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TITLE / JOURNAL TITLE:

Surface review and letters.

ISXN: 0218-625X

Volume/Issue: 03/01

Month/Year: 2 1996

Pages: 655-660

Article Title: RECOMBINATION OF
OPPOSITELY CHARGED AQUEOUS CLUSTER
IONS USING ELECTROSTATICALLY MERGED
ION BEAMS

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RECOMBINATION OF OPPOSITELY CHARGED AQUEOUS CLUSTER IONS USING ELECTROSTATICALLY MERGED ION BEAMS

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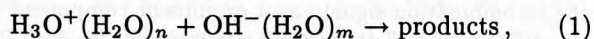
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A new method for studying cluster-cluster interactions is introduced which involves merging mass-selected beams of oppositely charged cluster ions with an electrostatic quadrupole deflector. Recombination is monitored by measuring the rate of fast neutral production. Relative rate constants have been measured for the reaction of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{OH}^-(\text{H}_2\text{O})_m$ as a function of cluster size ($m = n = 0-3$), which display a pronounced enhancement with clustering. Relative rate constants have also been measured as a function of center-of-mass collision energy for a heavily clustered reaction ($n = 3, m = 3$) and a lightly clustered reaction ($n = 1, m = 0$) revealing that clustering produces a dramatic change in the reaction mechanism.

1. Introduction

Molecules often behave quite differently at bulk than as free gas-phase monomers. In water, for example, a sodium-chloride molecule spontaneously dissociates into free aqueous ions; however, in the gas phase it costs 6 eV to dissociate into a pair of free ions. Clusters provide an opportunity to isolate collective interactions in a finite system whose properties can be studied with powerful and incisive gas-phase methods. One fundamental scientific goal is to explain the properties of matter based on its molecular constituents; therefore a fundamental strategy is to examine cluster properties as a function of cluster size to establish a connection to bulk.

The cluster approach is applied in this work to study water and aqueous solvation. Our experimental handle is the reaction of oppositely charged, aqueous cluster ions. The behavior of aqueous ions is central to understanding water itself because even pure water is partially ionized. We are examining the reaction of



which at infinite cluster size represents the forward reaction of the equilibrium that maintains the pH of bulk liquid water.

Cluster-cluster recombination has been addressed in a number of reviews.¹⁻⁴ Only two specific cluster-cluster binary reaction rates have been reported as deduced from flowing afterglow Langmuir probe (FALP) experiments,^{2,5-7} but these were deduced from data taken under conditions where three-body processes were dominant. Recombination has also been studied using magnetically merged ion beams^{1,8-11} and crossed beams,¹² but we have found no reports of cluster results. The present results are perhaps the first direct measurements of binary cluster-cluster recombination rates.

2. Experimental

A new ion-optical method has been developed^{13,14} to coaxially merge oppositely charged beams of mass-selected cluster ions as presented in Fig. 1. The apparatus has been described in detail elsewhere^{13,14} including the ion sources.¹⁵⁻¹⁸ The key ion-optical element is an electrostatic quadrupole deflector^{19,20} (QD) which has found widespread use for bending ion beams by 90° (usually for coaxial overlap^{21,22} with laser beams). This is the first application of a QD for merging oppositely charged ion beams.²³ Once the beams are merged, they interact for $\sim 1 \mu\text{s}$

