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Event-by-Event Analysis of Collision-Induced Cluster-Ion Fragmentation: Sequential Monomer Evaporation versus Fission Reactions

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The most abundant decay channels have been studied quantitatively for high-energy (60 keV/amu) cluster ions $\text{H}_3^+(\text{H}_2)_{m=1-14}$ colliding with He atoms employing a recently developed multicoincidence technique for the simultaneous detection of the correlated fragments on an event-by-event basis. This allows us to identify decay reactions and their underlying decay mechanisms responsible for the occurrence of the U-shaped fragmentation pattern.

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Spontaneous fragmentation of finite systems, e.g., nuclei, molecules, clusters, has recently attracted increased interest, in particular, because of the recognition that some of the general features in the decay of these systems are rather independent of the actual system studied [1]. Therefore, one important field in cluster science [2] is the study of the characteristics of the fragmentation of excited cluster ions produced by the excitation of neutral or ionized clusters by photons, electrons, ion impact, or surface collisions.

Fragmentation after low-energy deposition has been successfully interpreted in the frame of the evaporative ensemble model [3–6] invoking the sequential evaporation of neutral monomer units for singly charged cluster ions [7] or by sequential fissionlike reactions of multiply charged cluster ions [8]. In contrast, high-energy deposition, e.g., by collisions of the clusters with high-energy heavy particles or vice versa [9–12] and by collisions of clusters with multiply charged ions [13,14], has led to bimodal fragment ion distributions which have been interpreted (i) by the presence of sequential (monomer) evaporations (see above) leading to the production of fragment ions with large masses and (ii) by the presence of multifragmentation processes leading to the formation of the fragment ions with the small masses. These bimodal distributions, sometimes exhibiting a U shape [10,12], sometimes consisting of two peaks separated by a strong minimum [9,11,13,14] have also been observed for primary mass spectra after electron impact or photon impact ionization of C_{60} and after C_{60} ions impacting a surface (see [15] and references therein). Moreover, these

distribution patterns obtained are similar to what have been seen in nuclear fragmentation [16].

Although today several experiments have measured these “total (inclusive) fragment ion mass distributions,” mostly for fullerene targets, and although the origin of this bimodal distribution is generally thought to be due to these two differing fragmentation mechanisms, knowledge on the details of multifragmentation reaction mechanisms (and its contribution to the bimodal distribution) is very scarce and mostly due to molecular simulations [17,18]. In addition, some coincidence experiments have been carried out (using either highly charged ion projectiles or charged C_{60} ion projectiles) where two fragmentation products from C_{60} have been identified, thereby providing more information on the fragmentation dynamics [11,19–23]. The fragmentation behavior is observed to be strongly dependent on the charge state of the fullerene after the collision [24] and on the nature of the projectile ion used [25].

Here we have extended these studies in several aspects. On the one side, we are using hydrogen cluster ions with different sizes $\text{H}_{n \leq 31}^+$ instead of C_{60}^+ as in the earlier studies, thus allowing us to study fragmentation as a function of cluster size n . Moreover, the protonated hydrogen clusters represent a completely different class of systems where a quantum solute is solvated by a quantum solvent; the added proton becomes trapped and a tightly localized H_3^+ core is surrounded by solvating H_2 molecules, $\text{H}_3^+(\text{H}_2)_{m \leq 14}$ [26]. On the other side, we are employing here a recently developed multicoincidence technique for the simultaneous detection (on

an event-by-event basis) of the correlated, ionized, and neutral fragments from collision of 60 keV/amu hydrogen cluster ions with a He target. This allows us to investigate for the first time in a quantitative manner (absolute cross sections) the occurrence of the various possible decay channels and their relative importance as a function of m . Focusing here on some of the most abundant decay reactions (involving the production of neutral fragments and one charged fragment), we are able (i) to distinguish experimentally the two different decay channels most important for occurrence of the U-shaped total fragmentation distribution, and (ii) to obtain novel insights about the excitation and subsequent decay mechanisms in these molecular cluster ions.

