

## SOLVATING COLLISIONS BETWEEN DEUTERONS AND LIGHT-WATER OCTAMERS

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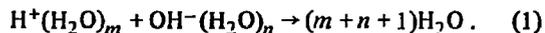
One hundred classical trajectories have been numerically generated for solvating collisions of  $D^+$  with the stable light-water cluster  $(H_2O)_8$ . Ten distinct open channels were discovered, with product-ion hydration numbers ranging from 1 to 6. The deuteron tends preferentially to be carried away in neutrals, particularly when large ions are formed. The results can be explained in terms of competition between charge transfer within, and decomposition of, the charged reaction complex.

### 1. Introduction

Formation and study of gas-phase clusters has become an exciting area of experimental chemical physics [1,2]. A wide variety of atomic and molecular substances has been examined, as both neutral and charged clusters. One of the interesting prospects offered by these developments is the chance to observe macroscopic materials properties develop as the cluster size steadily increases.

Experiments on gas-phase clusters containing water have provided information basic to understanding aqueous condensed phases. Determination of the water dimer structure [3], for example, yields vital insight into hydrogen bonding, which constitutes an indispensable part of the intermolecular forces in liquid water, aqueous solutions, and the ices. Similarly the experimental study of protonated water clusters [4] constitutes a background for understanding hydrogen ions in macroscopic solution phases.

This burgeoning experimental effort gives an extra impetus for theory to probe cluster structure and dynamics. In a recent series of papers [5–12] we have undertaken a modest response to this challenge. By employing the "polarization model" as a convenient approximation to the complex potential energy functions involved [5] we have studied selected aspects of the exothermic neutralization reactions [9–12]



Some of the results obtained (including effects of isotopic substitution) implied the presence of unanticipated phenomena, and to that extent the simple modelling may be beneficial in stimulating future experiments.

In this paper we wish to report on a computational study of hydrogen-ion hydration dynamics. Once again we have relied on the polarization model to supply the interactions, and classical dynamics has been used to follow the reactive collisions.

The specific system studied involves bare deuterons  $D^+$  colliding with light-water octamers  $(H_2^{16}O)_8$  in what is believed to be the stable structure for the latter [7]. The collisions produce a combination of solvated hydrogen ions and neutral water molecules in several possible channels. We have employed  $D^+$  (rather than  $H^+$ ) for the bare reactant ion because such simultaneous use of distinct hydrogen isotopes in the corresponding real experiment would help to sort out details of the solvation dynamics as explained below.

Interactions in the polarization model have an inherently many-body character. Consequently it is a non-trivial task numerically to integrate equations of classical motion for the twenty-five coupled nuclei involved in the present case. For that reason we had previously carried out and reported [8] a short feasibility study of the hydrogen ion plus water octamer system. That earlier work differs from the present study in several significant ways: (1) The hydrogen

ion was the light isotopic species  $H^+$  rather than  $D^+$ . (2) Only 5 reactive trajectories were generated in contrast to 100 in this study. (3) Initial conditions and termination criteria for the individual trajectories differ in details, as mentioned below, from those of the feasibility study. (4) An earlier (and inferior) version of the polarization model was employed to represent the interactions.

Section 2 explains how we generated the present set of trajectories. Results extracted from those trajectories are presented in section 3. Section 4 summarizes conclusions and discusses their implications.

## 2. Trajectory generation

The polarization model in version "PM6" has been employed for the present study [9]; this is the version that has been used to examine the neutralization reactions (1).

Fig. 1 shows the structure of the stable water octamer produced by the PM6 potential. It has a pattern of nine nearly linear hydrogen bonds that make it equivalent to the hydrocarbon bicyclo[2.2.2]octane [7]. Its binding energy compared to eight independent water molecules is 68.339 kcal/mol with the PM6 potential.

To initiate any given trajectory a deuteron was placed 30 Å from the centroid of the light-water octamer, to which a random orientation had been applied. The mutual potential energy  $\Delta\Phi$  of the two re-

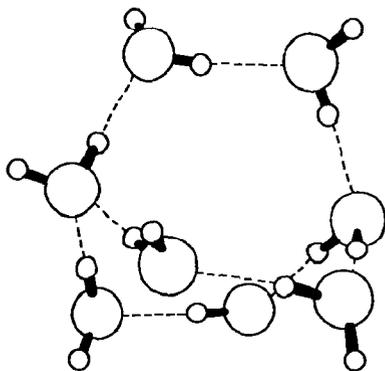


Fig. 1. Structure of the stable water octamer according to the polarization model (version PM6).

actants was then calculated, which at the distance involved would be dominated by the charge-dipole interaction. If this mutual interaction was positive (as found in 44% of the trials) the configuration was rejected. If it was negative, translational velocities were assigned to  $D^+$  and to  $(H_2O)_8$  that corresponded essentially to infall of unexcited reactants from infinity to 30 Å. Specifically, antiparallel velocity vectors  $v_1$  and  $v_2$  are applied respectively to  $D^+$  and to the twenty-four atoms of the octamer so that the following conditions were satisfied: (a) The reactants were aimed directly at one another. (b) The overall system center of mass was stationary. (c) The kinetic energy was equal to  $-\Delta\Phi$ .

