Ion induced radiation damage on the molecular level
Alvarado Chacon, Fresia

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H$_2$O dissociation by protons and alpha particles

The most common molecule in biological environments is water. Many studies have been devoted to the interaction of ionizing particles with water molecules. Those studies have yielded absolute cross sections for selected final products, for example H$_2$O$^+$ or H$^+$. Only few coincidence studies have been performed to identify individual dissociation channels. In this chapter, different H$_2$O dissociation channels after impact of 4-24 keV H$^+$ and He$^q$+ ions are identified and the associated kinetic energy releases are presented. Some general features of water molecules are discussed at the beginning of the chapter. Afterwards, proton average energies following single ionization of water molecules are presented. Dissociation pathways for double and triple ionization of water molecules can be identified on basis of the measured kinetic energy releases. For double ionization, the two–step process predicted by Nobusada and Tanaka [53] has been observed for the first time.

based on:

Dissociation of water molecules upon keV H$^+$- and He$^q$+-induced ionization
Fresia Alvarado, Ronnie Hoekstra, and Thomas Schlathölter
4.1. Gas phase water molecules

The current interest in understanding the molecular mechanisms underlying biological radiation damage has triggered the investigation of ion-induced ionization and dissociation of water molecules for ion energies covering the whole Bragg–peak region. In early studies, Toburen et al. [54] measured high energy charge transfer cross sections for protons and atomic hydrogen in the energy range 100 to 2500 keV in various gases, including water vapor. They measured the energy dependence for single electron capture and electron loss. Both quantities were found to decrease with energy. Some years later, Rudd et al. [55] measured ionization cross sections of water vapor by protons in a broader energy range of 7-4000 keV. They also determined ionization, capture and loss cross sections for H₂O in collisions with 5-450 keV He⁺ [56]. The obtained data provided cross sections for the production of positive ions and electrons after the collision.

It was only in 1995 when Werner et al. [57, 58] provided coincidence information of selected fragments for the complete Coulomb fragmentation of water molecules. In these studies, kinetic energy releases (KER) for a number of water dissociation channels after 100-350 keV H⁺ and He⁺, O⁶⁺ and O⁷⁺ impact were reported. Of special interest was the process H₂O → H⁺+H⁺+O⁺ for singly charged projectiles. Gobet et al. [23, 59] extended these results by separating direct ionization and electron-capture contributions to the partial and total absolute cross-sections in 20-150 keV proton collisions with water molecules. From their results, it is clear that around 50 keV, there is a transition from electron capture as the major contributor to direct ionization. A compilation for charge transfer cross sections for a wide energy range of protons and hydrogen atoms colliding with water molecules can be found in the atomic data tables [60].

In the lower energy range, the studies by Dagnac et al. [61] on collisions of H⁺ with a water vapor target provided total cross sections of charge exchange and electron loss for energies between 2 and 60 keV. More recent experimental studies on charge transfer and electronic excitation by 0.5-5 keV protons provided absolute differential and integral cross sections [62]. Very recently theoretical investigations on charge transfer and electronic excitation in proton collisions below 10 keV were performed using the molecular–orbital close–coupling approach [63]. In the energy range covered, this approach showed excellent agreement with the above mentioned experiments.

In the high velocity range, several studies using highly charged ion impact have been performed. Luna and Montenegro [64] used 1-3.5 MeV C³⁺ and O⁵⁺ to determine absolute water cross sections. Much stronger H₂O fragmentation was observed than for proton impact. This was attributed to many electron removal and subsequent Coulomb explosion: the predominant process for highly charged projectiles at MeV energies. At energies ≥1 MeV/amu, fast protons and F⁹⁺ [65] were used to study bond rearrangement within the water molecule, namely water dissociation into H₂⁺+O⁹⁺. For fast protons, a strong isotopic effect was observed when comparing the bond rearrangement effect in H₂O, HDO and D₂O. Dealing with isotopic effects, Legendre et al. [66] found evidence of a stronger O-H bond cleavage in comparison with the O-D cleavage on HDO cation and dication fragmentation. Recently wave-packet propagation calculations of the branching ratios for HDO²⁺ dissociation were shown to be in good agreement with the experimental data [67].