Mass selected hydrogen cluster ions with an energy of 60 keV/amu are prepared in a high-energy cluster-ion beam facility consisting of a cryogenic cluster jet expansion source (stagnation temperature of 34 K) combined with a high performance electron ionizer and a two step ion accelerator (consisting of an electrostatic field and a radio frequency quadrupole postaccelerator). After momentum analysis by a magnetic sector field, the mass selected high-energy projectile pulse (pulse length 100 ms, repetition frequency 1 Hz), consisting in the present study of $\text{H}_3^+(\text{H}_2)_{m \leq 14}$ cluster ions, is crossed perpendicularly by a helium target beam effusing from a cylindrical capillary tube. Prior to this, the ion beam is collimated by two apertures ensuring an angular dispersion of about 0.16 mrad. One meter behind this collision region the high-energy hydrogen collision products (neutral and ionized) are passing a magnetic sector field analyzer. The undissociated primary $\text{H}_3^+(\text{H}_2)_{m \leq 14}$ cluster projectile ion, or the neutral and charged fragments resulting from reactive collisions, are then detected approximately 0.3 μs after the collision event with a multidetector device consisting of an array of passivated implanted planar silicon surface barrier detectors located at different positions at the exit of the magnetic analyzer. This allows us to record for each event simultaneously the number (multiplicity) of each mass-identified fragment ion resulting from the interaction (for more experimental details, see Ref. [10] and references therein). Moreover, for each event we can also monitor in coincidence with the detected ions the sum of the masses of all the neutral fragments. From additional measurements, the identity of neutrals, either H atoms or H_2 molecules, can be inferred [27]. Thus, we are able to analyze on an event-by-event basis the identity of all fragments produced in a collision between the $\text{H}_3^+(\text{H}_2)_{m \leq 14}$ cluster ion and the He target atom, except for the distinction between H_2 and two H. The validity of single collision conditions has been ascertained by measurements at different He target pressures and allows also to derive absolute cross sections for the occurrence of specific reaction channels (partial cross sections) (for details, see [28]).

Figure 1 shows the absolute cross section as a function of cluster size m of the projectile ion $\text{H}_3^+(\text{H}_2)_m$ for one of the most abundant reaction channels, i.e., the production of

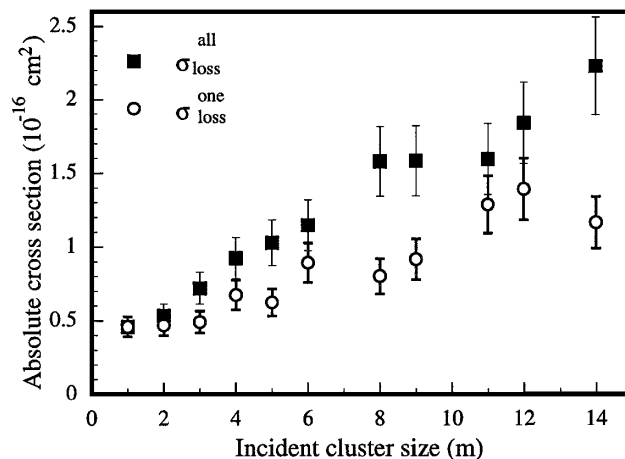
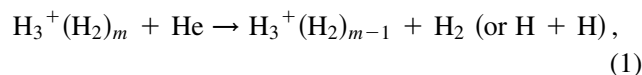
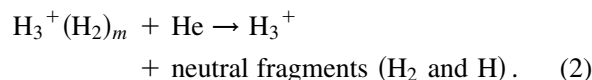


FIG. 1. Collision cross section as a function of cluster size m for the dissociation channel: $\text{H}_3^+(\text{H}_2)_m + \text{He} \rightarrow \text{H}_3^+(\text{H}_2)_{m-1} + \text{H}_2$ (or $\text{H} + \text{H}$), designated by $\sigma_{\text{loss}}^{\text{one}}$, and for the dissociation channel: $\text{H}_3^+(\text{H}_2)_m + \text{He} \rightarrow \text{H}_3^+ + \text{neutral fragments}$, designated by $\sigma_{\text{loss}}^{\text{all}}$.

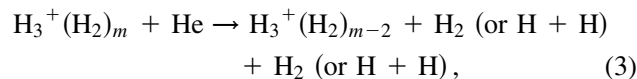
only one charged reaction product (fragment ion) by either the loss of one H_2 monomer leading to a $\text{H}_3^+(\text{H}_2)_{m-1}$ fragment ion,



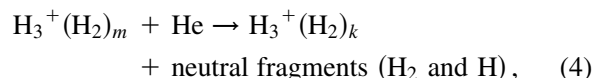
or by a reaction involving the production of the central H_3^+ core ion of these clusters via loss of all the neutral ligands:



