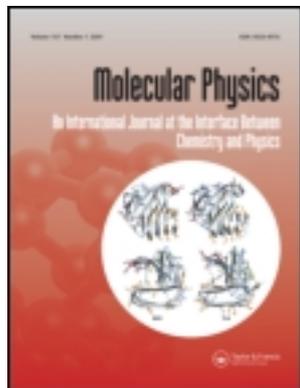


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Frank H. Stillinger^a & Thomas A. Weber^a

^a Bell Laboratories, Murray Hill, New Jersey, 07974, U.S.A.

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Asymmetry between protons and proton holes in gas-phase neutralization reactions

by FRANK H. STILLINGER† and THOMAS A. WEBER
Bell Laboratories, Murray Hill, New Jersey 07974, U.S.A.

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Energy distribution functions have been computed for neutral water molecules produced by reactive collisions of H_5O_2^+ with OH^- , and of H_3O^+ with H_3O_2^- . The potential energy hypersurface was approximated by the polarization model, and 500 classical trajectories were generated by computer for each reaction. The translational and the rotational-vibrational excitation energy distributions differ qualitatively for the two cases, thereby demonstrating an asymmetry under proton, proton-hole interchange between reactant clusters. The mean excitation energies for product molecules of anionic origin are found to be greater in both cases than those of cationic origin.

1. INTRODUCTION

As a result of the reversible molecular dissociation process



charge carriers are present in liquid water as well as in ice. These carriers, the positive solvated proton and the negative solvated "proton hole", are striking in that their liquid-phase mobilities far exceed those of any other ions [1] (with the possible exception of the solvated electron). It has been understood for some time that these high mobilities were due to the Grotthuss chain hopping mechanism [2] involving successive proton exchanges that is inapplicable to other ions. In an intriguing and long appreciated sense the protons and proton holes provide analogues in aqueous media to electrons and holes in semiconductors.

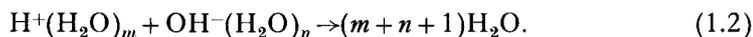
At a superficial level of understanding it might appear that protons and proton holes in water should have closely similar structural and kinetic behaviours. For every solvation structure that can be imagined for a proton in a condensed aqueous medium a conjugate structure can as well be imagined for a solvated proton hole. Yet the fact remains that protons and proton holes do *not* behave similarly (even aside from charge sign). The proton mobility in pure liquid water exceeds that of the proton hole by a factor of 1.8 at room temperature, and the discrepancy is aggravated by lowering the temperature [1].

We are not aware of any credible explanation for the proton, proton-hole dynamical asymmetry in liquid water. Furthermore no obvious experimental technique suggests itself for resolving the mystery. Nevertheless some hope

† To whom correspondence should be addressed.

exists that suitable gas-phase studies involving the solvated ions $\text{H}^+(\text{H}_2\text{O})_m$ and $\text{OH}^-(\text{H}_2\text{O})_n$ might be helpful for understanding asymmetry, at least to the extent that these ions can be regarded roughly as models for the proton and proton hole solvated by the extended liquid medium.

We have previously [3–5] carried out computational studies of gas phase neutralization reactions of the type



The polarization model (in version ‘PM6’) was employed to represent the multidimensional potential energy hypersurface for the collection of nuclei. Classical trajectories were numerically constructed carrying randomly oriented and widely separated reactants through reactive collision to widely separated products. Both of the cases $m, n=1, 0$ (hydronium ion plus hydroxide ion) and $m, n=2, 1$ (doubly hydrated proton plus singly hydrated hydroxide) have been examined in detail, including the influence of isotopic substitution [4]. Note that when

$$m = n + 1 \quad (1.3)$$

we can regard the reactant ions as protons and proton holes with equal extents of hydration, namely m water molecules.

One obvious form of proton, proton-hole asymmetry appeared in those earlier studies. Specifically the product water molecules whose oxygen originated in the proton-hole cluster emerged from the reaction with a greater average excitation than those whose oxygen originated in the proton cluster. This differential apportionment of energy released by the neutralization was manifest both in translational motion of the products as well as in the internal motions of vibration and rotation. The effect was found to be quite vivid for the 1, 0 case [3, 4]; it was clearly present as well for the 2, 1 case but with substantially diminished magnitude [5].

