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REGULAR ARTICLE

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Dissociation, solvation, and dynamics of HBr in small water clusters

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Abstract The dissociation of hydrogen bromide in a small water cluster $(H_2O)_n$ (n=3–5) has been studied with quantum chemical methods. The dynamics of dissociation was followed by classical molecular dynamics, and stationary points were studied in order to compute the free energy change associated with the ionization process. The nudged elastic band method was used to map out the energy profile of the reaction paths. The results show that HBr can dissociate in the presence of just four water molecules if they are in the correct configuration.The relation of our results to recent experiments is discussed.

1 Introduction

In conjunction with nitrogen oxides, bromine and chlorine are active agents in the depletion of ozone in the troposphere. Hydrogen chloride and hydrogen bromide are possible intermediates in atmospheric chemistry and their ionization at the surface of cloud particles is believed to be an important step in reactions involving ozone depletion in the Arctic and Antarctic [1]. This underlines the importance of studying the dissociation of these acids in very small clusters of water or ice, i.e. the proton transfer from the halide to a water molecule. Femtosecond laser spectroscopy has recently been used to probe the dissolution of HBr in water at the molecular level [2], whereas infrared spectroscopy was used to separate the different stages of HCl dissociation at the surface of ice nanoparticles [3]. The low temperature of these experiments (50–100 K) slows down the dissociation process, making various intermediates "visible".

From their experiment on HBr dissociation, Hurley et al. [2] concluded that five water molecules were necessary to produce a solvent-separated ion pair, $H_3O^+(H_2O)_4Br^-$in the ground state. Theoretical calculations performed on small clusters in the gas phase suggest that this solvation already occurs with four water molecules, the most stable species being $H_3O^+(H_2O)_3Br^-$ with three Br^- – water and three H_3O^+ – water hydrogen bonds [4,5]. Dissociation of HCl on ice clusters also occurs when three hydrogen bonds stabilize Cl^- [3].

Although many ab initio molecular dynamics studies have been devoted to water and ions in liquid water [6–15], the quantum chemical investigation of HCl and HBr dissociation at the molecular level has been restricted to static cluster calculations, and without consideration of the possible equilibrium with the H_3O^+– Br^- contact ion pair [16]. In fact, the ultrafast dynamics of mixed HBr – water clusters shows that the dissociation occurs in several steps. Initially, a contact ion pair is formed, and this is followed by a rearrangement of the water molecules, which precedes the final solvated ion-pair formation.

We have thus focused our interest on analysing how the dynamics of water clusters, water molecules and HBr couple to yield the solvent-separated ion pair. The present paper represents a progress report in that a relatively small number of trajectories have been examined so far. The trajectories studied do reveal, however, interesting possibilities for the dissociation mechanism and insight into the factors that change the nature of the dissociation as successive water molecules are added to the system.

2 Methodology

All the calculations have been performed with the density functional theory (DFT) program deMon [17]. Clusters including one HBr and from three to five water molecules are presented. The Born-Oppenheimer dynamics were started with different initial geometries having various numbers of $HBr\cdots HOH$ and $BrH\cdots OH_2$ hydrogen bonds. After various equilibration times, the different starting points on occasion yielded different equilibrated structures.

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Table 1 Comparison between DZVP[11], TZVP[12] and experimental results for the test set (bond lengths in Angströms, angles in degrees, binding energy BE in kcal/mol, without evaluation of the BSSE correction)

Molecules (parameter)	DZVP	TZVP	Exp.
H–Br	1.437	1.430	1.41443 [28]
H_2O O–H	0.973	0.973	0.957
(HOH)	104.4	104.1	104.4 [29]
H_3O^+ O–H	0.991	0.991	
$(H_2O)_2$O–H 1^{st}w	0.974/0.974	0.974/0.974	
(HOH) 1^{st}w	104.8	104.8	
OH$\cdots$O	1.900	1.911	
O–O	2.88	2.89	2.946[a] [30] / 2.952[a] [31]
(OH$\cdots$O)	172.5	172.9	≈ 174 [32]
(O–H 2^{nd}w)	0.984/0.972	0.987/0.977	
	104.3	104.5	
(HOH) 2^{snd}w	6.62	6.40	5.44 ± 0.7 [32]
BE (no BSSE)			5.44 ± 0.2 [33]
$H_2O\cdots$ HBr			
O$\cdots$H	1.763	1.822	
H–Br	1.478	1.463	
BE (no BSSE)	7.10	6.66	
$Br^-\cdots$ HOH			
Br$\cdots$O	2.318	2.372	
H–O	1.002	1.000	
O–H	0.974	0.974	
BE (no BSSE)	15.00	14.97	
H_2O–H^+-OH_2			
O–H^+	1.208	1.211	
O–H	0.979	0.980	
BE(no BSSE)	40.09	39.64	

