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Collision-induced dissociation of protonated water clusters

F. Berthias,^{1,2,3} V. Buridon,^{1,2,3} H. Abdoul-Carime,^{1,2,3} B. Farizon,^{1,2,3} M. Farizon,^{1,2,3} P. M. Dinh,^{4,5} P.-G. Reinhard,⁶

E. Suraud,^{4,5} and T. D. Märk⁷

¹Université de Lyon, F-69003 Lyon, France

²Université Lyon 1, F-69622 Villeurbanne, France

³CNRS/IN2P3, UMR5822, Institut de Physique Nucléaire de Lyon, F-69622 Villeurbanne, France

⁴Laboratoire de Physique Théorique (IRSAMC), Université de Toulouse, UPS, F-31062 Toulouse, France

⁵CNRS, LPT (IRSAMC), F-31062 Toulouse, France

⁶Institut für Theoretische Physik, Universität Erlangen, D-91058 Erlangen, Germany

⁷Institut für Ionenphysik und Angewandte Physik, Leopold Franzens Universität, Technikerstrasse 25, A-6020 Innsbruck, Austria

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Collision-induced dissociation (CID) has been studied for protonated water clusters $H^+(H_2O)_n$, with n = 2-8, colliding with argon atoms at a laboratory energy of 8 keV. The experimental data have been taken with an apparatus (Device for Irradiation of Molecular Clusters, 'Dispositif d'Irradiation d'Agrégats Moléculaire,' DIAM) that has been recently constructed at the Institut de Physique Nucléaire de Lyon. It includes an event-by-event mass spectrometry detection technique, COINTOF (correlated ion and neutral fragment time of flight). The latter device allows, for each collision event, to detect and identify in a correlated manner all produced neutral and charged fragments. For all the studied cluster ions, it has allowed us to identify branching ratios for the loss of i = 1 to i = n water molecules, leading to fragment ions ranging from $H^+(H_2O)_{i=n-1}$ all the way down to the production of protons. Using a corresponding calibration technique we determine total charged fragment production cross sections for incident protonated water clusters $H^+(H_2O)_n$, with n = 2-7. Observed trends for branching ratios and cross sections, and a comparison with earlier data on measured attenuation cross sections for water clusters colliding with other noble gases (He and Xe), give insight into the underlying dissociation mechanisms.

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I. INTRODUCTION

Studies on radiation mechanisms at the nanometer scale can provide insights into "radiative energy transfers" in terms of the involved molecular processes. They can pave the way for a better understanding of the consequences of a specific radiation dose deposited in living systems at the microscopic level. The first such studies have become possible owing to the ability to irradiate isolated molecular nanosystems at various stages of aggregation with various projectiles, e.g., see Refs. [1,2,3]. They allowed the investigation of initial radiation-induced interactions between molecules in these isolated nanosystems. which provides detailed information on some radiation effects at the nanoscale. The study of radiation mechanisms on such a scale requires specific nanosystems used as model cases for the rather complex biological in situ situation. In this context, small water clusters constitute a very relevant candidate for mimicking and possibly solving such biological questions.

A full understanding of radiation-induced phenomena at the nanometer scale requires both experimental and theoretical studies. Theoretical studies based on the time-dependent density functional theory (TDDFT) allow one to simulate the dynamics of various irradiated systems [4]. The more recent computations by Wang *et al.* [5] described the collision between an atom, or an ion, and a H₂O molecule. These models provide the possibility to explore the dynamics of water systems irradiated by various projectiles. In addition, there are a number of experimental studies, some involving collision-induced dissociation (CID) methods, concerning the interaction of water clusters (ions) with various targets at energies ranging from the thermal regime [6–9] up to 50 keV [10]. CID is a standard technique in mass spectrometry that is