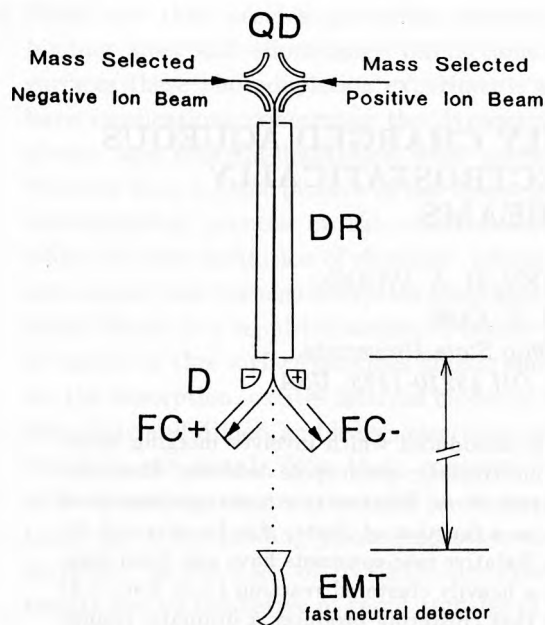


Fig. 1. Schematic of the apparatus. Oppositely charged hydrated cluster ions (produced in glow-discharge ion sources of neat water vapor) are mass-selected with Wien velocity filters and injected from opposite directions into an electrostatic quadrupole deflector (QD). The beams emerge coaxially overlapped in the drift region (DR) where they interact for $\sim 1 \mu\text{s}$ before being separated by a deflector (D) and monitored with different Faraday cups (FC+, FC-). Any fast neutrals created continue undeflected and impinge on an electron multiplier (EMT) which is placed 58-cm back from DR in order to reduce the background of fast neutrals resulting from interaction of the ions with residual gas in the chamber.

in a drift region (DR) until a deflector (D) separates the ion beams and directs them to different Faraday cups (FC+, FC-). Any fast neutrals created continue undeflected and crash (with a kinetic energy defined by the parent-ion beams) into an electron multiplier (EMT, either a Channeltron 4750G or HOT MCP 6025). The basic quantity determined in these experiments is the recombination rate (R) of fast-neutral production normalized to the positive and negative parent-ion currents (I_+ , I_-) which is related to the binary recombination-rate constant (α_2) as

$$\alpha_2 \propto \frac{R}{I_+ I_- f}, \quad (2)$$

where f depends on the detector response to fragments. It equals 1.0 when there is no fragmentation

as with simple electron transfer. It can be considerably less than 1.0 if the detector is not fast enough to respond independently to multiple-product fragments and/or response is nonlinear in kinetic energy.

The fast neutral detector is positioned downstream from the drift region in order to reduce the background of fast neutrals resulting from interactions of the parent ions with residual gas in the vacuum chamber. The backgrounds are presently ~ 50 times larger than the recombination signal, so an efficient modulation scheme is required to pull signal from the background.¹⁰ Each parent-ion beam is chopped at different frequencies by applying amplified square waves to corrective, parallel-plate deflectors near the start of the ion beamlines. The fast neutral detector response due to each ion beam and the recombination signal is given in Fig. 2. The fast neutral detector output, which is a weighted sum of the three lowest traces in Fig. 2, is sampled at equal increments in time producing an interferogram which is transformed to frequency space. The low-frequency portion of a fast Fourier transform is shown in Fig. 3 for the reaction of $\text{O}_2^+ + \text{O}_2^-$. Recombination signal (the Fourier transform of the bottom trace in Fig. 2) will have a prominent peak at the difference

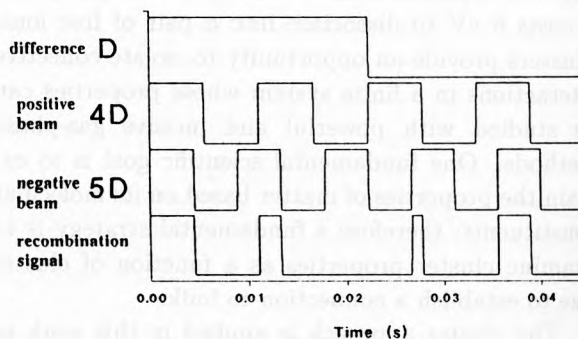


Fig. 2. Modulation scheme. Each ion beam is chopped at different frequencies by application of square waves to a parallel-plate deflectors near the beginning of each ion beam producing fast neutral background signals at the chopping frequencies. There is an additional fast neutral signal due to recombination which only occurs when both beams are on (bottom trace). The Fourier transform of the recombination signal has a prominent component at the difference of the modulating frequencies for each ion beam, while the Fourier transform of the backgrounds gives no signal below the chopping frequencies. Transforms of experimental data are shown in Figs. 3 and 4.