[a] Corrected for anharmonicity

The PBE exchange and correlation functionals [18] were used, since this combination has been shown to be one of the most accurate GGA functionals for hydrogen-bonded systems [19]. It is generally accepted that orbital bases of triple-zeta quality, augmented with polarization functions, are necessary for a good description of hydrogen-bonded systems (for an example on water clusters, see [20]). Since dynamics simulations are time consuming, we have used a DZVP basis optimized for DFT, after verification on test examples that DZVP [21] and TZVP [22] results provide very similar geometries and acceptable binding energies. We compare in Table 1 optimized geometries for HBr, H_2O, $H_2O\cdots H_2O$, H_3O^+, $H_2O\cdots HBr$, $HOH\cdots Br^-$ and $H_3O^+\cdots H_2O$, which correspond to the interactions of importance in our simulations. Polarization functions are necessary to provide good H-bonded structures, as the calculated structure of the hydronium ion is trigonal planar if they are not used. Diffuse functions are much less critical for structural work, and since the smallest exponents in the basis sets are already fairly diffuse, we opted not to add more functions in order to keep the basis set size to a minimum. As a test of the effect on the energetics, we found that the water dimer binding energy with the 6-311G^{**++} basis set is smaller by less than 0.4 kcal/mol than with the TZVP basis.

In order to improve the efficiency of calculations, deMon uses a set of auxiliary functions to fit the density. The auxiliary functions used in the fitting are optimized for the DZVP basis, and include up to *g* functions.

The dynamics was run with time steps of 0.5 fs, using the velocity Verlet algorithm [23] and the Berendsen thermostat (τ = 0.2 and 0.5) [24] after equilibration with simple scaling (about 1 ps). The simulation temperature was 50 K, close to the experimental conditions [2,3]. The results reported correspond to equilibrated trajectories of 2–3 ps in length.

Minimum energy paths for transitions from the contact ion pairs to the solvent-separated ion pairs have also been calculated for the clusters containing four and five waters, using the nudged elastic band (NEB) method [25,26]. The transition-state positions have been refined by following the negative frequency modes. All extrema have been checked using frequency analyses.

3 Results and discussion

It has been inferred that for HCl on small ice clusters, acid dissociation occurs when Cl is connected to at least two waters [2,27]. Therefore, several starting structures have been considered, with different numbers of waters bonded to the H and Br ends. Since the $HBr(H_2O)_4$ system is special in that a question remains as to whether the solvent-separated ion pair is more stable than the undissociated form, more starting structures have been considered for this case.

3.1 $HBr(H_2O)_3$

The two starting geometries $(H_2O)HBr(H_2O)_2$ and $(H_2O\cdots H_2O)HBr(H_2O)$ led to the same final stable species where the

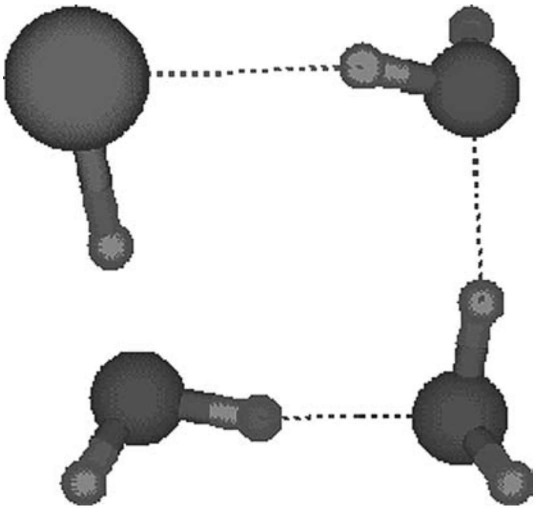

Fig. 1

four molecules are arranged with the O and Br atoms sitting at the four corners of a square, the molecules being linked by hydrogen bonds (Fig. 1).

No stable form with Br bonded to two waters could be found. In this species, the H–Br bond fluctuates rapidly, the proton moving back and forth between Br and OH_2, leading to an average Br–O distance of 2.97 Å (standard deviation = 0.03 Å), calculated over an equilibrated simulation of 4.4 ps. The corresponding average Br-H distance is 1.68 Å (standard deviation = 0.05 Å), whereas the minimum and maximum Br–H distance found during the simulation are 1.545 and 1.833 Å, respectively. The average Br–H bond is thus elongated with respect to that calculated at 0 K in the system $H_2O\cdots HBr$ (1.464 Å).The proton never remains attached to H_2O with its typical distance in H_3O^+(0.99 Å). One can thus conclude that HBr does not dissociate in the presence of three waters. Geometry optimization of this cluster leads to a minimum with Br–H = 1.838 and H–OH_2 = 1.126 Å (<Br–H–O = 172.4°).

