

# The Effect of Clustering on Mutual Neutralization Rates Using Electrostatically Merged Ion Beams: $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0-3} + \text{OH}^-(\text{H}_2\text{O})_{m=0-3}$

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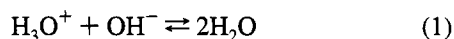
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Relative rate constants for the mutual neutralization of hydrated hydronium and hydrated hydroxide cluster ions have been measured using a new ion optical method which merges mass-selected beams of oppositely charged cluster ions with an electrostatic quadrupole deflector. Measurements are presented for all combinations of the reaction,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0-3} + \text{OH}^-(\text{H}_2\text{O})_{m=0-3}$ , under one ion optical setting of the interaction region (different relative velocities) and a few representative reactions as a function of relative velocity. A pronounced enhancement in the relative rate constant is seen with clustering which suggests that cluster specific rate constants may be required for accurate chemical modeling of the D region of the ionosphere. The neutralization reaction mechanism changes dramatically with clustering which is interpreted as a change from electron transfer at small cluster size to proton transfer with more clustering.

## Introduction

Clusters offer a means to study phenomena of interest at bulk with the power of incisive gas phase methods. Preliminary results from a new type of merged beam apparatus are presented concerning the effect of clustering on reactions of oppositely charged ions. The pH of bulk liquid water is maintained by the following equilibrium



which can be described as proton transfer in nature. However, the binary reaction of oppositely charged atomic and simple polyatomic species is well-known to proceed by electron transfer.<sup>1-4</sup> The present work examines the rates and relative velocity dependence of the forward gas phase reaction of eq 1 as a function of clustering with particular interest in evidence for progression from the electron transfer behavior of simple molecular ions to the proton transfer behavior characteristic of bulk.

Aside from the possibility of modeling bulk behavior, cluster ions are certainly interesting of their own accord. Clusters are the only form that ions take in the lower parts of the atmosphere,<sup>2,5,6</sup> and hydrated hydronium ions are the predominant ionic species at an altitude of  $\sim 75$  km<sup>5,6</sup> where binary ion-ion recombination is important. There are a number of reviews concerning reactions of oppositely charged ions which include sections on cluster ions.<sup>1-4</sup> Only two specific cluster-cluster binary reaction rates have been reported as deduced from flowing afterglow Langmuir probe (FALP) measurements<sup>2,7-9</sup> under conditions where three-body processes are important. The corresponding monomer-monomer reaction rates either are not available or are in dispute.<sup>1,2</sup> Mutual neutralization has also been studied using magnetically merged fast ion beams<sup>1,10-13</sup> and crossed beams,<sup>14</sup> but we have found no reports in which cluster ions have been studied with these methods.

A new type of apparatus is described which coaxially merges oppositely charged, mass-selected beams of cluster ions using an electrostatic quadrupole deflector. At the expense of making only relative measurements, this apparatus is simpler and more compact than a magnetically merged machine enabling more

