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On the Ultrafast Infrared Spectroscopy of Anion Hydration Shell Hydrogen Bond Dynamics

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Molecular Dynamics simulations are used to examine the title issue for the I^-/HOD/D_2O solution system in connection with recent ultrafast infrared spectroscopic experiments. It is argued that the long “modulation time” associated with the spectral diffusion of the OH frequency, extracted in these experiments, should be interpreted as reflecting the escape time of an HOD from the first hydration shell of the I^- ion, i.e., the residence time of an HOD in this solvation shell. Shorter time features related to the oscillation of the OH ···I^- hydrogen bond and the breaking and making of this bond are also discussed.

1. Introduction

The dynamics of water molecules in the first hydration shells of anions is of interest in connection with the wide range of aqueous phase chemical reactions in which these anions can participate; examples for the chloride ion include simple contact ion pair/solvent-separated ion pair dynamics,[1] S_N2 nucleophilic substitutions such as that involved in the reaction $Cl^- + CH_3Cl$,[2] S_N1 unimolecular dissociations,[3] and the acid dissociation of HCl.[4] These dynamics are also significant for anion transport in aqueous solution.[5] In a recent series of papers, Bakker and co-workers[6] have opened a new experimental window on the dynamics of water molecules in the hydration shells of anions in water via ultrafast infrared spectroscopy. In particular, OH stretch vibrations are pumped and probed for solutions of different halide anions (with alkali counterions) in HOD dilute in liquid D_2O. By subtraction of the spectra associated with the HOD molecules in the bulk of the solution, information concerning the dynamics of those HOD molecules in the hydration shells of the anions can be extracted. The OH vibrational population and the spectral diffusion of the OH frequency have been probed along these lines for the halides Cl^-, Br^-, and I^-. For the F^- case, comparable vibrational population time scales for bulk and solvation shell OH stretch dynamics preclude a similar analysis.

One striking feature of the experimental results for the spectral diffusion dynamics, which is the focus of the present article, is the finding of rather slow decay features, termed “modulation times” by the authors, compared to the corresponding times for bulk OH. Thus, while a characteristic time ∼500 fs has been assigned for bulk OH,[6a,b] Bakker and co-workers extracted[6a,c] times of 12 ± 3 ps for Cl^-, 25 ± 5 ps for Br^-, and 18 ± 5 ps for I^- from their analysis of the spectral data. The authors associated these times with the modulation of the OH···X^- bond due to the interaction of the halide ion (X^-) with the surroundings, with possibilities mentioned being that this time represents an overdamped motion of the OH···X^- hydrogen bond and/or is associated in some way with the hydration shell deformation. In any event, the interpretation of these modulation times remains to be established.

Here we present a theoretical analysis, using Molecular Dynamics simulations, of aspects of the spectral diffusion dynamics of an OH vibration for the case of the iodide ion in HOD dilute in liquid D_2O. We have selected I^- for this initial study because the red shift (with respect to the gas-phase OH frequency) of the frequency of the OH in its first solvation shell is sufficiently different from the red shift for the OH when the HOD is located in the bulk of the D_2O solution, a feature important for the analysis within. Our basic analysis procedures are similar to those employed for the study of HOD in liquid D_2O,[7] with the important difference of special sampling methods required for the anionic hydration shell examination. In addition to shorter time features—including an oscillation of the I^-···HO hydrogen (H) bond and breaking and making of this bond—similar to those found for theoretical studies of HOD in D_2O,[7−9] a longer time feature is found and is shown to be associated with the escape of the HOD molecule from the iodide’s first hydration shell, i.e., the HOD residence time. Raugei and Klein[10] have remarked on such a possibility by noting the similarity of a calculated residence time for the case of Br^- in water and the time initially reported by Bakker[6] for this ion.[11]

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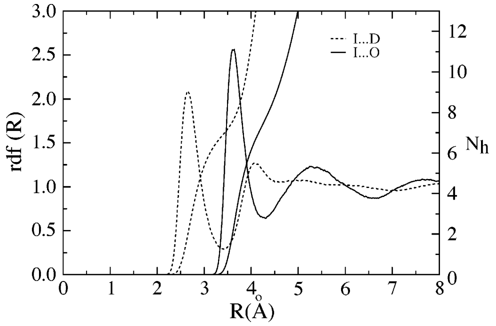

Figure 1. Radial distribution functions (rdfs) and running coordination numbers (N_h) for the $I^-\cdots O$ separation (—) and the $I^-\cdots D$ separation (- - -), for the simulation of I^- in liquid D_2O.

The outline of the remainder of this paper is as follows. We deal with the system definitions and computational details in Section 2, while Section 3 describes the results and interpretation of the OH frequency shift dynamics. Section 4 gives the conclusions.