The cross section values increase in both cases monotonously with cluster size n starting at $0.5 \times 10^{-16} \text{ cm}^2$ at the smallest cluster size $\text{H}_3^+(\text{H}_2)$ and reaching for $m = 14$ the value $1.4 \times 10^{-16} \text{ cm}^2$ for reaction (1) and $2.2 \times 10^{-16} \text{ cm}^2$ for reaction (2). This result is remarkable in two ways, firstly reaction (2) shows an unexpected strong size dependence and, secondly, reaction (2) is more effective than reaction (1). In contrast, the cross section for the loss of two H_2 monomers units via reaction (3),



stays in the $0.5 \times 10^{-16} \text{ cm}^2$ range or below for all cluster sizes studied; see also Fig. 2 which shows a biparametric (m, k) representation of the cross sections for the fragmentation channel:



with $0 \leq k < m$. It can be seen that, for each cluster size m , all possible reactions (4) (with $1 \leq k < m - 1$) have

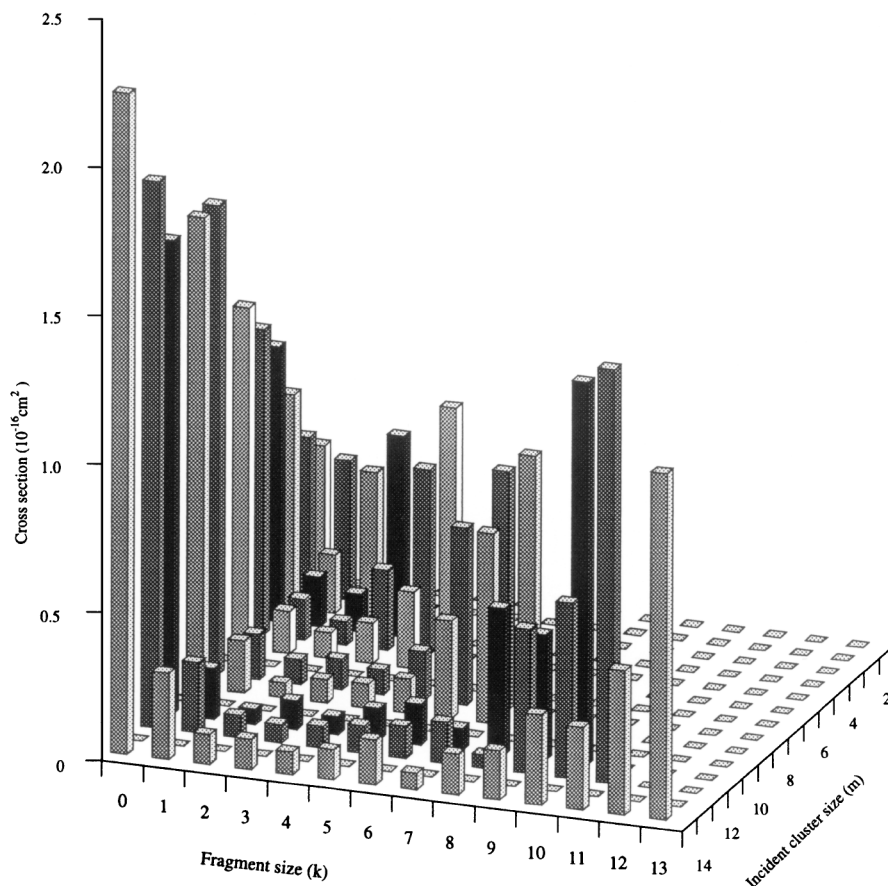
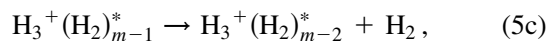
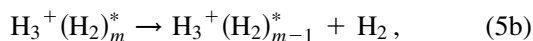
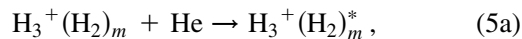


FIG. 2. Biparametric (m, k) representation of the collision cross sections for the fragmentation channel: $\text{H}_3^+(\text{H}_2)_m + \text{He} \rightarrow \text{H}_3^+(\text{H}_2)_k + \text{neutral fragments}$.

smaller cross sections than reaction (1) (with $k = m - 1$) and (2) (with $k = 0$), a fact which is responsible for the occurrence of the U-shaped total fragmentation patterns as other reactions involving more charged fragments in the exit channel are much less probable and thus have no leading influence on this pattern.

