

# Dynamical study of the $\text{H}_5\text{O}_2^+ + \text{H}_3\text{O}_2^-$ neutralization reaction using the polarization model

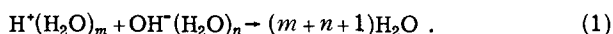
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Computer-generated classical trajectories have been used to simulate reactive collisions between the gas phase ionic species  $\text{H}_5\text{O}_2^+$  and  $\text{H}_3\text{O}_2^-$ . Two cases have been considered, corresponding, respectively, to the isotopic choices  $\text{H}_3\text{ }^{16}\text{O}_2^-$  and  $\text{D}_3\text{ }^{18}\text{O}_2^-$  for the anion. Two hundred trajectories were constructed for each case, with initial conditions corresponding to zero incident energy. The multidimensional potential energy hypersurface required for the dynamics was supplied by the "polarization model." Distributions were calculated for exit angles and for excitation energies of the water molecules produced by the exothermic reaction. Product molecules whose oxygens have anionic origin tend to be "hotter" than those with cationic origin. Most of the collisions entail simple proton transfer as expected for neutralization; however, approximately 3% exhibit concerted transfer of three protons or deuterons. Isotopic labeling of the anion causes little change in the various product distributions, and seems thereby to afford a means to verify present results experimentally.

## I. INTRODUCTION

One of the most fundamental reactions in aqueous chemistry is that which produces water through neutralization of hydrogen cations with hydroxide anions. In the gas phase this reaction can occur through collision of ion hydrate clusters ( $m, n \geq 0$ ):



In the event that both  $m$  and  $n$  are zero (bare ions) the presence of a third body normally would be required to permit the reaction to occur.

We have previously initiated a numerical study<sup>1</sup> of classical trajectories for Reaction (1) in the case  $m=1, n=0$ . The polarization model<sup>2</sup> supplied the requisite potential energy hypersurface. The most striking result that emerged from that study was asymmetric energy partitioning between the two water molecules formed in the neutralization. Specifically, that molecule whose oxygen originated in the hydroxide anion tends to emerge with more energy of translation and of rotation-vibration than that whose oxygen originated in the hydronium cation.

In view of the fact that energy asymmetry would be observable in a real experiment only through some sort of molecular labeling, we have also examined the effects of partial and of complete deuteration on the hydronium-hydroxide neutralization reaction.<sup>3</sup> It was verified that the marked asymmetry of energy distribution remained after deuteration, although significant isotope effects were perceptible. In regards to this last point we concluded that the isotope effects were primarily determined by the mass of the *transferred* hydrogen. Therefore, the closest experimentally significant analog to the undeuterated reaction



would be that in which only the anion were deuterated



For this pair of cases the reaction cross sections and product energy distributions were quite similar to each other. In analogous fashion the other pair

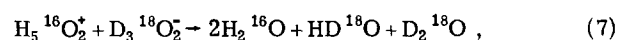


(for both of which a deuteron transfers) leads to its own similar cross sections and energy distributions.

This paper extends our previous studies to the case  $m=2, n=1$ . The primary objective was to see if the energy asymmetry effect persisted in the neutralization reactions with larger ion hydrates. Mindful again of the molecular labeling necessity, we have generated classical trajectories and examined results for the two versions of the reaction:



and



where in writing the latter it has been assumed that just a single hydrogenic particle transfers. The motivation behind selection of Eq. (7) for comparison with Eq. (6) was once again that the mass of the transferred particle was unchanged, and therefore genuine isotope effects would likely be at a minimum. It was felt that an exhaustive study of all possible isotopic variants of the basic case (6) would be unwarranted at present, and unduly expensive.

The Sec. II discusses the structures and energies of the reactant ions. This is followed in Sec. III by specification of initial conditions and computational details required in generation of the sets of classical trajectories. Section IV presents results. Concluding discussion appears in the final Sec. V.

## II. REACTANT STRUCTURES AND ENERGIES

Table I provides polarization model energies for the water molecule and for the small ion fragments that are relevant to gas-phase neutralization reactions. These potential energies required separate calculations on the respective isolated species, and refer to configurations of mechanical stability for the "PM6" version of the polarization model.<sup>3</sup> By construction, the polari-

TABLE I. PM6 potential energies for clusters at their respective global minima.