used to probe the structure and bond energies in molecular ions, and also provides a convenient means to study the dynamics of collision-to-internal energy transfers. For instance, Magnera et al. [11] determined the energy released by the loss of water molecules in such collisions at collision energies of a few eV. Armentrout et al. [6-8] measured various other physical quantities (reaction cross sections, solvation enthalpies) for $H^+(H_2O)_{1-4}$ ions colliding with deuterated ammonia and with acetonitrile, and for $H^+(H_2O)_{1-5}$ ions colliding with xenon in the energy range from thermal energies to 20 eV. Previous experiments on CID include also the estimation of branching ratios for the loss of one, two, and three water molecules, and the determination of cross sections for $H^+(H_2O)_{2-6}$ cluster ions colliding with methane and argon gas targets in the collision energy range up to 50 eV (see Ref. [12]). Finally, Tomita *et al.* [10] measured the attenuation and fragmentation cross sections for $H^+(H_2O)_{1-100}$ cluster ions colliding with helium and xenon gas at a collision energy of 50 keV.

In order to extend these few previous measurements we present here a complete set of total charged fragment production cross sections and branching ratios for CID of $H^+(H_2O)_n$, ions, with n = 2 up to 8, colliding with an argon gas target at an energy of 8 keV. The experimental data have been taken with an apparatus (Device for Irradiation of Molecular Clusters, 'Dispositif d'Irradiation d'Agrégats Moléculaire,' DIAM) recently constructed at the Institut de Physique Nucléaire de Lyon (IPNL). It involves an event-by-event mass spectrometry detection technique called correlated ion and neutral fragment time of flight (COINTOF) [13]. The latter device enables us to detect and identify in a correlated manner all the neutral and charged fragments produced for each collision event.



FIG. 1. (Color online) Schematic view of the COINTOF setup.

The present CID experiments focused on the determination of branching ratios of a protonated water cluster $H^+(H_2O)_n$, (with n = 2 up to 8) for the loss of i = 1 to i = n water molecules, all the way down to the formation of protons. Using a corresponding calibration technique we also were able to determine total charged fragment production cross sections for incident protonated water clusters $H^+(H_2O)_n$, with n = 2-7. The observed trends for branching ratios and cross sections as a function of n and i and a comparison with theoretical structure studies [see, for instance, the vibrational predissociation spectra and *ab initio* calculations on $H^+(H_2O)_{5-8}$ of Jiang *et al.* [14]] and earlier data on measured attenuation cross sections for water clusters colliding with other noble gases (He and Xe) [10] give insight into the underlying dissociation mechanisms.

II. EXPERIMENTAL SETUP

The principle of the present experimental method is shown in Fig. 1. As the COINTOF technique is a part of a tandem mass spectrometry technique (MS-MS), a prerequisite is to produce a mass-and-energy selected primary beam of parent (precursor) ions. The generation of such a mass-and-energy selected ion beam in the recently constructed DIAM device has been described in detail elsewhere [15]. Briefly, protonated water cluster ions are produced by electron impact ionization of neutral clusters produced in a supersonic nozzle expansion of water vapor. They are accelerated to energies in the 2–8 keV range and mass selected by a double focusing sector field mass spectrometer [5]. For the present CID experiments, the energy and mass-selected $H^+(H_2O)_n$, beam is crossed with an effusive argon gas jet, whose density is controlled in order to ensure single collision conditions in the CID region.

The time-of-flight apparatus COINTOF is mounted right after the collision region along the direction of the incident cluster ion beam, as shown in Fig. 1. In general, a single dissociative collision of a $H^+(H_2O)_n$, parent ion with an Ar atom will produce a daughter ion and one or more neutral fragments. The charged species thus formed are then extracted from the collision area and accelerated by an electric field in the acceleration zone (between 1.7 and 2.4 kV) before reaching a field-free zone. Consequently, the various charged fragments are separated from the neutral ones depending on their mass-to-charge ratio. On the other hand, the velocity of the neutral fragment(s) is close to the initial velocity of the parent ion, and the respective arrival time serves as an internal time reference for each single collision event. All fragments are then detected by the same detector with the charged fragment arriving significantly earlier than the neutral species.