The cross section dependence observed here for reaction (1) is similar to the one observed by Reuss and co-workers [29] for collision-induced dissociation of protonated hydrogen clusters in the 250–900 eV energy range. This type of decay can be interpreted by the evaporative ensemble model, where a primary excitation event initiated by the interaction of the He atom with one of the cluster constituents [see the excitation of specific vibrational modes of one solvent molecule in the $\text{H}_3^+(\text{H}_2)_m$ ion by infrared techniques [30]], is followed by energy transfer and partitioning between all of the cluster constituents (mostly in intracluster vibrational modes) and subsequent statistical (sequential) predissociation event(s) [3–8] via



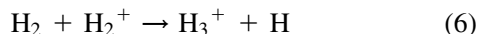
and so on. The observed increase with cluster size m at the same collision velocity simply reflects the increasing interaction volume between the reaction partners with increasing cluster size. It is interesting to note that we are operating the experiment at collision energies where direct vibrational excitation (or momentum transfer) is negligible as compared to electronic excitation (see, for instance, [31]), and thus we have to conclude that, in this case, excitation from the $\nu = 0$ of the H_2 electronic ground state to a electronically excited level into $\nu > 0$ providing the necessary (initial) vibrational motion for the statistical evaporation events.

In contrast, the size dependence for reaction (2)—reported here for the first time—cannot be explained in this way, as reaction (2) is not proceeding via sequential evaporation. The latter has been inferred indirectly from the U-shaped nature of the fragmentation pattern and other properties of the statistical decay mechanism [9,13,17,18,32], and it was concluded that reactions of type (2) are due to prompt multifragmentation events. The present results shed new light on the nature of this event. The cross section dependence immediately excludes reaction channels proceeding via a direct interaction of the He with the H_3^+ core (followed by a subsequent direct expulsion of all neutral solvent molecules by an excited H_3^+ core) as the probability for these reactions would not

depend on cluster size. Moreover, the much larger cross section for reaction (2), as compared to the one for reaction (1), excludes also the possibility of successive collisions of the He within the cluster as the probability for scattering on two solvent molecules can be estimated to be less than about 10% of the probability for single collision. In addition, we can conclude that reaction (2) does not necessarily involve the interaction of the He atom with an inner solvent molecule, but proceeds also in the case where the He interacts with a molecule of the outermost solvent shell. This can be seen by comparing the cross section for $\text{H}_3^+(\text{H}_2)_4$ [which is, according to *ab initio* calculations [26], a closed shell $\text{H}_3^+(\text{H}_2)_m$ ion with an additional weakly bound H_2 molecule] with the cross section for the closed shell $\text{H}_3^+(\text{H}_2)_3$ ion. The cross section for the former one ($0.72 \times 10^{-16} \text{ cm}^2$) is larger than for the latter one ($0.92 \times 10^{-16} \text{ cm}^2$) indicating that interaction of the He with the outer shell molecule is also contributing to the overall cross section for reaction (2) leading to the complete destruction of the cluster.

Turning now to the mechanism of reaction (2), the only plausible explanation is excitation of one of the molecules in a high enough electronic energy level to allow the subsequent destruction of the entire cluster by direct coupling of at least part of this energy into intracluster modes. In analogy to the reactions observed in argon clusters, where the excitation of a metastable excimer dimer state (within the ionized cluster) and the subsequent radiative decay of this excimer into the dimer ground state led to the sudden release of about 1 eV into two fast moving Ar atoms followed by the direct expulsion and evaporation of up to half of the monomers [33], we are proposing that reaction (2) proceeds via the excitation of a dissociative electronic state in one of the solvent molecules. It has to be noticed that the technique successfully achieved for the mass analysis of the neutral fragments (distinction between an H_2 molecule and two H atoms) in the H_3^+ fragmentation studies [34] is not practicable in the cluster case, due to the increase of the number of dissociation channels.

The dissociation of an excited H_2^* leads to the formation of two fast moving (possibly excited) hydrogen atoms in the vicinity of the H_3^+ core. Whereas part of the destruction of the cluster ion will proceed via a direct impulsive interaction (in a similar manner as observed for excimer decay reactions in rare gas cluster ions [33]), part of the destruction may also proceed via interaction of the hydrogen atom with the H_3^+ core. This is more likely, as it is well known that the reaction



is very efficient [35]. A hydrogen atom in the cluster could therefore induce a large change in the H_3^+ polarization and thereby weaken the interaction potential with the remaining neutral ligands leading to the evaporation of all the solvent molecules.

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