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Bond rearrangement, namely the dissociation of water ions into $H_2^+ + O^{(q-1)+}$ (q=1–4) following fast ion-impact ionization, unexpectedly occurs following multiple ionization of water in spite of the presumably fast "Coulomb explosion" of the transient molecular ion. Furthermore, the branching ratio of bond rearrangement is found to be nearly equal for each level of ionization, q. In addition, formation of H_2^+ is more than twice as likely to occur from the lighter water isotopologue H_2O^+ than D_2^+ from D_2O^+. These findings are consistent with the ground state dissociation mechanism in which a fast projection of the ground state nuclear wave function onto the vibrational continuum of the cation potential energy surface is sometimes followed by H_2^+ formation.

I. INTRODUCTION

Producing new complex molecules is one of the main goals driving research aimed at improved control of formation and cleavage of particular bonds [1–6]. An interesting process of this kind, which involves the cleavage of some bonds and formation of others within the molecule, is bond-rearrangement. Improved control of bond rearrangement and other similar processes requires a fundamental understanding of how these processes occur. One example of this intramolecular process involves the formation of hydrogen molecular ions, specifically H_2^+ [7–22] and even H_3^+ [23–40], from polyatomic molecules.

Out of the parent molecules in the above studies, water — the subject of the present investigation — is the simplest system for studying H_2^+ formation. The H_2^+ formation following ionization of water has been studied for a variety of ionizing interactions ranging from fast electron [10] or ion impact [13, 14], oxygen core excitation by synchrotron radiation [11, 12, 19, 21], and strong field ultrafast lasers [17, 18, 22].

These studies suggested a variety of H_2^+ formation mechanisms. Following core excitation in water, Piancastelli *et al.* [11] suggested that bending motion initiated after the excitation of the O(1s) to $H_2O(2b_2)$ resonance is responsible for the H_2^+ formation by $\sim$536 eV photons. This interpretation was verified by Hiraya *et al.* [12], who showed in a vibrationally-resolved measurement that mixed symmetric-stretch and bending nuclear motions in the O $\left(1s^{-1} 2b_2\right)$ core-excited state play a key role in the process. In addition, their structure calculations support the assessment that the hydrogen molecular

ion is formed from the water cation, specifically in the reaction $H_2O^+ \rightarrow H_2^+ + O$. Follow-up work by Sorensen *et al.* [21] and by Laksman *et al.* [19] focused on H_2^+ formation from the water dication following the same core excitation. They deduced from the measured angular distribution that in this case the formation mechanism of $H_2O^{2+} \rightarrow H_2^+ + O^+$ is very fast — below 10 fs.

The formation of H_2^+ by a strong laser field has been attributed by Rajgara *et al.* [17, 18] to stretching and bending motion on the ^1A state of the water dication, which occurs within the 9.3 fs duration of the driving laser pulse. The formation of H_2^+ from the transient H_2O^{2+} was further investigated by Garg *et al.* [18] who showed, through time-dependent wavepacket dynamics calculations on an *ab initio* potential energy surface of the dication, that breakup of one O–H bond followed by H^+ migration can lead to the $H_2^+ + O^+$ final state on a time scale of 10 to 15 fs. Moreover, their calculations, assuming vertical ionization and taking the H_2O ground state vibrational wavefunction to be the initial wavepacket that propagates under field-free conditions, were found to be consistent with the measured production rate of H_2^+ relative to H_2O^+ [18].

In contrast to the core-excitation work, strong laser fields as well as fast electron and proton impact ionize the water molecule by removing a valence electron in a large majority of cases. In fast collisions, this ionization occurs on a very short time scale, estimated to be of the order of 10 as for projectiles at 1 MeV/amu. Therefore, vertical transitions are expected to result from the collision, i.e. ionization and electronic excitation while the nuclear motion is "frozen". The transient water cation can later undergo unimolecular dissociation with H_2^+ (of interest in this study) being one of the possible products. Given the above scenario, it is expected that the H_2^+ production rate should be independent of the collision parameters, such as collision velocity (above some minimum) or projectile charge, as will be shown below.

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This work examines two main questions: First, what is the isotopic dependence of hydrogen molecular ion formation following single ionization of water? Second, can H_2^+ result from highly charged water ions produced by fast highly charged ion impact, namely $H_2O^{q+} \to H_2^+ + O^{(q-1)+}$ (q=1–4)? If this process is possible, how does the production rate depend on the ionization level?