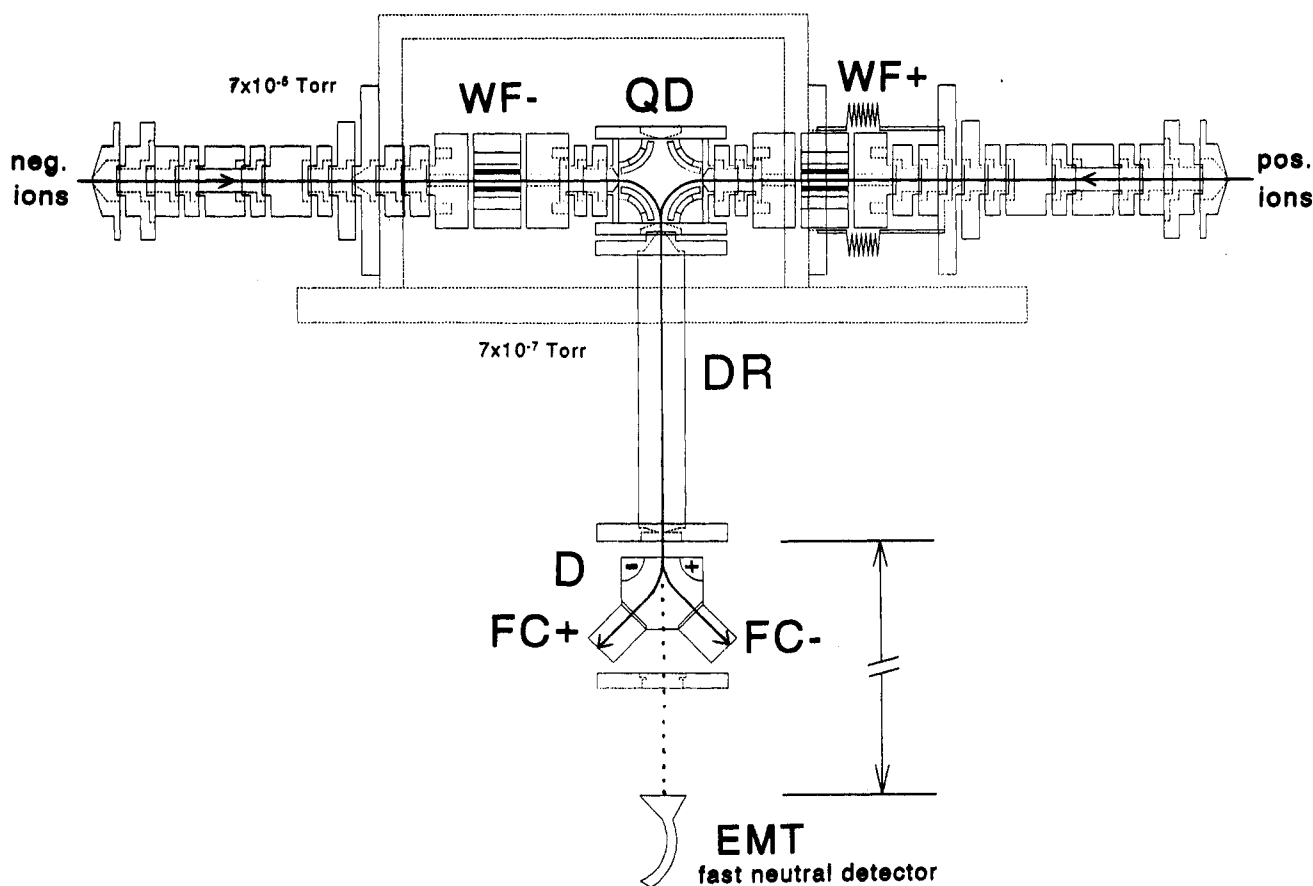
difficult systems to be studied. Relative neutralization rate constants have been determined for all 16 combinations of the reaction of  $\text{OH}^-(\text{H}_2\text{O})_{m=0-3} + \text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0-3}$  under one set of ion optical conditions, i.e., a set of conditions similar in terms of lensing and ion beam overlap. Since each of these reactions is being studied at a different relative velocity, we have also included data on the relative rate constant vs relative velocity for a heavily clustered and lightly clustered reaction, as well as for  $\text{O}_2^+ + \text{O}_2^-$ , a calibrating reaction for which the absolute rate constant is known.<sup>12,15</sup> Relative velocity measurements for two representative reactions have also been measured with a different fast neutral detector which is better able to respond to the multiple fragments produced in a cluster neutralization event.

## Experimental Section

A scaled drawing of the merged beam apparatus<sup>16</sup> is presented in Figure 1. The key ion optical element is an electrostatic quadrupole deflector (QD) which bends ion beams by 90°. It has found widespread use for the coaxial overlap of laser beams and ion beams,<sup>17,18</sup> but it can also be used to merge oppositely charged beams.<sup>19</sup> The QD was first described in theory and practice by Zeman.<sup>20</sup> We are using a simpler version without shims (built in a 4.572 cm square) as described by Farley.<sup>21</sup> Mass-selected positive and negative ion beams are directed to the QD from opposite directions to be merged. The positive and negative ion source apertures are maintained at potentials which are symmetric about ground, so that both ion beams will experience the same magnitudes of potential difference within the QD. If one beam is deflected by 90°, the other will be too. Given beams coming to the QD from opposite directions, the net result is that both beams will emerge from the same aperture of the QD, coaxially overlapped.

