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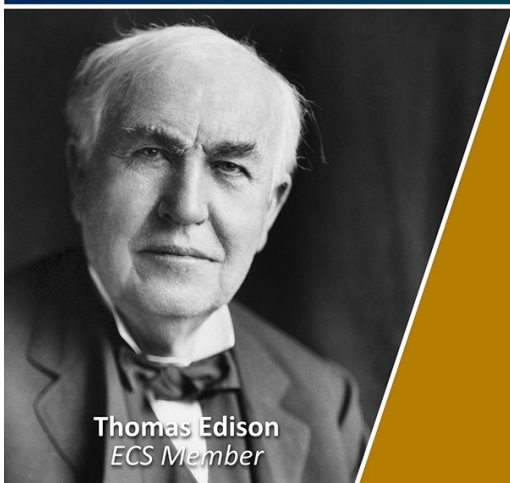
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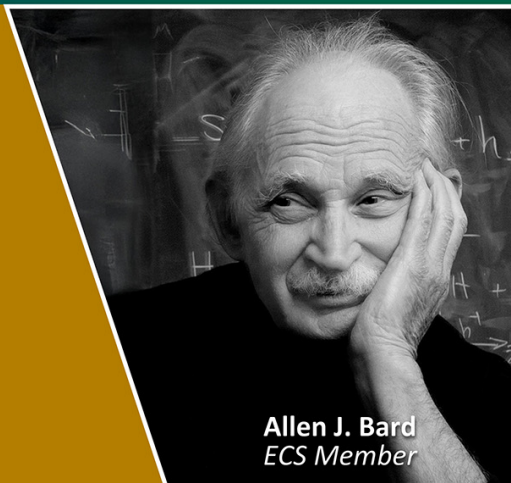
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High LET Highly Charged Ion–Induced Ionization and Fragmentation of Water Molecules and Clusters

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Abstract. Kinematically complete experiments lead to very substantial progress in the understanding of decay dynamics of multiply charged molecular ions. This paper is devoted to the study of dissociative ionization of water molecules and clusters induced by highly charged ions. We will present first how experimental results determined in the gas phase can provide information about the physical stage of liquid water radiolysis. Second, we will discuss strong bond cleavage selectivity in ion-induced dissociation of deuterium tagged water molecule. Finally, we will present first promising results about water cluster dissociative ionization. Stability, energetics and charge mobility in the charged cluster will be briefly discussed.

1. Introduction

Ionization of simple molecules by the impact of photons [1-3], electrons [4-5], and ions [6-8] has been the subject of extensive experimental and theoretical investigations for almost two decades. Among all of the possible ionizing sources, highly charged ion beams can produce highly charged transient molecular ions, mainly *via* valence charge stripping. In the case of swift projectiles, a comparison of the different characteristic times leads to a commonly accepted two-step picture for the molecule fragmentation. First, the electron removal takes place on an attosecond time scale with a fixed-in-space molecule. Second, molecule fragmentation occurs and nuclear motion starts driven by fragmentation dynamics. With the advent of kinematically complete collision experiments, in which the full momentum vector of all charged particles is determined, it is now possible to investigate fragmentation processes with unprecedented detail and precision. Very substantial progress in the understanding of the formation and the decay dynamics of multiply charged molecules have been realized these last years. It is now possible to scrutinize the stability or the dissociation of multiply charged molecular ion but also to use this dissociation to reveal the initial mechanisms between the projectile and the target.

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Among all the simple molecules, the description of water fragmentation is probably one of the most important tasks as it intervenes in a lot of applications on the border of many branches of science. For example, water is the major absorber of sunlight in our atmosphere [9]. Population of excited states of highly charged ion (HCI) in charge-exchange collisions with water (and other) molecules is to date the explanation for the recent and unexpected discovery of x-ray emission from comets [11-12]. Furthermore, water radiolysis can also play a major role in the understanding of radiation damage in biological tissue [13]. For this latter case, only scarce results have yet been reported in the case of high linear energy transfer HCI [13-14]. Thus, a refined description of water fragmentation is of interest to modelize the subsequent chemistry in solution. We will present in this paper (*cf.* section 3.1) how gas phase results can answer to still open questions and contribute to the understanding of the physical stage of liquid water radiolysis.