We conducted two types of measurements using the experimental method described briefly in Sec. II. In the first method, fast proton impact was used to study the formation of $H_2^+ + O$ following single ionization of a valence electron of H_2O. These measurements were repeated for heavier water isotopologues as described in Sec. III A. Next, in Sec. III B, studies of multiple ionization of water caused by fast highly charged ions are described. Specifically, the rate of $H_2^+ + O^{(q-1)+}$ formation up to quadruple ionization of water was determined. Both studies support the idea that a fast projection of the ground state nuclear wave function onto the vibrational continuum of the ion's potential energy surface, referred to as ground state dissociation (GSD) [41, 42], characterizes the relative amount of bond rearrangement leading to H_2^+ formation.

II. EXPERIMENTAL

Fast protons and highly charged ions were used to highlight single and multiple ionization, respectively. Fast (1-14 MeV) proton impact results predominantly in single ionization of water with about 1% double ionization [13, 14]. Thus, all the H_2^+ molecular ions created by fast proton impact were associated with neutral oxygen and none were found to be in coincidence with O^+ due to the low probability for this process to occur. In contrast, highly charged ions, such as the 1 MeV/amu F^{4+} and F^{7+} used in these measurements, efficiently ionize more than one target electron (typically resulting in ~30% multiple ionization [43]).

The projectile ions were accelerated, bunched, and directed through a target cell filled with water vapor and collected afterwards in a Faraday cup. The vapor pressure in the target cell was kept high enough, typically above 0.3 mTorr (i.e. 3 orders of magnitude above the base pressure in the vacuum system), to minimize the relative contribution of H_2^+ from the hydrogen residual gas [14]. The recoil ions produced in these collisions were extracted and accelerated by uniform electric fields onto the microchannel plate detector of a time-of-flight spectrometer [44]. The times of flight of the different recoil ions were recorded relative to a signal synchronized with the beam bunch, which was about 1 ns wide. Recoil ions produced in the same beam bunch were recorded in coincidence, event by event, thus separating single, double, and multiple-ionization events. The number of projectiles in a beam bunch was large enough to enable the study of the small fragmentation channels of interest in

this work, up to $H_2^+ + O^{3+}$, but small enough to keep the random coincidence rate under control. These random coincidences, i.e. fragments produced in the same beam bunch but from different molecules, were subtracted from the data employing the method described in Ref. [24].

III. RESULTS AND DISCUSSION

A. Single ionization — $H_2^+ + O$ formation

The measured yield of $H_2^+ + O$ relative to H_2O^+ following fast proton impact ionization of water is shown in Fig. 1 as a function of the proton velocity, together with the heavier water isotopologues HDO and D_2O. Note that the $H_2^+ + O$ data is less accurate by about a factor of three than the other isotopologues, because of the subtraction of the residual (H_2) gas contribution [14]. The fast proton impact data for H_2O and D_2O are in good agreement with the fast electron impact data of Straub et $al.$ [10]. Both show no significant velocity dependence of the $H_2^+ + O$ branching ratio above $v \sim 3$, and the 1 MeV/amu F^{9+} data shows that this branching ratio is also independent of the projectile charge. More importantly, the data shows that the H_2^+ formation rate is 2.5 times that of D_2^+, while HD^+ formation is in between, about 1.7 times larger than that of D_2^+.

Another measurable quantity that usually provides insight about the dissociation mechanism of molecules is the kinetic energy release (KER) upon dissociation [45]. The KER of the $H_2^+ + O$ dissociation can be evaluated from the width of the time-of-flight peak of the H_2^+, as explained in Ref. [24]. Specifically, we determined the KER distribution $H_2^+ + O$ to be peaked near zero and extend up to about 1.1 eV (FWHM). The KER distributions for the other water isotopologues, namely $HD^+ + O$
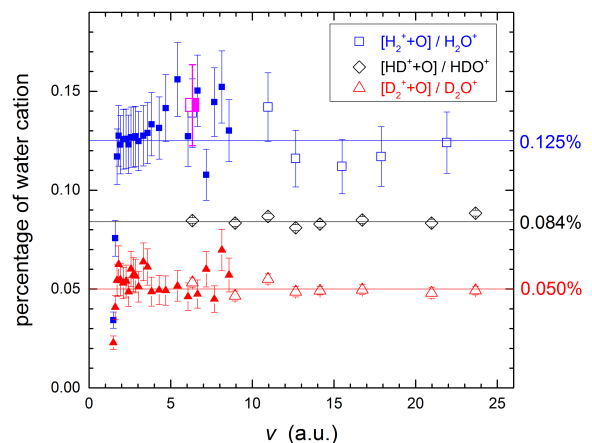