The hydrated hydronium and hydroxide cluster ions are produced in glow discharges (1000–1500 V dc, <1 mA, 0.5 MΩ ballast) of neat water vapor ( $\sim 0.5$  Torr, 2 mm diameter apertures). These sources have been described in detail elsewhere.<sup>22-25</sup> The only difference between the sources is a "spider" plate<sup>24,25</sup> on the negative ion source aperture to prevent the extraction of electrons. Ions of both beams are extracted, focused, and deflected through a 3.2 mm diameter differential pumping aperture by a set of two three cylinder lenses and a

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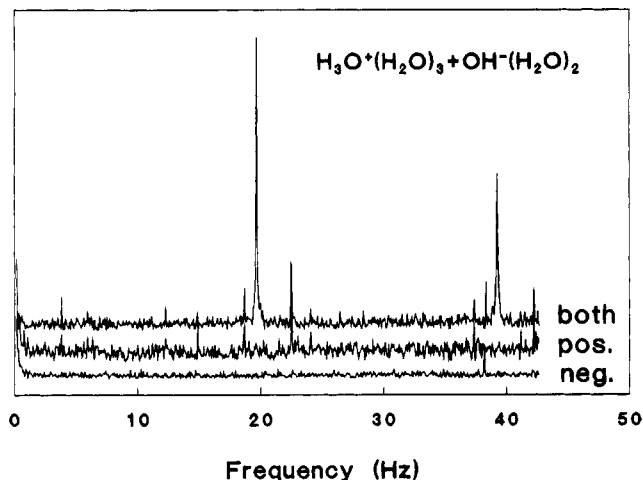
**Figure 1.** Schematic of the apparatus. Hydrated cluster ions are produced in glow discharge ion sources of neat water vapor whose source apertures are maintained at opposite voltages about ground. Oppositely charged beams are extracted toward each other and mass selected by Wien velocity filters (WF+, WF-). The beams are injected into an electrostatic quadrupole deflector (QD) from opposite directions and emerge coaxially overlapped in the drift region (DR). After interaction in the DR, the beams are separated by a deflector (D) and impinge on different Faraday cups (FC+, FC-). Any fast neutrals created continue undeflected and impinge on an electron multiplier (EMT). The EMT is placed 58 cm back from DR in order to greatly reduce the background of fast neutrals resulting from interaction of the ions with residual gas in the chamber.

pair of parallel plate deflectors. The ion sources and extraction optics are pumped by a 5000 L/s diffusion pump (Balzers DIFF-5000) with a water-cooled baffle (Balzers MCB 5000) which operates at about  $7 \times 10^{-5}$  Torr under load from both sources. The rest of the ion optical system is pumped on by a second, similar 5000 L/s diffusion pump with a liquid nitrogen cooled, high throughput baffle (Varian 326-10) which operates at  $\sim 7 \times 10^{-7}$  Torr under load. A box has been welded onto the flange separating the two differentially pumped chambers, so that the second chamber extends to as much of the ion optical system as feasible. After the ion beams are directed through the pumping apertures, they enter home-built Wien velocity filters (WF+, WF-) which are used to select the masses of interest. The Wien filters are 2.54 cm long, with permanent magnets (0.15 T), mild steel field terminators, and electrostatic shims. They are scanned electrostatically and have been built for optimal transmission. The mass-selected ion beams are injected into the QD from opposite directions. Pairs of perpendicular parallel plates are positioned in front of the QD which provide corrective deflection and independent vertical focusing.

The present application requires that both ion beams emerge perpendicular to the original ion beam axis and centered on the QD exit aperture. It is difficult to satisfy these two requirements with symmetric application of voltages to the QD. One set of voltages ( $\pm 0.75$  beam voltage) is applied to the two elements closest to the neutral detector, and another set ( $\pm 0.56$  beam voltage) is applied to the two other elements. This arrangement, which we call the "split quad", allows for different corrections at the input and output apertures. A complication of this

arrangement is that two knobs must be tuned to optimize transport instead of one. The positive and negative beams are coaxially overlapped in a 25 cm drift region (DR) with 3.2 mm diameter input and output apertures without any extra correctional deflection after the QD. A variable voltage ( $\delta$ ) can be applied to the DR in order to tune the barycentric energy or relative velocity of the mass-selected ions.