Understanding of the molecular bond breakage selectivity, in order to control the bond cleavage [15], is one of the most exciting challenges in chemistry. It requires a detailed knowledge of the potential energy surfaces as well as of the dynamics that governs the dissociation. Reaction dynamics experiments give a complete insight into the dynamics of the process and reveal the mechanism involved in the interaction [16]. The isotopomer of water HOD provides a three-atom prototype for studying bond cleavage selectivity. In particular, for such a hydrogenated molecule, one can take advantage of the large mass ratio between H and D which magnifies the isotopic difference. We will discuss here (*cf.* section 3.2) a strong “isotopic effect” leading to a clear preference for breaking the O-H bond rather than the O-D bond.

The properties of water clusters have been the subject of increasing research activities in recent years due to the ubiquity of H₂O as one of the most important polar solvents, as well as the importance of water clusters in atmospheric science. In the atmosphere, water clusters exist as a precursor to the formation of droplets in clouds. Intermediate size clusters of about ten molecules may represent the earliest stage of cloud formation [17]. We will present in section 3.3 the first experimental results about small water clusters in highly ionizing collisions. Such imaging experiment provides refined information not only about stability but also about energetics or charge mobility inside the charged cluster.

2. Experimental techniques

The principle of RIMS technique has been widely detailed especially when applied to ion-atom collision studies [18]. The principle is the same for an application for ion-molecule collision [19]. The main adaptations of this technique to molecule fragmentation study concerns multi-hit capability requirements and strong electric field needed to maintain the 4π solid angle efficiency. The experiments with swift projectiles were performed at the GANIL facility (Caen, France). The ions collide with a dense and localized molecular gas target provided by a supersonic jet in order to have initially highly monokinetic targets. In the case of water clusters, approximately 20 ml of distilled water is loaded into a heated reservoir (stagnation chamber). Its temperature is controlled by a thermocouple and is typically kept at $T_s \cong 80^\circ\text{C}$. The pressure of the water vapor p_s is determined by the temperature of the stagnation chamber, and is around 400 mbar. 1 bar Ar seeding gas is mixed with the water vapor at the exit of the sealed oven to increase the total stagnation pressure. The vapor flows to the nozzle (30 μm diameter, temperature 90°C) through an inox tube. The temperature of this tube is controlled separately, and is held slightly above the reservoir temperature to avoid condensation. The gas mixture undergoes isentropic expansion and the temperature drops rapidly with increasing distance from the nozzle. This leads to the supersaturation of the water vapor and subsequent clustering.

The fragments were extracted by a strong uniform electric field (approximately 200 V/cm), and directed onto a large diameter (80 mm) PSD – composed of microchannel plates and a delay-line anode – with a dead time of approximately 15 ns. In the case of ion-atom collisions, the main limitation to the momentum resolution originates from the size of the collision region, which has to be as small as possible. The time-focusing geometry of the spectrometer [20] overcomes the uncertainty

on the time of flight determination while the uncertainty on the impact position is limited by the supersonic jet extension (1–2 mm). In the case of molecule fragmentation study, more than one fragment is detected in most cases. The momentum conservation provides additional information which gives access to the collision point for each event in the collision region [19]. Thus, the time and the position resolutions lead to an achievable momentum resolution $\Delta p/p$ of about 5×10^{-3} , comparable with the one obtained by RIMS in ion–atom experiments.

We recently implement the experimental setup (depicted in figure 1) by adding a coincident detection of the electrons using the same imaging techniques, to study H_2 ionization. A weak magnetic field ($\cong 18$ G) is added using Helmholtz coils. The electrons are therefore forced into helical trajectories, allowing the detection of large transverse electron momenta (ensuring 4π electron solid angle collection for kinetic energies up to 60 eV). This multi-electron recoil ion momentum spectrometer (often called “reaction microscope” [21]) is the adequate experimental apparatus to measure fully differential cross-sections of the primary processes. Fragment ion momentum spectroscopy allows calculating the initial relative orientation between the molecule internuclear axis and the projectile direction, leading, in conjunction with electron spectroscopy imaging, to a detailed study of electron emission in the molecule frame [22-23].