3.2 $HBr(H_2O)_4$

For this system, we began with five different starting geometries. If the water molecules interacting with HBr are either discrete waters or dimers, we obtain a quasi-planar square structure including either four waters or three waters and HBr after about 200 fs of simulation and before equilibration is completed. When HBr interacts with a water trimer at the bromine end and a single water at the H end, we found two very different dynamics possible, according to the nature of the trimer: either an optimized stable trimer or a random arrangement of three H-bonded waters. In the first case, after some time, the dynamics is similar to the dynamics started with a water tetramer. In the second case, the ionization of HBr occurs very rapidly, about 10 fs after the cluster of three waters becomes H bonded to Br. Finally, the dynamics started with a tetramer of waters interacting with HBr followed, after some delay, by the dynamics started with four separated waters. These systems will be discussed individually.

For comparison, we present first the dynamics started with an already solvated ion-pair model. The average equilibrated structure corresponds indeed to the most stable form one can obtain for (HBr, $4H_2O$).

3.2.1 $H_3O^+ (H_2O)_3 Br^-$

This model contains both H_3O^+ and Br^- ions H bonded to three equivalent water molecules. The dynamics was started directly from this structure to have a comparison with the other dynamics started from non-dissociated HBr. Figure 2a displays a snapshot of this solvent-separated ion-pair dynamics.

Geometry optimization of this species leads to a very symmetrical structure of C_3 symmetry, Br^- and the oxygen of H_3O^+ being on the symmetry axis.

3.2.2 $(H_2O\cdots H_2O)HBr(H_2O)_2$

The square formed in this case consists of three water molecules and the HBr molecule. The fourth water is hydrogen bonded to the Br end of the square. Dissociation of the HBr occurs without much change in the relative positions of the waters and the Br. As an equilibrated structure is reached, a contact ion pair is formed, which rearranges slightly to form the structure shown in Fig. 2b. The quasi-planar square structure is maintained, with the water outside the ring being H bonded to the $H_3O^+$and Br^-ions.

3.2.3 $(H_2O)HBr(H_2O)_3$

Before dissociation, a quasi-planar (deviation from planarity = 15–20°) square is formed with all four water molecules. The HBr molecule is hydrogen bonded through both ends to two adjacent waters. The dissociation in this case is slower than in the other isomer, but a contact ion pair is formed, with the quasi-planar structure becoming highly distorted. The new structure can be seen in Fig. 2c, and contains the three water molecules and the hydronium ion. The bromide ion sits on top of the square, hydrogen bonded to the hydronium ion and to the water molecule diagonally opposite from it.

3.2.4 $((H_2O)_4$ *cyclic)HBr*

If HBr is to interact with a stable cluster of four waters, the starting point of the dynamics must thus be a four-member ring of waters with HBr bonded to two waters. These dynamics have thus been started with an optimized water tetramer. We found two isomers, with HBr bonded to two adjacent waters of the ring, or on top along the diagonal. In both cases, HBr dissociates after about 300 fs, and the bromide ion is inserted into the ring of waters, breaking it. The proton is first transferred to the adjacent water, and then may pass to the next water. Both dynamics, after equilibration, lead also to the structure illustrated in Fig. 2b.