In addition, the charged fragments can also be deflected by an electrode (pusher), thus allowing one to spatially separate the impact position of the charged fragments on the detector according to their mass-to-charge ratio.

The detector consists of a microchannel plate detector (MCP, Hamamatsu) hocked up to a delay line anode (DLA, RoentDek). The MCP setup is designed geometrically in such a way as to ensure that all the fragments from a single CID event can reach this detector. The signal(s) produced is (are) sampled by a fast analog-to-digital converter (ADC 8 GHz/10 bits from Acqiris[®], Agilent) during a given recording time window. In addition, the whole setup allows one to deduce the impact position of each detected fragment: The electron avalanche produced by a specific fragment at the MCP reaches the DLA located directly behind the MCP. The DLA is composed of two perpendicular layers of wires constituting a two-dimensional (2D) mesh, thus allowing one to collect the electrons from the MCP. Thereby the detection positions (vertical and horizontal) are determined by measuring the arrival time differences of the pulses propagating to both ends of the wires. The spatial resolution of the DLA is around 0.1 mm.

The intensity of the initial parent ion beam is controlled in such a way as to ensure that only the fragments of one single parent ion can reach the detector during the recording time window. Therefore, the correlation between the arrival times of the charged and neutral fragments produced by the dissociation of one single parent ion can be recorded. For each dissociated parent ion, the difference ΔT between the arrival time of the charged fragment and neutral fragment(s) is characteristic of the mass-to-charge ratio(s) of the charged species produced. A "charged fragment mass spectrum" is constructed from successive measurements of the arrival time differences ΔT for a large number of cluster ion dissociation events. A characteristic example is given in Fig. 2. The event-by-event analysis is performed by using the ROOT software [16].

The present CID measurements using the COINTOF technique have been carried out for $H^+(H_2O)_{n=2-8}$ cluster ions colliding at 8 keV with an argon gas target. At a collision energy of 8 keV the ensuing (limited) energy transfer mostly induces unimolecular evaporation of water molecules [17]. Therefore, after an interaction with the argon gas target $H^+(H_2O)_n$, parent ions can dissociate via *n* different dissociation channels, each one corresponding to the loss of a given number of water molecules. Each dissociation channel can then be identified by a specific product ion, $H^+(H_2O)_{n-1}$, $H^+(H_2O)_{n-2}...H^+$, with their respective branching ratio $R_{i=1}^n, R_{i=2}^n...R_{i=n}^n$. Branching ratios are labeled R_i^n , where *i* represents the number of water molecules lost from the



FIG. 2. The mass spectrum of charged fragments produced by CID of 8-keV $H^+(H_2O)_3$ on an argon gas target.

precursor ion $H^+(H_2O)_n$, after the collision. The protonated water trimer $H^+(H_2O)_3$, if used here (see Fig. 2) as an example to illustrate the method, can thus in principle dissociate via three decay channels leading to $H^+(H_2O)_2$, $H^+(H_2O)$, and H^+ fragments, with the respective branching ratios R_1^3 , R_2^3 , and R_2^3 .

The mass spectrum of the charged fragments as shown in Fig. 2 is generated by plotting the difference of the arrival times between the accelerated fragment ion and the respective neutral water molecule(s) produced via CID of the $H^+(H_2O)_3$ cluster ions. Thus, the arrival time difference characterizes the mass-to-charge ratio of the fragment ions and allows the identification of each peak in Fig. 2 to a given dissociation channel. The background noise corresponds to random events without correlation.