Species	Potential (kcal/mol)
$\text{H}^+$	0
$\text{OH}^-$	-644.056
$\text{H}_2\text{O}$	-1032.925
$\text{H}_3\text{O}^+$	-1204.287
$\text{H}_3\text{O}_2^-$	-1709.102
$(\text{H}_2\text{O})_2$	-2070.696
$\text{H}_5\text{O}_2^+$	-2268.266

zation model reproduces the correct gas-phase geometry and dipole moment for the water molecule. It also yields the proper proton affinity for water (171.4 kcal/mol), and the resulting hydronium ion exhibits the correct pyramidal shape.<sup>4</sup> It is designed to predict the potential energy of any configuration of hydrogen and oxygen ions.

Figure 1 shows the geometries of the reactant ions  $\text{H}_3\text{O}_2^-$  and  $\text{H}_5\text{O}_2^+$  at the mechanical equilibrium points predicted by the polarization model. These structures are independent of isotopic mass, of course. Both structures shown in the figure involve short hydrogen bridges, and in this feature they agree with crystallographic and quantum-computational studies of the ions. The anion geometry illustrated is planar and has a center of symmetry coincident with its bridging hydrogen. The cation geometry is nonplanar and asymmetric, although its bridging hydrogen falls essentially midway between the two oxygens. From Table I one finds that the energy required to remove an undistorted  $\text{H}_2\text{O}$  molecule from  $\text{H}_3\text{O}_2^-$  is 32.1 kcal/mol, while the corresponding energy for  $\text{H}_5\text{O}_2^+$  is 31.1 kcal/mol.

Accurate quantum mechanical calculations (at the Hartree-Fock level) have been carried out by Kraemer and Diercksen<sup>5</sup> for  $\text{H}_3\text{O}_2^-$ . They conclude that indeed this ion is planar, with off-axis terminal hydrogens in a *trans* configuration. They find an oxygen-oxygen separation of 2.51 Å, slightly larger than that shown in Fig. 1. Their water removal energy is smaller than ours, namely 24.3 kcal/mol. Furthermore, they suggest that the bridging hydrogen may reside preferentially toward one oxygen rather than in the middle, though the relevant potential barrier was found to be extremely small.

Kraemer and Diercksen have also studied  $\text{H}_5\text{O}_2^+$  computationally at the Hartree-Fock level.<sup>6</sup> On the basis of a limited geometry search their lowest energy structure was nonplanar and had a linear symmetric hydrogen bridge of length 2.39 Å. The water removal energy was found to be 32.24 kcal/mol.

Although the polarization model evidently entails moderate imprecision in its structural and energetic predictions, we regard it as satisfactory for qualitative study of the cited gas phase reactions.

From Table I we see that the prediction for the energy released in Reactions (6) and (7) is 154.332 kcal/mol.

### III. COMPUTATIONAL DETAILS

Our numerical analysis has been patterned after that employed previously<sup>1,3</sup> for hydronium reactions with hydroxide. The two ionic reactant species were initially placed in a standard configuration, with a 30 Å separation between their centroids. Random solid-body rotations about those centroids are then applied to each, and the shift  $\Delta\Phi$  in potential (compared to infinite ion separation) is subsequently computed. This quantity is invariably negative owing to the opposite charges on the reactant clusters. Uniform translational velocities are then given to each ion so that the respective centroids are directly aimed at one another; these velocities are chosen so that (i) the resulting kinetic energy is precisely  $-\Delta\Phi$ , and (ii) the overall system center of mass remains fixed. The classical equations of motion for the twelve nuclei on the polarization-model potential hypersurface were then numerically integrated as in our previous work.

The choice of initial conditions corresponds to reactants that have fallen toward one another from infinity, under mutual attraction, from initially unexcited states. In order to assure appropriate statistical sampling, 200 trajectories were generated for each of the Reactions (6) and (7).

For any given trajectory, the rms distance  $S_O$  of the four oxygens from the system center of mass was monitored as a function of time. A reactive collision was only regarded as complete if, after passing through a collision-complex minimum,  $S_O$  rose to 1.5 times its initial value, and then an *extra* 1 ps had elapsed. At this stage the neutral products were found to be widely dispersed and essentially noninteracting.

The corresponding quantity  $S_H$  for the hydrogen atoms was also calculated for each trajectory. In all cases  $S_O$  and  $S_H$  have similar behaviors.