2. System Definitions and Computational Procedures

We begin by performing standard MD simulations with a single iodide ion and 215 D_2O molecules at standard temperature and density (298.15 K and 1.1044 g/cm^3), to characterize several static aspects of the system. We adopt a SPC/E model for the water-like molecule[12] and a nonpolarizable potential for the iodide ion taken from ref 13. We use the SHAKE algorithm to keep the molecules rigid, the Ewald sum to account for long-range electrostatic interactions,[14] and a 1 ps coupling for the Berendsen thermostat.[15] The static properties of the solvation shell are displayed in Figure 1, where the radial distribution functions (rdf) for both separations $R(O\cdots I^-)$ and $R(D\cdots I^-)$ are shown, together with their running coordination numbers. The first shell extremals for $O\cdots I^-$ are in good agreement with ref 16, where the same potential for H_2O was used. The oxygen coordination number at the first minimum ($R_{min} = 4.26$ Å) is 7.5. For $R(D\cdots I^-)$, the coordination number at $R_{min} = 3.39$ Å is 6.8. The positions of these rdf's first maximum and mininum are generally in very good agreement with those reported in a recent work[17] using an optimized harmonic oscillator-type potential.[18] These results will be used below in constructing a definition of the $I^-\cdots HO$ H-bond.

In the simulation of the dynamics of this system, it turns out that, as anticipated in the Introduction, we must be concerned with the relatively rare process of the departure of an HOD molecule from the hydration shell in a D_2O solution. This requires sufficient statistics and has dictated our choice for the initial conditions as follows. In an already thermalized simulation with the iodide ion in a pure D_2O environment, we select one D_2O in the hydration shell and change it into an HOD molecule, paying attention to effect this for a D that is H-bonded to the iodide ion. The time instant for the mass change will be our time zero in the following analysis. A collection of 105 trajectories for an HOD molecule initially H-bonded to the ion has been used for analysis of the statistical behavior of the OH frequency and other properties of interest, each trajectory being followed for 12 ps. (This strict initial condition can be relaxed, and one can reduce the constraint to the requirement that the HOD is initially in the first hydration shell.) Particular attention has been paid to avoid possible artifacts of the perturbation in the short time behavior due to the mass change. First, a parallel simulation has been run for a system of one iodide ion in pure HDO solvent; the relaxation of the OH shift time autocorrelation function (as well as other quantities as residence time and H-bond dynamics) was not significantly different and, more importantly, the mass-changed system does not display any additional relaxation process (which would be of course ascribed to a spurious effect of the mass change). To further investigate possible effects stemming from the mass change, in test simulations fast thermalization has been forced by direct velocity scaling during the initial time steps following the mass change (time intervals lasting from 0.1 ps up to 0.5 ps have been used). No appreciable differences from the results obtained without fast thermalization were detected. These tests validate our basic procedure to follow the trajectories. Since on a time scale shorter than the trajectories' duration of 12 ps, the HOD molecule initially in the ion's hydration shell will be found to eventually leave the shell to reach the bulk water environment, we can directly probe the shift dynamics while the molecule departs from the iodide.

The frequency shift has been calculated via a semiclassical perturbative method[7,19] and the result compared to a direct one-dimensional (1D) vibrational quantum mechanical calculation in the Born−Oppenheimer approximation. The procedure is very like that used in refs 7 and 20 to which the reader is referred for further details. Briefly, we use the Reimers and Watts[21] local mode potential for the intramolecular water potential and treat the OH stretch as an independent local mode. The perturbative contribution of the solvent forces to the frequency shift from the (anharmonic) gas-phase value is easily computed, and is found to be in excellent agreement with the more computationally demanding B−O procedure.

The calculated averaged OH frequency 3575 cm^{-1} for the $OH\cdots I^-$ complex is shifted by -150 cm^{-1} from the calculated gas-phase OH frequency value 3725 cm^{-1}, while the calculated value 3513 cm^{-1} in bulk, i.e., (D)OH in D_2O, is shifted from the gas-phase OH frequency by -212 cm^{-1} as already reported in ref 7. There is thus 62 cm^{-1} less red shift for OH in the complex than in the bulk D_2O. We note that while the absolute value for the OH frequency in the presence of the ion (3575 cm^{-1}) is less red-shifted than the experimental value (3495 cm^{-1}),[22,6] the difference of 62 cm^{-1} between the average value for the $OH\cdots I^-$ complex and the bulk is in good agreement with the same experimental estimate. The width (fwhm) of the OH frequency distribution in the iodide ion solvation shell is 114 cm^{-1}.