Our goal in the present paper is to extend the previous studies to $m, n=2, 0$:



and to $m, n=1, 1$:



This is one of the simplest pair of reactions for which the proton and proton hole have different extents of hydration, yet yield the same products. We expect to find (and indeed do find below) the energy asymmetry in these new cases that was observed previously. But in addition new indications of asymmetry are possible as well. If indeed protons and proton holes were equivalent then one might expect that the distribution in energy of all molecules lumped together (regardless of cation or anion origin) might be the same for reaction (1.4) as for reaction (1.5). In fact we find below systematic and obvious differences that seem further to illuminate the asymmetry.

The next § 2 briefly outlines our computational procedure. Section 3 presents results. Implications of those results are discussed in the final § 4.

2. COMPUTATIONAL PROCEDURE

By drawing upon published PM6 energies for the ions and the water molecule [5] we can obtain the energy released in the two neutralization reactions under

consideration. The results† are 186·453 kcal mol⁻¹ for reaction (1.4), and 185·386 kcal mol⁻¹ for reaction (1.5). These represent the differences in energy between reactants and products all of which are at their mechanical equilibrium geometries, and in isolation from one another.

Five hundred reactive collision trajectories have been generated numerically for each of reactions (1.4) and (1.5). These trajectories were used to infer distributions for neutral product molecules. For most of the properties discussed in the following § 3 this number seemed to be sufficient to ensure statistical significance.

To initiate each trajectory, the reactant ions were placed with their centroids 30 Å apart, with random orientations. Each ion at this stage possessed its stable geometry, i.e. no vibrational deformation was present. The ions were given translational velocities (but no rotation) so that their centroids were directly headed toward one another, and so that the total system centre of mass was stationary. In all cases the energy was set equal to that of infinitely separated, stationary, and unexcited ions. Thus the initial conditions corresponded to infall of the ions from infinity under their mutual coulombic attraction.

The polarization model involves a manifestly non-additive description [6] of the potential energy hypersurface for the nine atom system. Consequently it is a non-trivial task to integrate the classical equations of motion [7]. Nevertheless it is possible to do so using a standard numerical algorithm, and time increment [3–5]

$$\Delta t = 6 \cdot 28 \times 10^{-5} \text{ ps.} \quad (2.1)$$

During the generation of each trajectory the rms distances $S_O(t)$ and $S_H(t)$, for oxygens and for hydrogens respectively, from the system centre of mass were monitored. The initial value of S_O was approximately 15 Å for each trajectory, but varied a bit with orientational angles initially applied to the reactants. When S_O for any given trajectory had risen to 1·5 times its initial value that trajectory was extended for an additional 1 ps and then terminated. At this stage the three monomers produced by the reaction were invariably widely dispersed and essentially non-interacting.

The calculations reported in this paper required approximately 15 h of computer time on a CRAY-1.

3. PRODUCT DISTRIBUTIONS

Figure 1 shows the distribution of molecules produced by reaction (1.4) according to the amount of excitation energy they carry away from the collision complex, that is, the energy excess above that of a stationary undeformed molecule. This excitation energy comprises both translational kinetic energy, as well as energy of internal vibration-rotation motion. The data in this figure represents 1500 emerging neutrals, and has been collected in bins of width 5 kcal mol⁻¹. Figure 2 provides exactly the same type of plot for reaction (1.5).

No neutral water molecule can carry away more than the maximum energy released. Both distributions in figures 1 and 2 reflect that obvious constraint, and in fact show very small probability beyond about 150 kcal mol⁻¹. If one

† 1 kcal = 4·184 kJ.