After interaction for about a microsecond in the drift region, the merged beams are separated with a deflector and impinge on different Faraday cups (FC+, FC-) whose currents (typically  $\sim 1-10$  nA) are measured with an electrometer (Keithley 610C). Any fast neutrals that result continue undeflected and impinge directly with kiloelectronvolt energies on a Channeltron 4750G electron multiplier which is set 58 cm downstream from the end of the drift region. The detector is set back from the interaction region because mutual neutralization signal is expected to be defined by the ion beam overlap region while background (from the ion beams interacting with residual gas in the chamber) is broad and diminishes more rapidly than the signal as the detector is pushed back. The multiplier has an active area 20 times larger than the area of the drift region output aperture in order to catch product fragments which have obtained off-axis kinetic energy in the neutralization process. Detector output is measured with an electrometer (Keithley 610C) using a multiplier gain voltage of 2200 V for each experiment. It was very important to suppress the fast neutral backgrounds due to the ion beams after separation with an extra 6.4 mm diameter, on-axis aperture. The ion beams after separation do not contribute mutual neutralization signal but (being the closest

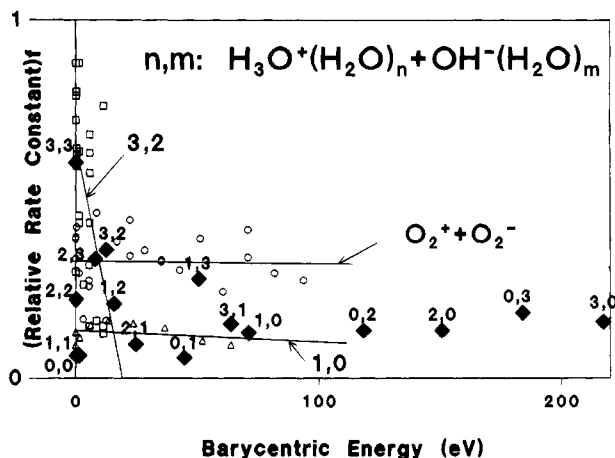


**Figure 2.** Representative signal for the  $n,m = 3,2$  reaction obtained by fast Fourier transformation of the fast neutral detector output. The difference in modulation frequency for the positive and negative ion beams was 20 Hz. The top trace is the signal when both positive and negative ion beams are on and the bottom two traces are each ion beam by itself. A signal-to-noise ratio of  $\approx 42$  was obtained in 90 s (40 s for the interferogram and 50 s for transformation) with 4.8 nA of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$  and 2.7 nA of  $\text{OH}^-(\text{H}_2\text{O})_2$ .

parts of the ion beams to the fast neutral detector) can contribute greatly to the background.

Typical conditions for the  $\text{H}_3\text{O}^+ + \text{OH}^-$  reaction (1 nA of each ion, background pressure of  $8 \times 10^{-7}$  Torr) correspond (assuming the manufacturer's gain) to a 60 kHz background rate and a 2.5 kHz signal rate, so an efficient modulation scheme is required to pull the signals from the background. The double modulation scheme of Aberth and Peterson<sup>10</sup> is employed to pick out only the additional signal present when both beams are on. A TTL circuit was built which takes a reference input frequency (1600 Hz) and provides a  $\div 20$  (80 Hz),  $\div 16$  (100 Hz), and difference frequency (20 Hz) output. One beam is modulated with an amplified square wave (Control Technics CTC 260-3) at 100 Hz and the other with a separate amplifier at 80 Hz by applying these wave forms to corrective, parallel plate deflectors near the start of the ion beam line. The fast neutral detector output is sampled at equal increments over a 40 s interval by a PC (386SX with 80387 math coprocessor and Metrabyte DASH-16 analog/digital I/O board) producing a 64K interferogram which is transformed by a fast Fourier routine in about 50 s. The low-frequency portion of the transform is shown in Figure 2 for the reaction of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{OH}^-(\text{H}_2\text{O})_2$ , which shows a prominent feature at the difference frequency (20 Hz) and its first harmonic when (and only when) both beams are on. The other smaller features result from aliased (folded over) high-frequency harmonics of the backgrounds from each ion beam, and each can be assigned to one ion beam or the other. To obtain reproducible results, one must simultaneously optimize the ion currents and the fast neutral signals that each beam produces though this is not a trivial task.