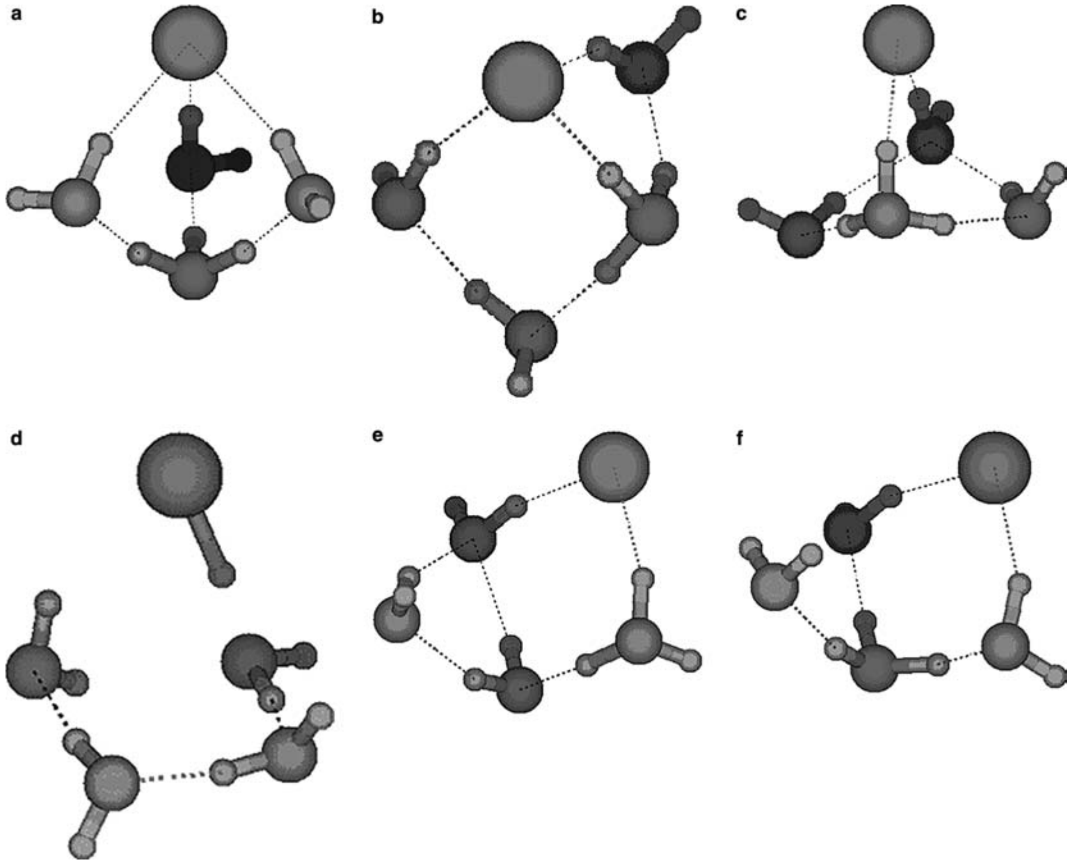

Fig. 2

3.2.5 $(H_2O)HBr(H_2O\cdots H_2O\cdots H_2O)$

Two types of 'trimer' have been used: either the optimized cyclic isomer or a non-stable form, taken from a snapshot of water dynamics, where the central water has its two O–H forming H-bonds with the oxygens of the two other waters. These two structures are both cyclic, with similar $H_2O\cdots HOH$ distances (1.83 Å for the optimized trimer and 1.85 Å for the other) and (OOO) angle (60°); they only differ by the orientations of the OH's.

$(H_2O)HBr((H_2O)_3$ optimized trimer) The trimer is H bonded to the Br end of HBr and the isolated water to the H end. The structure evolves very quickly (50 fs) to a deformed tetramer of waters interacting with HBr. The dynamics then follows a path very similar to that of HBr bonded to two adjacent waters of the cyclic tetramer. After about 270 fs, HBr dissociates, and, later, the proton is transferred to the next water, leading to a structure equivalent to that of Fig. 2b.

Geometry optimization of the starting structure of the dynamics leads to a minimum, which consists of a quasi-planar trapezoidal tetramer of waters, H bonded on the largest side with HBr, which does not dissociate. This minimum is shown in Fig. 2d.

$(H_2O)HBr(H_2O\cdots HOH\cdots OH_2$ cyclic) The trimer is also H bonded to the Br end of HBr and the isolated water to the H end. After only 50 fs, a contact ion pair is formed (Fig. 2e). About 250 fs later, the proton of the contact H_3O^+ ion is transferred to the next water of the trimer (Fig. 2f), the potential energy remaining stable during this period. As visible on Fig. 2f, H_3O^+ is now H bonded to three waters and Br^- to only two waters. In the next 100 fs of the dynamics, the hydronium ion and the trimer water, which is still far from Br^-, rotate towards this ion, generating a stable solvated ion-pair species of similar geometry and potential energy with that illustrated in Fig. 2a and described in the previous paragraph.

Geometry optimization of the first image of this dynamics leads to a stable minimum, identical in structure and energy with the optimized snapshot of the solvent-separated ion-pair dynamics.

The present simulation has thus led to the dissociation of HBr into a contact ion pair, followed by the transfer of the proton to the next water and the formation of a solvated proton without a barrier.

To summarize, all these dynamics, except one, have led to three stable contact ion pairs, which, then, remained similar throughout the remainder of the simulation time.

The only dynamics which has led to a stable solvent-separated ion pair is the one started with the non-optimized trimer.

As shown in Table 2, the two stable clusters with contact ion pairs have very similar average potential energies (within 0.5 kcal/mol). In contrast to Gertner et al. [5], these clusters (along the trajectories, but also after geometry optimization of trajectory snapshots), include real contact ion pairs, with clearly separated Br^- and H_3O^+ entities. The typical distance range for O–H in H_3O^+, bonded to Br^- and two waters, is 1.02–1.10 Å, whereas the $Br \cdots H_3O^+$ distance varies within 1.9–2.2 Å. These values are different from those found in Ref. [5] for the $HBr(H_2O)_4$ cluster, which was reported as 3.6 kcal/mol less stable than the solvent-separated ion pair. Indeed, in this species, the H-Br bond is elongated to 1.489 Å, whereas the $H \cdots OH_2$ distance is 1.566 Å, showing that, in these calculations, no contact ion pair has been found.

It is obvious from Fig. 2b and c that these two clusters, each of which contain a $(Br^-–H_3O^+)$ contact ion pair, cannot lead to a solvent-separated ion pair without an important rearrangement. Indeed, a proton transferred from H_3O^+ to any water molecule bonded to Br^- produces another contact ion pair, whereas a proton transferred to a water not bonded to Br^- leads to a transition state, as verified by frequency analysis of such models, after geometry optimization at 0 K.