For the CID of $H^+(H_2O)_n$, the branching ratio of the first dissociation channel, R_1^n , associated with the loss of a single water molecule is defined as

$$\frac{1}{R_1^n} = 1 + \sum_{i=2}^n \frac{R_i^n}{R_1^n},$$
(1a)

$$\frac{1}{R_1^n} = 1 + \sum_{i=2}^n \frac{N_i}{N_1} \frac{1}{\sum_{j=1}^i \frac{i!}{(i-j)!j!} (\varepsilon_0)^{j-1} (1-\varepsilon_0)^{i-j}},$$
 (1b)

where R_i^n is the branching ratio associated with the loss of *i* water molecule(s) for the protonated water cluster H⁺(H₂O)_n, and N_1 is the number of H⁺(H₂O)_{n-1} ions detected in correlation with a water molecule resulting from the loss of a single water molecule. The quantity N_i is the number of H⁺(H₂O)_{n-1} ions detected in correlation with at least one of the water molecules resulting from the loss of *i* water molecules. The values for N_i and N_1 are obtained by calculating the area under each of the peaks in the fragment ion mass spectrum using Lorentzian fits and background noise corrections.

Finally, ε_0 is the detection efficiency for the neutral water molecule. It has to be determined from a specific dissociation channel. In particular, for the loss of a single molecule, in this case an adapted voltage value set on the pusher is used to separate spatially the H⁺(H₂O)_{*n*-1} ions from the incident H⁺(H₂O)_{*n*}, cluster ion beam (see Fig. 3). The number of H⁺(H₂O)_{*n*-1} ions detected in coincidence with the water





FIG. 3. (Color online) Distribution of impact positions on the detector surface of the charged fragments and the neutral fragment for CID of 8-keV $H^+(H_2O)_3$ on an argon gas target. Also shown to the left (y axis) and below (x axis) are the respective projections of these impact signals.

molecule divided by the total number of $H^+(H_2O)_{n-1}$ ions detected gives the detection efficiency for the water molecule. The value for this detection efficiency value lies in the range of 4%–34%, with the larger values at larger velocities of the molecule. These values are in agreement with those available in literature [18].

The corresponding total charged fragment production cross sections for 8-keV $H^+(H_2O)_n$, σ , can be calculated as follows:

$$\frac{N_{\text{undiss}}}{N_{n-i}} = \frac{\varepsilon_+ N_{\text{inc}} (1 - \sigma x)}{\varepsilon_+ N_{\text{inc}} R_i^n \sigma x},$$
(2a)

$$\sigma = \frac{1}{\left(1 + \frac{N_{\text{undiss}}}{N_{n-i}} R_i^n\right) x},$$
(2b)

where N_{undiss} is the number of undissociated $\text{H}^+(\text{H}_2\text{O})_n$, ions from the incident beam, N_{n-i} is the total number of $\text{H}^+(\text{H}_2\text{O})_{n-i}$ resulting from the loss of *i* water molecules, N_{inc} is the number of incident projectiles, ε_+ is the detection efficiency for the charged fragment, *x* is the argon gas target thickness, and R_i^n is the branching ratio associated with the loss of *i* water molecules. The cross sections determined by Eq. (2b) do not include electron-capture processes.

Note that the detection efficiency of $H^+(H_2O)_n$, and $H^+(H_2O)_{n-1}$ ions is assumed to be equal. Indeed, Peko and Stephen showed that the detection efficiencies for charged fragments are almost independent of the mass-to-charge ratio above a kinetic energy of 1 keV upon impact on a MCP detector [18].

As for the determination of the detection efficiency of water molecules, the determination of N_{undiss} and N_{n-i} requires the use of the pusher in order to separate spatially the incident projectiles $\text{H}^+(\text{H}_2\text{O})_n$, from the $\text{H}^+(\text{H}_2\text{O})_{n-1}$ fragment ions. Later on, σ [Eq. (2b)] will be deduced from R_1^n since



FIG. 4. (Color online) Ion impact distribution as projected onto the y axis corresponding to the detected $H^+(H_2O)_2$ fragments (solid blue line) and $H^+(H_2O)_3$ fragments (solid red line) and their respective fit (dotted blue line and dotted red line).

