chem. Phys.* **1998**, *109*, 4726−4733.

(23) Dodaro, F. A.; Herman, M. F. *J. Chem. Phys.* **1998**, *108*, 2903−2911.

(24) Walrafen, G. E. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1972; Vol. 1, Chapter 5.

(25) Eisenberg, D.; Kauzmann, W. *The structure and properties of water*; Oxford University Press: London, 1969.

(26) Gregory, J. K.; Clary, D. C. *J. Phys. Chem.* **1996**, *100*, 18014−18022.

(27) Ziman, J. M. *Principles of the theory of solids*; Cambridge University Press: Cambridge, 1965.

(28) Goodyear, G.; Stratt, R. M. *J. Chem. Phys.* **1997**, *107*, 3098−3120.

(29) Goodyear, G.; Stratt, R. M. *J. Chem. Phys.* **1996**, *105*, 10050−10071.

(30) Billing, G. D.; Mikkelsen, K. M. *Adv. Molecular Dynamics and Chemical Kinetics*; John Wiley and Sons: New York, 1997.

(31) Atkins, P. W.; Friedman, R. S. *Molecular Quantum Mechanics*; Oxford University Press: Oxford, 1997.

(32) Li, Z.; Gerber, R. B. *Chem. Phys. Lett.* **1995**, *243*, 257−263.

(33) Fredj, E.; Gerber, R. B.; Ratner, M. A. *J. Chem. Phys.* **1996**, *105*, 1121−1130.

(34) Åstrand, P.-O.; Linse, P.; Karlstroem, G. *Chem. Phys.* **1995**, *191*, 195−202.

(35) Mas, E. M.; Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **2000**, *113*, 6687.

(36) Toukan, K.; Rahman, A. *Phys. Rev. B* **1985**, *31*, 2643−2648.

(37) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.

(38) Reimers, J. R.; Watts, R. O.; Klein, M. L. *Chem. Phys.* **1982**, *64*, 95.

(39) Coker, D. F.; Miller, R. E.; Watts, R. O. *J. Chem. Phys.* **1985**, *82*, 3554−3562.

(40) Stone, A. J. *The theory of intermolecular forces*; Clarendon Press: Oxford, 1996.

(41) Frisch, M. J.; Trucks, G. W.; et al. *Gaussian 98*, Rev. A.9; Gaussian Inc.: Pittsburgh, PA, 1998.

(42) Helgaker, T.; Joergensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; John Wiley and Sons: Chichester, 2000.

(43) Hartke, B.; Schytz, M.; Werner, H.-J. *Chem. Phys.* **1998**, *239*, 561−572.

(44) Wilson, J.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.

(45) Franks, F. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1972; Vol. 1, Chapter 5.

(46) Hobbs, P. V. *Ice Physics*; Clarendon Press: Oxford, 1974.

(47) Paschek, D.; Geiger, A. *MOSCITO 3.9*; Department of Physical Chemistry: University of Dortmund, 2000.

(48) Ryckaert, J. P.; Ciccotti, G.; Berendsen, H. J. C. *J. Comput. Phys.* **1977**, *34*, 327−341.

(49) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A. *J. Chem. Phys.* **1984**, *81*, 3684−3690.

(50) Darden, T. A.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089−10092.

(51) Paschek, D.; Geiger, A. *Users guide and manual, MOSCITO 3.9*; Department of Physical Chemistry: University of Dortmund, 2000.

(52) Frenkel, D.; Smit, B. *Understanding Molecular Simulation*—*From Algorithms to Applications*; Academic Press: San Diego, 1996.

(53) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.