FIG. 1: The yield of H_2^+ relative to H_2O^+ (and isotopologues) as a function of the projectile velocity. Proton impact – open symbols, 1 MeV/amu F^{9+} impact – half-full (magenta) symbol, and electron-impact data (from Ref. [10]) – full symbols (see text). The error bars are at a 1σ level.

and $D_2^+ + O$, are also peaked at zero, but are much narrower, having FWHM of 0.41 and 0.20 eV, respectively.

This KER data prompts one to ask why the heavy water has a narrower KER distribution than the $H_2^+ + O$ dissociation and how this might be related to the lower D_2^+ formation probability as compared to the H_2^+ case. The answers can be found by looking at ground state dissociation (GSD) of hydrogen molecules [46, 47], which exhibits a similar isotopic preference and KER distributions.

The mechanism responsible for GSD in the hydrogen molecule involves a vertical ionization of the molecule to the vibrational continuum of the ground state of the molecular ion. The likelihood of this transition, determined by the overlap of nuclear wave functions (assuming a weak dependence of the electronic coupling on the internuclear distance), peaks at a threshold associated with zero KER and becomes rapidly smaller with increasing energy. This is similar in shape to the measured KER distributions from $H_2^+ \to H^+ + H(1s)$ dissociation [41, 42, 46, 48] and also the current water experiments. The nuclear wave function of the heavier hydrogen isotopologue, in this case D_2, has a smaller spread in internuclear distance and therefore a smaller overlap with the vibrational continuum of D_2^+ in comparison to H_2. As a result, the KER distribution of D_2^+ drops off faster with increasing energy and the GSD probability is smaller than for the lightest isotopologue [46, 47]. The GSD probability of the HD isotopologue is in between H_2 and D_2 when the two final products associated with HD GSD, namely $H^+ + D(1s)$ and $D^+ + H(1s)$, are added together. These products exhibit a small preference for the lower dissociation limit, $H^+ + D(1s)$ [41, 42]. The HD GSD products also have KER distributions that fall between the wider H_2 and narrower D_2 cases [41, 42, 48].

The water data suggests by analogy to hydrogen that the process leading to H_2^+ formation in water also involves GSD following the single ionization by the fast protons or electrons. Here too, the nuclear wave function of the neutral water can be projected onto the vibrational continuum of the ground electronic state of the water cation resulting in its dissociation. To this end, potential energy surfaces (PES) for the ground electronic states of the neutral and cation water molecules were calculated within Gaussian09 [49] using fourth-order Møller-Plesset perturbation theory [50] to add higher order corrections to the potential energy surfaces calculated by Hartree-Fock theory with the 6-31G basis set. The calculations are done as a function of R_{Oz} (where z can represent a proton (p) or deuteron (d) as appropriate for the particular isotopologue) and α. The results for the symmetric stretch mode $(\beta = 90°)$, shown in Fig. 2, are presented in Jacobi coordinates, where R_{zz} is the distance between the protons (deuterons) and R is the distance between the oxygen nuclei and the midpoint between the hydrogen nuclei, as illustrated in the inset of Fig. 2(a). The square of the neutral ground state nuclear wave function is approximated for illustration purposes by obtain-
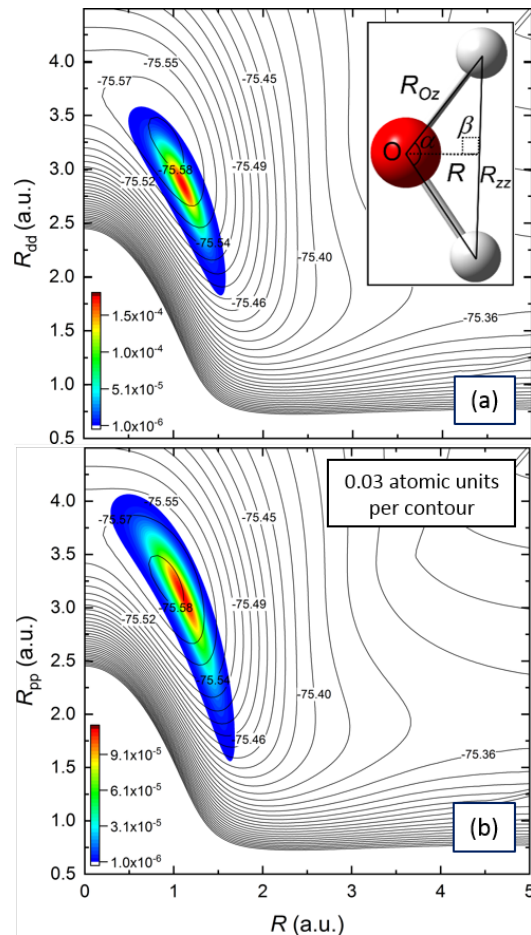