### IV. RESULTS

The usual behavior observed for  $S_O(t)$  is that it declines over the first 0.8 ps to a minimum value (of

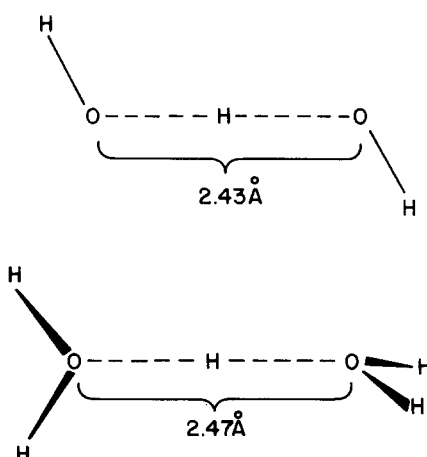


FIG. 1. Geometries predicted for  $\text{H}_3\text{O}_2^-$  and  $\text{H}_5\text{O}_2^+$  by the polarization model (version PM6).

approximately 2 Å), then within the following 0.2 ps begins to rise rapidly as product molecules recede from one another. In all of the 400 trajectories examined the ultimate products were neutral monomers. However, in a few cases transient hot dimers ( $\text{H}_2\text{O}_2$ ) were observed to emerge from the initial collision complex, and later to undergo spontaneous decomposition into separating monomers.

Our calculations occasionally produced anomalous "rebound" collisions, similar to those found earlier in hydronium-hydroxide reactions.<sup>1,3</sup> Figure 2 shows  $S_0(t)$  for one such event [trajectory #68 for Reaction (6)], with a distinct pair of minima. In contrast to the usual situation neutralization did *not* occur on first encounter. The still-ionic fragments separated, and then came together again under mutual attraction approximately 1 ps later, to undergo reaction upon second encounter.

On account of the initial randomness of reactant orientations, the product water molecules have a distribution that is cylindrically symmetric about the original axis connecting reactant ion centers of mass. Figure 3 provides the angular distribution about this axis determined by our calculations for Reaction (6). The "forward" direction (cosine of exit angle = 1) is the direction from which the anion entered the reactive collision; the cation entered from the opposite "backward" direction (cosine of exit angle = -1). The histogram shown

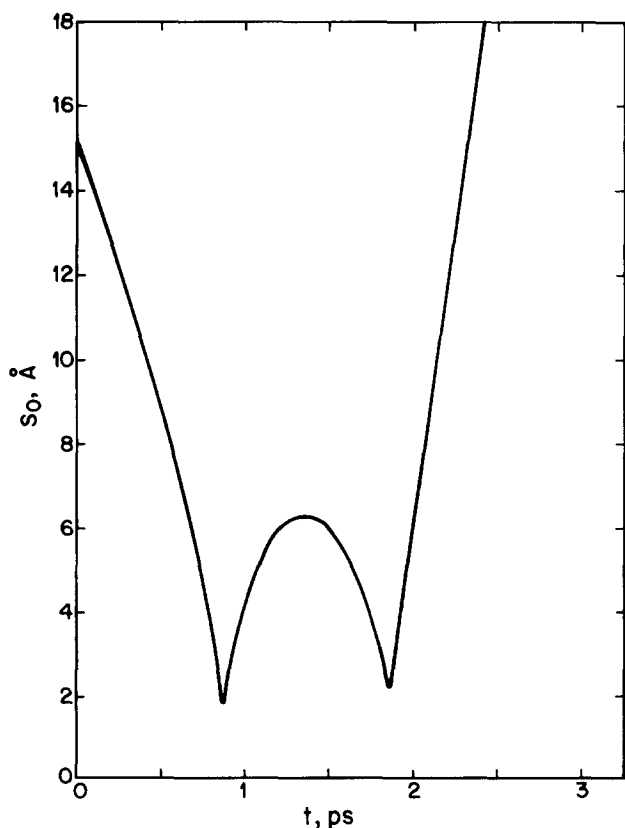


FIG. 2. Time dependence of  $S_0$  for trajectory #68 in the light-isotope reaction (6). This is one of the infrequently encountered "rebound" collisions.