Comparing the average potential energies of the three models, the solvent-separated ion pair (Fig. 2a) is the most stable. The difference with respect to the model of Fig. 2b is 2.7 kcal/mol (2.0 kcal/mol with the TZVP basis). Table 2 displays the respective energies obtained from the dynamics compared with energy (non-ZPE corrected) and free energy (ΔG) differences. The ΔG values have been evaluated by geometry optimization of snapshot structures from the equilibrated trajectories (calculation at 50 K using the harmonic oscillator and rigid rotor approximations). It can be seen that the average potential energy differences provided by the dynamics are in good agreement with the free energy differences.

3.3 HBr, $(H_2O)_5$

Four initial starting structures for the dynamics were tested, and the results will be discussed separately.

3.3.1 *$(H_2O \cdots H_2O)HBr(H_2O)(H_2O \cdots H_2O)$*

Dissociation of the HBr molecule occurs before equilibration, and the resulting equilibrated structure is shown in Fig. 3a. The bromide ion sits above a quasi-planar square (distortion = 10°), which contains three water molecules and the hydronium ion. The fifth water sits below the ring, and is hydrogen bonded to one of the waters in the ring and the hydronium ion. This water can be very easily protonated by the hydronium, and will then transfer a proton to another water molecule. These models, when optimized at 0 K, result in two minima (Fig. 3a and c) and a transition state (Fig. 3b). The energies (without ZPE correction) are very similar, differing by less than 0.6 kcal/mol.

3.3.2 *$(H_2O)HBr(H_2O \cdots H_2O)_2$*

After HBr dissociation, this isomer results in a quasi-planar five-membered ring, with the ions occupying adjacent positions on the ring, and a single water below the ring, which is hydrogen bonded to both ions (Fig. 3d). The energies of the two stable structures 3a and 3d are quite similar (within 1 kcal/mol), but the two forms do not interconvert during the 2-ps trajectory.

3.3.3 *$(H_2O)_2HBr(H_2O \cdots H_2O \cdots H_2O)$*

The same two forms of water trimer as for $HBr(H_2O)_4$ have been compared.

$(H_2O)_2HBr(H_2O)_3$ (optimized trimer) The original structure is equivalent to that described in the four water case, but including an additional water molecule at the H end of HBr. In contrast to the four-water case, the evolution of the dynamics leads very rapidly to the dissociation of HBr to a contact ion pair (after 70 fs). A structure, very similar to that shown in Fig. 3a, is obtained.

$(H_2O)_2HBr(H_2O \cdots HOH \cdots OH_2$ cyclic) This structure includes the water trimer, as described for $HBr(H_2O)_4$, H bonded to bromine. After H–Br dissociation (25 fs), a structure very similar to that shown in Fig. 2b for $HBr(H_2O)_4$ is obtained, but including a fifth water (Fig. 3e). The two ions of the contact ion pair and two water molecules form a quasi-planar square, and a water molecule is found above and below the square. During the next 250 fs of the dynamics, the potential energy of the system forms a plateau, during which the proton oscillates between the contact ion H_3O^+ and the closest water belonging to the water trimer (distance $H_2O \cdots HOH_2^+$ moving between 1.409 Å and 1.198 Å). In the same time, the two other waters in the trimer rotate to become quasi-parallel to each other, breaking their H-bond, but the trimer water next to H_3O^+ remains H bonded to them (Fig. 3f). Once each of the two trimer waters has set up a H-bond with Br^-, the proton is transferred from the contact pair to the closest trimer water (Fig. 3g). The system then evolves rapidly (50 fs) to a final structure which corresponds to a solvent-separated ion pair (Fig. 3h). At this point, the structure remains the same, with only rocking motions of the four water molecules being seen (no more proton transfer occurs). This solvent-separated ion pair is 4.8 kcal/mol more stable than the contact ion pair shown in Fig. 3a.

The energies of the isomers as provided by the dynamics are shown in Table 2, along with the non-ZPE-corrected and free energy differences obtained from the geometry optimization of the snapshots, leading to minima in the potential energy surface. In this case (five waters), the potential energy differences given by the dynamics are significantly smaller than the free energy differences. This indicates that the entropy differences sampled from the dynamics are larger than in the four-water system. This may be related with the larger fluctuations of the potential energy (0.80–0.95 kcal/mol) for the five-water system as opposed to those (0.30–0.40 kcal/mol) for the four-water system. The origin could also be due to the frequency modes calculated for the systems. The five-water systems in particular are quite floppy,

Table 2 Comparison of the relative stabilities of the $Br^-(H_3O^+)(H_2O)_3$ and $Br^-(H_3O^+)(H_2O)_4$ models in kcal/mol

Model	<Epot> (dynamics at 50 K)	ΔU (0 K)	ΔG (50 K)
$4H_2O$, HBr Contact ion pair 2b	2.7	2.5	2.2
$4H_2O$, HBr Contact ion pair 2c	3.1	2.6	3.4
$4H_2O$, HBr Solvent-separated ion pair 2a	0	0	0
$5H_2O$, HBr Contact ion pair 3a	4.8	5.8	5.4
$5H_2O$, HBr Contact ion pair 3d	4.0	6.7	5.1
$5H_2O$, HBr Contact ion pair (plateau in the dynamics) 4a	5.0	6.0	6.1
$5H_2O$, HBr Solvent-separated ion pair 4d	0	0	0

so the accurate calculation of the frequencies are very dependent on the extent of the geometry optimization, and in fact the validity of the harmonic oscillator and rigid rotor approximations for these systems is quite suspect.