In non-coincidence studies on 1-5 keV He²⁺ and 2-90 keV Ne⁹⁺ induced water frag-
4.1 Gas phase water molecules

Figure 4.1: Ground state geometry of the water molecule with the parameters calculated using MP2 theory with aug-cc-pVQZ basis set. In brackets the experimental data is given [71].

mentation [68–70], a number of different dissociation channels has been invoked. The assignment of the kinetic energies observed for the dissociation channels was done using only a Coulomb explosion model. Therefore the correspondence between the energy assigned to particular dissociation channels remained tentative. However, the absolute cross sections for the different dissociation channels obtained at these projectile energies are very valuable. Then, complementary studies on coincident detection of the fragments at the same projectile energies will provide additional information to unambiguously assign the channels observed.

Electronic and geometric features of H$_2$O

In fig. 4.1 a schematic representation of the water molecule is shown. It consists of two light atoms (H) and a relatively heavy atom (O). The ground state geometry can be described by the O-H bond lengths and the angle in between the two O-H bonds. The values in the figure correspond to the result of a geometry optimization using GAUSSIAN [49] with MP2 theory and the aug-cc-pVQZ basis set. For comparison, the experimental values are given in brackets.

Electronically, the H$_2$O molecule is dominated by the central oxygen atom. The valence molecular orbitals (MO’s) are largely centered around the O atom and H$_2$O accordingly appears almost spherical. Fig. 4.2 displays the molecular orbital shapes for the ground state of the water molecule. Binding energies obtained with MP2 theory are compared with binding energies given by TD-DFT theory [72] and experimental results [73]. The orbital labels in the figure denote the five occupied molecular orbitals of the water molecule ($C_{2v}$ geometry) corresponding to the $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ ground state configuration. The geometry of the orbitals does not depend on the theoretical model employed. It can be seen that the HOMO of the molecule corresponds to the oxygen lone-paired electrons (not involved in chemical bonding). The HOMO-1 has mixed bond pair and lone pair character and HOMO-2 is only related to O-H chemical bonding. The orbitals $2a_1$ and $1a_1$ correspond to inner valence and core MO’s, dominated mostly by contributions of the oxygen 2s and 1s orbitals respectively.
Figure 4.2: Molecular orbitals of the water molecule from GAUSSIAN calculations using MP2 theory with the 6-311+g(3df,3pd) basis set. The schematic representations of the different molecular orbitals are given for an isovalue of 0.07. Binding energies calculated using TD-DFT [72] and experimental values [73] are given for comparison.
Two important consequences arise from the geometry and electronic properties of the water molecules: 1) charge is not equally distributed over the molecule, the dipolar characteristics can be represented by 2 positive point charges at the positions of the hydrogen atoms and 2 negative point charges on the oxygen atom; 2) the lone-pairs on the oxygen atom and the polarity of the OH bonds give rise to tetrahedral coordination when several H₂O molecules are present.

Electron transfer to keV singly and multiply charged ions is known to involve mainly the most weakly bound target electrons. For water molecules, inelastic atomic interactions will involve HOMO, and to a less extent HOMO-1 and HOMO-2. Only when large amounts of energy can be deposited into the target, inner valence and core electrons will play a role.

### 4.2. Fragmentation of water molecules

When a keV ion collides with a water molecule, a variety of processes can take place. It is known that in this velocity range not only charge transfer processes but also direct ioniza-
Figure 4.4: Percentage of fragment formation relative to the $H_2O^+$ formation for the different fragments formed after impact with 6 keV $H^+$, $He^+$ and $He^{2+}$.

