Fragmentation of Water by Heavy Ions

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Abstract. The connection between single and double electron removal and the fragmentation yields of water by heavy ions is analyzed. The contribution from the Auger-like decay of vacancies in the 2a$_1$ molecular orbital to the asymptotic branching ratios for water fragmentation by fast particles is obtained. A model assuming the independence of double and single electron removal due to collisional processes is proposed, from which double electron removal cross sections can be obtained from the fragmentation pattern obtained in single coincidence experiments. The proposed scheme helps in the comparison between theoretical calculations for electron removal from ionization, electron capture and electron loss and the observed fragmentation pattern of water.

1. Introduction
Molecular fragmentation induced by fast particles is initiated by the removal of one or more electrons from the molecular orbitals. The population of vacancies created depends on the collision dynamics, i.e., the velocity and charge state of the projectile, as well as the collision channel which, for heavier ions, besides ionization, can be electron capture and electron loss, or any combination of these channels in case of multiple electron removal. The creation of vacancies can then be followed by fragmentation [1-5]. The yields for the various possible molecular fragments depend in which one of the molecular orbitals the vacancies are produced, i.e., depends on the dynamics of the collision. A key point in this whole process is the link between the population of vacancies and the branching ratios of the fragmentation products. These branching ratios are very difficult to calculate because the ejection of fragments occurs in conjunction with an equally fast rearrangement of the electrons and, presently, almost all available information concerning these branching ratios comes from experiment. Without knowing the branching ratios, theoretical calculations for electron removal for a particular ion and collision channel cannot be compared with the fragmentation yields produced by the experiment. This scenario brings an important question concerning the universality of these branching ratios, at least for fast collisions, where the molecular rearrangement occurs long after the ion has left the target. In these conditions, these "asymptotic" branching ratios can be considered simply as a spectroscopic property of the molecule which, although difficult to calculate, could be directly associated with the primary population of vacancies irrespective to the dynamical characteristics of the collision. However, if the collision is not too fast, as in the important region of velocities located around the Bragg peak, double electron removal contributes to the fragmentation yields, in a fashion which is strongly dependent on the collision dynamics, the fragmentation yields and the use of the asymptotic values can be questioned.
In this Report we focus our attention in the fragmentation of water by heavy ions, with different charge states and covering a wide range of velocities, to study, in a comprehensive way, the role played by double electron removal and the asymptotic yields in the observed fragmentation pattern.

2. Water basics and high velocity limit of fragmentation

The collision mechanisms that will be studied here are related to the four valence molecular orbitals of water, $1b_1$ (12.6 eV), $3a_1$ (14.84 eV), $1b_2$ (18.78 eV) and $2a_1$ (32.61 eV), where the number in parenthesis are the ionization energies. The first two orbitals are non-bonding while the last two are bonding orbitals, with two electrons in each.

In their study of fragmentation of water by high energy electrons, Tan et al. [6] were able to set values for the branching ratios associated to the vacancy production for each of the above molecular orbitals. This is shown in Fig. 1 and this scheme is the starting point from which more recent analysis on the connection between vacancy production and fragmentation pattern have been carried out [7,8]. This set of values are the high-velocity asymptotic branching ratios for the fragmentation rates. As shown by Montenegro et al. [8] these branching ratios essentially reflects the population of vacancies given by the first order Born Approximation.

To go further and to consider cases where the collisional dynamics are more complicated, it is useful to have a simple way to visualize the level of agreement between the experimentally measured fragmentation fractions and the scheme presented in Fig. 1. In Fig. 2, the fractions obtained by Tan et al. were replaced by indetermined fractions $f_0$ to $f_5$. Because the $OH^+$, $H^+$ and $O^+$ yields come from just the $1b_2$ and $2a_1$ orbitals, it is straightforward to show that these three yields are not independent, being interconnected through the relation:

$$f_1f_4\sigma_{H^+} = f_4(1-f_1-f_0)\sigma_{OH^+} + f_1(1-f_4)\sigma_{O^+}. \tag{1}$$

If $\sigma_{H^+}$, $\sigma_{OH^+}$ and $\sigma_{O^+}$ are plotted in a ternary graph, the former relation states that the data points should lie in a straight line intercepting the $\sigma_{OH^+}$ side at the point $f_1(1-f_0)$ and the $\sigma_{H^+}$ side at the point $(1-f_4)$. Figure 2 displays this ternary plot together with the line obtained considering the asymptotic branching ratios of Tan et al. and the experimental data for electron impact fragmentation.
impact fragmentation of water from Refs. [8-12]. The tendency of the experimental data to coalesce along the asymptotic line is clear.