The OH frequency shift has been correlated via density of state distributions with the intermolecular H-bond distance $R(OH\cdots I^-)$ in a HOD/I^- pair and the bending angle (α). As in the pure water case, even in the iodide hydration shell, the frequency shift increases with the distance R, but with considerable dispersion (see Figure 2), thus reproducing the characteristic "banana" shape already found in the pure water case.[7−9] We return to this below. In defining the geometrical parameters for the H-bond, we have chosen for the maximum bond length $R(OH\cdots I^-)$ the first minimum in the oxygen−anion radial distribution function for the HDO/I^- system (4.26 Å; cf. Figure 1). For the angular definition, we choose a maximum angle of $\alpha = 32°$ (almost identical to the usual definition[7] for a pair of water molecules, $\alpha = 30°$), which corresponds to the boundary at which the population of H-bonded molecules reaches a plateau behavior for which 95% of the molecules are H-bonded.

3. OH Frequency Dynamics

3.1. Short Time Behavior. We begin the analysis with the results of a spectral "hole" calculation similar to that of bulk HOD/D_2O calculations in ref 7. At an initial time, we create a

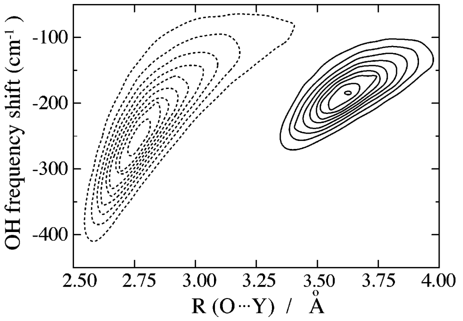

Figure 2. "Banana plot" of the OH frequency shift (from the gas-phase value) versus the I$^-\cdots$O separation (—) for I$^-\cdots$HOD in D$_2$O. The corresponding plot for the HOD in D$_2$O case is also shown (- - -), where the distance should be understood to be that of O$\cdots$O, with one O in HOD and the other one in D$_2$O.

Gaussian hole, of fwhm 80 cm^{-1}, in the (conditional) equilibrium distribution of OH frequencies for the OH in the ion's first hydration shell, and subsequently monitor the dynamical distribution. The laser pulse time duration is ignored, and the laser promotion is mimicked by assigning to each configuration in the equilibrium distribution at time zero the probability $1 - f(\omega_{\mathrm{OH}})$, where $f(\omega)$ is the laser (Gaussian) frequency pulse. Such holes are created either to the red or to the blue of the equilibrium value (-150 cm^{-1}). This procedure mimics an important part of the signal of the experiments,[6] although it does not account explicitly for any dynamics in the vibrationally excited state of the OH. Nonetheless, as was the case in ref 7, such distributions are extremely revealing for the interpretation of the experiments. Figure 3 displays the calculated OH frequency distribution (P_{r}) after creation of a hole to the blue of the average OH frequency in the I$^-$ hydration shell, the hole being centered at $\omega = -120$ cm^{-1}. In panels a and b of Figure 3, there is a subpicosecond drift in which the equilibrium frequency distribution for OH within the first hydration shell is largely recovered in approximately 200−400 fs. Panel c in Figure 3, however, shows an important subsequent spectral dynamics on a much longer time scale: the frequency distribution P_{r} approaches the bulk OH frequency distribution (recall that the average OH frequency shift in the bulk is -212 cm^{-1}). The obvious interpretation, which will be discussed in detail in the following section, is that these slower dynamics are associated with the escape of the HOD from the iodide ion's first hydration shell.

The short and long time dynamics are also clearly visible in Figure 4 where the average frequency shift for an HOD initially in the ion shell is displayed (together with nonequilibrium hole-dynamics average shifts both for blue and red excitation with respect to the equilibrium in-shell frequency shift of -150 cm^{-1}), with a drift of the OH frequency from the value -150 cm^{-1} toward the bulk value -212 cm^{-1}. One can see that both of the curves associated with hole creation converge, after ~2 ps, to the average curve, thus signaling the end of the initial short time equilibration. We can add further details about this earlier time dynamics by analyzing in more detail the time-dependent average frequency shifts associated with the hole distributions, as displayed in Figure 4 for both red and blue excitations. As was the case for the HOD/D$_2$O system,[7] the subpicosecond hole distribution at 100 fs is clearly asymmetric, i.e., not Gaussian. Another clear evidence of the non-Gaussian nature is visible in Figure 4 where the nonequilibrium shifts for the blue and red excitations are clearly different. If the frequency shift were a Gaussian variable, the nonequilibrium distribution dynamics can be expressed solely in terms of the frequency shift correlation function, and both the red and blue nonequilibrium frequency shifts would be proportional to the correlation function,[7b] and would not show the disparity evident in Figure 4. We note for later reference, however, that this signature of non-Gaussian behavior has largely disappeared by ~2 ps.

