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Fragmentation of water molecules by proton impact: The role of multiple electron processes

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Proton collisions with water molecules are analyzed at impact energies ranging from 20 keV to several MeV to distinguish fragmentation patterns in collisions involving capture and ionization. Solutions of the time-dependent Schrödinger equation restricted to an independent-electron model are complemented with a fragmentation model for water molecules. Recent measurements can be explained when electron processes up to triple electron removal are taken into account.

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Collisions of simple ions with water molecules are of direct interest in atmospheric physics [1,2] and radiation medicine [3,4]. This has motivated the experimental study of fragmentation of water molecules by proton impact. Werner *et al.* [5] recorded absolute yields of H_2O^+, OH^+, H^+, and O^+ at 100–350 keV proton energies without separating capture, direct ionization, and transfer ionization events. Gobet *et al.* [6,7] extended this work to the 20–150 keV energy range and separated fragmentation yields for capture vs direct ionization events. Luna *et al.* [8] performed measurements at lower energies (15–100 keV), which did not determine the projectile charge state after the collision but detected electrons in the continuum in coincidence with the charged fragments.

The analysis of experimental data is complicated by the fact that the proton-water collision system supports a relatively strong transfer ionization channel at low energies. This process, where one electron is captured and one is transferred to the continuum, can be separated from direct ionization when the projectile charge state is known after the collision. In the work of Gobet *et al.* [6,7] it appears as part of the data labeled as capture. In the data of Luna *et al.* [8] it is included in both the capture and ionization channels.

The comparison of fragmentation yields reported in Refs. [5–8] shows some interesting trends. Some of the fragmentation cross sections agree well, while others do not. The data of Luna *et al.* [8] were potentially affected by neglecting simultaneous singly charged fragment arrival, e.g., when the removal of $q = 2$ electrons from the water molecule would lead to quickly moving H^+ recoils together with relatively slowly moving OH^+ (or O^+) ions, the heavier ions might have been missed in the measurement. Clearly, the situation warrants a critical look at the data.

Two theoretical models capable of looking into multiple electron processes at the level of a statistical independent-electron analysis have been put forward recently. One of them involves a nonperturbative solution of the quantum electron dynamics within an independent particle model (IPM) [9]. The other assumes that the electron dynamics can be treated classically [10]. Both models predict significant contributions from multielectron processes, as is shown by the large difference between single-electron and net ionization cross sections.

The purpose of this paper is to provide a systematic explanation of the fragmentation yields as measured by the above-mentioned experiments [5–8]. Our aim is to validate a fragmentation model which is based on the following assumptions: for single-electron removal we follow ideas which originated in high-energy electron scattering [11], which are known to work in proton scattering at high energies where single-electron removal dominates [10,12]; for double- and triple-electron removal we propose to split the recoil production between the OH^+,H^+, and O^+ ions based upon coincidence measurements of Werner *et al.* [5].

The theoretical framework for the present study is an extension of previous work for ion-atom collisions, e.g., proton-argon [13,14]. The water molecule introduces the following new challenges: (i) the rotational-vibrational motion, (ii) the multicenter geometry, and (iii) the possibility of partial or complete breakup of the molecule.

Problem (i) can be safely neglected for fast collisions, while problem (iii) occurs on time scales longer than the collision time and will be treated by a fragmentation model in the final-state analysis. As outlined in Ref. [9], the basis generator method (BGM) has been adapted to simple molecular targets to deal with problem (ii). To avoid matrix elements involving multicenter integrals, a self-consistent field (SCF) solution of Ref. [15] forms the basis for an energy representation of the molecular Hamiltonian. The approximate eigenfunctions are then expanded in a large set of atomic oxygen eigenstates obtained from the optimized potential method of density functional theory (DFT) [16,17]. The representation of the molecular SCF wave function in terms of atomic eigenstates of oxygen is not complete—the worst-case overlap is of the order of 0.9. This approach gives reasonable predictions for the net cross sections for both proton [9] and He^+ [18] projectiles.