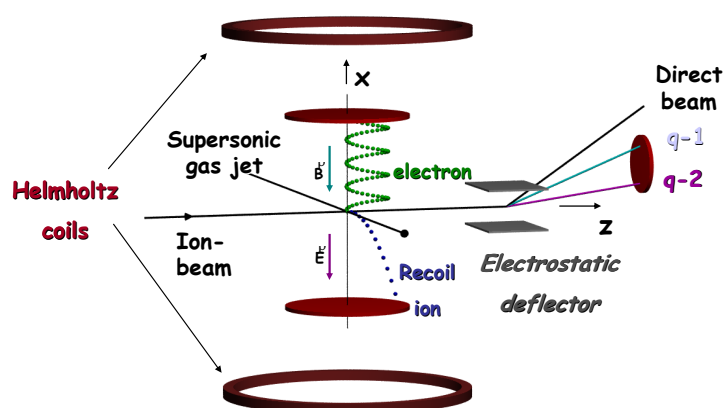


Figure 1. Experimental set-up

3. Results and Discussion

3.1. Contribution to the physical stage of water radiolysis

Liquid water radiolysis is now a relatively well understood phenomenon for irradiation at low linear energy transfer (electrons, X-rays, fast and low charge state projectile...). Monte-Carlo simulations are able to reproduce quantitatively the radiolytic yields of the different species produced and thus to provide a clear description of the mechanisms at work. The situation is not as clear for higher LET values [24]. In particular, simulations hardly account for the large amount of the HO_2 species experimentally measured and that seems to be typical of high LET radiations. It has been suggested by several authors that the formation of HO_2 could be due to multiple ionization of the water molecule [25]. For example, dissociation of doubly ionized water molecule can produce atomic oxygen ($H_2O^{2+} \rightarrow H^+ + H^+ + O$) assumed to be a precursor of formation of this HO_2 radical. If produced in the ground electronic state (3P), oxygen is supposed to contribute to the HO_2 production by the direct reaction $O + OH \rightarrow HO_2$ while excited oxygen atom will form this radical in two steps, reacting quickly with a water molecule $O^* + H_2O \rightarrow H_2O_2$ and then forming the HO_2 radical by the reaction $H_2O_2 + OH \rightarrow H_2O + HO_2$. As the measurements of interest (relative cross section, branching ratios, and electronic

state of the oxygen atom) are very difficult to realize in the liquid phase, gas phase measurements can contribute to the understanding of the “physical stage” of water radiolysis (for time shorter than 10^{-15} s after the passage of the ion) and provide valuable inputs for the Monte-Carlo simulations that calculate the radiolytic yields of the different species on long time scales (up to the micro-second) [24].

Branching ratios for almost all of the dissociation channels can be determined in the case of 12 MeV/u Ni^{25+} projectiles colliding with H_2O molecules [26]. This experiment is able to provide some precise information even for channels including one neutral fragment. This is possible since nearly no momentum is transferred from the projectile to the target in this high projectile velocity regime. Thus, the momentum conservation law leads in most cases to the momentum determination of the neutral (and obviously undetected) fragment.

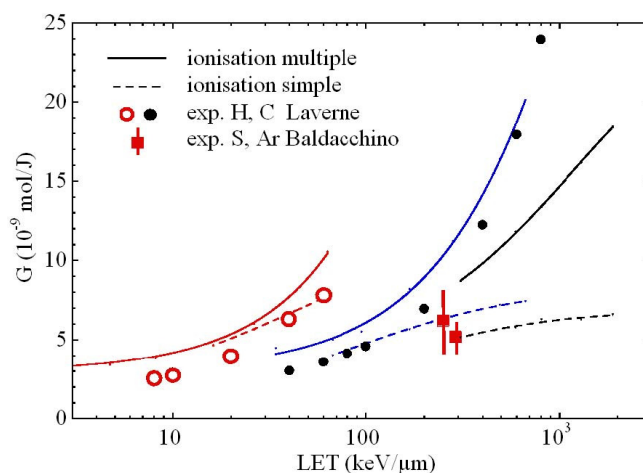


Figure 2. (Colour online) Variation of the chemical “ HO_2 ” yields [24] as a function of LET. Comparison between experimental results and Monte-Carlo simulations with inclusion of multiple ionization (straight lines) or without (dashed lines)