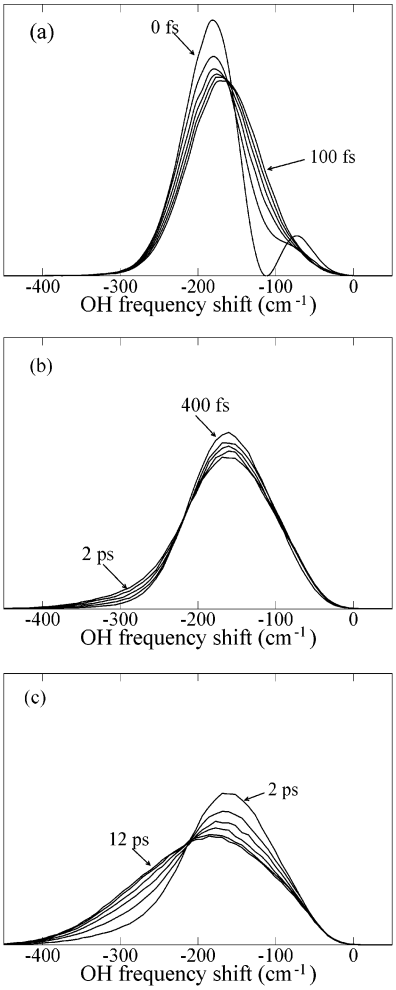

Figure 3. Time evolution of the remaining distribution P_{r} of the OH frequency shift after creation of a hole, at $t = 0$, to the blue of the average in-shell equilibrium shift (-150 cm^{-1}). Note that in panel a the creation of the hole to the blue (at -120 cm^{-1}) of the average produces an apparent peak near -200 cm^{-1}, whereas before the creation of the hole, the equilibrium distribution is peaked at -150 cm^{-1}.

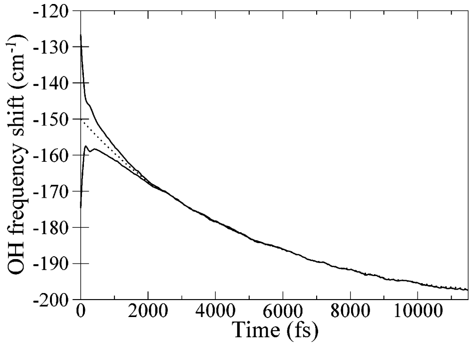

Figure 4. Time dependence of several average OH frequency shifts. The dashed line denotes the average shift with the initial condition of an equilibrium distribution for the HOD in the first hydration shell of the I$^-$ anion, with average frequency shift -150 cm^{-1}. The upper and lower solid lines are averages corresponding to the initial conditions where a hole is created respectively to the red of -150 cm^{-1} (at -180 cm^{-1}), so that the initial average shift is reduced in magnitude, and to the blue of -150 cm^{-1} (at -120 cm^{-1}), so that the initial average frequency shift is increased in magnitude.

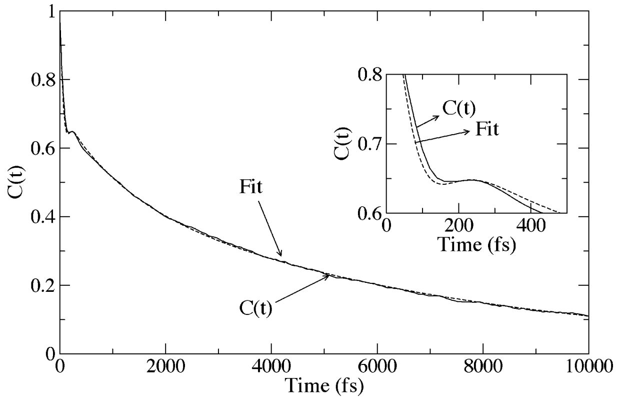

Figure 5. Normalized OH frequency shift correlation function $C(t)$ versus time (—), with the initial condition of an equilibrium distribution of OH frequencies of the HOD in the first hydration shell of the I^-. This simulation result is well fit by three terms (- - -), one an oscillation with the $I^-\cdots O$ H-bond frequency of ~100 cm^{-1} times an exponential, and two further exponentials: $A_0 \exp^{-t/A_1} \cos(0.018t) + A_2 \exp^{-t/A_3} + (1 - A_0 - A_2) \exp^{-t/A_4}$, with the amplitudes $A_0 = 0.289$, $A_2 = 0.216$ and the time constants being $A_1 = 70$ fs, $A_3 = 1108$ fs, and $A_4 = 6657$ fs. Insert: Focus on the "bump" feature at ~250 fs. See the text for discussion.