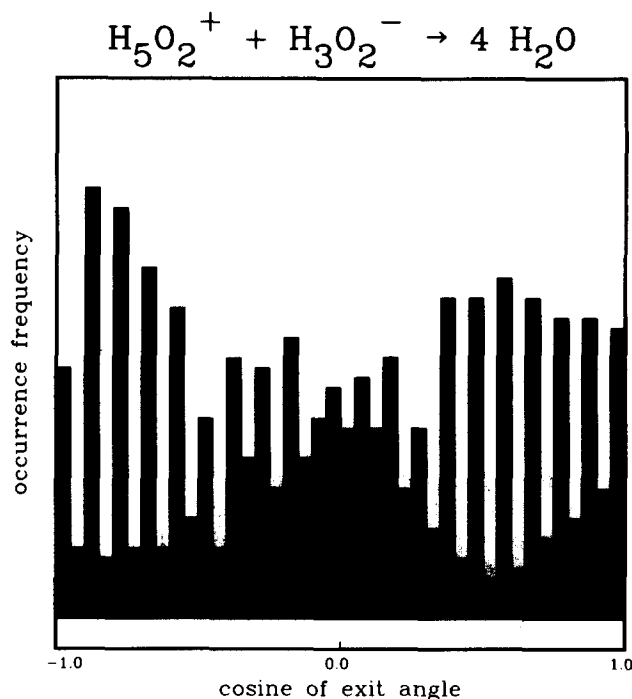


FIG. 3. Angular distribution of water molecules produced by reaction (6). The shaded bars comprise molecules originating in  $\text{H}_5\text{O}_2^+$  (oxygens O1 and O2), while black bars comprise those originating in  $\text{H}_3\text{O}_2^-$  (oxygens O3 and O4). The polar axis defining exit angles extends from the initial cation centroid position toward the initial anion centroid position.

distinguishes exiting water molecules according to the source of their oxygens: shaded bars comprise O1 and O2 originating in  $\text{H}_5\text{O}_2^+$  while black bars comprise O3 and O4 originating in  $\text{H}_3\text{O}_2^-$ . Twenty bins of equal width were provided for classifying molecules according to the value of their exit angle cosines.

While Fig. 3 suggests that both cationic waters (shaded bars) and anionic waters (black bars) can come away from the reaction zone at any angle, an obvious bias is present. In short, there is a tendency for the oxygens to return to their points of origin. The water molecules containing O1 and O2 preferentially emerge at large angles, while O3 and O4 tend to emerge at small angles. This phenomenon in much more vivid form has been observed for the simpler reaction of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , where the corresponding angular distributions concentrate strongly at forward and backward directions with no overlap.<sup>1,3</sup> It seems obvious that the greater diversity of geometric structures available for a reaction complex in the present case (with 12 atoms) would have to produce a more nearly isotropic distribution.

The corresponding angle distribution for product monomers emerging from collision of  $\text{H}_5^{16}\text{O}_2^+$  with  $\text{D}_3^{18}\text{O}_2^-$  is shown in Fig. 4. Considering the statistical uncertainties that inevitably are present with our small trajectory samples, one cannot conclude that Figs. 3 and 4 demonstrate a genuine isotope effect. This appears to support our initial presumption that little change should result if the mass of the transferred hydrogen remains unchanged.

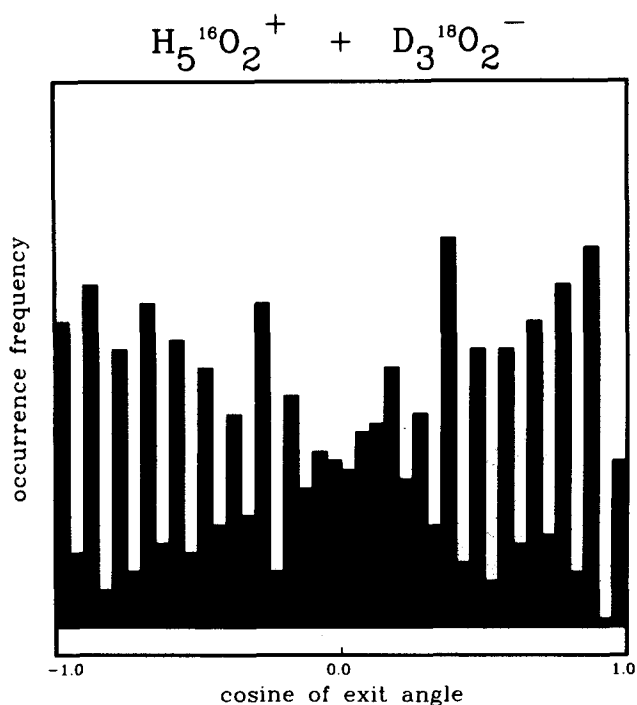


FIG. 4. Angular distribution of water molecules produced by reaction (7) involving the isotopically substituted anion  $\text{D}_3^{18}\text{O}_2^-$ . Polar axis and bar color coding are the same as for Fig. 3.