Our results thus show that HBr ionization at 50 K takes place as soon as the number of waters is at least equal to four. The dissociation of HBr at 50 K into a contact ion pair occurs very rapidly (within the first 200 fs of the simulations), whenever HBr is mixed with four waters or more, no matter what the pre-existing structure of the waters is (monomers or dimers). In the case of the $HBr(H_2O)_4$ ring, the dissociation to a contact ion pair is delayed by about 100 fs, the time needed to insert the bromide ion into the ring. Simulations at 200 K of the same four-water models show that no HBr dissociation occurs, whereas the HBr remains dissociated if the solvent-separated ion-pair form is used as an initial structure. Contact ion pairs are also formed rapidly in the case of five waters and, due to the large number of degrees of freedom, one can find many isomers for these ion pairs, 4.5 – 5.5 kcal/mol less stable than the solvated ion pairs.

Moreover, we found that, if a water trimer is present in the initial molecules, and if one water of this trimer is oriented in such a way that (i) it can receive H^+ from the contact pair; (ii) it is stabilized by *two H-bonds* with the other waters of the trimer (compare Figs. 3d and 4a), the dynamics does not remain at the contact ion pair but evolves very rapidly (300 fs) to a stable solvated ion pair, *both in the four- and five-water cases.*

From our simulations at 50 K on four-water and five-water clusters, we found a path leading from the contact ion pair to a solvent-separated pair, but, only when the starting structures include a particular water trimer H bonded to BrH. In both cases, the solvent-separated ion pair is more stable, and this difference in stability is increased with five waters.

It seems to be difficult to reach a solvated ion pair from ionization of HBr in the presence of only four water molecules, due to the difficulty of proton transfer from the contact ion pair to a water molecule that is separated from the bromide by another water. Comparing Fig. 2a with 2b or c, it can be seen that this process would involve the breaking of hydrogen bonds and a large-amplitude rotation of the released water around the bromide ion. In the five-water case, it appears that no bond breaking is needed, but essentially rocking two waters would be sufficient to achieve proton transfer and obtain the largest possible number of hydrogen bonds.

3.4 Reaction paths

To get more insight into the mechanism of the solvation process, we have also used the NEB method (completed by following the negative frequency mode) to calculate the two reaction paths going from structures 2b and 2c to the solvent-separated ion pair model 2a in the four-water systems. For the five-water clusters, we calculated the path described in Fig. 3. The results are shown in Fig. 4a and b for the two paths involving $HBr(H_2O)_4$, and Fig. 4c and d for the two paths involving $HBr(H_2O)_5$.

The results clearly show that the transition states to $H_3O^+(H_2O)_3Br^-$ cannot be reached easily at 50 K from the contact ion pairs (18.1 and 8.0 kcal/mol from 2c and 2b, respectively), whereas, in the five-water case, the barrier is smaller (6.0 kcal for 3a). Obviously, as already shown by the geometry optimization and the dynamics, the paths for $(H_2O)HBr(H_2O\cdots HOH\cdots OH_2$ cyclic) and $(H_2O)_2HBr$ ($H_2O\cdots HOH\cdots OH_2$ cyclic) lead without barrier to the solvent-separated ion pair, as shown for five waters on Fig. 4d.

Comparing the structures on the minimum energy paths 4a and 4b, it is easy to understand the much higher barrier coming from structure 2b (Fig. 4a). In fact, the way to transform the contact ion pair to a solvent-separated ion pair for 2b is to break first all of the hydrogen bonds involving the three waters and the hydronium ion, which corresponds to a transition state illustrated in Fig. 5a. At this point, the distance between the bromide ion and the four oxygen atoms is comparable (3.20–3.25 Å). The hydronium then rotates to form three hydrogen bonds with the three waters as shown on Fig. 2c, whereas its distance to the bromide ion increases to 3.75 Å. In the case of the isomer 2a (CIPa on Fig. 4b), the number of bonds broken is much less because the path involves the inversion of the hydronium ion, as a first and highest transition state of 8.0 kcal/mol (Fig. 5b). At least two intermediates have been distinguished, the second one (CIPc), similar to 2a but with an inverted H_3O^+ is only 1.3 kcal less stable than the initial contact pair. Rotation of the water originally not bonded to Br^- generates the next transition state where the hydronium is only bonded to two waters. Further rotations of waters and stabilization through the formation of a $H_5O_2^+$ ion leads finally to the solvent-separated ion pair (SIP).