It might be noted in passing that for the prior feasibility study [8] of the  $H^+ + (H_2O)_8$  reaction the initial distance was 20 Å, and the reactants were motionless at this point.

The polarization model dynamical equations were integrated numerically as in our previous work [8, -12], with time increment

$$\Delta t = 6.25 \times 10^{-17} \text{ s} . \quad (2)$$

During the course of the numerical integration the rms distance  $S_O(r)$  of the eight oxygens from the system center of mass was computed. When  $S_O$  had risen above 10 Å (this is possible only if the octamer had suffered a fragmenting collision), a sequence of product-cluster tests was begun to identify the final pattern of diverging fragments.

A product cluster is defined as a set of H and O atoms such that any pair in the set is either closer than 3.0 Å, or is indirectly connected by a chain of other atoms in the set which obey this distance criterion. One picosecond after having made the first cluster identifications the criterion was applied again. If the same sets of atoms appeared in each cluster the second time the trajectory was terminated. If a different cluster pattern appeared, the trajectory was extended for another picosecond and the clusters were re-identified. This procedure would be repeated until two successive cluster patterns separated in time by 1 ps were identical. These clusters were taken to be the reaction products.

The bare proton  $H^+$  or deuteron  $D^+$  has a large affinity for water. Consequently the reaction under study is strongly exothermic. However the amount of energy released depends upon the pattern of products pro-

duced. For that channel which produces  $H_3O^+$  and seven independent water molecules, the energy released is 103.024 kcal/mole according to the PM6 prediction.

### 3. Product distributions

As a result of reactive collision between  $D^+$  and  $(H_2O)_s$ , hydrated hydrogen ions containing from 1 to 6 water molecules were observed to emerge from the reaction. These are listed in table 1, which shows the corresponding occurrence probabilities for each of these ion hydration numbers. It should be kept in mind that these probabilities include both cases where the incoming  $D^+$  respectively does, and does not, ultimately reside in the ionic cluster. Table 1 shows that the most probable degree of hydration is 3, with probabilities declining to either side of this maximum. While none of the 100 reactive trajectories examined yielded hydration number 7 it is conceivable that this would have appeared with very low frequency in a much larger trajectory sample.

Table 1 also presents information about the energy carried from the reaction by the ions. Column 3 shows the mean translational kinetic energy for ions with the various degrees of hydration. The more massive ions naturally move less rapidly away from the reaction complex, and within the expected statistical uncertainty it appears that the mean translational kinetic energy declines monotonically with increasing hydration number.

Column 4 in table 1 shows mean values determined for kinetic energy of internal (vibration-rotation)

motion of the ions. These energies are considerably larger than those shown for translation and possibly reveal a rising trend with increasing mass, due probably to the larger number of degrees of freedom that are present in the larger ions.

Neutral products from the 100 reactive collisions predominately were water monomers. In fact each collision produced at least one monomer, i.e. the occurrence probability for neutral monomers was found to be unity. Four of the reactions also produced neutral bound water dimers. Three of the cases yielded neutral bound water trimers. Table 2 summarizes these occurrence frequencies in column 2; note that the probabilities in sum exceed unity because of simultaneous occurrences of monomers with higher oligomers.

Columns 3 and 4 in table 2 show mean kinetic energies of translational and of internal motion for the emerging neutrals. As was observed for the ionic products, the translational energy declines with increasing mass. However the internal kinetic energy pattern is unlike that for the ionic case, declining sharply from the neutral monomers to the neutral dimers and trimers. This distinction reflects the much weaker binding present in neutrals compared to the ions, since unimolecular decomposition would more easily degrade neutral dimers and trimers that were initially highly excited, in comparison to their ionic counterparts. Only those neutral dimers and trimers with low internal excitation energy would survive long enough to be picked up by our cluster accounting procedure.

The various reaction channels and their probabilities (regardless of the fate of the deuteron) have been summarized in table 3. Ten such channels have been discovered in the present study. The size of the ionic cluster is designated by the position of an asterisk in table 3.