Figures 5 and 6 show, for Reactions (6) and (7), respectively, how the 154.3 kcal/mol released in the reaction is carried away by the products. These figures indicate the relative probabilities for various excitation energies (translation, vibration, and rotation combined)

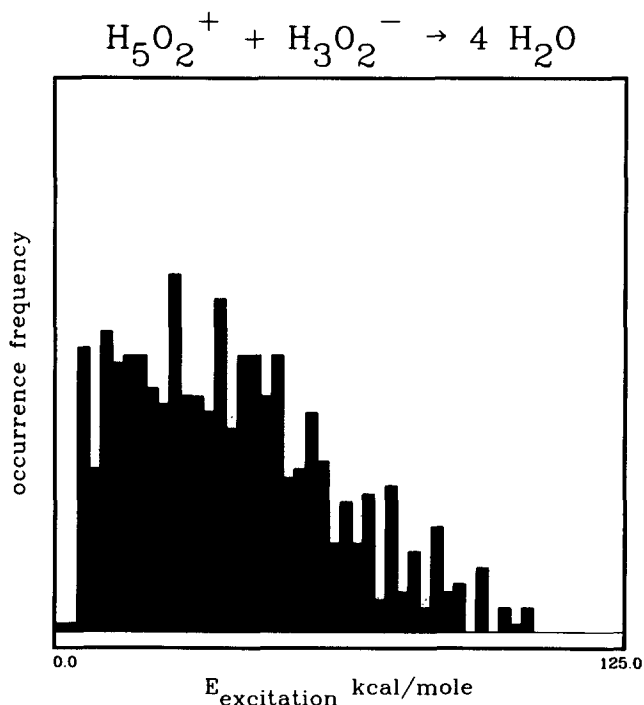


FIG. 5. Distribution of excitation energy among product molecules from Reaction (6). The bin width is 5 kcal/mol and bar color coding is the same as in Fig. 3.

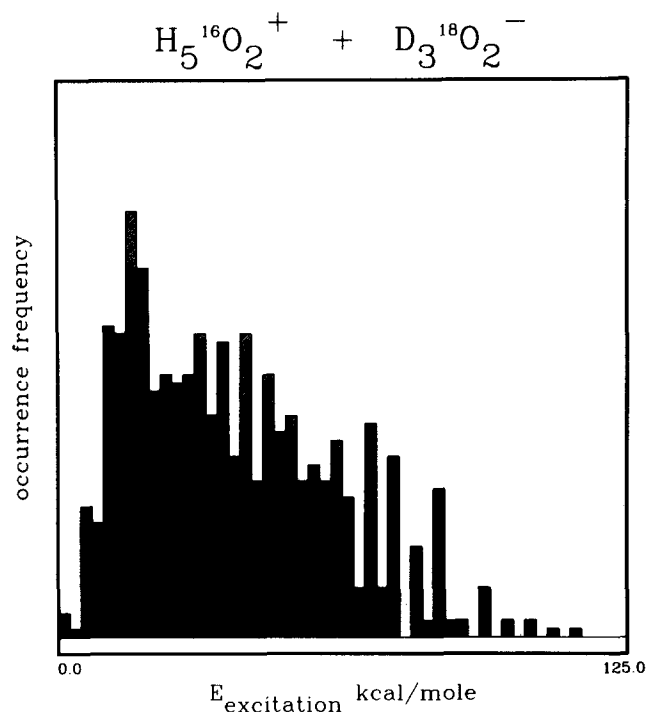


FIG. 6. Distribution of excitation energy among product molecules from Reaction (7). Bin width is 5 kcal/mol and the bar color code is the same as in previous figures.

to appear. The water molecules are distinguished as before (shaded for O1 and O2, black for O3 and O4) according to their reactant source. The plots are similar and show (i) that a negligible fraction of the product molecules achieves 120 kcal/mol excitation, and (ii) water molecules originating in the anion tend to be more highly excited than those originating in the cation. This latter feature confirms the original guess that excitation-energy asymmetry should extend beyond the hydronium-hydroxide case.<sup>1,3</sup>

A somewhat more instructive view of the energy disposal statistics results from distinguishing product molecules further, according to whether or not they end up containing a hydrogen atom with which their oxygens were originally associated in the ionic reactants. In all cases, of course, one of the anionic molecules with O3 or O4 *must* contain a transferred hydrogen. Figure 7 presents the resolved distributions for Reaction (6), with the top portion of the figure showing results for the molecules containing a transferred hydrogen, and the bottom portion showing results for the molecules emerging with only hydrogens with which their oxygens were initially linked. Not surprisingly the top distribution exhibits a greater average excitation energy than the bottom distribution. Figure 8 shows the same types of distributions for the isotopically substituted Reaction (7), with quite similar results.