A cluster ion neutralization reaction is expected to produce a large number of fragments which would arrive at the detector closely spaced in time (within  $< 100$  ns). The spacing of these fragments corresponds to frequencies well above 10 MHz on average. The initial measurements were made with a Channeltron 4750G electron multiplier which was operated at the maximum gain which comfortably kept the background from saturating the detector (2200 V). At this gain closely spaced fragments arrive at frequencies well into the Channeltron's nonlinear response region, so it may produce less signal than a



**Figure 3.** Relative neutralization rate constants for all 16 combinations of the reaction  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{OH}^-(\text{H}_2\text{O})_m$  plotted with large diamonds vs barycentric energy using  $\delta = 0$ ,  $V_b = 900$  eV, and a Channeltron 4750G detector. ( $f$  may be less than 1 for the heavily clustered reactions.) Each point is indexed by  $n,m$  where  $n$  is the number of waters on the  $\text{H}_3\text{O}^+$  and  $m$  is the number on  $\text{OH}^-$ . The reactions with  $n = m$  can be compared at similar and minimal barycentric energies and display a factor of 10 difference between the 0,0 and 3,3 reactions. Measurements at different barycentric energies are given for the 3,2 reaction (open squares), the 1,0 reaction (open triangles), and the calibrating reaction of  $\text{O}_2^+ + \text{O}_2^-$  (open circles), which is  $\sim 1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  in this range. These three reactions have been fitted with least-squares lines to reveal the general trend.

case without fragmentation. Relative velocity measurements for two representative reactions have also been made with a Galileo HOT microchannel plate detector (MCP 6025) which maintains linear response at unusually high input rates sufficient to respond linearly to multiple fragments produced in neutralization events.

## Results

The rate ( $R$ ) of mutual neutralization in terms of ion densities ( $\rho$ ) is

$$R = -\frac{\partial \rho_{\pm}}{\partial t} = \alpha_2 \rho_+ \rho_- \quad (2)$$

where  $\alpha_2$  is the binary rate constant. Since ion densities are proportional to the ion currents ( $I$ ), the rate constant is

$$\alpha_2 \propto R/(I_+ I_- f) \quad (3)$$

where  $f$  depends on the detector's response to multiple fragments. Electrostatic merging requires equal beam energies, so different mass ions will have different velocities in a grounded interaction region once merged. The barycentric energy ( $W$ ), i.e., center-of-mass collision energy, and relative velocity ( $v_{\text{rel}}$ ) are changed by applying a variable voltage ( $\delta$ ) to the drift region/interaction region (DR). These quantities are related as<sup>10</sup>

$$W = \frac{1}{2} \mu v_{\text{rel}}^2 = \frac{m_+ m_-}{m_+ + m_-} \left( \sqrt{\frac{V_{b+} - \delta}{m_+}} - \sqrt{\frac{V_{b-} + \delta}{m_-}} \right)^2 \quad (4)$$

where  $\mu$  is the reduced mass,  $m$  is mass of each ion, and  $V_b$  is the beam energy before the drift region.

Averages of multiple measurements of rates normalized to positive and negative ion currents for all 16 combinations of the reaction of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0-3} + \text{OH}^-(\text{H}_2\text{O})_{m=0-3}$  are plotted (using large diamonds) vs barycentric energy in Figure 3 for the case where the drift region was grounded ( $\delta = 0$ ) and  $V_b =$

900 eV. Each point is indexed by  $n,m$  where  $n$  is the number of water molecules solvating the  $\text{H}_3\text{O}^+$  reactant and  $m$  is the number of waters solvating the  $\text{OH}^-$  reactant. These data were obtained using the Channeltron 4750G detector which ideally has  $f = 1$ , so  $R/(I_+I_-)$  is simply the relative rate constant; however, results with a faster detector suggest that  $f$  could be less than 1 for reactions with extensive fragmentation. Although many of these reactions were studied at disparate barycentric energies, the series of reactions with  $n = m$  presents a set at similar and minimal barycentric energies. This set reveals a factor of 10 increase in the relative rate constant between the 0,0 reaction and the 3,3 reaction and a factor of 5 increase in the relative rate constant between the 1,0 reaction and the 3,3 reaction.