Table 1  
Distribution of ionic reaction products

Ion hydration number	Occurrence probability	Mean translational energy <sup>a)</sup>	Mean internal kinetic energy <sup>a)</sup>
1	0.06	5.71	20.83
2	0.18	2.99	22.62
3	0.39	2.10	22.01
4	0.28	2.04	27.48
5	0.06	1.38	31.69
6	0.03	1.54	26.25

<sup>a)</sup> Energies in kcal/mole

Table 2  
Distribution of neutral reaction products

Cluster size	Occurrence probability	Mean translational energy <sup>a)</sup>	Mean internal kinetic energy <sup>a)</sup>
1	1.00	5.18	11.55
2	0.04	1.66	3.32
3	0.03	0.73	5.01

<sup>a)</sup> Energies in kcal/mole.

Table 3  
Reaction channels and probabilities<sup>a)</sup>

Cluster size						Probability
1	2	3	4	5	6	
8*						0.01
6*	1					0.02
6	1*					0.17
5*		1				0.02
5		1*				0.39
4	2*					0.01
4			1*			0.28
3*	1	1				0.01
3				1*		0.06
2					1*	0.03

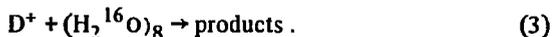
<sup>a)</sup> The size of the ionic cluster is indicated by an asterisk.

We have also examined the disposition of the incoming deuteron. This is the reactant particle that initially bears the excess charge, so it might have been reasonable to suppose it would appear with high probability in the ionic product cluster. However that is not the case. D<sup>+</sup> was contained in the ionic cluster in only 27 of the 100 cases. This frequency is substantially less than the probability that corresponds to complete scrambling of all hydrogenic particles during reaction, namely 0.434, that can be inferred from the last column in table 3. This discrimination effect appears to be amplified for those cases producing large ions. Among the 37 trajectories that led to ion hydration numbers of 4, 5, or 6 there were only 2 for which the deuteron was found within those ions.

The statistical tendency for the incoming hydrogenic ion to end up in neutral products was observed earlier in our rudimentary feasibility study [8].

#### 4. Conclusions and discussion

Using classical mechanics, and the polarization model to represent interactions, we have studied the following gas-phase reaction family:



Even disregarding isotope distribution among products, ten distinct channels were discovered among the 100 trajectories numerically generated. These channels differ according to the hydration number of the solvated

ion produced, and whether or not any of the ancillary neutrals are bound. Mean translational and internal kinetic energies have been determined for products, with results that correlate with mass, number of internal degrees of freedom, and binding energy.

The use of D<sup>+</sup> rather than H<sup>+</sup> as the incoming charged particle offers an important experimental tool for clarifying some aspects of the solvation dynamics. Because the masses of the products would reflect the presence or absence of a deuteron, this would in principle permit an experimental test of our conclusion that D<sup>+</sup> tends to be excluded from ionic products.

Our statistical results seem to be consistent with a relatively simple picture of the solvation dynamics involved in reaction (3). Under the zero-incident-energy condition employed, the D<sup>+</sup> will collide with the polar octamer near its negative end (at the right in fig. 1). A large solvation energy should suddenly be released at this impact point, creating a "hot spot". At this stage charge transfer within the octameric aggregates begin to compete with decomposition. If the latter immediately dominates then the "hot spot" should ablate, carrying the excess charge away in a small-mass ion (more than likely to contain D<sup>+</sup>, compared with random expectation), leaving a reduced-size water oligomer with enough internal excitation usually to break up into monomers.

On the other hand the excess charge could quickly transfer to the other, cooler, end of the octamer by concerted hydrogen ion exchange (the Grotthuss hopping mechanism [13]) along one of the two properly oriented hydrogen-bond chains that connect the ends of the octamer. This charge transfer would leave D<sup>+</sup> behind as part of a neutral HDO molecule at the hot end of the aggregate. Subsequent break-up would drive this HDO away as a neutral, while tending to leave behind a relatively cool (and thus larger) ion containing only light hydrogen.

Although some modification would be warranted by the lower mobility of D<sup>+</sup> compared to H<sup>+</sup>, the scenario just provided should apply to the analogous case of H<sup>+</sup> impinging on (D<sub>2</sub>O)<sub>8</sub>.

An exciting prospect for future theoretical study, perhaps utilizing a suitably adapted [14,15] polarization model, is the study of H<sup>+</sup> or D<sup>+</sup> colliding reactively with bound oligomers of HF and NH<sub>3</sub>, as well as with mixed clusters of these species with H<sub>2</sub>O. Present expectations are that each of the qualitative

features observed in the present project would continue to appear in this broader context.

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