FIG. 2: A contour plot of a cut of the water cation ground state potential energy surface (keeping $\beta = 90°$), which is identical for the three water isotopologues within the Born-Oppenheimer approximation. The internuclear distances R_{Oz} – oxygen-proton or oxygen-deuteron distance, and R_{zz} – the distance between the two light nuclei (see text) are shown in the inset of panel (a). The square of the nuclear wave function of the ground state of neutral water is plotted on the PES as a linear-scale color-filled contour plot. The spatial extent of the ground state nuclear wave function increases with lighter hydrogen nuclei. Panel (a) shows the situation for D_2O and (b) for H_2O.

ing the normal mode force constants using the method described by Gocker and Tung [51]. These force constants and their associated vibrational frequencies [52] are used to construct ground state harmonic oscillator wave functions for each mode. This approximate probability distribution, $|\Psi|^2$, is then transformed into the R_{zz}—R coordinate system and shown in Fig. 2.

The main observation to be drawn from Fig. 2 is that the initial nuclear wave function has a wider spread for the lighter water isotopologue, and thus overlaps a different region of the cation PES, including more of the repulsive region towards small R and small R_{zz}. As a result, the KER distribution is wider for the lighter isotopologue, and the likelihood for H_2^+ formation should

also be higher than for the heavier cases based on the reflection approximation [53–56] in the diatomic molecule case, or a multidimensional analog specifically in the case of a polyatomic molecule. However, given the higher complexity of the potential surface in comparison to the one-dimensional hydrogen-molecule case [46, 47], calculating the dissociation probability into $H_2^+ + O$ is much more challenging. This is because just being above the dissociation limit is insufficient, as in addition, part of the wave packet has to propagate on the potential surface toward the configuration which leads to $H_2^+ + O$, i.e. $R_{pp} \sim 2$ (a.u.) and a large R on Fig. 2, and not toward other breakup channels.

Furthermore, as we expect only the tail of the projected wave packet to be above the $H_2^+ + O$ dissociation limit, then in analogy to GSD in hydrogen, the KER distribution should be near zero. What leads us to expect a higher likelihood for low KER is that projection of the ground state wavefunction to the vibrational (nuclear) continuum is more likely when the continuum wave function does not oscillate rapidly, i.e. near turning points and energy barriers. The qualitative interpretation above can be quantified, for example, by calculating the multichannel nuclear scattering states on the cation's electronic ground state and projecting them onto the ground-state vibrational wave function. The absolute square of this overlap would provide an approximate channel-resolved energy distribution, but is beyond the scope of this report.

It is reasonable to consider, as pointed out by the reviewer, whether this dissociation mechanism is unique to the ground electronic state or if it can be extended to excited states. In particular, the lowest two excited states of the water cation, namely the $1\,^2A_1$ and $1\,^2B_2$ states [57, 58], which are energetically accessible given the appearance energy of the H_2^+ fragments [59], may be candidates for the low-KER H_2^+ formation observed in our experiment. The potential surfaces of these two states, calculated by Schneider, Giacomo and Gianturco [58], suggest that the first $1\,^2A_1$ state is not a likely source of low-KER H_2^+ fragments because it is correlated with the $O^+(^2D_u) + H_2$ dissociation limit when the oxygen is stretched away from the H_2, while keeping the two hydrogens close to each other. In contrast, the lowest $1\,^2B_2$ state, i.e the second excited state of H_2O^+, does correlate to the $O(^3P_g) + H_2^+$ dissociation limit and has a minimum in its PES, and therefore this state is likely to contribute to the measured signal. It is worth noting that projecting the H_2O ground state wave function onto the $1\,^2B_2$ state requires about 6.3 eV more energy than the excitation to the H_2O^+ ground state $(X\,^2B_1)$, and, since the cross section typically falls off with increasing excitation energy (except near threshold), we expect this state to have a smaller contribution. The same arguments are valid for a few highly excited states of H_2O^+, also reported in Ref. [58], which have a low KER and are correlated to $O + H_2^+$ dissociation limits. The experimental data does not allow one to distinguish between the paths involving different intermediate states of H_2O^+, however, it does support the same fragmentation mechanism and requires a similar landscape of intermediate potentials, thus reducing the number of possible states.