Both Figs. 7 and 8 contain an unexpected feature. They show that infrequently a water molecule originating in the cation can carry away a transferred hydrogen. We find that this occurs by means of a triple hydrogen transfer: Two hydrogens pass from the cation to the anion, while

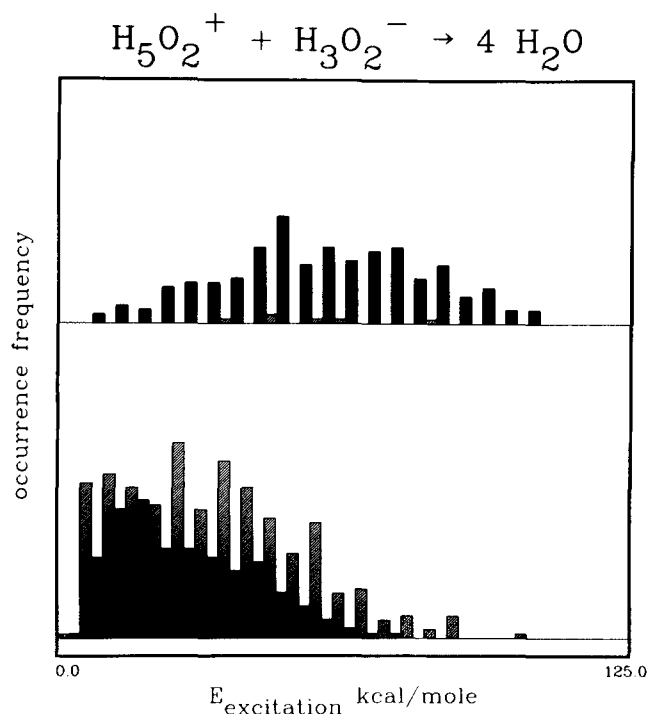


FIG. 7. Excitation energy distributions for reactions (6) resolved according to hydrogen transfer. The top portion shows results for molecules which carry away a transferred hydrogen, i.e., one with which they were not originally associated in a reactant ion. The lower portion shows results for all other molecules. Shaded bars represent cationic waters, black bars represent anionic waters.

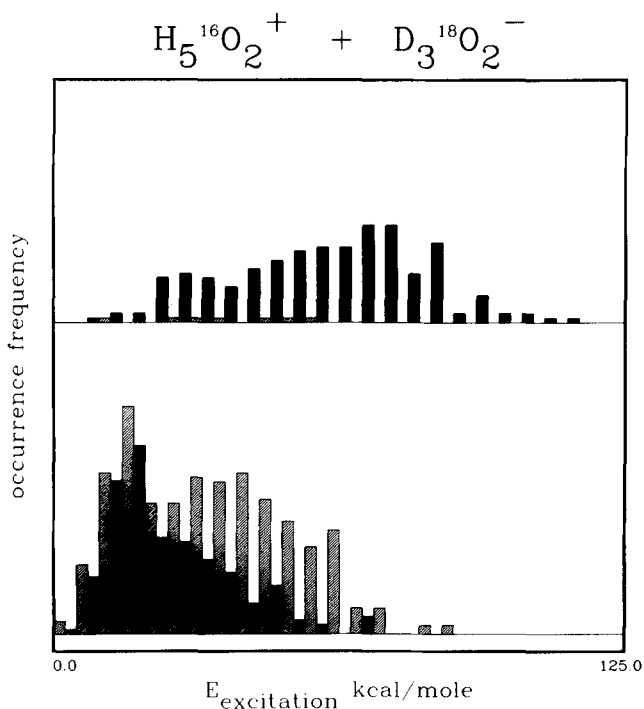


FIG. 8. Excitation energy distributions for Reaction (7) resolved according to hydrogen transfer. Top: molecules with transferred hydrogen; bottom: molecules with only hydrogens with which the oxygens were originally associated. Bar color coding as before.