A relevant feature apparent in Figure 4, especially for the blue excitation, is the "bump" at ~250 fs, suggestive of an oscillation. As was the case for HOD in D_2O, this feature is clearly visible in the shift tcf,[7,9] displayed in Figure 5, and defined with the initial condition that the HOD is in the hydration shell of the iodide and H-bonded to it. To interpret it we have examined the Fourier transform of the velocity time correlation function for the $I^-\cdots O$ bond in D_2O, from 200 ps of a separate simulation. We found a frequency ~100 cm^{-1},[23] corresponding to a period of 334 fs, thus identifying the source of this feature. This H-bond frequency is slightly lower than the experimental (135 cm^{-1}) and ab initio estimates (111 cm^{-1}) for an I^- water cluster,[24] the only data available for comparison. Indeed, one might anticipate a frequency lowering due to the extra solvation in water. This short time feature was not observed in the Bakker group experiments[6] due to time resolution issues. In the experiments, it should be the H-bond frequency involving the vibrationally excited HOD rather than for the ground vibrational state HOD calculated here. Since an H-bond typically strengthens in the excited vibrational state,[25] one could expect a slightly higher frequency to be observed.

An additional feature of importance is that there is also a somewhat longer time scale (of ~1 ps) evident in Figure 4 before the slower convergence to the average shift. This can be associated with the making and breaking of the $I^-\cdots O$ H-bond, without, however, having an HOD departing from the hydration shell. This interpretation is supported most directly by the significant suppression of this feature if one restricts the calculation to a subensemble that remains continuously H-bonded for 2 ps, just as was done for the water case in ref 7 (this restriction naturally also suppresses the beginning of the longer time relaxation due to the exit of the HOD from the ion hydration shell, as will be shown below). A second, indirect support is via a separate calculation of the so-called continuous H-bond relaxation function[26] such that an H-bond is not broken from time 0 to time t; this yields a time of 0.9 ± 0.3 ps consistent with the H-bond breaking and making character of the ~1 ps time scale noted above. Thus, the interpretation of the short time features for the hydrated I^- problem, while differing in detail, are qualitatively quite similar to those for HOD in liquid D_2O.[7−9]

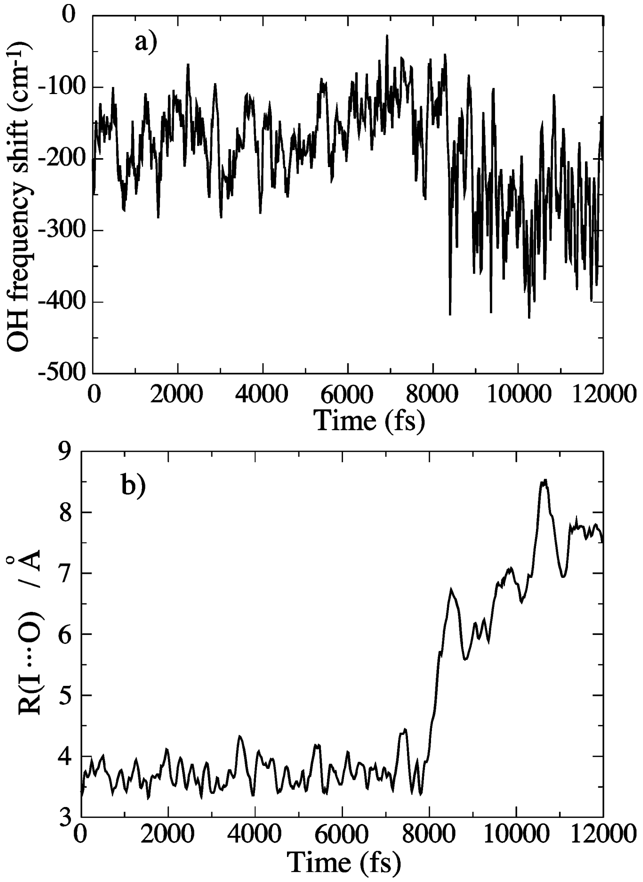

Figure 6. Representative trajectory results versus time for an initial condition taken from an equilibrium distribution of HOD in the first hydration shell of I^- for (a) the OH frequency shift and (b) the $I^-\cdots O$ H-bond separation.

3.2. Long Time Behavior. We now turn to the central issue of this work, namely, the interpretation of the long time decay as due to the escape of the HOD molecule from the ion's first shell. First, it is worth noting that Figure 4 shows that while the initial features differ in detail, the longer time decay associated with escape from the first hydration shell is common for any of the initial conditions. It is interesting to note that with the interpretation proposed here it is rather straightforward to explain why such a tail would appear for the ion hydration shell case, and not for an experiment or calculation for HOD dilute in D_2O. For the ion case, there is a significant shift of the OH frequency for an HOD in the first hydration shell and outside of it; for example, the difference from the bulk value is $(-150\ cm^{-1}) - (-212\ cm^{-1}) \approx 62\ cm^{-1}$. By contrast, if an HOD leaves the first hydration shell centered on some D_2O, it simply enters into another hydration shell centered on another D_2O and there is no change in the OH frequency shift.