Up to eight electrons can be removed from the water molecule in a single collision. Multi-ionization is found to represent more than 35% of the ionizing events [23]. Thus, the production of atomic oxygen cannot be neglected. Moreover, evidence for a high proportion of excited oxygen atom has been reported recently [27]. New simulation of liquid water radiolysis by swift carbon ions taking explicitly into account multiple ionization and the results issued from the gas phase exhibits a good agreement with all the molecular or radical species radiolytic yields experimentally measured in this high LET regime (figure 2).

3.2. Reaction dynamics : high bond cleavage selectivity

HOD molecule provides a three-atom prototype for studying bond cleavage selectivity. Extensive studies have been performed in the case of resonant vibrationally mediated photodissociation (see, for example, [15] for a review). A few results are known for isotopic effects in water cation fragmentation. Saylor *et al* [28] reported on an isotopic effect in the bond-rearrangement channel $\text{X}_2\text{O}^+ \rightarrow \text{X}_2^+ + \text{O}$, where $\text{X} = \text{H}$ or D for light ion-induced single ionization of H_2O and D_2O molecules, respectively. Only scarce results have been reported on the HOD^{2+} fragmentation. Richardson *et al.* [29] presented a systematic deduction of the branching ratios for HOD molecule ionized by HeII light. They deduced from coincident time-of-flight measurement of the two first charged fragments an OD^+/OH^+ ratio around 5. They found a similar mean KER value of 4.7 ± 0.5 eV for the two channels $\text{H}^+ + \text{OD}^+$ and $\text{D}^+ + \text{OH}^+$.

Compared to photoionization, the situation is much more complex in the case of non-resonant HCI impact. In this case, bond selectivity cannot be monitored by a wavelength variation of the ionizing radiation. In order to look for any isotopic effect in the HCI-induced HOD fragmentation in an unambiguous way, we propose to look to the HOD^{2+} fragmentation by comparing the H^+OD^+ and D^+OH^+ production. Experimentally, the detection is obviously complete (since there is no neutral fragment to detect). From a theoretical point of view, accurate calculations have recently been published on potential energy surfaces of this dication ground and excited states [30-31].

KER distributions experimentally measured are presented in figure 3 for three fragmentation pathways, namely $\text{HOD}^{2+} \rightarrow \text{H}^+\text{OD}^+$, D^+OH^+ , $\text{H}^+\text{D}^+\text{O}$. A large difference is found between two- and three-body fragmentation channels. The fact that full atomization of the molecule gives higher mean KER value (around 9 eV) than the partial dissociation pathways reveals that the full dissociation occurs mainly *via* population of excited dication repulsive states. The D^+OH^+ and H^+OD^+ channels are centered at 6 eV and 7 eV, respectively. No such difference has yet been reported. Regarding the isotopic effect, a clear (6.5 ± 0.5) -fold excess of OD^+ versus OH^+ yield is observed. This result clearly evidences a preferential cleavage of O–H bond rather than O–D bond in swift ion-induced fragmentation. Note that a same conclusion has recently been drawn by Saylor *et al* [32] for fast proton and F^{7+} induced double ionization with a ratio of (5.2 ± 0.3) . They also point a similar behavior following single ionization though the asymmetry is found smaller at about a factor of two.