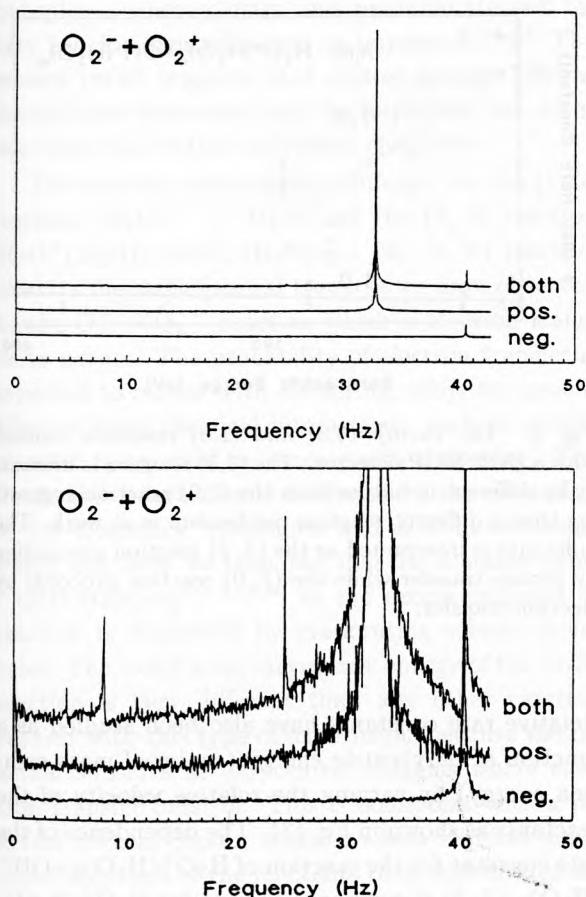


Fig. 3. Low-frequency portion of the Fourier transform of a 32-K interferogram recorded for the reaction of $\text{O}_2^+ + \text{O}_2^-$. The plots show traces for each ion beam alone and both beams together. The top plot shows large features at 32 and 40 Hz for O_2^+ and O_2^- , respectively, which are backgrounds due to interaction with residual gas in the chamber. When both beams are on, additional peaks arise at 8 Hz (the difference frequency) and 24 Hz (the first odd harmonic of the recombination signal). Aliased peaks due to high harmonics of the parent-beam backgrounds also occur, but are easily identified in the traces of the parent beams alone.

of the modulating frequencies of the positive (32 Hz) and negative (40 Hz) ion beams which can be seen in the bottom plot of Fig. 3 at 8 Hz. This feature (and its first odd harmonic) occur only when both beams are on. The top plot in Fig. 3 shows that the recombination signal is small compared to the parent-ion backgrounds. The recombination signal-to-noise ratio is obtained under circumstances requiring 90 s of data acquisition and transform time.

A useful feature of this experimental configuration is the ability to vary the relative velocity of the reactants and consequently the center-of-mass collision energy, i.e., barycentric energy. Electrostatic merging requires equal beam energies, so different mass ions will have different velocities once merged in a grounded drift region. The barycentric energy (W) or reactant relative velocity (v_{rel}) are changed by applying a variable voltage (δ) to the drift region (DR) after merging as⁸

$$W = \frac{1}{2} \mu v_{\text{rel}}^2 = \frac{1}{2} \frac{m_+ m_-}{(m_+ + m_-)} \quad (3)$$

$$\times \left(\sqrt{\frac{2q(V_{b+} - \delta)}{m_+}} - \sqrt{\frac{2q(V_{b-} + \delta)}{m_-}} \right)^2,$$

where μ is the reduced mass, q is the electron charge, m is the mass of each ion, and V_b is the absolute value of the beam voltage at the quadrupole deflector. Each perspective pair of reactants has a specific value of δ which gives the reactants zero average relative velocity and a root-mean-squared value⁸ which corresponds to ~ 0.1 eV. The recombination reactions can be studied at temperatures approaching room temperature in spite of the fact that the reactants have keV laboratory beam energies. Different reaction mechanisms can produce different behavior of the rate constant as function of barycentric energy.