Anion and excitation can occur. In our experiments we can directly observe the fragmentation pathways after ionization but we cannot directly infer how the molecule was ionized in the first place. For a projectile $A$ with charge $q$ colliding with water molecules, the following specific collision processes are possible:

\[ A^{q+} + H_2O \rightarrow A^{q+} + H_2O^* \]  \hspace{0.5cm} \text{(excitation)} \hspace{0.5cm} \text{(4.1)}

\[ A^{q+} + H_2O \rightarrow A^{q+} + H_2O^+ + e^- \]  \hspace{0.5cm} \text{(direct ionization)} \hspace{0.5cm} \text{(4.2)}

\[ A^{q+} + H_2O \rightarrow A^{(q-r)+} + H_2O^{r+} \]  \hspace{0.5cm} \text{(electron capture)} \hspace{0.5cm} \text{(4.3)}

The full process, including the previous three can be described by the following equation:

\[ A^{q+} + H_2O \rightarrow A^{(q-r)+} + H_2O^{(r+s)+} + se^- \]  \hspace{0.5cm} \text{(total)} \hspace{0.5cm} \text{(4.4)}

Here, $r$ is the number of electrons captured from the target into the projectile and $s$ is the number of electrons released during the collision. As described in chapter 3, close collisions lead to excited molecules (eq. 4.1), singly charged intact molecules with electron release (eq. 4.2), or a combination of them: singly charged molecules in an excited state which can, in turn, dissociate. On the other hand, distant collisions are characterized by gentle charge transfer from the target to the projectile (eq. 4.3). In the experiments described in this chapter, excitation, ionization and capture can occur during the collision, leading to a more general process described by eq. 4.4. The consequence of this general process can be surprising effects such as triply charged target molecules after collisions with doubly charged projectiles.
4.3 Single ionization

Table 4.1: Average kinetic energies of protons stemming from single ionization of H$_2$O induced by different projectile ions at 6 keV.

<table>
<thead>
<tr>
<th>projectile</th>
<th>H$^+$</th>
<th>He$^+$</th>
<th>He$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>average kinetic energy (eV)</td>
<td>2.1</td>
<td>1.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>

In fig. 4.3 the fragmentation patterns of water molecules after impact by different projectiles are shown. It can be seen that the total fragment formation yields are strongly influenced by the projectile’s electronic structure and charge state. All spectra are normalized to the maximum intensity of the surviving H$_2$O$^+$. It can be seen that the relative fragmentation yields are the highest for He$^+$. The fragment O$^{2+}$ is observed for He$^{2+}$ projectiles and in traces also for He$^+$. In fig. 4.4 the branching ratios for fragment formation are plotted for the different projectiles. The highest fragment yields are observed for He$^+$, followed by the He$^{2+}$ and the lowest yields are observed for H$^+$. For the fragment OH$^+$ the branching ratios are higher for H$^+$ projectiles than for He$^{2+}$.

In the following the second step of the collision process will be discussed, i.e. possible dissociation paths followed after single, double or triple ionization will be explored and compared for different projectiles.

### 4.3. Single ionization

H$_2$O$^+$ → H$^+$ + OH$^0$ and H$_2$O$^+$ → H$^+$ + O$^0$ + H$^0$

There are several fragmentation channels that can result from the single ionization of water molecules. The channels involving formation of protons are H$_2$O$^+$ → H$^+$+OH$^0$ and H$_2$O$^+$ → H$^+$+O$^0$+H$^0$ [74]. To our knowledge, the cross-section for the second mentioned channel as compared to the first one is not known. There are two other channels leading to formation of either O$^+$ and two neutral hydrogens or OH$^+$ and a neutral H. Due to the lower yields for these processes as compared to the ones leading to H$^+$ formation, they will not be treated in this study.

