

3D Imaging of the Collision-Induced Coulomb Fragmentation of Water Molecules

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The multiple ionization and fragmentation of H_2O by fast H^+ and He^+ ions was studied using a position- and time-sensitive multiparticle detector. By the coincident measurement of correlated fragment momenta a complete three-dimensional image of the breakup process can be obtained for *each individual event*. Of special interest is the process $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^+$ where a simple Coulomb explosion model is insufficient to explain the measured fragmentation energies and angular correlations. Better agreement is achieved with *ab initio* multiconfiguration self-consistent field calculations of the intermediate H_2O^{3+} parent ion.

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Ion impact-induced fragmentation of molecules is a process of fundamental importance in many areas of science and technology, for example, radiation damage to biological tissue (especially in the case of H_2O) [1], in astrophysics and the physics and chemistry of upper planetary atmospheres [2]. In spite of this broad ranging interest, and in contrast to studies of molecular breakup following electron bombardment (cf., e.g., [3,4] and references therein), ion impact-induced fragmentation has yet received comparatively little attention. Most work so far has concentrated on individual reaction products without further attention to the correlated behavior of the remaining fragments (cf., e.g., [5] and references therein). Exceptions can be found in studies of the dissociation of diatomic molecules where the correlation of both fragments has been studied in detail (e.g., [6–9]), and in the “Coulomb explosion” studies of the Argonne/Weizmann cooperation [10–12]. This latter work is of particular interest since *all* fragments from a particular breakup of even larger molecules can be detected *in coincidence*. To achieve this, the molecule under study is passed at great speed through a very thin foil. The outer electrons are stripped off, and the fragments from the ensuing Coulomb explosion are detected typically with MeV laboratory kinetic energies in a time- and position-sensitive device. Recently, for example, this technique has been employed to determine the H_2O^+ bond angle [13]. As powerful as it may be, this technique is in practice only applicable to molecular ions with energies of at least several MeV, and the data analysis is complicated by the complex ion-foil interaction. In the great majority of experimental situations, however, fragments from a molecular breakup process will emerge with low kinetic energies only. A typical experiment employs, after the dissociation process, an ionization or acceleration of the reaction products to keV energies, and fragment detection in a time-of-flight (TOF) spectrometer.

In this Letter we report on the application of a new device to the study of the ion impact-induced Coulomb fragmentation of H_2O molecules. We are able to establish correlations between low-energy fragments from

the molecular breakup process by coincident detection of *all* fragments in a time- and position-sensitive detector. Thus, a three-dimensional image of the breakup process can be obtained. In contrast to earlier correlation studies (e.g., [6–8]) more than two fragments can be detected in coincidence; in other work we have already detected as many as five fragments in coincidence [14].

Details of the experimental technique have already been published [15]. We will therefore give only a brief account of the experimental setup. Collimated beams of H^+ and He^+ projectiles from a 350 keV ion accelerator interact with a H_2O gas target. Slow ions and electrons generated in the collision are separated by a weak homogeneous electric field ($E_s = 200$ V/cm) perpendicular to the primary beam. Electrons are detected in a channeltron at one side of the interaction region; positive ions are accelerated toward the position- and time-sensitive multiparticle detector [15] at the other side, being essentially a channelplate multiplier with a crossed-wire anode structure. The ions pass a field-free time-of-flight region before they are accelerated a second time to a few keV to increase the detector efficiency. The first electron registered in the channeltron serves as a start pulse for the detection system. For all positive fragments from one particular breakup process their position on the detector (x_i, y_i) and the time of flight τ_i relative to the start electron are recorded.

The present setup allows the separation and simultaneous measurement of all reaction channels which result in at least one electron and one or more positive fragments. From the data the associated relative rates can be obtained; furthermore, the fragmentation energy and angular correlations for *each individual event* can be derived. As a first example Fig. 1(a) shows the production rates for several ion species which appear in 100–350 keV $\text{H}^+-\text{H}_2\text{O}$ collisions. The measured relative data were normalized at 350 keV to absolute cross sections from Edwards and co-workers [16–18] for H^+-H_2 collisions using a mixed $\text{H}_2 + \text{H}_2\text{O}$ gas target [19]. The total positive ion production cross section is compared to absolute cross sections for the production of positive ions from