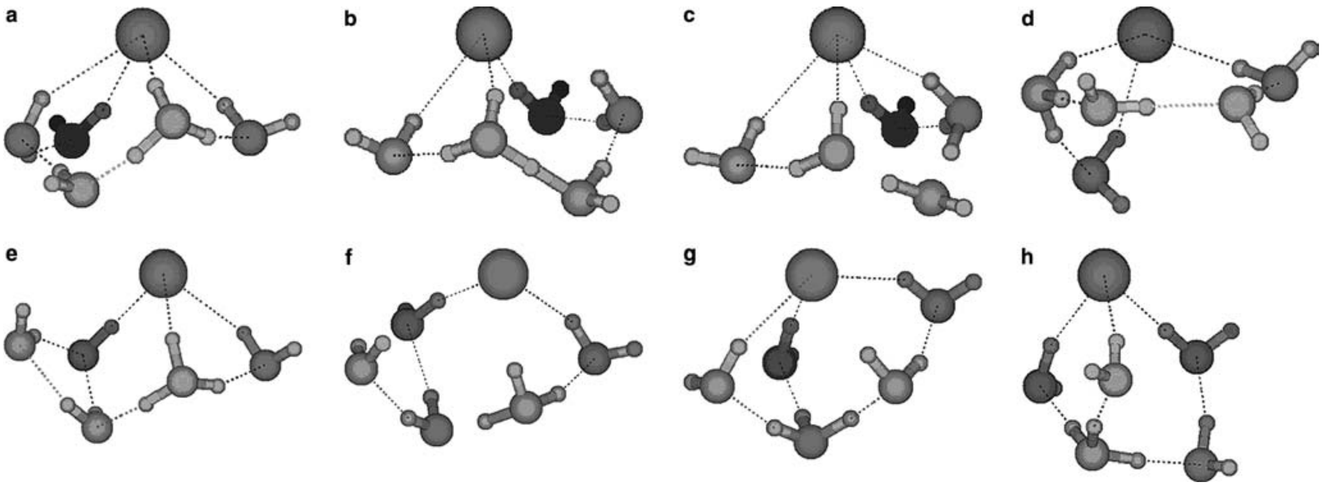

Fig. 3

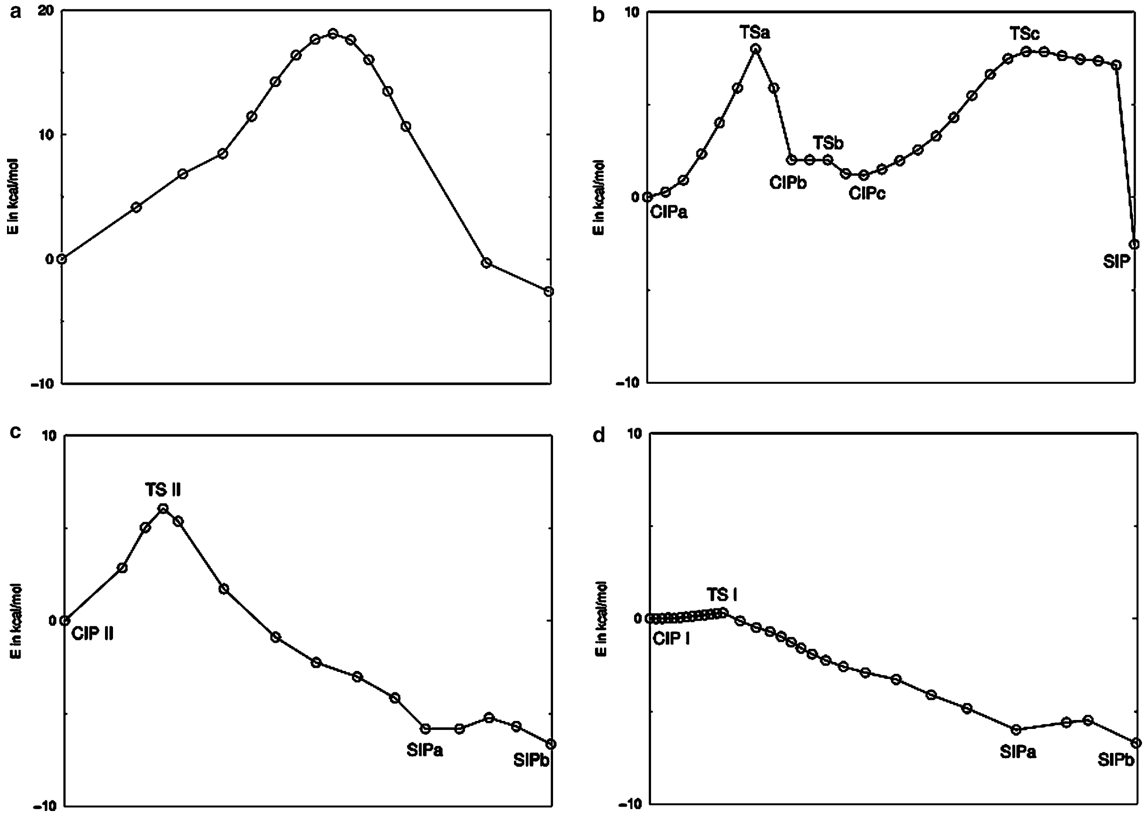

Fig. 4

In the case of the five-water system, no hydrogen bond is broken and the solvent-separated ion pair is reached by small rotations of the waters with a barrier of 6 kcal/mol when starting from the isomer 3a or 3c (CIP II on Fig. 4c).