 $H^+(H_2O)_{n-1}$ is the most relevant fragment when charged fragments are spatially separated.

Again, in the example of the protonated water trimer, Fig. 3 allows one to identify three different products from top to bottom: the undeflected neutral water molecules located around the center of the detector, below that the undissociated $H^+(H_2O)_3$ ions, and, even further down in the y position, the fragment ions $H^+(H_2O)_2$ resulting from the loss of one water molecule.

It can be seen from Fig. 3 that the distribution of fragments is homogeneous in both spatial directions. However, as a consequence of the direction of the applied pusher voltage, the incident $H^+(H_2O)_3$ ion beam and the $H^+(H_2O)_2$ fragment ion beam are slightly shifted to negative y positions, and we use in the following the y-axis projection of the impact position for further analysis (see Fig. 4). Figure 4 represents a closeup of the y-axis projection, where N_{n-i} and N_{undiss} can be extracted owing to Gaussian fits (dotted blue curve and dotted red curve, respectively).

The target thickness *x* necessary to determine absolute cross sections [Eq. (2)] can be obtained by using a known cross section as a reference point. Here the calibration is performed with the cross section for single electron capture of a 7-keV He⁺ colliding with an argon atom target from Rudd *et al.* [19]. In the flow regime and the range of target thickness used, the target thickness appears to be proportional to the residual gas pressure in the collision chamber. This result is in agreement with Troitskii's vapor flow model [20].

III. RESULTS AND DISCUSSION

Table I gives the values for branching ratios measured for each dissociation channel for a given size of the protonated water clusters (n = 2-8). Each mean value of R_i^n is obtained from several experimental runs. The accuracy given by the standard deviation lies between 5% and 10% for R_1^n to R_{n-1}^n , respectively. It arises from the accuracy of the determination of N_{n-i} and N_{undiss} and from the accuracy of the measured efficiency ε_0 for the detection of the neutral fragments. The statistical error for the branching ratios for the production of the H⁺ ions is much larger, i.e., 20%–50%, mainly due to the small number of such events.

Figure 5 displays the branching ratios associated with the dissociation of a given precursor size as a function of the number of water molecules lost. Several conclusions can be drawn from the results shown in this figure.

(i) The general trend shows a decrease of R_i^n with the increase of *i*. This would be in line with the general understanding of a sequential evaporation process leading to this type of distribution of fragment ions. The smaller the precursor size, the larger is the trend. It is especially large for very small precursors n = 2 and 3, moderate for n = 4 and 5, and very soft for larger precursor sizes, indicating that the underlying mechanisms are certainly size dependent. In addition to this general trend, the figure exhibits interesting specific trends to be noted.

(ii) The loss of a single molecule (as expressed by R_1^n) is the dominant fragmentation channel for *n* up to 5. See also below the discussion of the variation between the two ion groups, i.e., the H⁺(H₂O)_{*n*=2-5} and H⁺(H₂O)_{*n*=6-8} cluster ion groups.

(iii) Nevertheless, for each studied size n (n > 3), we observe a relative maximum in the value of the branching ratio for the formation of the H₃O⁺ ion by the loss of n - 1 water molecules (R_{n-1}^n). This would indicate that at least two different mechanisms are operative, one involving sequential evaporation from the initially excited parent ion leading to a fragment n - 1, n - 2, and so on, and one where in one step the H₃O⁺ ion is produced.

(iv) Finally, a weak production of H^+ ions, representing at most 2.5% of the total dissociation of any of the precursor ions, is observed and reported here.

The change in the general evolution of branching ratio values between the $H^+(H_2O)_{n=2-5}$ and $H^+(H_2O)_{n=6-8}$ cluster ion groups deserves some more comments. For *n* from 2 up to

TABLE I. Values for the branching ratios for CID of 8-keV $H^+(H_2O)_{n=2-8}$ cluster ions colliding with an argon gas target. The branching ratio R_i^n is related to the loss of i water molecules.

