Bond rearrangement during Coulomb explosion of water molecules

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Bond rearrangement, namely the dissociation of water ions into \( \text{H}_2^+ + \text{O}^{q-1} \) \((q = 1–4)\) 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 \( \text{H}_2^+ \) is more than twice as likely to occur from the lighter water isotopologue \( \text{H}_2\text{O}^+ \) than \( \text{D}_2\text{O}^+ \). 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 \( \text{H}_2^+ \) formation.

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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 \( \text{H}_2^+ \) [7–22] and even \( \text{H}_3^+ \) [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 \( \text{H}_2^+ \) formation. The \( \text{H}_2^+ \) 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 \( \text{H}_2^+ \) formation mechanisms. Following core excitation in water, Piancastelli et al. [11] suggested that bending motion initiated after the excitation of the \( \text{O}(1s) \) to \( \text{H}_2\text{O}(2b_2) \) resonance is responsible for the \( \text{H}_2^+ \) formation by \(*\approx 536 \text{ 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 \( \text{O}(1s) \rightarrow 2b_2 \) 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 \( \text{H}_2\text{O}^+ \rightarrow \text{H}_2^+ + \text{O} \). Followup work by Sorensen et al. [21] and by Laksman et al. [19] focused on \( \text{H}_3^+ \) 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 \( \text{H}_2\text{O}^{2+} \rightarrow \text{H}_2^+ + \text{O}^+ \) is very fast—below 10 fs.

The formation of \( \text{H}_2^+ \) by a strong laser field has been attributed by Rajgara et al. [17,18] to stretching and bending motion on the \(^1\text{A}\) state of the water dication, which occurs within the 9.3 fs duration of the driving laser pulse. The formation of \( \text{H}_2^+ \) from the transient \( \text{H}_2\text{O}^{2+} \) was further investigated by Garg et al. [18] who showed, through time-dependent wave-packet dynamics calculations on an \( \text{ab initio} \) potential energy surface of the dication, that breakup of one O-H bond followed by H\(^+\) migration can lead to the \( \text{H}_2^+ + \text{O}^+ \) final state on a time scale of 10 to 15 fs. Moreover, their calculations, assuming vertical ionization and taking the \( \text{H}_2\text{O} \) ground state vibrational wave function to be the initial wave packet that propagates under field-free conditions, were found to be consistent with the measured production rate of \( \text{H}_2^+ \) relative to \( \text{H}_2\text{O}^+ \) [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 \( \text{H}_2^+ \) (of interest in this study) being one of the possible products. Given the above scenario, it is expected that the \( \text{H}_2^+ \) production rate should be independent of the collision parameters, such as collision velocity (above some minimum) or projectile charge, as will be shown below.

This work examines two main questions: First, what is the isotopic dependence of hydrogen molecular ion formation following single ionization of water? Second, can \( \text{H}_2^+ \) result from highly charged water ions produced by fast highly
charged ion impact, namely $\text{H}_2\text{O}^{q+} \rightarrow \text{H}_3^+ + \text{O}^{(q-1)+}$ ($q = 1–4$)? 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 $\text{H}_2^+ + \text{O}$ following single ionization of a valence electron of $\text{H}_2\text{O}$. 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 $\text{H}_2^+ + \text{O}^{(q-1)+}$ 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 $\text{H}_2^+$ formation.

II. EXPERIMENT

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 $\text{H}_3^+$ 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 $\text{F}^{13+}$ and $\text{F}^{17+}$ used in these measurements, efficiently ionize more than one target electron (typically resulting in $\sim 30\%$ 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., three orders of magnitude above the base pressure in the vacuum system), to minimize the relative contribution of $\text{H}_2^+$ 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 $\text{H}_3^+ + \text{O}^{1+}$, 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—$\text{H}_2^+ + \text{O}$ formation

The measured yield of $\text{H}_2^+ + \text{O}$ relative to $\text{H}_2\text{O}^+$ 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$_2$O. Note that the $\text{H}_2^+ + \text{O}$ data is less accurate by about a factor of three than the other isotopologues, because of the subtraction of the residual ($\text{H}_2$) gas contribution [14]. The fast proton impact data for H$_2$O and D$_2$O are in good agreement with the fast electron impact data of Straub et al. [10]. Both show no significant velocity dependence of the $\text{H}_2^+ + \text{O}$ branching ratio above $v \sim 3$, and the 1 MeV/amu $\text{F}^{9+}$ data shows that this branching ratio is also independent of the projectile charge. More importantly, the data shows that the $\text{H}_2^+$ 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 $\text{H}_2^+ + \text{O}$ dissociation can be evaluated from the width of the time-of-flight peak of the $\text{H}_2^+$, as explained in Ref. [24]. Specifically, we determined the KER distribution $\text{H}_2^+ + \text{O}$ 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 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 $\text{H}_2^+ + \text{O}$ dissociation and how this might be related to the lower D$_2^+$ formation probability as compared to the $\text{H}_2^+$ 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
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.

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 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.

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What leads us to expect a higher likelihood for low KER is that projection of the ground state wave function 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 paper.

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 Giaturco [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 $O(^3P_u) + H_2$ 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 $H_2O^+$ and $D_2O^+$ (see Table I).

The potentials of highly-charged ions are hard to compute, but one would expect the highly-charged water ion to

<table>
<thead>
<tr>
<th>Dissociation channel</th>
<th>Relative yield (%)</th>
<th>Isotopic ratio</th>
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<tbody>
<tr>
<td>$H_2^+ + O / H_2O^+$</td>
<td>0.125 ± 0.013</td>
<td>2.50 ± 0.30</td>
</tr>
<tr>
<td>HD$^+$ + O / HDO$^+$</td>
<td>0.084 ± 0.002</td>
<td>1.68 ± 0.18</td>
</tr>
<tr>
<td>D$^+_2 + O / D_2O^+$</td>
<td>0.050 ± 0.003</td>
<td>1</td>
</tr>
<tr>
<td>H$^+_2 + O^+ / H^+ + OH^+$</td>
<td>0.209 ± 0.006</td>
<td>1.80 ± 0.11</td>
</tr>
<tr>
<td>D$^+_2 + O^+ / D^+ + OD^+$</td>
<td>0.116 ± 0.006</td>
<td>1</td>
</tr>
<tr>
<td>H$^+_2 + O^{2+} / H^+ + OH^+$</td>
<td>0.067 ± 0.003</td>
<td>1</td>
</tr>
<tr>
<td>H$^+_2 + O^{3+} / H^+ + OH^+$</td>
<td>0.032 ± 0.005</td>
<td>1</td>
</tr>
</tbody>
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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$_2$O$^q+$ 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$_2$O$^2+$, namely H$_2^+$ + 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 F$^7$+ + H$_2$O 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$_2$O$^+$, 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$_2$O$^q+$ (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. The statistics of the quadruple ionization H$_2^+$ + O$^+$ channel are too low to show a time correlation, but these peaks are not caused by random coincidences between 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$_2$O$^q+$ → 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$_2$O than for D$_2$O 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 $\text{H}_2^+ + \text{O}^{(v-1)+}$. 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 $\text{H}_2^+$ 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 $\text{H}_2^+$ 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.

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