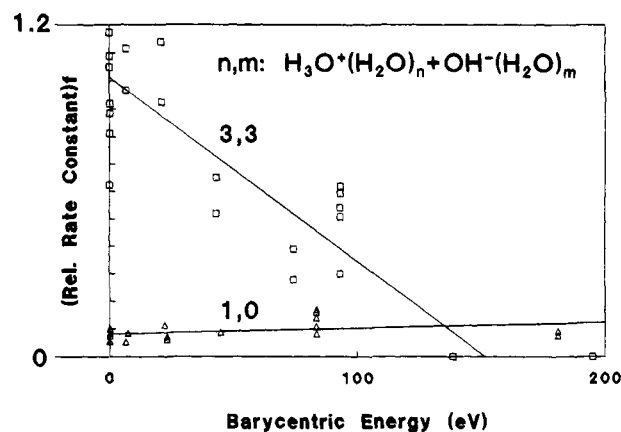
Two of these reactions ( $n,m = 3,2$  and  $1,0$ ) have been studied at a variety of barycentric energies by applying different voltages ( $\delta$ ) to the drift region. The reaction of  $\text{O}_2^+ + \text{O}_2^-$  has also been studied as a calibrant whose rate constant<sup>1,12,15,26</sup> in this range of barycentric energies is taken<sup>27</sup> as  $1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ . In order to reveal the general trends in these reaction rates with barycentric energy, the data are presented in Figure 3 with least-squares, best fit lines. This should not be taken to imply that the actual trends are linear.<sup>1</sup> The 1,0 reaction exhibits a trend which is qualitatively similar to the  $\text{O}_2^+ + \text{O}_2^-$  reaction but very different from the 3,2 reaction.

To address the issue of detector fragment response, measurements were made with a Galileo HOT MCP 6025 detector which exhibits linear response over an unusually large range of input rates, large enough to respond to the individual fragments of a neutralization event. Rates normalized to positive and negative ion current as a function of barycentric energy using the HOT MCP detector are presented in Figure 4 for the  $n,m = 3,3$  and  $1,0$  reactions with  $V_0 = 1300 \text{ eV}$ . The 3,3 reaction displays 10 times more signal than the 1,0 reaction at the minimum barycentric energy as compared to a factor of 5 using the Channeltron 4750G detector, suggesting that there is a difference in the average number of fragments created by these two reactions and that the HOT MCP is responding better to them. Also evident in this data set is a distinctly different trend in the data with barycentric energy for the 3,3 and 1,0 reactions. The points above 100 eV in the 3,3 data set represent multiple measurements in which no signal was detected.

## Discussion

In general, a significant increase in the rate constants with clustering is observed. The addition of only three waters to both  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  produces an order of magnitude increase (or more) in the rate constant and a change in the reaction mechanism. Early FALP experiments<sup>2,28,29</sup> on different reactions concluded (on admittedly limited evidence) that there was no significant increase in the neutralization rate constant with clustering. FALP cluster ion studies are limited because it is difficult to create plasmas containing a single species of cluster ion, only negative ions with large electron affinities could be used ( $\text{OH}^-$  could not be studied), and binary results are extrapolated from three-body experimental conditions. There are regions of the earth's atmosphere, such as the stratopause, where cluster ions predominate and binary ion-ion neutralization is important.<sup>6</sup> The present result suggests that cluster-specific neutralization rate constants may be important for accurate modeling of the ionosphere's chemistry.

A change in the reaction mechanism between  $\text{H}_5\text{O}_2^+ + \text{OH}^-$  (the 1,0 reaction) and  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{OH}^-(\text{H}_2\text{O})_3$  (the 3,3 reaction) is evident. The 1,0 reaction exhibits the same general trend as the  $\text{O}_2^+ + \text{O}_2^-$  reaction, which is an electron transfer



**Figure 4.** The 3,3 and 1,0 reactions studied with a HOT MCP detector which is more sensitive to multiple product fragments ( $f = 1$ ). The 3,3 reaction is dramatically different in nature than the 1,0 reaction, suggesting that a different reaction mechanism is at work. It is likely that the 3,3 reaction proceeds by proton transfer while the 1,0 reaction proceeds by electron transfer.