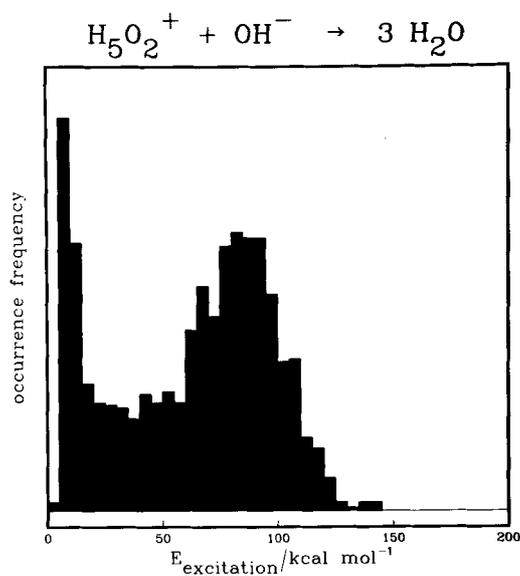


Figure 1. Distribution of excitation energy for all neutral water molecules produced by reaction (1.4). Results have been collected in bins of width 5 kcal mol^{-1} .

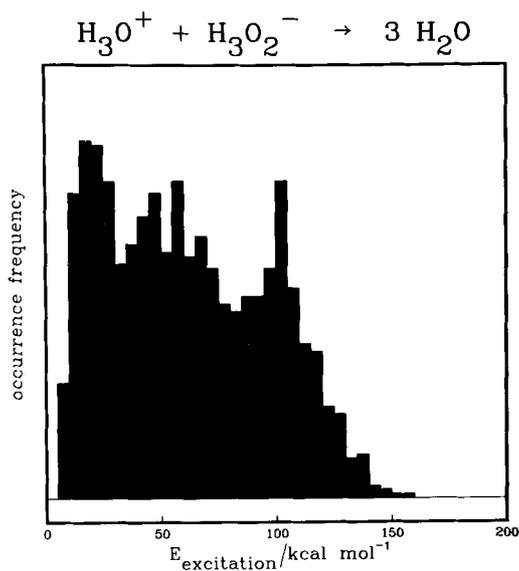


Figure 2. Distribution of excitation energy for all neutral water molecules produced by reaction (1.5). Results have been collected in bins of width 5 kcal mol^{-1} .

of the product molecules is to have an excitation energy approaching the maximum available to all three, the available phase space shrinks toward zero measure. As a result the probability for such processes becomes small, and should vanish strongly at the upper energy limit.

The distributions in figures 1 and 2 clearly differ in overall shape and in detail, thereby illustrating proton, proton-hole asymmetry. In particular that shown in figure 1 for reaction (1.4) appears to have clearly resolved maxima at about 5 and 85 kcal mol⁻¹. The distribution shown in figure 2 has a form which at best has less well developed maxima, perhaps at about 20 and 105 kcal mol⁻¹.

Because figures 1 and 2 do not distinguish monomers according to cationic or anionic source, they have no indication of the previously found energy asymmetry alluded to in the Introduction. However such distinctions can be made, and the corresponding results are presented in figures 3 and 4 for reactions (1.4) and (1.5) respectively. These latter figures split each 10 kcal mol⁻¹ of the previous distribution into three parts corresponding to the three oxygens involved. For reaction (1.4) the oxygens labelled O1 and O2 originated in H₅O₂⁺, while O3 originated in OH⁻. In the case of reaction (1.5), O1 started out in H₃O⁺, while O2 and O3 started out in H₃O₂⁻. It is certainly clear from figures 3 and 4 that water molecules of anionic origin tend to carry away more energy from the neutralization reaction than those of cationic origin, and indeed the respective distributions in both figures 3 and 4 have distinctively different shapes.

An independent view of the products arises by focusing on just the energy of internal motion (rotation and vibration). Figures 5 and 6 show how this energy of coupled rotation and vibration is distributed among all product molecules for

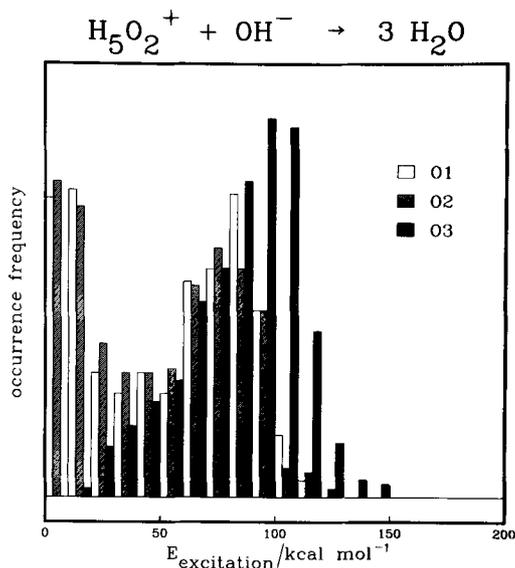


Figure 3. Excitation energy distributions for products from reaction (1.4), distinguished by reactant source. Molecules with oxygens labelled O1 and O2 originated in H₅O₂⁺, those with O3 originated in OH⁻.