3. Auger-like rates

The asymptotic branching ratios reported by Tan et al. [6] are related to measurements which include both single and double ionization, without discriminating between these two channels. Thus, part of the branching ratios presented in Fig. 2 comes from contributions from double ionization, producing OH\(^{+}\) + H\(^{+}\), O\(^{+}\) + H\(^{+}\), H\(^{+}\) + H\(^{+}\) or O\(^{2+}\) recoil ions. The results of measurements of double ionization of water by electron impact by Scully et al. [13], which are shown in Fig. 3, show that the rate of change of cross section with projectile energy for single ionization (H\(_{2}\)O\(^{+}\)) and double ionization (open symbols in Fig. 3) are essentially the same, at high velocities. This result means that in the "asymptotic" regime, double ionization is related to the single ionization dynamics and the removal of the second electron comes from an Auger-like post-collisional mechanism. It was proposed in Ref. [13] that this Auger-like processes comes from the decay of a vacancy produced in the 2\(a_{1}\) orbital, and it is an alternative decay mode for a vacancy produced in this state.

![Figure 3.](image1)

**Figure 3.** Single and double ionization of water by electron impact. Experiments: Ref. [8,13]. Closed symbols are single coincidence data and open symbol double coincidence ones.

These considerations indicate that the scheme shown in Fig. 1 can be improved to include this decay mode. This is displayed in Fig. 4. The Auger rates can be determined from the above-mentioned measurements of double ionization in the asymptotic regime. This will be done below. Note, however, that the branching ratios obtained by Tan et al. already include the Auger rates, as they are determined from measurements which do not discriminate single or double ionization. Thus, the Auger-like branching ratios indicated in Fig. 4 are part of the total contribution. For example, \(f_{4}\) already includes the contribution \(f_{4A}\). This last factor is needed if we are interested in the products coming from double electron removal (e.g., O\(^{+}\) + H\(^{+}\)). From

![Figure 4.](image2)

**Figure 4.** Scheme for asymptotic fragmentation of water including Auger-like decay. The three arrows pointing to H\(^{+}\) indicates the Auger contributions from OH\(^{+}\) + H\(^{+}\), O\(^{+}\) + H\(^{+}\), and H\(^{+}\) + H\(^{+}\) dissociation channels. The fraction \(f_{3A}\) is the sum of these three contributions to the production of H\(^{+}\). In the same way, \(f_{2A}\) is the OH\(^{+}\) + H\(^{+}\) contribution to OH\(^{+}\), and \(f_{4A}\) is the O\(^{+}\) + H\(^{+}\) contribution to O\(^{+}\).
the measurements of Ref. [13] it is also clear that the product OH$^+$ + H$^+$ is not only important but also has the same energy dependence as single ionization for high energies. These findings indicate that a new branch, denoted by $f_{24}$ in Fig. 4, not present in Tan’s scheme, is needed to account for the energy dependence of the OH$^+$ + H$^+$ fragmentation channel.

4. Water Fragmentation by heavy ions

Most of the data presently available involving heavy ion fragmentation of water is obtained from "singles" measurements. In this case the single and double ionization channels are mixed. For example, in the ionization measurements, single and double ionization (or higher ionization states) are recorded together. The same happens for electron capture and transfer-ionization, as well as for loss-ionization. Thus, collisional (and not post-collisional as above) double electron removal is likely to occur, mainly if the velocity is not too high, as for example in the vicinity of the Bragg peak, or if the charge state of the ion is large. If these effects are not too large, as in the case of protons, the fragmentation pattern is similar to that for electrons, as shown in Fig. 5, where the line is drawn with the same parameters as in Fig. 2. Thus, the scheme displayed in Fig. 1 is also suitable to describe the proton case for energies above 20 keV. However, if we do the same plot by including heavier ions, as shown in Fig. 6, some deviation from the straight line is observed, although there is a clear tendency of the experimental data points to lie in the vicinity of the above mentioned line and not to be completely scattered all over the area of the plot. So, even for heavy ions, much of the signature of the asymptotic behavior still remains.

Figure 5. Ternary plot of water fragmentation by proton impact. Experiment: Refs. [14-16].

Figure 6. Ternary plot of water fragmentation by heavy ions impact. Experiment: Refs. [17-19].