3. Results

Typical recombination signal for the cluster-cluster reaction of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{OH}^-(\text{H}_2\text{O})_2$ is shown in Fig. 4. A signal-to-noise ratio of 42:1 is obtained in 90 s of data acquisition and transform time. The recombination signal is normalized to the positive and negative ion currents producing a quantity proportional to the binary rate constant. In the first set of experiments, this quantity was monitored for the reaction of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n + \text{OH}^-(\text{H}_2\text{O})_m$ as a function of aqueous cluster size with a grounded drift region ($\delta = 0$) and the Channeltron 4750G detector. The merger of the beams requires equal beam energies, so different mass reactants will not have the same velocity in a grounded drift region. Relative rate constants vs cluster size are plotted in Fig. 5 for the reactions with a similar number of solvating waters on each reactant ($n = m$) which have similar

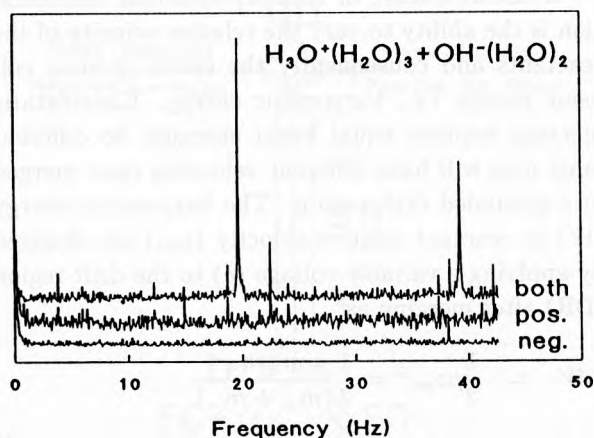


Fig. 4. Representative signal for the $(n, m)=(3, 2)$ reaction obtained by fast Fourier transformation of the fast-neutral detector output (Channeltron 4750G) with a difference frequency of 20 Hz. The top trace is the signal when both positive- and negative-ion beams are on and the bottom two traces are each ion beam by itself. A signal-to-noise ratio of ≈ 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 $\text{OH}^-(\text{H}_2\text{O})_2$.

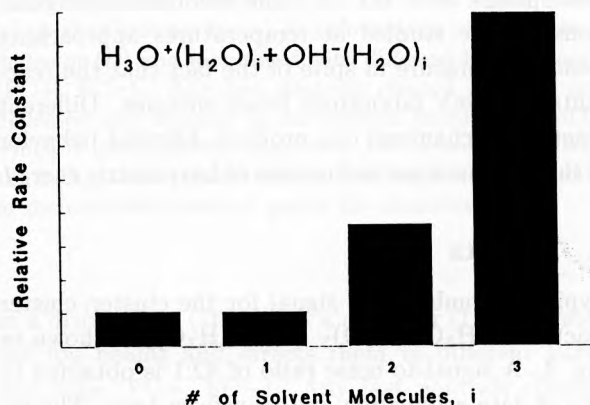


Fig. 5. Plot of the relative binary recombination-rate constant as a function of clustering for the case where the number of solvating water molecules is equal on each reactant. Initial calibrations of the fast-neutral detector indicate that extensive product fragmentation will be under-represented, so the actual cluster enhancement of the $i = 3[(n, m) = (3, 3)]$ reaction over the monomer reaction may be more than a factor of 10.

masses and can be examined with $\delta = 0$ at small barycentric energies (< 1.6 eV). The addition of only three water molecules to each reactant produces an order of magnitude increase in the rate constant.