The assignment of KER values to dissociation channels following single ionization is more difficult than for the multiple ionization cases. Using the technique sketched in fig. 2.8, the contributions from single ionization can be separated. Within our experimental resolution, structure-less KER distributions peaking at 0 eV are obtained. Table 4.1 shows the average kinetic energies of protons stemming from single ionization events. Whereas for singly charged projectiles, average KER’s of $\approx$ 2 eV are found, these values almost double to 3.6 eV for the He$^{2+}$ case. This hints at the population of higher excited H$_2$O$^+$ intermediate states from which the dissociation starts.
4.4. Double ionization

As already mentioned in chapter 2, time-of-flight spectrometry experiments on molecular dissociation products might be hindered by the occurrence of neutral fragments, which cannot be detected without employing post-ionization methods. Therefore, the KER of some dissociation channels after double ionization of the molecule, namely the ones leading to neutral fragments, are not directly accessible in our experiment. Furthermore, the dead-time of the timing electronics does not allow the coincident detection of two protons from one \( \text{H}_2\text{O} \) dissociation event. Detection of two fragments from a dissociation into three fragments is often insufficient to unambiguously identify the respective fragmentation channel. However, two-body breakup into two charged fragments can be investigated kinematically complete and serves as a starting point for the further analysis.

\[
\text{H}_2\text{O}^{2+} \rightarrow \text{H}^+ + \text{OH}^+
\]

For singly charged projectile ions at lower energies, this is the most intense fragmentation channel involving at least two ionic fragments. Its two-body nature requires zero total momentum of the two fragment ions leading to a \(-1\) slope of the respective islands in the correlation plot (see fig. 2.10 and discussion in section 2.4.2). The KERs for this process
were determined to be \((3.4 \pm 0.18) \text{ eV} \approx 3.6 \text{ eV}\) and \((3.6 \pm 0.16) \text{ eV} \approx 3.8 \text{ eV}\) for 6 keV \(\text{H}^+\) and \(\text{He}^+\) projectiles, respectively. At 23 keV, only slightly higher KER values are observed.

For \(\text{He}^{2+}\) projectiles, the \(\text{H}^+ + \text{OH}^+\) channel has a smaller relative cross section but the KER is much higher than for \(\text{H}^+\) and \(\text{He}^+\) projectiles. At 6 keV projectile energy, a KER of \((6.5 \pm 0.31) \text{ eV} \approx 6.8 \text{ eV}\) is observed (see fig. 4.5). At 23 keV projectile energy, this value decreases by more than one eV to 5.6 eV total KER. This dissociation channel can be assigned to double electron capture from the water molecule. The possible scenario is described in the following paragraph.

The short \(\text{He}^{2+}\)-\(\text{H}_2\text{O}\) interaction time (of the order of 1 fs) implies a Franck-Condon transition from the \(\text{H}_2\text{O}\) ground state to a \(\text{H}_2\text{O}^{2+}\) dication state, \(\text{i.e.}\) a vertical transition with \(\text{H}_2\text{O}^{2+}\) in bent \((\text{C}_2\text{v})\) geometry. Fig. 4.6 shows the ionization energies of the lowest \(\text{H}_2\text{O}^{2+}\) states relative to the \(\text{H}_2\text{O}\) ground state. The dissociation products of these (unstable) states are \(\text{H}^+\) and \(\text{OH}^+\), the latter either in the \(3\Sigma^-\) ground state or in the \(1\Delta\) excited state. Because of spin-conservation, the \(3\text{B}_1\text{ H}_2\text{O}^{2+}\) can only decay to the \(3\Sigma^-\) ground state of \(\text{OH}^+\). This dissociation would be accompanied by a KER of about 8.3 eV, which clearly exceeds our experimental value. Dissociation from the \(1\text{A}_1\text{ H}_2\text{O}^{2+}\) to \(\text{H}^+ + 1\Delta \text{OH}^+\) on the other hand leads to a KER of about 7.3 eV, only 0.5 eV off the 6.8 eV we observe experimentally for 6 keV \(\text{He}^{2+}\) projectiles. The decrease of the measured KER with increased projectile kinetic energy might be due to population of higher excited \(\text{H}_2\text{O}^{2+}\) states leading to higher excited states of the product \(\text{OH}^+\) or vibrationally excited \(\text{OH}^+\). A similar trend of decreasing kinetic energy release with increasing velocity has been observed before, for \(\text{He}^{2+}\) collisions with...
Table 4.2: Percentage of \( H^+ \) fragments stemming from different ionization/dissociation channels following \( He^+/H^+ \) interactions with \( H_2O \). Our experiment discriminates against the \( H^++O^++H^+ \) channel.