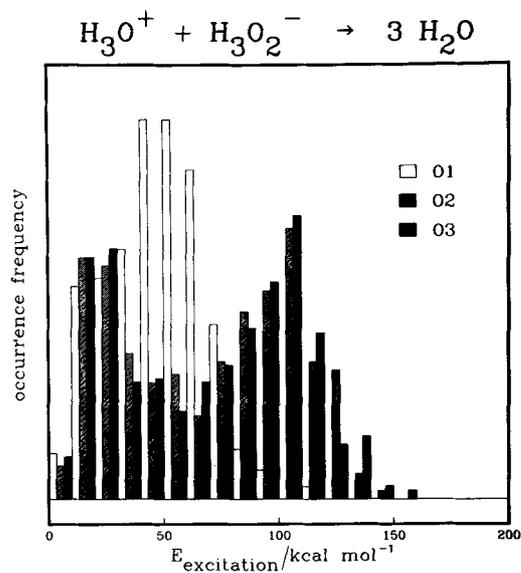


Figure 4. Excitation energy distributions for products from reaction (1.5), distinguished by reactant source. Molecules with oxygens labelled O1 stemmed from H_3O^+ , while those with O2 and O3 stemmed from H_3O_2^- .

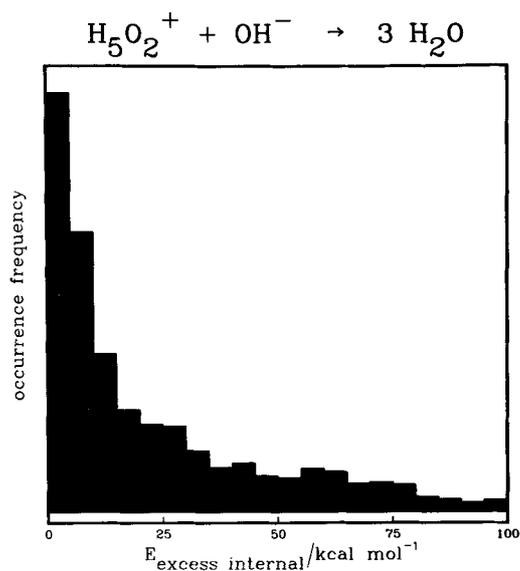


Figure 5. Energy distribution for internal motions of all molecules produced by reaction (1.4).

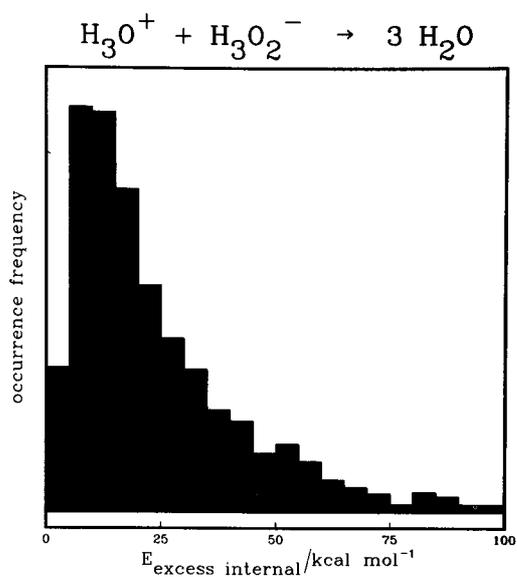


Figure 6. Energy distribution for internal motions of all molecules produced by reaction (1.5).

Mean excitation energies and rms deviations for water molecules produced by gas phase neutralization†

		Mean	R.m.s. dev.
$\text{H}_5\text{O}_2^+ + \text{OH}^-$ [reaction (1.4)]‡			
Internal	O1	11.4	17.2
	O2	10.8	15.7
	O3	48.3	54.7
Total	O1	51.9	61.3
	O2	49.9	59.5
	O3	84.7	88.2
$\text{H}_3\text{O}^+ + \text{H}_3\text{O}_2^-$ [reaction (1.5)]§			
Internal	O1	17.4	20.8
	O2	27.3	34.4
	O3	28.5	36.1
Total	O1	47.5	51.7
	O2	68.7	78.2
	O3	69.2	79.1

† All energies in kcal mol⁻¹.