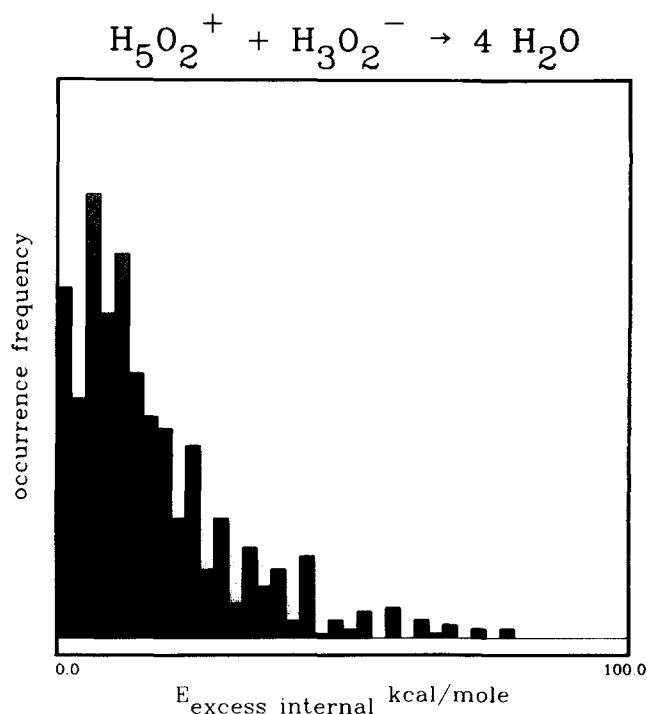
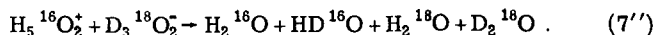


FIG. 9. Distribution of internal excitation energy (vibration-rotation) for all molecules in Reaction (6). Bar color coding as before.

the anion gives a third hydrogen back to the cation. The net result is as before that neutralization occurs and produces four neutral molecules. These molecules have the same mass (18) in Reaction (6) as with single hydrogen transfer. However, it is significant that Reaction (7) as written for single transfer produces a set of masses (18, 18, 21, 22) which is distinguishable from that produced by this triple-transfer channel:



specifically the mass set (18, 19, 21, 21). We observed 6 of these triple transfers among the 200 trajectories for Reaction (6), and 7 among the 200 trajectories nominally intended to model Reaction (7). Among all 400 trajectories there were *no* occurrences which in the isotopically substituted reaction would proceed into the following channel:



Because translational motion is separable from internal (vibration-rotation) motion, it is possible to produce distributions just for internal excitation energy of the emerging water molecules. Figures 9 and 10 present those results for Reaction (6), respectively without, and with, hydrogen transfer distinction. Figures 11 and 12 provide the corresponding distributions for the isotopically substituted case (7) [including Eq. (7')]. The energy asymmetry phenomenon continues to be obvious even for just internal degrees of freedom.

## V. CONCLUSIONS

The principal conclusions which emerge from the present study are the following:

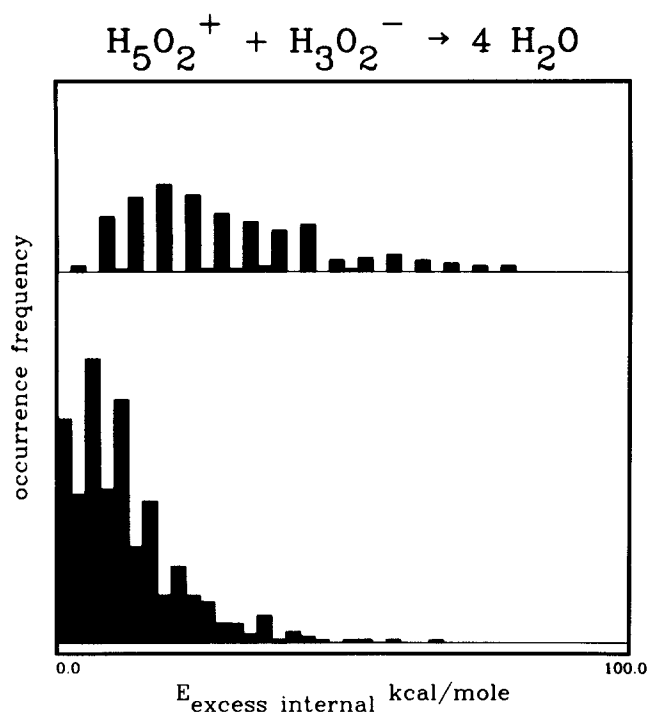


FIG. 10. Distributions of internal excitation energy from Reaction (6). Molecules with a transferred hydrogen are shown in the upper portion, all others in the lower portion. Bar color coding as before.