<table>
<thead>
<tr>
<th>projectile</th>
<th>ionization:</th>
<th>products:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>single</td>
<td>double</td>
</tr>
<tr>
<td>6 keV ( He^+ )</td>
<td>84.2%</td>
<td>15.8%</td>
</tr>
<tr>
<td>23 keV ( He^+ )</td>
<td>82.6%</td>
<td>17.4%</td>
</tr>
<tr>
<td>ratio (23keV/6keV)</td>
<td>0.98</td>
<td>1.10</td>
</tr>
<tr>
<td>6 keV ( H^+ )</td>
<td>86.5%</td>
<td>13.5%</td>
</tr>
<tr>
<td>23 keV ( H^+ )</td>
<td>88.4%</td>
<td>11.6%</td>
</tr>
<tr>
<td>ratio (23keV/6keV)</td>
<td>1.02</td>
<td>0.86</td>
</tr>
</tbody>
</table>

CO [79]. Note that population of higher excited states does not lead to a lower KER. If the excited state decays into low lying product states, also an increase in KER is possible, as will be invoked in a later section. A thorough theoretical analysis of the excited states of the water dication and its products would be needed for a detailed understanding of their role.

In collisions of MeV highly charged ions with water, Siegmann et al. [80] and Legendre et al. [66] also observed a KER around 6.5 eV for the \( H^++OH^+ \) and \( H^++OD^+ \) breakup channels, respectively. No dependence of the energy distribution on the projectile charge state was observed [80].

On the other hand, in photofragmentation/charge transfer studies on \( H_2O \) two KER contributions at lower energies of 3±1 eV and 4.8±0.5 eV have been observed for the \( D^++OD^+ \) pair [76], and they are assumed to be similar for isotopic congeners. The energies were attributed to an adiabatic double ionization to \( 3\Sigma^- \) \( H_2O^{2+} \) in linear (\( D_{ohl} \)) geometry which subsequently dissociates into \( H^+ \) and \( 3\Sigma^- \) \( OH^+ \) or \( 1\Delta \) \( OH^+ \), supposedly giving rise to KERs of about 2.6 eV and 4.8 eV, respectively (see fig. 4.6). Note, that the low KER channel is spin-forbidden. The KER of about 4 eV that we measure for the \( H^+ \) and \( He^+ \) induced dissociation of the water dication (see fig. 4.5) lies in between the values obtained by Richardson et al. [76] and also can only be explained by an adiabatic double ionization. For \( He^+ \) and \( H^+ \) projectiles, double charge transfer is either ruled out or very unlikely and other ionization processes have to be invoked. A possible scenario is resonant capture or ionization of an inner \( H_2O \) electron and a subsequent Auger-deexcitation. Auger processes take place on timescales similar to molecular rearrangement times which would explain the apparent adiabatic nature of the ionization process. For \( H^+ \) projectiles, the responsible process could be direct ionization of a lower lying electron followed by Auger deexcitation.

Using the procedure sketched in fig. 2.8, chapter 2 the fraction of fragment \( H^+ \), which is due to single or double ionization can be obtained. For double ionization, it is furthermore possible to distinguish between two dissociation channels. The results for \( H^+ \) and \( He^+ \) projectiles at 6 keV and 23 keV can be found in table 4.2. The balance between single and double ionization remains virtually unchanged when increasing the projectile energy and also
Figure 4.7: Kinetic energies of $H^+$ (left) and $O^+$ (right) fragment ions formed in 6 keV $H^+$ and $He^+$ collisions with $H_2O$. The values in parentheses were obtained for 23 keV projectiles.