‡ O1 and O2 come from H₅O₂⁺, O3 from OH⁻.

§ O1 comes from H₃O⁺, O2 and O3 from H₃O₂⁻.

the two reactions. Once again the bin width is 5 kcal mol⁻¹ for these histograms. These distributions are most obviously different in the small energy region. We remark in passing that if the water molecules are distinguished by source, the previously noted energy asymmetry continues to appear in the internal motions.

The table shows the mean energies and the inherent rms deviations for distributions of the various populations of neutral water molecules.

One more aspect of proton, proton-hole asymmetry uncovered in the present study deserves to be mentioned, even though it is frankly of marginal statistical significance. Two of the five hundred trajectories created for reaction (1.5) involved concerted three proton transfer rather than a single proton transfer as is normally the case. In these anomalous events the cation cluster gives up two protons to the anion cluster, while the anion gives back a third proton to the cation. Such three proton neutralizations were observed before in our computational study of the H₅O₂⁺ + H₃O₂⁻ neutralization reaction [5]. In contrast to the two events of this kind found with reaction (1.5), none occurred with reaction (1.4) even though nothing in principle is present to prevent them.

4. DISCUSSION

The polarization model studies of gas phase neutralization reactions have now been extended to include two cases [reactions (1.4) and (1.5)] in which the proton and proton hole have different degrees of hydration. The previously observed form of asymmetry continues to appear: Neutral water molecules with anionic origin emerge from the reaction with greater average excitation energy than those with cationic origin. This bias applies both to translational kinetic energy and to internal motion of rotation-vibration.

Examination of reactions with distinct degrees of proton and of proton-hole hydration leads to observation of a new form of asymmetry, namely that the energy distributions of *all* emerging neutrals (regardless of origin) depend on which way the proton and the proton hole were placed on the different sized reactant clusters. It seems reasonable to suppose that this new asymmetry would continue to appear for larger reactant cluster pairs. Specifically we would anticipate systematic differences to be found in comparing energy distributions for all product molecules from the reactions:



Although statistically adequate study of these two cases would require somewhat more computing effort than that devoted to (1.4) and (1.5), it is still feasible.

In order to distinguish experimentally between energy distributions of water molecules with different reactants, some sort of labelling obviously is necessary. Isotopic substitution of deuterium for light hydrogen is the most straightforward option. The effect of deuteration has been examined before in the context of the polarization model studies [4]. It was found (for hydronium plus hydroxide, $m, n = 1, 0$) that deuteration involves yet another manifestation of asymmetry. Specifically it was concluded that deuteration of the anionic reactant caused substantially less change in reactant angular and energy distributions than did

deuteration of the cation. In other words the mass of the transferring hydrogen was decisive. It is attractive to suppose that the same isotopic asymmetry applies to both reactions (1.4) and (1.5) separately. However confirmation of that hypothesis would require an impractical extension of the present project and will have to await future effort.

A wide gap still exists between the dynamics of the gas phase clusters studied in this series of papers, and the dynamics of proton and proton-hole motion in condensed aqueous phases. It is conceivable that this gap could be partially filled by suitable computational study of larger gas phase clusters, namely those with m and n in the range

$$12 \leq m, n \leq 20. \quad (4.3)$$

Ionic clusters of this size should begin to partake of some attributes of macroscopic 'droplet' behaviour. In particular they should exhibit relative sizes for protons and for proton holes that are indicative of which of these charged species has the larger partial molar volume in pure water, an unresolved problem of long standing. By carefully following the dynamics of neutralizing collision between two such 'droplets' it should be possible to observe which of the excess charges moves more from the centre of its cluster to effect neutralization at droplet contact; this would provide insight into the discrepancy between liquid phase mobilities for the two solvated ions mentioned in the Introduction. Whether or not the polarization model is sufficiently realistic to represent these phenomena accurately remains to be seen.

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