B. Multiple ionization — $H_2^+ + O^{(q-1)+}$ (q=2–4)

Formation of H_2^+ following double ionization of water, identified by $H_2^+ + O^+$ coincidences, has been studied experimentally and theoretically [17–19, 21]. The H_2^+ formation was determined to be fast, of the order of 10 fs, following double ionization by either a strong laser field [17, 18] or a core excitation of the $O(1s)$ by an x-ray photon [19, 21].

We also observe $H_2^+ + O^+$ formation following double ionization of water by fast highly-charged ion impact, as shown in Fig. 3(a). Taking advantage of the relatively high rate of multiple ionization in such collisions, we explore the formation of H_2^+ in higher charge states of the transient water ion. To increase the bond-rearrangement rate, we use the H_2O isotopologue, because H_2^+ formation is more likely than from other isotopologues, as indicated by the single ionization results discussed in Sec. III A and by directly comparing this process in H_2O^{2+} and D_2O^{2+} (see Table I).

The potentials of highly-charged ions are hard to compute, but one would expect the highly-charged water ion to disintegrate faster due to the larger Coulomb repulsion. This expected faster fragmentation raises the question of whether the chances for H_2^+ formation are reduced with increasing ionization level, i.e. with larger oxygen charge. The ratio of $H_2^+ + O^{(q-1)+}$ to H_2O^{q+} is proportional to this probability. However, small three-body breakup channels make it hard to evaluate this ratio directly. Instead, we measure the rate of $H_2^+ + O^{(q-1)+}$ formation relative to the main ion-pair breakup channel of H_2O^{2+}, namely $H^+ + OH^+$ (see Table I), and use this information to evaluate the relative H_2^+ formation probability of interest for each water ion as discussed below.

The spectrum of ion pairs resulting from 1-MeV/amu

TABLE I: Relative bond rearrangement in single and multiple ionization of water and heavy water. The isotopic ratio of each ionization level is relative to the heavy water (marked as 1).

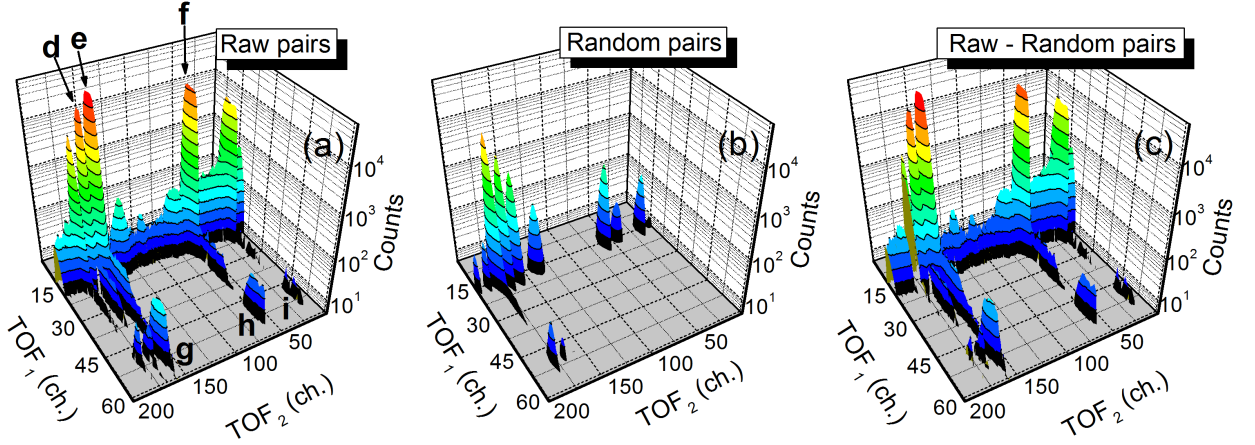| Dissociation channel	relative yield (%)	Isotopic Ratio
$H_2^+ + O$ / H_2O^+	0.125 ± 0.013	2.50 ± 0.30
$HD^+ + O$ / HDO^+	0.084 ± 0.002	1.68 ± 0.18
$D_2^+ + O$ / D_2O^+	0.050 ± 0.003	1
$H_2^+ + O^+$ / $H^+ + OH^+$	0.209 ± 0.006	1.80 ± 0.11
$D_2^+ + O^+$ / $D^+ + OD^+$	0.116 ± 0.006	1
$H_2^+ + O^{2+}$ / $H^+ + OH^+$	0.067 ± 0.003	—
$H_2^+ + O^{3+}$ / $H^+ + OH^+$	0.032 ± 0.005	—