Deviations from the asymptotic scheme in the heavy ions case has been observed by Olivera et al. [7], who tried to make a better agreement between calculated cross section for electron removal and the observed fragmentation fractions by modifying the set of parameters proposed by Tan et al. This line of reasoning was also followed by Errea et al. [20] in their study by proton impact. Luna and Montenegro [17] in their work with C$^{3+}$ projectiles observed a large decrease of the H$_2$O$^+$ yield compared to the other products, as the collision becomes harder. That happens in a systematic way, irrespective to the projectile charge or to the collision channel. This finding was interpreted as due to the contribution of double electron removal (double ionization, transfer-ionization or loss-ionization) which feeds all other products except H$_2$O$^+$. 
The above scenario indicates that the inclusion of double electron removal is necessary if one wishes to obtain a more general scheme for water fragmentation by heavy ions. However, this would also imply in the inclusion of too many alternatives for the removed electron pair, hindering the usefulness of a simple model. To avoid this, just the total double electron removal cross section, $\sigma_D$, which is the sum of all alternatives to take two electrons off the four molecular orbitals, is included in the model. This simplification will result in a case-to-case adjustment of some parameters, but the main point of this scheme is to add double electron removal without the need to make changes in the asymptotic parameters, either for single removal or the Auger-like decay. This general scheme is displayed in Fig. 7

From Fig. 7 it is straightforward to show that:

$$\sigma_{H_2O^+} = \sigma_{1b_1} + \sigma_{1b_2} + f_0 \sigma_{1b_2},$$  
$$\sigma_{OH^+} = f_1 \sigma_{1b_2} + f_\alpha \sigma_D,$$  
$$\sigma_{H^+} = f_2 \sigma_{1b_2} + f_3 \sigma_{2a_1} + f_\beta \sigma_D,$$  
$$\sigma_O^+ = f_4 \sigma_{2a_1} + f_\gamma \sigma_D,$$  
$$\sigma_{O^2+} = f_5 \sigma_{2a_1} + f_\delta \sigma_D,$$  
$$\sigma_{(OH^+)+(H^+)} = f_2 \sigma_{2a_1} + f_\alpha \sigma_D,$$  
$$\sigma_{(O^+)+(H^+)} = f_4 \sigma_{2a_1} + f_\beta \sigma_D.$$  

$$\sigma_{(H^+)+(H^+)} = 1/2[(f_3 \sigma_{2a_1} - f_2 \sigma_{2a_1} + (f_\beta - f_\alpha - f_\gamma) \sigma_D].$$

From Eqs. 3 - 5 one obtain:

$$\lambda \sigma_D = f_1 f_4 \sigma_{H^+} - f_4 (1 - f_1 - f_0) \sigma_{OH^+} + f_1 (1 - f_4) \sigma_{O^+},$$

where

$$\lambda = f_1 f_4 f_\beta - f_2 f_3 f_\alpha - f_1 f_3 f_\beta.$$  

It is clear from Eq. 10 that, if $\sigma_D = 0$, Eq. 1 is recovered. Thus, according to this model, the amount of the deviation of the measured yields of $OH^+$, $H^+$ and $O^+$ from the asymptotic values given by Eq. 1 is directly related to the cross section for double electron removal. The parameters $f_\alpha$, $f_\beta$, $f_\gamma$, and $f_\delta$ are not independent but related through

$$f_\beta = 2 - f_\alpha - f_\gamma - 2f_\delta,$$

with

$$f_\beta - f_\alpha - f_\gamma \geq 0.$$  

In practice, $f_\delta$, is small, so only two parameters are free in the whole scheme.
5. Results
To apply the above model, the parameters associated to the Auger-like decay of the $2a_1$ molecular orbital are determined from the high-energy asymptotic branching ratios between double and single ionization by electron impact [8,13] and from Eqs. 5-8 (note that, from Eq. 5, $\sigma_{2a_1} = (1/f_4)(\sigma_{O^+} - f_2\sigma_D)$). The contribution from $\sigma_D$ is negligible for all the $\text{OH}^+ + \text{H}^+$, $\text{O}^+ + \text{H}^+$ and $\text{O}_2^{2+}$ cross sections. These branching ratios are shown in Table I, and are slightly different from those reported by Tan et al. [6] or Olivera et al. [7] because the $f_{2A}$ Auger rate was included. The $f_{3A}$ rate was obtained from the ($\text{H}^+ + \text{H}^+)/(\text{O}^+$ cross section ratio given by Ref. [7].

|      | $f_0$ | $f_1$ | $f_2$ | $f_3$ | $f_4$ | $f_{2A}$ | $f_{3A}$ | $f_{4A}$ | $f_{5A}$ |
|------|-------|-------|-------|-------|-------|----------|----------|----------|----------|
|      | 0.08  | 0.70  | 0.22  | 0.68  | 0.20  | 0.11     | 0.54     | 0.10     | 0.007    |

Figure 8 shows the measured double ionization cross section by electron impact, reported in Refs. [8,13], together with the cross sections obtained from singles measurements, according to the present scheme. Apart from those shown in Table I, the remaining parameters used are $f_\alpha=1$, $f_\beta=1$, $f_\gamma=0$ and $f_\delta=0$. The final result for the cross sections are not particularly sensitive to these choices as the contribution from $\sigma_D$ is small in all cases.