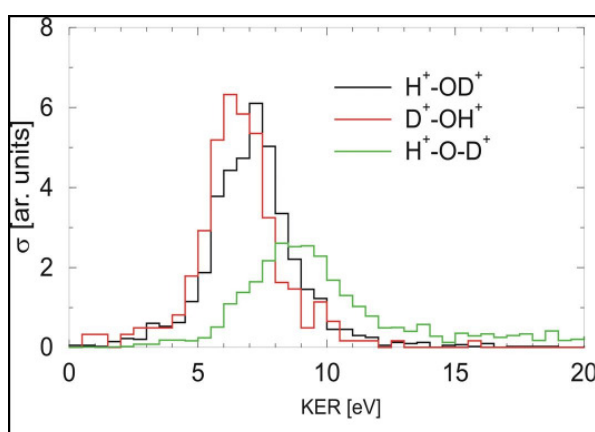


Figure 3. (Colour online) Experimental KER distributions for three different 11.7 MeV/u Ni^{25+} ion-induced fragmentation channels of HOD^{2+} (the three distributions are normalized to the same number of events)

It is instructive to simulate the dynamics of the fragments on the potential energy surface (PES) of the excited states of H_2O^{2+} . For a given PES, it is straightforward to mimic the ionic dynamics of the three bodies by means of classical dynamics. Such a simulation is quite general, still we have to restrict our investigation to the X^3B_g ($X^3\Sigma_g^-$ in linear geometry) [30] H_2O^{2+} ground electronic state, which is the only state for which a complete parameterization of the PES is available [31]. This surface has a saddle point which separates the dissociation path into two- and three-body. For the simulation, the momenta and position of the three atoms are generated from the Wigner distribution deduced from the harmonic approximation of a precise PES of H_2O groundstate. Assuming a Franck-Condon transition, the system is then propagated classically on the X^3B_g groundstate surface of the dication. We make sure to propagate for a sufficiently long time, so that dissociation is complete when it occurs, and so the remaining Coulomb repulsion energy between the charged fragments becomes negligibly small with respect to the kinetic energy of the system. We simulated 10^6 trajectories to achieve a good statistics. We checked the sensitivity to initial conditions by scaling the PES so that the

vibrational frequencies match closely the experimental frequency measurements. The simulated isotopic ratio then changes from 7.5 in the pure harmonic approximation to 7.2 when matching experimental frequencies. The difference with our previously published ratio (13.2) [27] arises from a too short time (and thus an incomplete) propagation in our previous simulation.

The calculation reproduces nicely a preferential cleavage of the O–H bond as experimentally observed. Three-body fragmentation proportion is found to be highly underestimated by taking into account only the dissociation via the H_2O^{2+} electronic ground state, which is consistent with our conclusion that it comes from excited states. For the X^3B_g ground state, the numerical simulation gives access to phase-space correlations for each final channel. Figure 4 provides a picture of the part of the initial phase-space distribution function that contributes to each of the final dissociation channel. We consider the three possible pairs of atom (O–H, O–D and H–D). For each pair, we represent the distribution of their relative distance and the distribution of their relative momentum along the internuclear axis direction. No strong correlation is evidenced for the $HOD^{2+} \rightarrow H^+ + OD^+$ channel. The results reflect mainly the position and velocity distributions of the initial HOD state. It corresponds to the main fragmentation channel. At the opposite, the $HOD^{2+} \rightarrow D^+ + OH^+$ exhibits correlations which consist in a preference for shorter O–D bond length and for longer O–H and H–D distances. These position correlations are also associated with positive relative velocity between O and D (D atom moving away from O) and negative relative velocity between O and H (H atom moving towards O). Similar correlations are found for the three-body fragmentation channel, except that the H–D distance is compressed in this case, corresponding mainly to smaller bending angles. Emission of two protons is found to be preferential for rather low bond angles i.e. small $H^+ - D^+$ distances that maximize the Coulomb repulsion between the fragments and thus the molecule dissociation.

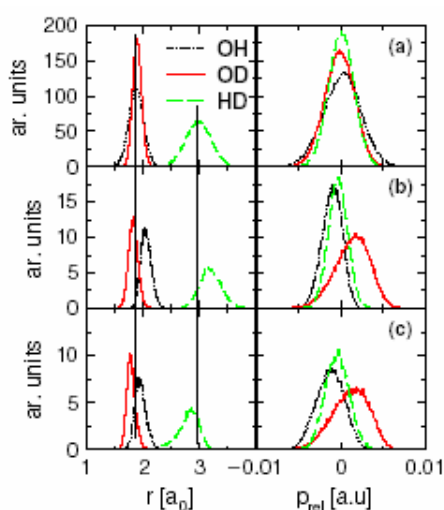


Figure 4. (Colour online) On the left side, distributions of the relative distances between pair of atoms for each final channel: (a) $H^+ + OD^+$ channel; (b) $D^+ + OH^+$ channel; (c) $H^+ + D^+ + O$ channel. Vertical lines indicate average equilibrium positions for the HOD ground state. On the right side, distributions of the relative momentum along the internuclear axis direction of each pair of atoms for each final channel (negative values correspond to atom getting closer from each other) [27].

