

ISOTOPIC AND ASYMMETRIC EFFECTS IN H_2O^{q+} FRAGMENTATION

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All fragmentation channels of water and its isotopes, namely H_2O , D_2O , and HDO , due to fast ion impact have been measured using the coincidence time-of-flight (CTOF) technique. These measurements were motivated by the need to understand the effects of ionizing radiation on water in biological cells. In addition to the expected fragmentation channels, unexpected and interesting phenomena such as asymmetric bond cleavage [1] and bond rearrangement [2] have been seen.

Measurements of the fragmentation of deuterium tagged water molecules, namely HDO , by fast proton and F^{7+} impact exhibit a very strong isotopic preference for cleavage of the OH bond over the OD bond. Explicitly, the former is about five times more likely than the latter for HDO^{2+} dissociation. HDO^+ exhibits similar behavior, though the asymmetry is smaller at about a factor of 2. In addition, wave-packet propagation calculations, as shown in Fig. 1, are in good agreement with the measured branching ratio for HDO^{2+} dissociation, as well as with measurements of Legendre *et al.* [3].

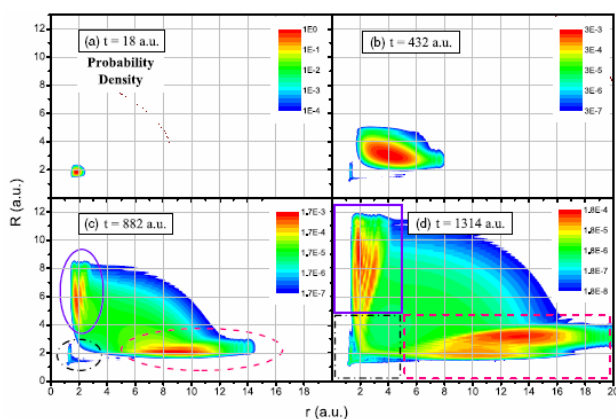


Fig. 1 Time evolution of the wave packet shown on a 2D ‘cut’ through the HDO^{2+} potential energy surface, where r is the distance between the O and H atoms and R is the distance from the centre of mass of the O and H to the D atom. In panels (c) and (d) the reaction channels are marked within a solid line – $\text{D}^+ + \text{OH}^+$, dashed line – $\text{H}^+ + \text{OD}^+$, and dashed-dot line – HDO^{2+} , while the three-body break-up, $\text{H}^+ + \text{D}^+ + \text{O}$, is the area with large r and R outside the boundaries marked on panel (d).

Bond rearrangement, namely the dissociation of water into $\text{H}_2^+ + \text{O}^{q+}$ ($q = 0$ to 3) following fast ion-impact ionization, unexpectedly occurs following multiple ionization of water in spite of the fast ‘‘Coulomb explosion’’ of the transient molecular ion. Furthermore, it is found to be approximately equally likely for each level of ionization. In addition, this process exhibits a strong counterintuitive isotopic effect [2,4], favoring bond rearrangement of the lighter water isotopes. Explicitly, H_2^+ production is about twice as likely as D_2^+ with HD^+ in between. These findings suggest that bond rearrangement does not happen during the relatively slow molecular dissociation, but rather proceeds via a sudden mechanism.

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References

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