In principle, it is necessary to perform calculations for all possible orientations of the molecule. However, as demonstrated in Ref. [9], an average over only two orientations results in satisfactory cross sections for net capture and net ionization. A comparison with more detailed experimental information shows that this cost-saving averaging procedure also works for cross sections with specified charge states on projectile and target [19].

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The calculations, thus, propagate a set of four single-particle wave functions for the active molecular orbitals (MO's) $\{1b_1,3a_1,1b_2,2a_1\}$, which play the role of time-dependent Kohn-Sham orbitals. Currently the target representation is frozen, i.e., response effects from the change in the electron density are not included. This can lead to some overestimation of multiple electron processes at the lowest energies considered in this work. A Slater determinant is formed from the MO's and interpreted as a many-electron wave function in order to apply the correct many-electron analysis including the Pauli exclusion principle [20]. The orientation average and summation over impact parameters allows us to obtain cross sections $\sigma_{k,l}$ for k-fold capture ($k = 0,1$) and simultaneous l-fold ionization ($l = 0,1,2,\ldots$). The number of electrons removed from the water molecule equals $q = k + l$.

In Fig. 1 we compare our calculated q-fold electron removal cross sections with the available data of Werner *et al.* [5]. For $q = 3$ we show the reported coincidence data for complete fragmentation resulting in three singly charged ions ($H^+ + H^+ + O^+$), which represent a close lower bound to the triple-electron removal cross section (σ_T). For $q = 1$ and 2, we applied a model-dependent procedure: on the basis of the measured H_2O^+ yield in Ref. [5], the single-electron removal cross section (σ_S) can be estimated by $(0.68)^{-1}\sigma_{H_2O^+}$, as explained below. Since σ_T is assumed to be given by the measured $H^+ + H^+ + O^+$ cross section, the double-electron removal cross section (σ_D) in Ref. [5] can be derived by subtracting the σ_S and the σ_T contributions from the sum of the four singly charged ion yields. In our present IPM-BGM calculations, $\sigma_{S,T,D}$ are given by [19]

$$\sigma_S = \sigma_{1,0} + \sigma_{0,1}\,, \quad \sigma_D = \sigma_{1,1} + \sigma_{0,2}\,, \quad \sigma_T = \sigma_{1,2} + \sigma_{0,3}. \tag{1}$$

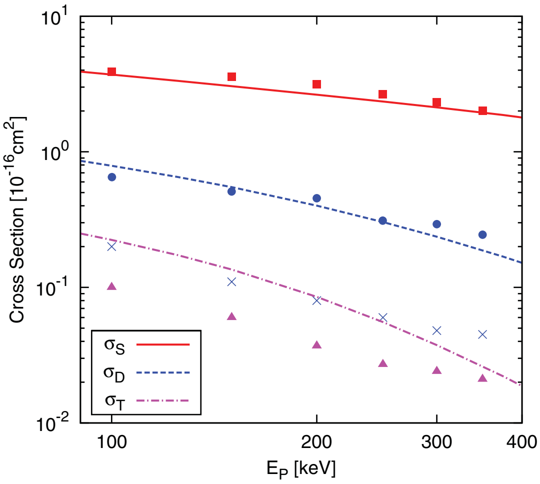

FIG. 1. (Color online) Cross sections for single- (σ_S), double- (σ_D) and triple- (σ_T) electron removal processes calculated with the present independent particle model. Also shown are the experimental values obtained from the measurements of Werner *et al.* [5] for σ_S (■), σ_D (●), and σ_T (▲). The σ_S and σ_D data are estimated in a model-dependent way as explained in the text, while the σ_T data represent measured triple coincidences ($H^+ + H^+ + O^+$). Also shown with crosses ($\times$) are the coincidence measurements of Ref. [5] for $H^+ + H^+ + O^{0,-}$.