Starting from the isomer 3e (CIPI on Fig. 4d), the path presents no barrier. The optimized isomers CIPI (3e) and CIPII (3c) have the same potential energy (a difference of only 0.2 kcal/mol). A similar barrierless path can describe the evolution of the corresponding model with four waters.

4 Conclusions

The dynamics simulations and the reaction path calculations lead to a convergent picture of the mechanism of HBr dissociation with four and five waters. In all cases, contact ion pairs are formed. The transfer of the proton to the next water molecule, yielding the solvent-separated ion pair, is exothermic, but most of the reaction paths have activation barriers larger than a few kcal/mol, explaining why the passage from

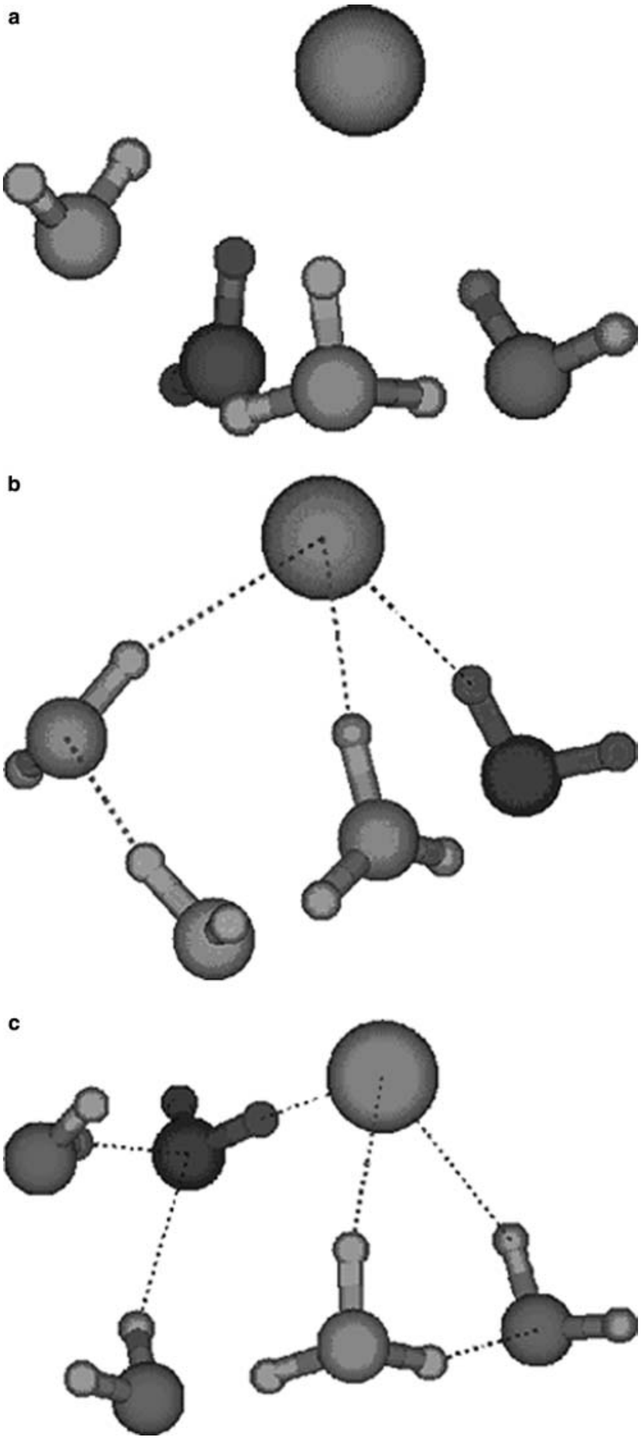

Fig. 5

the contact ion pair to the solvent-separated ion pair is not observed in most of the dynamics and during the simulation time (2–3 ps). However, experimental evidence indicates the existence of solvent-separated ion pairs when HBr interacts with at least five waters.

In fact, we found that when the cluster $H_2O \cdots HOH \cdots OH_2$ is present with HBr and one or two other waters, the dynamics and the reaction paths lead to HBr dissociation to a contact ion pair, followed by a barrierless transformation to a solvent-separated ion pair. This starting structure is certainly much less probable than either single waters or interactions of stable dimers, trimers, or tetramers of water. Moreover, it is much less probable with fewer water molecules. Increasing the number of water molecules will increase the chance to generate this kind of water trimer. This could be an explanation of the experimental results, making more probable the barrierless process with five waters than with four.

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