Luna et al. [14] measured the fragmentation cross sections by proton impact for the ionization and electron capture channels. These two channels, for the low energy set of the reported

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Figure 8. Cross sections for double ionization by electron impact. The closed squares are double coincidence data from Refs. [8,13]. The closed circles are obtained from the $\text{OH}^+$, $\text{H}^+$ and $\text{O}^+$ yields from single coincidence experiment [8,13] and using Eqs. 10 and 11 to calculate $\sigma_D$ and Eqs. 5-8 to calculate the cross sections. The contribution from $\sigma_D$ is not shown because it is too small. The $f_{4A}$ and $f_{5A}$ Auger rates are obtained combining the single and double coincidence data. The $f_{2A}$ is obtained through a best fit between experiment and the present model (see Table I for the values).
data, include transfer-ionization (TI). This is a two-electron removal channel that contributes to fragmentation but has not been measured in that experiment. However, the measured OH$^+$, H$^+$ and O$^+$ yields retain the information about TI, which can be recovered using Eqs. 10 and 11, from the OH$^+$, H$^+$ and O$^+$ yields, for both channels. The resulting TI cross section, calculated using the same $f_\alpha=f_\beta=1$, $f_\gamma=f_\delta=0$ as above, is shown in Fig. 9, together with calculations by Errea et al. [20]. Values of $f_\alpha$ smaller than one decreases $\sigma_D$, meaning that the better agreement with theory occurs if TI contributes essentially to the OH$^+$ + H$^+$ fragmentation channel. This conclusion also indicates that the outermost 1b$_1$ and 3a$_1$ are the more likely contributors to TI.

**Figure 9.** Cross sections $\sigma_D$ corresponding to transfer ionization (TI) by protons. Closed squares and triangles are obtained from the OH$^+$, H$^+$ and O$^+$ yields of the ionization and electron capture single coincidence measurements, respectively, of Luna et al. [14]. The dashed line is the TI cross sections calculated by Errea et al. [20].

**Figure 10.** Cross sections $\sigma_D$ corresponding to transfer ionization (TI) by C$^+$. Closed circles and triangles are obtained from the OH$^+$, H$^+$ and O$^+$ yields of the ionization and electron capture single coincidence measurements, respectively, of Montenegro et al. [18]. Closed squares are double-coincidence direct measurement of TI, also from Ref. [18].

Montenegro et al. [18] reported double coincidence measurements of transfer ionization by low energy C$^+$ ions together with single coincidence ones for ionization (including double ionization) and single capture (including TI) channels. From the OH$^+$, H$^+$ and O$^+$ yields of the single coincidence experiments $\sigma_D$ can be obtained as above, and compared with the values given by direct TI measurements. This is shown in Fig. 10, using $f_\alpha=f_\beta=1$, $f_\gamma=f_\delta=0$ as before. The general agreement is quite good in this case. The result indicates not only that cross sections for double ionization and TI are of the same order, but that the OH$^+$ + H$^+$ is the predominant fragmentation channel for TI also in this case. This seems to be the main fragmentation channel induced by TI in soft collisions.

6. Conclusions
The fragmentation branching ratios are an essential link to allow the comparison between theoretical calculations and measurements in heavy ions collisions with water. In this work, we present a scheme based on the assumption that the effects in the fragmentation yields due to single and double electron removal are independent. As a consequence, the asymptotic values for the fragmentation branching ratios due to single electron removal can be used for both
light and heavy ions, in all collision channels, as long as the collision time is smaller than the fragmentation time. Auger-like decay of the $2a_1$ molecular orbital play an important role in the fragmentation and its rates were obtained from electron impact measurements. Within this model, theoretical calculations for single and double electron removal can be compared with experimentally measured yields through a few adjustable parameters, all of them associated to the collisional process of taking two electrons off. Besides the scarcity of data where double electron removal cross sections by heavy ions are directly measured, some cases were analyzed to show how the proposed methodology works. The possibility to obtain double electron removal cross sections from more common single coincidence measurements (Eqs. 10 and 11) helps to improve estimates in applications where double ionization plays a major role, as, for example, in the production of HO$_2$ radicals in water radiolysis [21-23].

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