reaction. Ion-ion neutralization rates will be affected by two opposing trends upon clustering by polar solvent molecules. The probability of electron transfer reduces<sup>1</sup> with clustering because the ionic charges are shielded by increasing amounts of high dielectric material, the electron affinity of the negative ion increases with clustering, the positive ion's ionization potential decreases with clustering, equilibrium molecular geometries of ions and their corresponding neutrals may be significantly different, and the reduced mass increases. The probability of dissociative neutralization (in this case proton transfer) increases with clustering because the Coulombic interaction is mediated by the excitation of weak intermolecular vibrations and solvent molecule rotations which can help to trap the ions in a stable orbit ("tidal trapping"),<sup>1,2,30,31</sup> and the excess enthalpy of reaction can be dissipated by evaporating solvent molecules. These considerations and the observed trends with barycentric energy suggest that the most probable explanation has the hydronium-hydroxide reaction proceeding by electron transfer at small cluster size (as do most simple polyatomic species) with switching over to proton transfer at larger cluster size (as in bulk water) by the addition of three waters per reactant ion.

With this interpretation, one can predict the number of fragments for the 3,3, 1,0, and 0,0 reactions. The proton transfer reaction of hydronium and hydroxide is exothermic by 9.87 eV,<sup>32</sup> while the electron transfer reaction<sup>33</sup> is only 3.4 eV exothermic. To facilitate proton transfer, the two product waters would have to carry away about 4.9 eV each in kinetic or internal energy to dissipate the excess heat, which is not very likely. Electron transfer would produce  $\text{OH}$  and  $\text{H}_3\text{O}$  radicals, the latter of which is unstable and decays rapidly<sup>34</sup> ( $< 0.1 \mu\text{s}$ ) to a hydrogen atom and water molecule. The 0,0 reaction can be expected to produce three fragments. However, by the addition of only three waters to each reactant, the proton transfer reaction becomes<sup>34,35</sup> only 4.07 eV exothermic. This is enough heat to evaporate away all of the water molecules in the product, but each water only needs to dissipate 0.51 eV on average by means of kinetic and internal energy. For reasons mentioned in the above paragraph, the probability of electron transfer becomes very unlikely when this many solvating molecules are involved, so the 3,3 reaction proceeds by proton transfer producing eight water fragments on average. The similarity of the barycentric energy trend of the 1,0 reaction to that of  $\text{O}_2^+ + \text{O}_2^-$  and the arguments made in the above paragraph make it very likely that the 1,0 reaction proceeds by electron transfer. While the stability of  $\text{H}_5\text{O}_2$  radical is unknown, the electron

transfer reaction will certainly be strongly exothermic, so we expect that the  $\text{H}_2\text{O}_2$  radical will decay into an H atom and two water molecules producing four product fragments. The factor of 2 increase seen in the ratio of the 3,3 reaction vs the 1,0 reaction in Figure 4 (HOT MCP detector) vs Figure 3 (Channeltron 4750G detector) is consistent with this assessment of fragment numbers. Clearly, the HOT MCP detector is more sensitive to multiple fragments, although more work is required to make quantitative calibrations.

The trend with barycentric energy of the 3,3 reaction is very different than any other reaction studied with this type of experiment because the reaction subsides at barycentric energies where electron transfer is still going strong. This is consistent with a reaction such as proton transfer which requires much closer approach of the reactants than needed for electron transfer. Simple classical trajectory calculations on opposite polarity point charges support this picture. For example, the minimum distance of approach between reactants obtained with a barycentric energy of 100 eV and an impact parameter of 10 Å is 9.8 Å, which is not very different than what would be obtained with neutral particles. However, a 1 eV barycentric energy and the same impact parameter result in a minimum distance of approach of 3.5 Å, which is considerably smaller than the impact parameter. Therefore, trajectories for a given impact parameter have a greater chance of coming within some critical reactive distance as the barycentric energy is lowered.

Work is underway to assess the confidence with which absolute rate constants for cluster reactions can be assigned by comparison to calibrating reactions. Estimates made from Figure 3 by comparison to  $\text{O}_2^+ + \text{O}_2^-$  should still be considered preliminary as these issues are still being addressed. Similarly, work is underway to determine the average number of product fragments by electronically discriminating against fast neutral output pulses which arrive within  $\sim 1 \mu\text{s}$  of other pulses. Future work will involve measurements over a range of barycentric energies for all 16 reactions and a push to larger cluster size. Prospects look good for the direct measurement of product fragment average kinetic energy by fast neutral spot size and of the average number of fragments by real time observation in these reactions. Ultimately, this type of experiment at larger cluster size will enable the study of the stepwise solvation of mutual neutralization products, such as water in this case.

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## References and Notes

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