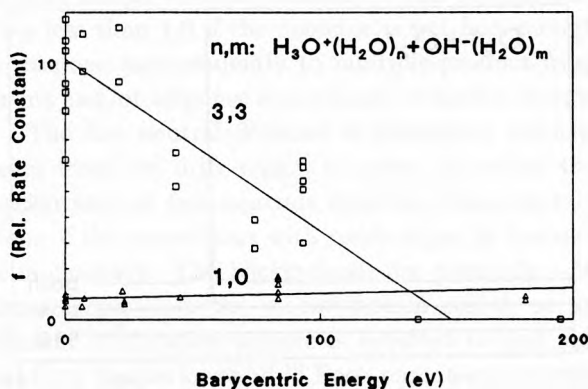


Fig. 6. The $(n, m)=(3, 3)$ and $(1, 0)$ reactions studied with a HOT MCP detector. The $(3, 3)$ reaction is dramatically different in nature than the $(1, 0)$ reaction suggesting that a different reaction mechanism is at work. The difference is interpreted as the $(3, 3)$ reaction proceeding by proton transfer while the $(1, 0)$ reaction proceeds by electron transfer.

Relative rate constants have also been studied as a function of barycentric energy (center-of-mass collision energy) by varying the relative velocity of the reactants as shown in Eq. (3). The dependence of the rate constant for the reaction of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{OH}^-(\text{H}_2\text{O})_3$ $(3, 3)$ is compared to that for $\text{H}_3\text{O}^+(\text{H}_2\text{O})_1 + \text{OH}^-$ $(1, 0)$ in Fig. 6 using the HOT microchannel plate 6025 detector. The addition of only three solvating water molecules to the monomer reactant ions produces a dramatically different trend which demonstrates that a different reaction mechanism is at work in the heavily clustered reaction.

4. Discussion

The addition of only three waters to both H_3O^+ and OH^- produces an order of magnitude increase in the rate constant and a change in the reaction mechanism. The fast-neutral detectors are in the process of being calibrated and show nonlinear response with respect to fast-neutral kinetic energy. The product fragments of reactions with extensive fragmentation [as is suspected for the $(3, 3)$ reaction] are grossly under-represented as compared to electron-transfer reactions without fragmentation, so the cluster enhancements in recombination rate are bigger than presently indicated. There are regions of the earth atmosphere, such as the D region of the

ionosphere, where cluster ions predominate and binary ion-ion neutralization is important.²⁴⁻²⁷ The present result suggests that cluster specific neutralization-rate constants may be important for accurate modeling of the ionosphere chemistry.

The reaction mechanism is different for the (1, 0) reaction ($\text{H}_5\text{O}_2^+ + \text{OH}^-$) and the (3, 3) reaction [$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3 + \text{OH}^-(\text{H}_2\text{O})_3$]. The (1, 0) reaction exhibits the same general trend as we have observed for the $\text{O}_2^+ + \text{O}_2^-$ reaction which is electron transfer in nature. The probability of electron transfer is expected to reduce with clustering, while the probability of more chemical interactions, such as proton transfer, is expected to increase with clustering.¹ The Coulombic interaction is mediated by the excitation of low-frequency vibrations and solvent rotations which can help to trap the ions in a stable orbit ("tidal trapping")^{1,2,28,29} as the excess enthalpy of reaction is dissipated by evaporating solvent molecules. 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 persists. This is consistent with a reaction such as proton transfer which requires much closer approach of the reactants than that needed for electron transfer, i.e., trajectories for a given impact parameter have a greater chance of coming within some critical reactive distance as the barycentric energy is lowered. These results are interpreted as the hydronium-hydroxide reaction proceeding by electron transfer at small cluster size (as do most atomic and simple polyatomic species) with a transition, by the addition of three waters per reactant ion, to proton transfer at larger cluster size (as in bulk water). This represents a poignant example of the use of clusters to embody bulk behavior in finite systems approachable with gas-phase methods.

Work is under way to determine absolute rate constants for these reactions by comparison to electron-transfer reactions such as $\text{O}_2^+ + \text{O}_2^-$ using a fast neutral detector calibrated with OH fast neutrals from collisional activation of OH^- . Future work will involve measurements over a range of barycentric energies for all reactant combinations of the available cluster ions. The most interesting results no doubt involve a push to larger cluster size, perhaps into the region ($n, m > 7$) where there is no longer enough excess enthalpy to evaporate all of the water molecules.

Prospects look good for the direct measurement of product fragment average kinetic energy by fast neutral spot size and of the average number of product fragments by real-time observation.

Acknowledgment

We thank the NSF (CHE-9204204) for support of this work.

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