

## COMPUTER SIMULATION OF PROTON HYDRATION DYNAMICS

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Classical trajectories have been numerically constructed for a proton interacting with an octameric water cluster. The "polarization model" was used to represent the 75-dimensional potential energy hypersurface. The most probable outcome is production of  $H_7O_3^+$  and five diverging water monomers, with one of the latter carrying away the incoming proton.

The "polarization model" for water was recently introduced to permit computer simulation of liquid and solid forms with inclusion of proton transfer processes [1,2]. Specifically, it permits study of the water-molecule dissociation process and solvation of the resulting  $H^+$  and  $OH^-$  ionic fragments. We report here some preliminary illustrative results on the dynamics of a simple type of proton solvation, using classical mechanics and the polarization model to describe the relevant potential energy hypersurface.

The particular process examined is the gas-phase collision of a bare proton  $H^+$  with a water cluster  $(H_2O)_8$ . The latter octameric species has the stable form reported in our earlier study. It is linked internally by nine nearly linear hydrogen bonds so as to form an aqueous analog of the saturated hydrocarbon bicyclo[2.2.2]octane, and aside from minor distortion it constitutes a portion of the hexagonal ice lattice [3]. The octamer has dipole moment 4.61 D, pointing essentially from one bridge-head oxygen to the other.

Six distinct dynamical trajectories have been generated with outcomes listed in table 1. In each case the proton (designated H17) was initially placed at rest 20 Å from the center of the octamer. Its six starting positions (+x to -z in table 1) were located along cartesian axes centered in the octamer, with the -z axis pointed along the cluster dipole direction. The nuclei comprising the octamer had small random momenta corresponding to a typical molecular beam temperature (=30 K), but no center of mass transla-

tion or rotation were initially permitted for the octamer.

On account of the many-body polarization forces that are present the newtonian equations of motion are more complicated than those usually encountered. However, they can be put into relatively compact form that permits numerical integration [4]. The slowest aspect of the integration procedure is the necessity to invert matrices ( $24 \times 24$ ) generated by the self-consistent polarization of the eight oxygens. A fifth-order Gear algorithm [5] was used with a time increment  $\Delta t = 1.25 \times 10^{-4}$  ps. Each of the six trajectories was run for a time interval of 10 ps. Computer running time for such a trajectory was  $\approx 20$  min on the CRAY-1.

Table 1 summarizes the results. Five of the six cases underwent a strongly exothermic solvation

Table 1  
 Outcome of  $H^+ + (H_2O)_8$  encounter

Initial position	Ionic product	Product temperature (K)	H17
+x	$H_7O_3^+$	1667	m
-x	$H_7O_3^+$	1302	m
+y	$H_7O_3^+$	1462	m
-y	$H_{11}O_5^+$	1862	m
+z	$H_7O_3^+$	1333	1
-z	(n.r.)		

reaction producing an ionic cluster and several escaping monomers. The non-reacting case (-z) initially put the bare proton along the positive end of the cluster dipole so that the two reactants simply flew apart

On the basis of the five reactive trajectories it appears that the most probable outcome of the solvation reaction is formation of a proton trihydrate cation  $H_7O_3^+$  plus five water monomers rapidly diverging from the ion in a non-planar pattern. The case "-y" provides an interesting exception since only three monomers emerge from the reaction, leaving behind a proton pentahydrate cation. On account of the possibility that this hot  $H_{11}O_5^+$  might undergo unimolecular decomposition to produce a lower proton hydrate this one trajectory was extended to 20 ps, but no such decomposition occurred.

The third column in table 1 lists product temperatures evaluated via average nuclear kinetic energies over the last 5 ps of the trajectories. This interval follows the occurrence of any reactive collision and rearrangement which typically last only  $\approx 1$  ps. Not surprisingly the average product temperature (1441 K) for those cases where five water monomers have evaporated is lower than that producing only three (1862 K).

The last column in table 1 indicates the final disposition ( $m$  = monomer,  $i$  = ion) of the incoming bare proton H17. Although one exception is noted there seems to be a high probability for this nucleus to be carried away on an evaporating monomer. This prediction has interesting implications for conceivable molecular beam experiments wherein cluster hydrogen have different isotopic identity from that of the bare proton. A possible explanation of this result is that first contact of the incoming proton with the cluster produces a "hot spot" from which evaporation occurs before thermal equilibration of the reaction complex appears.

Detailed study of the oxygen positions for all five reactive cases shows that those in the final ion cluster

initially constituted a subset of water molecules in the octamer that were connected among themselves by hydrogen bonds. This is consistent with the "hot spot" presumption and the observed hydrogen exchange that occurs at the moment of reaction.

Obviously classical dynamics can be inappropriate to describe hydrogen motions under many circumstances. However, we believe it is reasonably reliable to predict the statistical course of strongly exothermic reactions such as that reported here.

It is clearly desirable to generate a more comprehensive and exhaustive set of trajectories than those in table 1. In particular we expect to find initial conditions that will produce the intermediate ion  $H_9O_4^+$ . We also anticipate examining the collision of  $H^+$  with larger ice fragments to generate some insight into the astronomically important process of the radiation erosion of ice [6]. However the non-trivial cost implied above for trajectory generation suggests that empirical functions in the polarization model ought to be carefully optimized before undertaking exhaustive (and expensive) statistical studies of proton solvation dynamics.

Finally we mention early studies which show that gas-phase dynamics for the polarization model can also conveniently be carried out for neutralization reactions between  $H^+(H_2O)_m$  and  $OH^-(H_2O)_n$ .

## References

- [1] F H Stillinger and C W David, *J Chem. Phys.* 69 (1978) 1473
- [2] C W David, *Chem Phys* 40 (1979) 229
- [3] F H Stillinger and C.W David, *J Chem. Phys.* 73 (1980) 3384.
- [4] F H Stillinger, *J Chem Phys* 71 (1979) 1647
- [5] C W Gear, *The Numerical Integration of Ordinary Differential Equations of Various Orders*, Argonne National Laboratory Report ANL-7126, January 1966
- [6] L. Spitzer Jr., *Physical processes in the interstellar medium* (Wiley, New York, 1978) p. 209.