The theoretical results for σ_S are seen to agree well with experiment. We find that σ_D is smaller than σ_S by about a factor of 5 at 100 keV impact energy and a factor of 10 at 350 keV. The estimates based upon the experimental data are consistent with this result. For σ_T, the IPM overestimates the cross section by a factor of 2 at low energies; at high energies the experimental data display a different falloff, which may serve as an indication that auto-ionizing transitions begin to play a significant role. Auto-ionizing processes are not included in the present theoretical model.

Our calculations represent a theoretical explanation of $q = 2,3$ electron removal processes in proton-H_2O collisions. The IPM appears to be adequate for these processes at intermediate energies. At high energies (above 400 keV) it is known that the double-electron process also is dominated by autoionization [21], which can only be described if the IPM is supplemented by a statistical postcollision model [22,23]. The overestimation of the σ_T data is understandable within the IPM, which relates the q-fold removal probabilities (for a given impact parameter and orientation) to the theoretical single-particle removal probability in a statistical way. This method is accurate for the dominant processes only.

In order to analyze the fragmentation yields observed in Refs. [5–8] we need to supplement the predicted q-fold electron removal cross sections with a semiphenomenological model describing the postcollisional breakup of H_2O^{q+}. At high collision energies it is possible to evaluate the fragmentation cross sections in terms of the experimental branching ratios of Tan *et al.* [11]. It is known in this high-energy limit (e.g., Refs. [10,21]) that the MO-specific single-vacancy production cross sections scale as the inverse of the ionization energy, so that the population ratio of singly charged fragment ions according to the SCF ionization potentials of Ref. [15] can be given as

$$\sigma_{H_2O^+} : \sigma_{H^+} : \sigma_{OH^+} : \sigma_{O^+} = 68 : 16 : 13 : 3. \tag{2}$$

For slow collisions, however, multiple-electron removal becomes important, and the above formulation breaks down [19].

In this work, we complement Eq. (2) for $q = 1$ removal with the following model for $q = 2,3$ removal: $H_2O^{2+} \xrightarrow{60\%} H^+ + OH^+$, $\xrightarrow{20\%} H^+ + O^+ + H^0$, $\xrightarrow{20\%} H^+ + H^+ + O^0$; $H_2O^{3+} \xrightarrow{100\%} H^+ + H^+ + O^+$. The choice to split the $q = 2$ case is motivated by the coincidence measurements of $H^+ + H^+ + O^{0,-}$ in Werner *et al.* [5] (shown as crosses in Fig. 1) which accounted for 20% of σ_D, and by the assumption that complete fragmentation for $q = 2$ results in an equal amount of neutral O and H production. In principle, O^{2+} can also be formed, but measurements reveal that it plays a very minor role [5,7].

It then follows that

$$\begin{aligned} \sigma_{H_2O^+} &= 0.68\sigma_S, \\ \sigma_{OH^+} &= 0.16\sigma_S + 0.6\sigma_D, \\ \sigma_{H^+} &= 0.13\sigma_S + 1.2\sigma_D + 2.0\tilde{\sigma}_T, \\ \sigma_{O^+} &= 0.03\sigma_S + 0.2\sigma_D + 1.0\tilde{\sigma}_T. \end{aligned} \tag{3}$$

We multiplied σ_T by a factor of 0.5 to correct the overestimation in the IPM-BGM calculation found in Fig. 1, i.e.,

$$\tilde{\sigma}_T = 0.5\sigma_{0,3} + 0.5\sigma_{1,2}. \tag{4}$$

The electron-removal cross sections in Eqs. (1) can then be split into capture and ionization channels as follows:

$$\sigma_S^{\mathrm{cap}} = \sigma_{1,0}, \quad \sigma_D^{\mathrm{cap}} = \sigma_{1,1}, \quad \sigma_T^{\mathrm{cap}} = 0.5\sigma_{1,2}. \tag{5}$$

$$\sigma_S^{\mathrm{ion}} = \sigma_{0,1}, \quad \sigma_D^{\mathrm{ion}} = \sigma_{0,2}, \quad \sigma_T^{\mathrm{ion}} = 0.5\sigma_{0,3}. \tag{6}$$