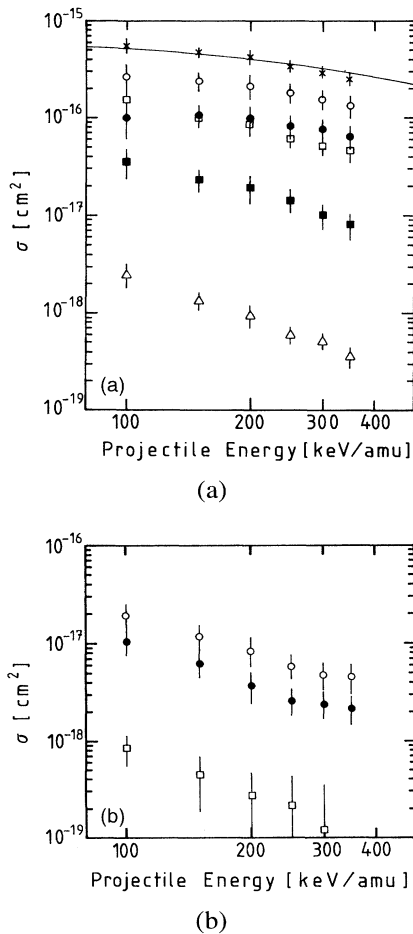


FIG. 1. (a) Cross sections for production of selected positive ions in H^+ - H_2O collisions: \circ H_2O^+ , \square H^+ , \bullet OH^+ , \blacksquare O^+ , and \triangle O^{++} . The sum of these data (\times) is compared to the total cross section for the production of positive ions from Rudd *et al.* (—). (b) Cross section for complete fragmentation in H^+ - H_2O collisions: \circ , $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^{0,-}$; \bullet , $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^+$; and \square , $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^{++}$.

Rudd *et al.* [1] showing good agreement. Figure 1(b) shows cross sections for the complete fragmentation channels $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^+$ and $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^{++}$ obtained by the coincident detection of correlated fragments. The rates of these processes are surprisingly large, e.g., in the first case about 1 order of magnitude larger than for $\text{H}_2 \rightarrow \text{H}^+ + \text{H}^+$. Since at present the setup is sensitive to positive ions only, neutral O and O^- fragments cannot be detected, and the data for the $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^{0,-}$ channel were derived from the $\text{H}^+ + \text{H}^+$ coincidences.

Of special interest is the dynamics of the complete fragmentation processes $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^{q+}$ ($q \geq 1$) where all three resulting positive ions are detected in coincidence. The measured flight times and positions on the detector allow the calculation of angular correlations and

the released total kinetic energy for each individual event. A practical choice of characteristic variables consists of the angles χ and θ_v in velocity space as defined in the inset in Fig. 2. These velocity-space coordinates contain the information about the geometric structure of the molecule at the instance of fragmentation. In particular, the angle χ between the velocity of the O^{q+} ion and the $\text{H}^+ - \text{H}^+$ relative velocity may be used as a criterion to decide whether the two H-O bonds break simultaneously or in a sequential (stepwise) fashion. Following the notation of Strauss and Houston [20] the process $ABC \rightarrow A + B + C$ is called *concerted* if all bonds of the parent molecule break in a time which is short on the time scale defined by the rotation and vibration periods of the system. The interpretation of χ is facilitated by a closer look at the extreme cases. In a strictly concerted fragmentation which always results in a particular set of momentum vectors, the value of χ would be fixed, and the distribution of $\cos \chi$ would be a δ function. A molecule, however, is not a rigid structure, and thus the δ function degenerates into a more or less narrow peak. In case of a stepwise fragmentation, on the other hand, the intact OH subsystem may rotate around its center of mass before dissociation. This should result in a uniform distribution of $\cos \chi$ if the associated breakup times were long compared to the time of rotation. Figure 2 shows a measured $\cos \chi$ spectrum for 100 keV H^+ impact together with a Monte Carlo simulation of a strictly concerted fragmentation which is based on the multiconfiguration self-consistent field (MCSCF) calculation described below. The widths of both distributions are in reasonable agreement, thus indicating that the $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^+$ fragmentation is mainly a concerted process, i.e., both H-O bonds break almost at the same time. The same holds in case of $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O}^{++}$ for both H^+ and He^+ impact at all energies studied.

The angle θ_v defined by the $\text{H}^+ - \text{O}^+$ relative velocities is shown in Fig. 3. In case of known molecular potentials a backtransformation from velocity space to internal

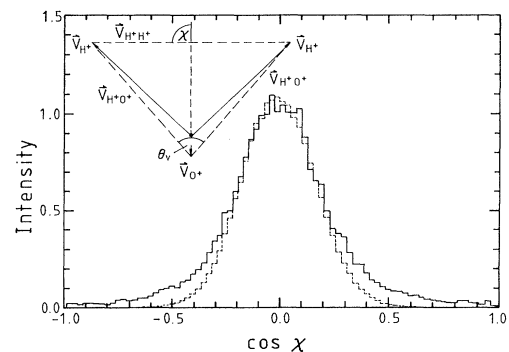


FIG. 2. $\cos \chi$ distribution of $\text{H}^+ - \text{H}^+ - \text{O}^+$ coincidences from collisions of 100 keV He^+ on H_2O (—). (---) Simulation based on a MCSCF calculation assuming a concerted breakup of both H-O bonds.