3.3. Imaging water clusters in highly ionizing collisions : stability, energetic, charge mobility

Small water clusters in collision with 12 MeV/u Ni²⁵⁺ projectiles (the same ion used for the determination of fragmentation patterns of the water molecule) are studied. Time of flight spectrum is presented in figure 5. Typically, the mass spectrum is dominated by protonated cluster ions (H₂O)_nH⁺. The detection of these species evidences the rapid intracluster proton transfer dissociation upon the following ionization scheme: (H₂O)_n → [(H₂O)_n]⁺* + e⁻ → (H₂O)_{n-1}H⁺ + OH + e⁻, where [(H₂O)_n]⁺* stands for the vertically ionized water clusters. It is well known that for clusters with n ≥ 3, water molecules within the cluster will rearrange themselves rapidly after ionization and release a large amount of energy. The high mobility of the proton might promote this process as pointed for example by Radi *et al.* [33] in the case of femtosecond photoionization. This mass spectrum is characteristic of the initial size distribution produced in the supersonic expansion as it has been demonstrated [34] that only a few of these monomers are evaporated in the case of small clusters while the number of evaporated molecules increases linearly with increasing cluster size. Stability of these protonated clusters as a function of n can also be studied. These results will be published in a forthcoming paper.

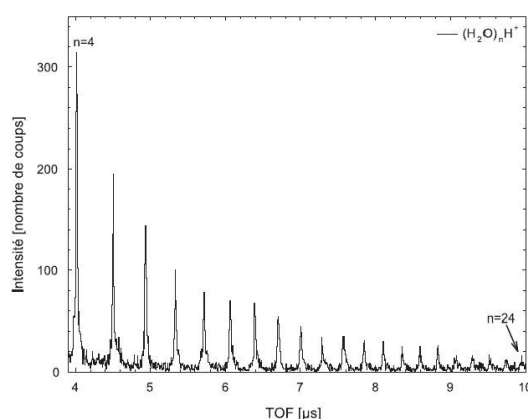


Figure 5. Mass spectrum (*time of flights longer than 4 μs*) for 12 MeV/u Ni²⁵⁺ + (H₂O)_n collisions

Coincidence experiments have also been realized. We can unambiguously evidence coincident emission of singly charged cluster fragments. High resolution energy distributions and angular distributions of the charged fragments are measured using the experimental determination of the momentum vector of each fragment. These experimental measurements will also allow exploring the question of the charge mobility and to which extent the excess charge is mobile or localized in highly charged water clusters. In order to clarify the situation, mass spectra which correspond to a given multiplicity, which means where a given number of charged fragments have been detected per event, have been plotted. First results seem to evidence that no multiply charged fragment is detected even for 5-fold ionization of the clusters.

4. Conclusion

We have explored dissociation dynamics of water molecules in collision with fast multiply charged ions. In order to bring information on the physical stage of liquid water radiolysis, fragmentation patterns (dissociation channels, branching ratios, relative multi-electron removal cross sections) are determined together with fragmentation dynamics. Strong bond cleavage selectivity is also evidenced in the dissociation of the HDO²⁺ dication. Experimental data analysis requires detailed Potential Energy Surface calculations as well for the simulation of this isotopic effect as for the determination of the excited states populated before and after dissociation. Dissociative ionization of water molecules could now be imaged by the recently developed reaction microscope.

First results are presented for collision of swift heavy ions with water clusters. More detailed results will be presented in a forthcoming paper. In order to have a complete balance of the dissociation, next step would be the study of stability and/or fragmentation of size-selected water clusters. We can imagine, in connection with the study of radiation damages, that these results are the first on the road of stability studies of even more complex systems.

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