$H^+(H_2O)_n$, precursor	R_1^n	R_2^n	R_3^n	R_4^n	R_5^n	R_6^n	R_7^n	R_8^n
$H^{+}(H_{2}O)_{2}$	0.975 ± 0.049	0.025 ± 0.005						
$H^{+}(H_{2}O)_{3}$	0.552 ± 0.028	0.439 ± 0.027	0.009 ± 0.002					
$H^{+}(H_{2}O)_{4}$	0.449 ± 0.022	0.240 ± 0.012	0.306 ± 0.015	0.005 ± 0.002				
$H^{+}(H_{2}O)_{5}$	0.400 ± 0.020	0.229 ± 0.011	0.158 ± 0.008	0.211 ± 0.011	0.0024 ± 0.0005			
$H^{+}(H_{2}O)_{6}$	0.214 ± 0.011	0.269 ± 0.013	0.157 ± 0.008	0.156 ± 0.009	0.203 ± 0.010	0.0021 ± 0.001		
$H^{+}(H_{2}O)_{7}$	0.214 ± 0.011	0.228 ± 0.011	0.181 ± 0.018	0.119 ± 0.011	0.114 ± 0.006	0.143 ± 0.010	0.0010 ± 0.0003	
$\rm H^+(\rm H_2O)_8$	0.181 ± 0.009	0.182 ± 0.017	0.157 ± 0.014	0.149 ± 0.013	0.100 ± 0.009	0.109 ± 0.005	0.120 ± 0.011	0.0008 ± 0.0002



FIG. 5. (Color online) Values of the branching ratios for CID of 8-keV $H^+(H_2O)_{n=2-8}$ cluster ions colliding with an argon gas target.

5, the loss of a single molecule (R_1^n) prevails over all the other dissociation processes, and the value of $R_{i>1}^n$ decreases significantly with *n* except for the observed relative increase of R_{n-1}^n . For the three largest clusters studied here (n = 6, 7, and 8), no branching ratio value clearly stands out. However, the loss of two water molecules appears to be more favorable than the loss of a single molecule (e.g., $R_2^6 = 26.9 \% > R_1^6 = 21.4 \%$ and $R_2^7 = 22.8 \% > R_1^7 = 21.4 \%$) or is of the same order of magnitude ($R_2^8 = 18.2 \% > R_1^8 = 18.1 \%$). These losses of two H₂O lead to the production of $H^+(H_2O)_4$, $H^+(H_2O)_5$, and $H^+(H_2O)_6$, respectively. Note that Dawson [12] also observed the increase of R_2^6 relative to R_1^6 for CID of H⁺(H₂O)₂₋₆ on argon gas targets in the collision energy range up to 50 eV. Besides, Armentrout et al. [8] observed the decrease of the branching ratio for the loss of i water molecules for the $H^+(H_2O)_{2 \le n \le 6}$ on the xenon gas target at a much lower energy (20 eV) only involving the sequential evaporation process. We observe that the branching ratio $R_{i>2}^{n=6-8}$ decreases less significantly with larger *i*; this effect is more and more pronounced for larger cluster sizes n (see Fig. 5). In addition, an increase in the production of H₃O⁺ is also observed, but a rise in the production of $H^+(H_2O)_2$ fragments is noted, growing with $n \ (R_4^6 = 15.6\%, R_5^6 = 20.3\%; R_5^7 = 11.4\%, R_5^7 = 14.3\%; R_6^8 = 10.9\%, R_7^8 = 12.0\%).$