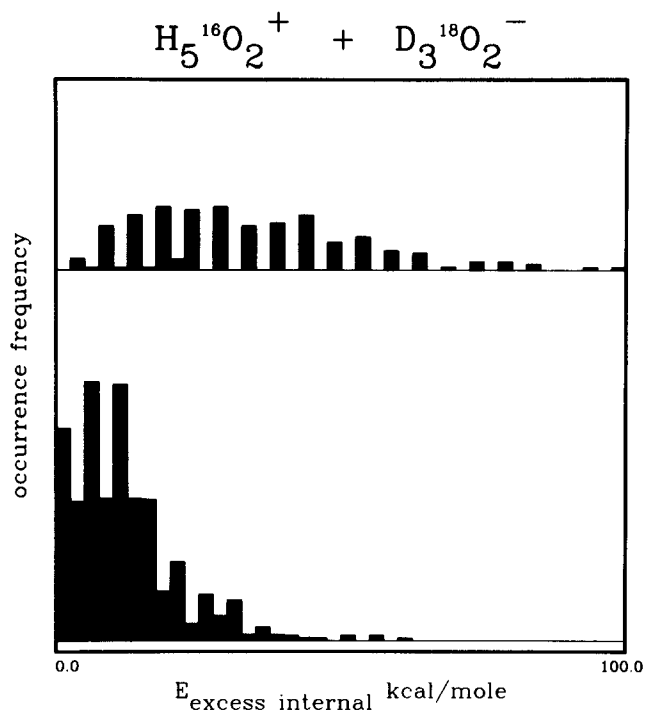


FIG. 12. Distributions of internal excitation energy from Reaction (7) [or (7')]. Molecules bearing a transferred hydrogen are shown in the upper portion, while all others appear in the lower portion. Bar color coding as before.

(1) Product water molecules are biased toward the forward or the backward direction according to whether their oxygen had an anionic or a cationic source, respectively.

(2) Product water molecules of anionic origin tend to emerge with higher translational and internal excitation than those of cationic origin.

(3) Triple hydrogen transfer occurs in roughly 3% of the collisions.

(4) Substitution of  $\text{D}_3^{18}\text{O}_2^-$  for  $\text{H}_3^{16}\text{O}_2^-$  causes little change in reaction dynamics.

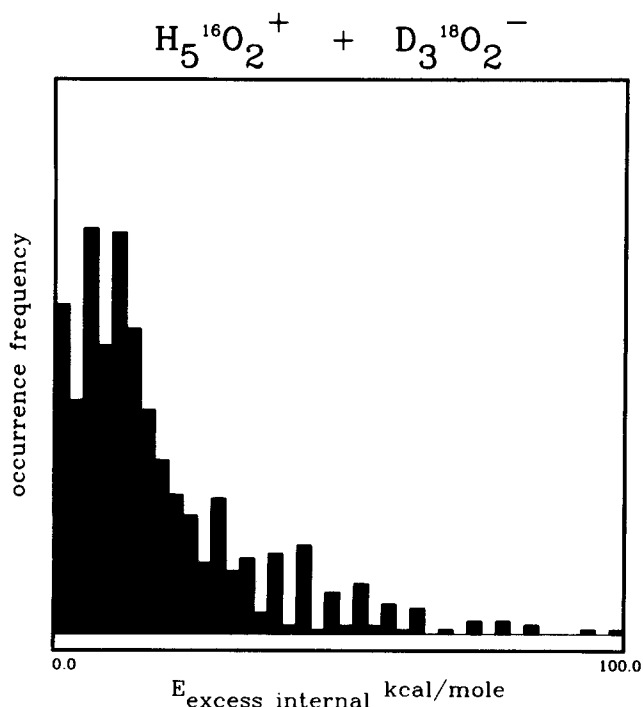


FIG. 11. Distribution of internal excitation energy for all molecules from Reaction (7) [or (7')]. Bar color coding as before.

The first two of these conclusions represent extensions to the present case of observations made previously on the simpler hydronium-hydroxide reaction. However, they appear now in much less vivid form than before.

Conclusion (4) suggests that future experiments directed at examining the present neutralization reaction can safely utilize isotopically labeled anions. This will permit laboratory testing of conclusions 1, 2, and 3.

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<sup>2</sup>F. H. Stillinger and C. W. David, *J. Chem. Phys.* **69**, 1473 (1978).

<sup>3</sup>F. H. Stillinger and T. A. Weber, *J. Chem. Phys.* **76**, 4028 (1982).

<sup>4</sup>G. H. F. Diercksen, W. P. Kraemer, and B. O. Roos, *Theor. Chim. Acta (Berlin)* **36**, 249 (1975).

<sup>5</sup>W. P. Kraemer and G. H. F. Diercksen, *Theor. Chim. Acta (Berlin)* **23**, 398 (1972).

<sup>6</sup>W. P. Kraemer and G. H. F. Diercksen, *Chem. Phys. Lett.* **5**, 463 (1970).