A first, qualitative, element of support for this interpretation of the longer time process is contained in Figure 6, which displays a representative trajectory for both the fluctuating $O\cdots I^-$ H-bond length and the fluctuating OH frequency shift. An increase of the (rather noisy) red shift is clearly apparent as soon as the molecule leaves the first shell, an exchange event that takes place at ~8 ps. Turning to results averaged over an ensemble of trajectories, an exponential fit to the long time tail in Figure 4 gives a time $\tau = 7.4 \pm 1.5$ ps. An almost identical decay time is obtained from a fit to the shift tcf (displayed in Figure 5). We have performed a separate simulation to determine a water molecule's residence time in the first hydration shell of I^- along standard lines[16,27] for D_2O, with the result $\tau_{res} = 8.4$

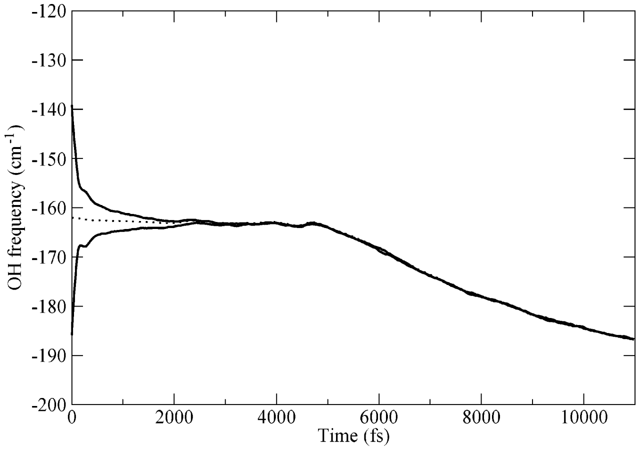

Figure 7. Same as Figure 4 for the time dependence of average frequency shifts, with the difference that only trajectories for which the HOD remains in the I$^-$ first hydration shell for at least 4.5 ps are included.

± 0.2 ps (the corresponding result for H_2O is 8.8 ± 0.6 ps), quite similar to the τ value just quoted, reinforcing the idea that the long time tail is due to the escape of the HOD from the ion shell. Since the average OH frequency varies continuously between hydration shell locations, the characteristic time will not be exactly the residence time (see ref 7 for related discussions concerning the hydrogen bond lifetime).[28]

A more stringent test of the connection between the long time tail and the exchange time is possible by restricting the computation of the average shift to those molecules that do not leave the first hydration shell of the anion before a given time limit (irrespective of whether they remain H-bonded or not). If the long time tail is indeed due to the exchange process, then it should not be present in this restricted function within the specified time limit. Figure 7 displays the result for such a calculation, with the restriction that only HOD molecules that stay within the first shell for at least 4.5 ps are considered. It is clear that there is no appreciable decay of the shift up to 4.5 ps, and that a long time tail sets in immediately after, which again is well represented with an exponential decay of some 9 ps. For the upper and lower curves there is a relaxation toward the mean shift characteristic of the hydration shell for HOD molecules initially on the blue or red sides, but it is crucial to note that this equilibration is not followed by a long time decay until they are able to escape toward the second shell.

From our calculations above we have assigned a characteristic time $\tau = 7.4$ ps to be associated with the escape from the first shell. The "modulation time" τ_c extracted by Bakker and co-workers in their analysis of their I$^-$ experiments is $\tau_c = 18 \pm 5$ ps for a 6 M solution. (While no value was extracted for the 1 M solution experiments, we provide an estimate below.) This is a significant difference and we devote some comments to it here (bearing in mind that the extraction from the experiment must be done on a signal that is rather small). As we have noted above, our calculations ignore the polarizibility of the water and especially that of the I$^-$ ion. This might lengthen the calculated time somewhat,[30,31] although this remains to be investigated for the present system. In addition, the high concentration (6 M) of the experimental iodide solution will have some effect: Chandra[31] has found in simulations that water residence times for a chloride ion lengthen from 10 ps at ~0 M NaCl to 14.3 ps at 4.5 M. In any event, our simulations are for low ionic concentration (one I$^-$ per 215 water-like molecules) without any countercation, and are not appropriate for a 6 M solution.[32] In the discussion to follow, we make a comparison for the less concentrated 1 M case.