...the relevance of the $H_2O^{2+} \rightarrow H^++OH^+$ channel changes only weakly. It is difficult to draw conclusions from these trends alone, since two additional dissociation channels for the water dication exist. For the $H_2O^{2+} \rightarrow H^0+O^++H^+$ channel, a strong increase with projectile velocity is observed. This channel is relatively stronger for $He^+$ than for $H^+$. In the next section, this fragmentation channel is discussed in more detail. The third channel, namely $H_2O^{2+} \rightarrow H^++O+H^+$, was found to be the most important one for double ionization of water after MeV $Xe^{44+}$ collisions [74]. A qualitatively similar result has been observed for 100-350 keV $H^+$ projectiles [58]. This channel cannot be observed in the present experiment.

$H_2O^{2+} \rightarrow H^0 + O^++H^+$

For $H^+$ and $He^+$ projectiles, a strong $O^++H^+$ fragmentation channel associated with a $H^+$ fragment kinetic energy of about 14-15 eV (see fig. 4.7) is observed. This value is too low to be due to a Coulomb explosion of $H_2O^{3+}$ ($H^+$ kinetic energy $\approx$ 18 eV, see next section). Furthermore, triple ionization by singly charged projectiles at keV energies is a very unlikely process and should therefore be negligible in our experiment. Therefore the $H^+-O^+$ fragment ion pair is most probably due to $H_2O^{2+}$ fragmentation.

A two–step dissociation of $H_2O^{2+}$ proceeding via the process discussed in the last section is ruled out, since it yields $^1 \Delta OH^+$, which dissociates into $O$ and $H^+$. The resulting $H^+-H^+$ coincidence has been observed as a very weak channel in the photofragmentation study of Richardson et al. [76]. Some excited states of $H_2O^{2+}$ however eventually can dissociate into $H^+$, $O^+$ and $H$, according to calculations using spin coupled valence bond theory [81]. In the photofragmentation study, a weak $H_2O^{2+} \rightarrow OH^++H^+ \rightarrow O^++H+H^+$ channel was also identified. The KER associated with this channel amounts to $5\pm1$ eV [76] and therefore clearly falls short to the 15 eV obtained here.
Nobusada and Tanaka [53] calculated that if H$_2$O$^{2+}$ is formed by removal of the 2 oxygen lone-paired 2$p$ electrons (corresponding to the most loosely bound 1$b_1$ molecular orbital in fig. 4.2) accompanied by a shake-up of an electron from 3$a_1$ to 4$a_1$, then another decay process occurs: H$_2$O$^{2+}$ → OH$^{2+}$+H→ O$^+$+H$^+$+H. With the two charges localized on the oxygen atom, the authors conclude that the two O-H bonds start to stretch almost symmetrically on a rather flat potential energy surface (PES), before the intermediate OH$^{2+}$ dissociates. The total KER is expected to be $\approx 15$ eV.

The latter value is in good agreement with the experimental data presented in fig. 4.7 and we therefore conclude that we have experimentally identified this predicted decay channel. It has to be noted that in a non-coincidence experiment for 4 keV He$^+$ induced water fragmentation, Seredyuk et al. [69] already observed H$^+$ fragment ions of about 15 eV kinetic energy. However, in their study this peak was tentatively attributed to the one step H$_2$O$^{2+}$ dissociation into OH$^+$ and H$^+$ or O$^+$+H$^+$+H.

From table 4.2 it can be seen, that the relative importance of this channel increases by about 50% when going from 6 keV to 23 keV projectiles. This suggests that the process is due to collisional ionization rather than electron transfer.