Inserting Eq. (5) or Eq. (6) into the fragmentation model (3) allows us to compare theoretical fragmentation yields with the data of Refs. [5,7]. For comparison with the data of Luna *et al.* [8], who include transfer ionization both in the capture and in the ionization data, we add $\sigma_{1,1}$ in the ionization channel, i.e.,

$$\hat{\sigma}_D^{\mathrm{ion}} = \sigma_{0,2} + \sigma_{1,1}. \tag{7}$$

The production of H_2O^+ can only be associated with pure single capture or pure single ionization. The consistency of the data of Gobet *et al.* [7] and Luna *et al.* [8] for $\sigma_{H_2O^+}$ (top left panel) in Fig. 2 shows that their respective normalization procedures are in agreement. Comparison with our theory shows that $\sigma_{H_2O^+}$ is reasonably predicted in the capture channel with the tendency to overestimate at energies above 100 keV. The direct ionization data, on the other hand, appear to be underestimated at low energies at the 30% level.

The display of the data as population ratios in the right panel of Fig. 2 shows sensitivity to the other fragment yields. Here we observe that the theoretical model predicts less H_2O^+ at low energies, where the transfer ionization channel is open down to 20 keV. Note that the experimental capture data approach the limit set by Eq. (2) at these energies. However, the comparison of the ionization data (direct only vs electron-ion coincidences) displays a widening gap between these results as the impact energy is lowered. The present model appears to exaggerate this gap, and it does not follow the trend of the experimental data in the direct ionization channel. One concern about the data of Luna *et al.* [8] is that the population ratio does not merge with the other experimental data at 100 keV impact energy. This is an indication that their experiment may have missed heavier fragments produced in coincidence with recorded H^+ ions.

The cross section for OH^+ production in the direct ionization channel is underestimated in our model by about 30%. The capture channel, on the other hand, follows the trend of the experimental data fairly well. Inclusion of transfer ionization in Eq. (7) leads to a substantial increase in the theoretical cross section, particularly at low energies. The experimental data of Luna *et al.* [8] do not show this behavior; this could be caused either by the $H^+ + OH^+$ channel not appearing in transfer ionization (as argued in Ref. [8]) or by a lack of detection of the heavy OH^+ ions produced in coincidence with H^+.

There are substantial differences between the theoretical calculations and the experimental data for OH^+ in the right panel of Fig. 2 above 50 keV impact energy. The trend in the data of Werner *et al.* [5] signals an increase of the OH^+ production at high energies, almost in parallel with the H_2O^+ fraction, but with larger population ratios than our model predicts. The data of Luna *et al.* [8] also fall short as compared to Refs. [5,7] above 50 keV impact energy.