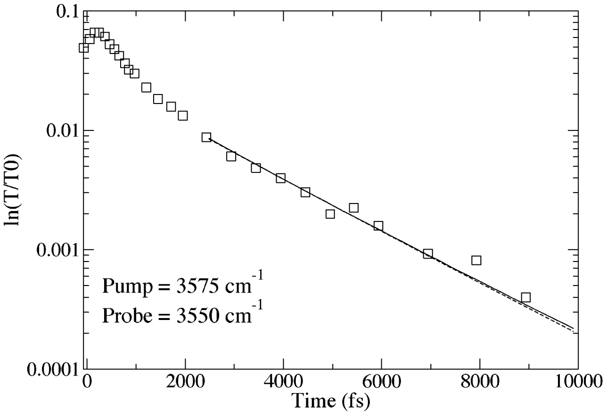

Figure 8. Theoretical spectral transmission versus time (—), using the calculated $C(t)$ representation (see Figure 5), and the result of the fit assuming $C(t) = \exp(-t/\tau_c)$ (- - -) to experimental data points as described in the text. For reference, the 1 M NaI experimental results extracted with permission from Figure 4 in ref 6a (Kropman, M. F.; Bakker, H. J. *J. Chem. Phys.* **2001**, *115*, 8942) are displayed as squares.

However, even beyond the issues raised above, it appears that extraction of a characteristic time is not completely straightforward. We illustrate this by simply assuming, following Bakker and co-workers, that the contribution from the ion solvation shell can be represented as a Gaussian random process, multiplied by a decaying exponential with the population lifetime of the OH vibration. In view of our previous remarks about the limitations of any such Gaussian description, we restrict all subsequent discussions to times equal to or greater than 2.5 ps, where non-Gaussian effects should be minimal (cf. Section 3.1). This restriction to longer times also minimizes any more rapidly decaying contribution to the experimental signal coming from the bulk HOD OH vibrations. Accordingly, we will only be concerned with a single Gaussian random process, associated with the OH vibrations for HOD in the anion hydration shell; this also avoids complex issues of the possibly differing intensities of bulk and hydration shell OH vibrations,[33] which will introduce an amplitude factor required to adjust various results to the experimental transmission spectrum, shown in Figure 8, at the "initial" time of 2.5 ps, a point to which we will return below. We focus on the experimental case[6] of the pump and probe frequencies at 3575 and 3550 cm^{-1}, respectively. Details of the calculations now to be described are given in ref 34.

For our first calculation, we simply insert in the single Gaussian expression[33] the three-term representation (see Figure 5 caption) of the calculated time correlation function $C(t)$ of the fluctuating OH frequency shown in Figure 5. This would be the correct procedure in the context of a Gaussian random process assumption, without any further assumption as to the fluctuating frequency being, e.g., directly proportional to the I$^-$···O H-bond length (this assumption in any case would be incorrect due to the dispersion, H-bond breaking and making, and hydration shell escape features discussed earlier in this paper). The result is shown in Figure 8 (solid line), in good agreement with the experimental points for a 1 M iodide solution[6] (squares).

We next ask, what would be the time τ_c extracted as in the studies of ref 6, which assume, in effect and at a minimum, that the frequency correlation function decays exponentially as $C(t) = \exp(-t/\tau_c)$[33] here assumed after 2.5 ps. We perform such a fit[34] to our theoretically generated curve in Figure 8 (solid line) and extract $\tau_c = 13.7 \pm 0.2$ ps (at a probe frequency of 3600 cm^{-1}, the extracted time is 10.4 ± 0.1 ps). If we perform a similar fit, again assuming an exponential correlation function $C(t) = \exp(-t/\tau_c)$ after 2.5 ps, to the experimental data points in ref 6a for a 1 M iodide solution and a probe frequency of 3550 cm^{-1}, we obtain a time 14.6 ± 9.8 ps (see Figure 8, dashed line). Both calculations thus give approximately the same time $\sim$14 ps.

We recall that the long time tail of our calculated $C(t)$ has a characteristic time of $\sim$7 ps, approximately half of the two times just extracted. In fact, if we take into account that our calculated $C(t)$ has, to within better than 10% to times greater than 2.5 ps, the time behavior $C(t) = 0.495 \exp(-t/6657)$, i.e., the third term in the three-term expression in the Figure 5 caption whose decay time is $\sim$7 ps—and is not an exponential with a unit prefactor—this representation reproduces the full $C(t)$ generated solid curve in Figure 8, which as noted above gives $\tau_c = 13.7 \pm 0.2$ ps when an exponential with a unit prefactor is assumed. These conflicting times can result from fits involving different amplitude factors at 2.5 ps mentioned above.[34] Further analysis would require knowing what the actual amplitude factor should be for the experimental data, whose theoretical calculation would involve extensive electronic structure calculations in solution.[35,36] The scatter evident in the data points in Figure 8 suggests that such an effort would be worthwhile when more refined experimental data become available.