### 4.5. Triple ionization

H$_2$O$^{3+}$ → H$^+$ + O$^+$ + H$^+$

For He$^{2+}$ projectiles, the H$^+$ and O$^+$ kinetic energies associated with the H$^+$ + O$^+$ fragment channel amount to 17.8 eV and 0.45 eV, respectively (see fig. 4.8). The H$^+$ value is higher than the 15 eV observed for He$^+$ and H$^+$ projectiles and therefore indicates that the origin of these fragments is mainly triple ionization followed by a dissociation into H$^+$ + O$^+$ + H$^+$+. In a non-coincidence experiment, Pešić et al. obtained similar H$^+$ fragment energies for 21 keV Ne$^{9+}$ induced dissociation of H$_2$O [68].

In the higher energy range 100-350 keV H$^+$ and He$^+$, induced dissociation of triply ionized water into H$^+$+O$^+$+H$^+$ was studied by Werner et al. [58]. They found only a slight increase of the H$_2$O bond-angle during a symmetric H$_2$O$^{3+}$ breakup. The KER for this process was calculated by means of Monte-Carlo techniques based on the *ab initio* potential
4.6 Conclusions

Figure 4.9: Kinetic energies of $H^+$ (left) and $O^{2+}$ (right) fragment ions formed in 6 keV He$^{2+}$ collisions with H$_2$O. The values in parentheses were obtained for 23 keV projectiles.

energy surfaces of the 9 lowest H$_2$O$^{3+}$ states. In agreement with their experimental data, KER peaking between 32 eV and 41 eV with an overall maximum at 36 eV are obtained. This value fits well to the $(2 \times 17.8 + 0.45) eV \approx 36 eV$ observed in our experiment (see fig. 4.8). Note that one expects 39 eV from a pure Coulomb explosion model.

\[
H_2O^{3+} \rightarrow H^+ + O^{2+} + H
\]

For He$^{2+}$ projectiles, formation of O$^{2+}$ fragment ions becomes an important channel. For fast Xe$^{q+}$ [80] as well as keV O$^{q+}$ [57] induced water ionization peak KER values of about 67 eV have been observed for H$^+$ and O$^{2+}$ ions originating from quadruple ionization (H$_2$O$^{4+} \rightarrow$H$^+$ + O$^{2+}$ + H$^+$). This value is again smaller than the prediction of the Coulomb explosion model but in agreement with Monte-Carlo simulations based on ab initio PES [80]. A KER of 67 eV corresponds to H$^+$ kinetic energies of $\approx$ 33 eV, as observed for keV Ne$^{q+}$ projectiles [68].

In the experiments presented here, a much lower H$^+$ fragment kinetic energy of about 27.5 eV (see fig. 4.9) is observed. This can be explained by the fact that H$^+$-O$^{2+}$ coincidences can also be observed for a triple ionization followed by the process H$_2$O$^{3+} \rightarrow$H$^+$ + O$^{2+}$ + H$^+$. A Coulomb explosion of the transient OH$^{3+}$ complex alone leads to H$^+$ and O$^{2+}$ kinetic energies of 28.3 eV and 1.8 eV, respectively. In the experiment, these energies are expected to be influenced by the presence of the neutral H fragment.

4.6. Conclusions

Fragmentation channels for water molecules upon interaction with protons, He$^+$ and He$^{2+}$ projectiles in the energy range 4-24 keV were investigated. It is clear that the projectile electronic structure very strongly influences the dissociation patterns. The corresponding KER distributions for a variety of dissociation channels were obtained and the underlying fragmentation processes identified. In particular, for singly charged projectiles we identified a H$_2$O$^{2+}$ fragmentation channel with a KER of about 15 eV. This KER can be attributed to the dissociation sequence H$_2$O$^{2+} \rightarrow$OH$^{2+}$+H $\rightarrow$ O$^+$+H$^+$+H recently predicted by theory [53]
and observed experimentally for the first time. Charge states of $q \geq 2^+$ of the transient water molecular ion lead to fragment proton energies which often exceed 10 eV. This is particularly interesting in the context of biological radiation damage, since these energetic protons have the potential to induce further damage in a cellular environment.