In collision processes, the energy transferred during the collision to the colliding partners influences the subsequent fragmentation. The production of H⁺ fragments from CID experiments suggests that sufficient energy has been deposited to dissociate $H^+(H_2O)_n$, all the way down to the naked proton. Cooks and co-workers evaluated the distribution of internal energy after CID for 7-keV $Fe(CO)_5^+$ ions with a gas-phase argon target [21]. From these and other collision experiments in the keV energy range, we can deduce that the internal energy transfer to the molecular ion systems is distributed roughly in the following way: $< 4 \text{ eV} (70\%), 4 - 8.5 \text{ eV} (20\%), 8.5 - 8.5 \text{ e$ 12 eV(8%), and > 12 eV(2%) [21–24]. Moreover, the energy threshold to evaporate a single water molecule is between 0.4 and 1.2-1.4 eV [8,25,26] for the sizes studied here. In contrast, the proton affinities of $H^+(H_2O)_{n=2-8}$ have been estimated to increase from 7.2 to 9.3 eV [9,11,27] when going from n = 2 to 8. These values explain also the low H⁺ production probability

which represents the least favorable dissociation process for each cluster size studied.

The structure of protonated water clusters has been extensively studied and it is admitted that they are built from two possible protonated cores: the Eigen and the Zundel structures [28]. The Eigen type consists of a proton strongly bound to a single water forming H_3O^+ , the hydronium ion, while in the Zundel type the proton is shared between two water units forming $H_2O \dots H^+ \dots OH_2$. Looking at the different studies on the structures of protonated water clusters [14,29–31], it appears that the isomers of the $H^+(H_2O)_{n=3-5}$ ions preferentially exist in Eigen forms and $H^+(H_2O)_{n=2,6-8}$ ions in Zundel forms.

For H⁺(H₂O)₆, in the results presented in Refs. [30,31], the minimum energy isomers are shown to be composed of a mixture of Zundel and Eigen types. Nevertheless, the Zundel form is predicted to be lowest in energy by the *ab initio* calculation performed by Jiang *et al.* [14]. For H⁺(H₂O)₇ the five-membered-ring structure is identified to be minimum in energy in Refs. [14,29]. These configurations could explain our values of branching ratios for the loss of one and two water molecules (R_1^7 and R_2^7). Indeed, it seems easier to lose the water molecules outside of the ring, the inside ones being more strongly bound. For H⁺(H₂O)₈, Refs. [14,29] identified a Zundel-type geometric shape as the minimum energy isomer. *Ab initio* calculations by Jiang *et al.* [14] tend to show that the isomer containing a five-membered ring is lowest in energy.

In regard to these calculated and observed isomer structures, it seems easier or of the same order of magnitude for a protonated water cluster $H^+(H_2O)_{n=6-8}$ to lose two water molecules rather than a single molecule. This could explain the increase of $R_2^{n=6-7}$ observed for these clusters. The increase of $H^+(H_2O)_2$ production suggests that $H^+(H_2O)_{n=6-8}$ indeed exists in Zundel form. However, we still observe a high rate of R_1^n , which can be interpreted as reflecting the coexistence of several isomers including Eigen isomers. Indeed, in the present experiment, the protonated water clusters are produced with a relatively large internal energy because of their formation by electron impact [15]. As the different isomers are close in energy [14], several isomers can coexist in the mass-selected incident beam.

It has to be noted that the present experiments have been done for incident beams of the same energy and not of the same velocity. Nevertheless, in this relatively low-energy range, a

TABLE II. Values of the CID cross sections (without considering electron-capture processes) for 8-keV $H^+(H_2O)_{n=2-7}$ ions on an argon gas target.