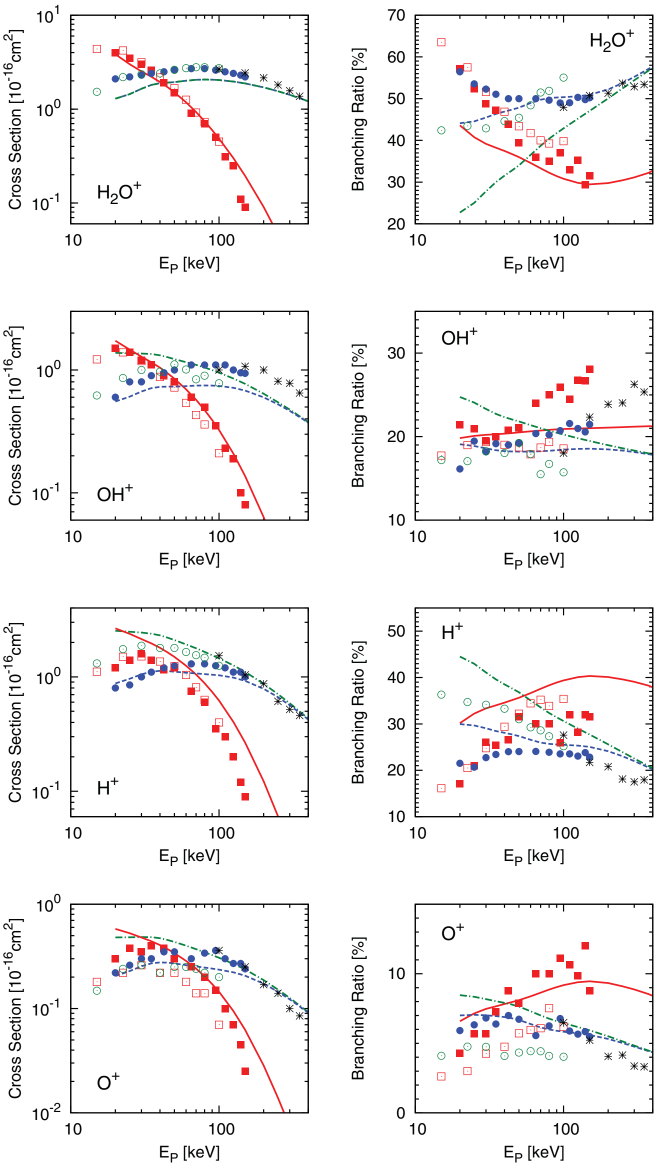

FIG. 2. (Color online) Left column: partial cross sections for fragment-ion production in the capture channel (red solid lines), the ionization channel (blue dashed lines), and the ionization channel calculated with transfer ionization included (green dash-dotted lines), cf. Eq. (7). Experimental data are from Werner *et al.* [5] (∗); Gobet *et al.* [7]: cap (■), ion (•); Luna *et al.* [8]: cap (⊡), ion (⊙). Right column: partial cross sections divided by the sum of the four fragment-ion production cross sections.

Our prediction of the H^+ production cross sections follows the opposite trend to the OH^+ case, i.e., it makes an error on the high side for the capture channel, but is in fairly good agreement with experiment in the direct ionization channel. It overpredicts the gap between direct ionization and direct-plus-transfer ionization: the split extends up to 200 keV, while the data of Refs. [7,8] appear to merge at 100 keV.

Considering the population ratio for H^+ ions, we note that the present model obtains the right order of the splitting between the data of Refs. [7,8] without the assumption made by Luna *et al.* [8] that transfer ionization leads predominantly to the $H^+ + H^+ + O^0$ channel. In fact, any enhancement of this channel in the fragmentation model results in a dramatic overprediction of the H^+ branching ratio.

For the relatively small O^+ production cross sections and branching fractions we find reasonable agreement between theory and experiment in the capture and direct ionization channels. Adding transfer ionization to the direct ionization channel according to Eq. (7) leads to some enhancement for σ_{O^+} in the theoretical analysis. However, the experimental data of Luna *et al.* [8] are significantly below those of Refs. [5, 7]. This again raises the possibility of missing the heavier ion in the $H^+ + O^+$ measurements of Ref. [8]. Unfortunately, Werner *et al.* [5] did not report results for this coincident channel.

In conclusion, we find that an *ab initio* IPM calculation coupled with a fragmentation model is capable of providing the general picture of fragmentation processes in proton-water collisions at moderate collision energies. At low impact energies some discrepancies are observed. They might be remedied when dynamical response is incorporated in the spirit of time-dependent DFT. At low energies there is also the need to revisit the question of the simple orientation average over molecular geometries employed in the present work. A recent single-electron capture calculation suggests that extensive orientation averaging does make a difference at impact energies below 50 keV [24]. The present work should serve to inspire further experimental and theoretical study of molecular fragmentation.