All of this discussion suggests that perhaps a very important source of discrepancy between the times calculated for fundamental quantities such as the correlation function (or hole dynamics) and those extracted from the experimental results might lie in the requirement to have a more complete description of the former rather than a simple exponential representation.

4. Concluding Remarks

We have argued on the basis of Molecular Dynamics simulations that the long "modulation time" for the modulation of the OH frequency for HOD molecules in the hydration shell of the I^- ion inferred from ultrafast infrared spectroscopy experiments[6] should be interpreted as being associated with a residence time for an HOD, i.e., the time for an HOD to escape this hydration shell (this escape could be separately analyzed by using the methods of ref 37). For lower ionic conentrations, this escape displaces the HOD toward an approximately bulk aqueous environment, the case examined here. At higher ionic concentrations, this escape will displace the HOD into a more complex environment, which remains to be examined. It is anticipated that the same basic interpretation of first anionic hydration shell escape applies to the other halide ions examined experimentally;[6] these will be reported elsewhere, again for low ionic concentrations. For shorter times, we have found an oscillatory feature associated with the $I^- \cdots O$ H-bond, as well as dynamics associated with the breaking and making of this H-bond, features similar to those found for the HOD in D_2O system. These shorter time features have not been discussed in the experimental papers,[6] but could be looked for in future experiments. We have noted at the end of Section 3.2 that the extraction of long time scales from the experimental data is not at all straightforward and depends on the system modeling. Photon echo peak shift experiments could be useful in this regard as well as in the investigation of shorter time dynamics since it is assumed that such experiments provide a direct measure of the frequency time correlation function.[9a,38]

Calculations corresponding to the present ones should be performed taking explicitly into account the polarizabilities of the anion and the water-like molecules. While this might change the times somewhat, we do not believe that the basic interpretation would change.[39,40] A major issue deserving future attention is the role of the cationic counterions as well as the other ions at high concentrations;[32] at some point, first hydration shell escape will place the HOD not in an environment resembling bulk water but rather in a different ionic environment.

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(32) At high concentrations of the salt, the countercation can even be in the first solvation shell of the anion, i.e., a contact ion pair, or the HOD could form a bridge between the two ions, i.e., a solvent-separated ion pair. In either of these cases or related variants of them, the escape process for the HOD would obviously be altered from that simulated in the present work.

(33) Actually the authors of ref. 6 adopt a sum of such Gaussian random process descriptions for the bulk OH vibrations and those in the ion solvation shell. We do not adopt this route since there are, for example, issues of the differing intensities of these OH absorptions.

(34) Our fits use the expression $a_0(T/T_0)$, where T is the pump−probe signal given by: Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995. T_0 is the time zero signal. The scaling factors (a_0), 0.03 and 0.01 for the 3550 (dashed line in Figure 8) and 3600 cm^{-1} probe signals, are adopted to match the experimental points at 2.5 ps. The corresponding a_0 value for the 3550 cm^{-1} probe signal adopted to match the theoretically generated curve to the experimental data (solid line in Figure 8) is $a_0 = 0.03$. The parameters used for fits are the following: central frequency 3490 cm^{-1}, fwhm 105 cm^{-1} (ref 6), and the T_1 vibrational lifetime 2.2 ps. In ref 6, T_1 is given only for the 6 M solution. T_1 depends on the concentration (see: ref 6a), and 2.2 ps is an extrapolated value for the ~1 M solution.

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(39) We have calculated the D_2O residence times under the same conditions as in Section 3.2 with two different polarizable ion and solvent models. The model of Fincham and Mitchell (Fincham, D.; Mitchell, P. J. *J. Phys. Condens. Matter* **1993**, *5*, 1031) gives 9.9 ± 1.6 ps while that of Lamoureux and Roux (Lamoureux, G.; Roux, B. *J. Phys. Chem. B* **2006**, *110*, 3308) gives 12.9 ± 2.3 ps. Both are somewhat longer than the SPC/E result 8.4 ± 0.2 ps for D_2O quoted in Section 3.2.

(40) In fact, the contribution to the IR spectral diffusion of a time scale associated with the escape of a water molecule from one environment to another one should be quite general, provided of course that the OH frequency is different in the different environments. We have already determined that a similar behavior occurs for the Cl^- and Br^- ions in water (unpublished). An interesting example could be that of biological water (see e.g.: Nandi, N.; Bagchi, B. *J. Phys. Chem. B* **1997**, *101*, 10954.)