FIG. 3: The (a) raw, (b) random, and (c) true coincidence time-of-flight (TOF) spectra of H_2O ionized by $1\,MeV/amu$ F^{7+} collisions. The labeled peaks are: (d) $H^+ + OH^+$; (e) $H^+ + O^+$; (f) $H^+ + O^{2+}$; (g) $H_2^+ + O^+$; (h) $H_2^+ + O^{2+}$; (i) $H_2^+ + O^{3+}$.

$F^{7+} + H_2O$ collisions, shown in Fig. 3(a), indicates that bond rearrangements occur in all levels of ionization, as $H_2^+ + O^+$ and $H_2^+ + O^{2+}$ peaks are clearly seen — even the $H_2^+ + O^{3+}$ peak is visible. These peaks are a small fraction of the multiple ionization, as was the $H_2^+ + O$ channel following single ionization. Given their small magnitude, it is crucial to verify that these peaks are not caused by random coincidences between two ions originating from different molecules ionized within the same beam bunch. To that end, we generated the spectrum of random ion pairs, shown in Fig. 3(b), by pairing two single ions from different beam bunches, taking advantage of the event-mode data collection (see Ref. [14]). The random spectrum is normalized to match a purely random ion-pair peak, like $H_2^+ + H_2O^+$, and then subtracted from the raw data to yield the random-free spectrum shown in Fig. 3(c). The random contribution to the $H_2^+ + O^{(q-1)+}$ channels is clearly small, thus confirming the bond rearrangement from Coulomb exploding H_2O^{q+} (for q up to 4).

To further verify that bond rearrangement occurs in multiple ionization, we present the coincidence times-of-flight of the dissociating fragments correlated by momentum conservation in Fig. 4, following a similar analysis to that presented by Sayler *et al.* [14]. Two-body breakup channels are spread along the expected two-body breakup line marked on the figure, though statistics are worse for the smaller triple ionization $H_2^+ + O^{2+}$ channel. The statistics of the quadruple ionization $H_2^+ + O^{3+}$ channel are too low to show a time correlation, but the presence of this dissociation channel is clearly supported by the data.

Finally, the ratios of bond rearrangement relative to the main ion-pair breakup, shown in Table I, were evaluated from the number of true ion pairs. Interestingly, the ratio $H_2^+ + O^{2+} / H_2^+ + O^+ = 0.32 \pm 0.02$, which we can write as

$$\frac{H_2^+ + O^{2+}}{H_2^+ + O^+} = \frac{H_2^+ + O^{2+} / H_2O^{3+}}{H_2^+ + O^+ / H_2O^{2+}} \frac{H_2O^{3+}}{H_2O^{2+}} \sim \frac{1}{3}, \quad (1)$$

is similar to the typical triple- to double-ionization ratio of $1/3$ measured for other multielectron targets undergoing similar collisions [60]. For example, $Ne^{3+} / Ne^{2+} = 0.390$ and $Ar^{3+} / Ar^{2+} = 0.326$ for 1-MeV/amu F^{7+} [43], and $CO^{3+} / CO^{2+} = 0.35$ for 1-MeV/amu F^{4+} collisions [61]. Therefore, we also expect H_2O^{3+} / H_2O^{2+} to be about $1/3$. Substituting this value in Eq. 1 yields

$$\frac{H_2^+ + O^{2+}}{H_2O^{3+}} \sim \frac{H_2^+ + O^+}{H_2O^{2+}} \ . \quad (2)$$