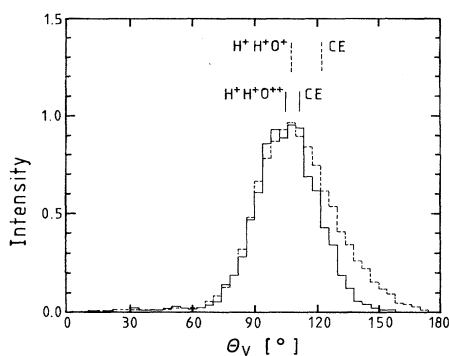


FIG. 3. Distribution of θ_v for coincident $\text{H}^+-\text{H}^+-\text{O}^+$ (---) and coincident $\text{H}^+-\text{H}^+-\text{O}^{++}$ triples (—) in 250 keV $\text{He}^+-\text{H}_2\text{O}$ collisions. The maxima of the experimental curves and the values calculated by a pure Coulomb model are marked.

molecular coordinates is in principle possible [13]. Note that due to the H^+-H^+ repulsion the observed θ_v values are in general somewhat larger than the bond angle $\theta_0 \approx 105^\circ$ of the water molecule. With higher charge states $\text{H}_2\text{O}^{(q+2)+}$ the H^+-O^{q+} repulsion becomes dominant, and θ_v approaches the bond angle; at even higher charge states even values $\theta_v < \theta_0$ are possible. In the case of H_2O^{3+} and H_2O^{4+} , however, the model of a simple Coulomb explosion (CE) is insufficient: The angles predicted by a pure Coulomb potential are significantly larger than the maxima of the measured distributions (Fig. 3), although the deviation is already smaller in the case H_2O^{4+} .

The weakness of the pure Coulomb explosion model becomes even more obvious in the total kinetic energy spectrum of correlated $\text{H}^+-\text{H}^+-\text{O}^+$ triples (Fig. 4). Whereas the angular distributions are similar for all projectiles, the shapes of the corresponding energy distributions show a strong dependence on the projectile species, again in contrast to a simple Coulomb explosion model. Several competing processes which all result in three positive fragments must be involved to explain the observed behavior. To account for the most dominant reaction

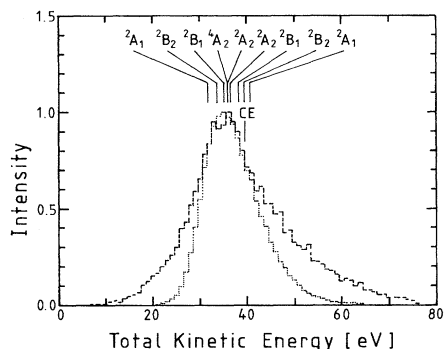


FIG. 4. Total kinetic energy distribution of coincident $\text{H}^+-\text{H}^+-\text{O}^+$ fragments from collisions of H_2O with 250 keV He^+ (—). The dotted line is a MCSCF calculation taking into account the indicated molecular states of H_2O^{3+} .

paths, we applied the MOLPRO code [21,22] to an *ab initio* MCSCF calculation of the nine lowest molecular states in the intermediate H_2O^{3+} ion. For each of the nine energy surfaces the resulting total kinetic energy spectrum of the fragment ions was calculated by Monte Carlo techniques. In a first step a Franck-Condon transition from the H_2O ground state to the particular dissociating H_2O^{3+} state was assumed in order to derive the starting point for the subsequent dissociation along the potential surface. This method is a generalization of the “reflection approximation” which is often used to analyze the dissociation of diatomic molecules [23,24]. The calculated energy and angular distributions show a distinct dependence on the occupation of the orbitals in the H_2O^{3+} ion [25]. The simulated energy spectra were convoluted with the response function of the detector system. Since no detailed calculations of transition strengths are available, we assumed an $1/E_i^2$ dependence (with E_i the excitation energies of the corresponding intermediate states of H_2O^{3+}) which has proven to be a useful approximation in other fields as, e.g., inner shell ionization. The maxima of the individual distributions and their weighted sum are shown in Fig. 4. A comparison with the spectrum measured in 250 keV $\text{He}^+-\text{H}_2\text{O}$ collisions reveals reasonable agreement, though there are deviations at the low- and high-energy edge of the distribution which may be attributed to the neglect of even higher excited states in H_2O^{3+} (note that a higher excited state does not necessarily imply a higher released kinetic energy). First measurements at the KVI in Groningen show an even better agreement for 96 keV $\text{O}^{6+}-\text{H}_2\text{O}$ collisions; in such “gentle” multiply ionizing collisions excited states are expected to be less important in agreement with the experimental finding.

To conclude, we presented first results of the complete ionic fragmentation of H_2O . The experimental technique allows a very detailed study of such fragmentation processes. To our knowledge, this is the first time that the *complete* impact-induced molecular breakup with more than two fragments has been studied. The obtained data include cross sections for the production of individual ions and for various complete fragmentation processes as well as information on the dissociation dynamics, as, e.g., dissociation energies and angular correlations. An application of the detector system to other fields, e.g., photodissociation and cluster collisions appears straightforward and may provide an interesting extension to the correlation method used in the work of Codling and co-workers [26]. Since the results of such studies are very detailed and thus also more accessible to interpretation, we are confident that such measurements will also provide a stimulus to further theoretical work which is as yet quite scarce.

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