Incident protonated water cluster $H^+(H_2O)_n$	Cross sections of the 8-keV H ⁺ (H ₂ O) ₂₋₇ CID on an argon gas target (10^{-16}cm^2)
$H^{+}(H_{2}O)_{2}$	1.59 ± 0.11
$H^+(H_2O)_3$	3.82 ± 0.26
$H^+(H_2O)_4$	5.27 ± 0.18
$H^+(H_2O)_5$	7.71 ± 0.56
$H^{+}(H_{2}O)_{6}$	13.53 ± 0.87
$H^+(H_2O)_7$	16.22 ± 0.41



FIG. 6. Present cross-section values for CID of 8-keV $H^+(H_2O)_{n=2-7}$ colliding with an argon gas target as a function of *n*, the protonated water cluster size, in a log-log scale (inset: the same results in a linear scale), designated by solid circles. Open diamonds represent the value measured by Tomita *et al.* [10] for attenuation cross sections of 50-keV $H^+(H_2O)_n$, on an xenon gas target. Open squares represent the values measured by Tomita *et al.* for attenuation cross sections of 50-keV $H^+(H_2O)_n$, on a helium target.

comparison between the various sizes, as is usually done in CID experiments, remains relevant.

Table II gives CID cross sections (without considering electron-capture processes which are not accounted for in the present experimental arrangement) of the 8-keV $H^+(H_2O)_{n=2-7}$ ions colliding with an argon gas target. For these clusters, the cross-section value increases with increasing cluster size. Uncertainties in Table II range from 2% up to 7%. As in the case of the branching ratios, the cross sections are also determined with a standard deviation derived from several experimental runs.

As already mentioned above, only a few experiments on CID of mass-selected protonated water clusters include the measurement of CID cross sections. For instance, Dawson [12] reported the estimation of branching ratios for the loss of one, two, and three water molecules and the determination of cross sections for $H^+(H_2O)_{2-6}$ cluster ions colliding with methane and argon gas targets in the collision energy range up to 50 eV. Tomita *et al.* [10] measured attenuation and fragmentation cross sections for $H^+(H_2O)_{1-100}$ cluster ions colliding with helium and xenon gas at a collision energy of 50 keV. In the present case the electron-capture process is excluded in the measured cross section, thus our cross sections are total charged fragment production cross sections.

Taking into account that the gas target and the incident ion energy are different, a relatively good order of magnitude agreement is observed between the two experiments (the present one and the one of Tomita *et al.* [10]) shown in Fig. 6. Nevertheless, the present results increase more rapidly when increasing the incident cluster size than the data from Tomita et al. [10]. This could be explained by the relative importance of the electron-capture process in comparison to the other dissociation channels as a function cluster size, i.e., the former being approximately constant with increasing cluster size [32]. We can mention that, in collision-induced fragmentation of water-solvated anions of adenosine 5'-monophosphate (AMP) with Na atoms, Liu et al. [33,34] observed that the electron-capture process leads to a more important damaging effect when increasing the number of initially attached water molecules while they observed a protective behavior of the water molecules for collision-induced dissociation processes without electron transfer.

In addition, we observe a break in the value of the cross sections between n = 5 and 6 (see the inset in Fig. 6). This break cannot be explained by the fact that the sixth or the seventh water molecule of $H^+(H_2O)_{n=6-7}$ is less bounded than the fifth. Indeed, the branching ratio value associated with the loss of a single water molecule is smaller than the one associated with the loss of two molecules $(R_1^{n=6-7} < R_2^{n=6-7})$ for these two clusters. Thus this break could be induced by a structural change in the cluster, as already observed in the branching ratio results between the two $H^+(H_2O)_{n=2-5}$ and $H^+(H_2O)_{n=6-8}$ cluster ion groups.

IV. CONCLUSION

In this paper we have demonstrated the ability to measure cross sections and branching ratios using the recently developed COINTOF technique [13]. The present study is dedicated to the interaction of mass-and-energy selected $H^+(H_2O)_{2-8}$ beams with an argon gas target at an energy of 8 keV. The set of cross sections for the $H^+(H_2O)_{2-7}$ clusters presented here corresponds to the measurement of total charged fragment production cross sections after excitation without electron capture. The corresponding branching ratios are given for the protonated water cluster $H^+(H_2O)_n$, in the size range up to n = 8 and for each possible dissociation channel all the way to the production of H^+ .

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