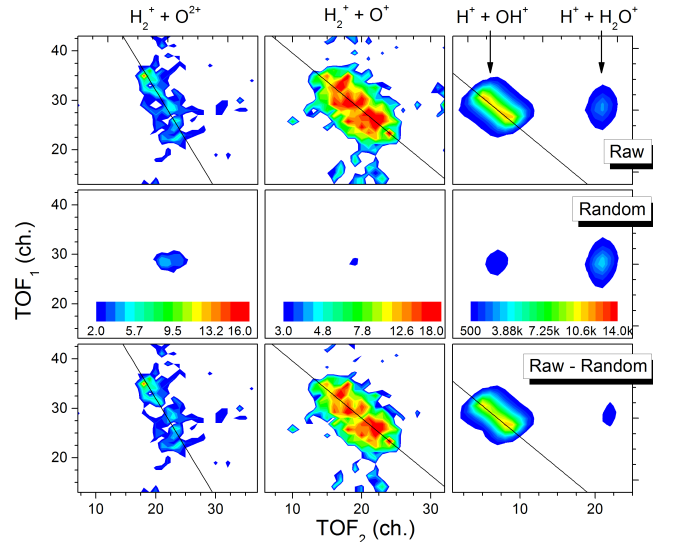This approximate equality suggests that the bond-rearrangement fraction out of each ionization level, such

FIG. 4: Coincidence time-of-flight (CTOF) spectra of water molecules ionized by $1\,MeV/amu$ F^{7+} collisions. The main two-body breakup, $H^+ + OH^+$, is shown for comparison. Note that the spread of events perpendicular to the lines is caused by our timing resolution, which was limited by instabilities in bunching over the 11 hours of measurement.

as $H_2^+ + O^+$ / H_2O^{2+} and $H_2^+ + O^{2+}$ / H_2O^{3+}, are similar to each other.

The curious observation that the H_2^+-formation probability is about the same for different highly-charged water ions, which are expected to fall apart rapidly, can be explained by a mechanism similar to the one leading to GSD. Specifically, the projection of the initial nuclear ground state wave function onto the final potential surface leads partly to a favorable configuration of the two protons that can result in their binding by one of the remaining electrons. Simply stated, one would expect a higher likelihood of H_2^+ formation if the distance between the two protons is similar to the H_2^+ bond length. In such a case, only a small fraction of the configuration space occupied by the constituents of the water molecule contributes to the process, which is consistent with the small H_2^+ formation probability. Moreover, if the nuclear configuration is key to H_2^+ formation then the likelihood for this favorable configuration is independent of the ionization level. Of course, this simple picture requires further work, especially if one expects to be able to quantitatively predict such bond rearrangement processes.

IV. SUMMARY

To summarize, we have shown that bond rearrangement, i.e. $H_2O^{q+} \rightarrow H_2^+ + O^{(q-1)+}$ (q=1–4), happens in single as well as multiple ionization of water by fast ion impact. This process is about twice as likely for the lighter H_2O than for D_2O for both single and double ionization. Furthermore, the data suggests a similar fraction of $H_2^+ + O^{(q-1)+}$ at each ionization level, q. These findings are consistent with a sudden mechanism involving the projection of the ground state nuclear wave function to the vibrational continuum of the ion's ground electronic state, or excited states with similar landscapes, where it is followed by the dissociation of a very small fraction of the wave packet into $H_2^+ + O^{(q-1)+}$. This suggested mechanism is similar to the one leading to ground state dissociation in hydrogen molecules. It is qualitatively in agreement with the observed small bond-rearrangement rate in water, the isotopic preference of bond rearrangement leading to hydrogen molecular ion formation from lighter isotopologues due to their broader internuclear distance spread, and the observed changes in the KER distributions for the different isotopologues. Moreover, it suggests that H_2^+ may be formed even following multiple ionization of water molecules with a similar bond-rearrangement fraction for each ionization level as observed. We have demonstrated that the ground state dissociation mechanism is consistent with H_2^+ formation from water. We have not, however, excluded other possible mechanisms leading to the same result, thus leaving room for further exploration of this curious bond rearrangement process.

V. ACKNOWLEDGMENTS

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