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[1] T. E. Cravens, Science **296**, 1042 (2002).

[2] J. J. Olivero, R. W. Stgat, and A. E. S. Green, J. Geophys. Res. **77**, 4797 (1972).

[3] H. Nikjoo, S. Uehara, D. Emfletzoglou, and A. Brahme, New J. Phys. **10**, 075006 (2008).

[4] B. Gervais, M. Beuve, G. H. Olivera, and M. E. Galassi, Radiat. Phys. Chem. **75**, 493 (2007).

[5] U. Werner, K. Beckord, J. Becker, and H. O. Lutz, Phys. Rev. Lett. **74**, 1962 (1995).

[6] F. Gobet, B. Farizon, M. Farizon, M. J. Gaillard, M. Carré, M. Lezius, P. Scheier, and T. D. Märk, Phys. Rev. Lett. **86**, 3751 (2001).

[7] F. Gobet, S. Eden, B. Coupier, J. Tabet, B. Farizon, M. Farizon, M. J. Gaillard, M. Carré, S. Ouaskit, T. D. Märk, and P. Scheier, Phys. Rev. A **70**, 062716 (2004).

[8] H. Luna, A. L. F. de Barros, J. A. Wyer, S. W. J. Scully, J. Lecointre, P. M. Y. Garcia, G. M. Sigaud, A. C. F. Santos, V. Senthil, M. B. Shah, C. J. Latimer, and E. C. Montenegro, Phys. Rev. A **75**, 042711 (2007).

[9] H. J. Lüdde, T. Spranger, M. Horbatsch, and T. Kirchner, Phys. Rev. A **80**, 060702(R) (2009).

[10] C. Illescas, L. F. Errea, L. Méndez, B. Pons, I. Rabadán, and A. Riera, Phys. Rev. A **83**, 052704 (2011).

[11] K. H. Tan, C. E. Brion, P. E. V. D. Leeuw, and M. J. V. D. Leeuw, Chem. Phys. **29**, 299 (1978).

[12] G. H. Olivera, C. Caraby, P. Jardin, A. Cassimi, L. Adoui, and B. Gervais, Phys. Med. Biol. **43**, 2347 (1998).

[13] T. Kirchner, M. Horbatsch, and H. J. Lüdde, Phys. Rev. A **66**, 052719 (2002).

[14] T. Kirchner, M. Horbatsch, M. Keim, and H. J. Lüdde, Phys. Rev. A **69**, 012708 (2004).

[15] S. Aung, R. M. Pitzer, and S. I. Chan, J. Chem. Phys. **49**, 2071 (1968).

[16] E. Engel and S. H. Vosko, Phys. Rev. A **47**, 2800 (1993).

[17] T. Kirchner, H. J. Lüdde, M. Horbatsch, and R. M. Dreizler, Phys. Rev. A **61**, 052710 (2000).

[18] T. Kirchner, M. Murakami, M. Horbatsch, and H. J. Lüdde, J. Phys.: Conf. Ser. (2012) (to be published).

[19] M. Murakami, T. Kirchner, M. Horbatsch, and H. J. Lüdde, Phys. Rev. A **85**, 052704 (2012).

[20] H. J. Lüdde and R. M. Dreizler, J. Phys. B **18**, 107 (1985).

[21] E. C. Montenegro, J. Phys.: Conf. Ser. **194**, 012049 (2009).

[22] T. Spranger and T. Kirchner, J. Phys. B: At. Mol. Opt. Phys. **37**, 4159 (2004).

[23] C. C. Montanari, E. C. Montenegro, and J. E. Miraglia, J. Phys. B: At. Mol. Opt. Phys. **43**, 165201 (2010).

[24] P. M. M. Gabás, L. F. Errea, L. Méndez, and I. Rabadán, Phys. Rev. A **85**, 012702 (2012).