Electron capture in the collision of mass-selected hydrogen-cluster ions with helium atoms

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The electron capture cross sections of hydrogen-cluster ions H_n^+ colliding with atomic helium have been measured in a large range of cluster size ($5 \leqslant n \leqslant 35$) for the same velocity ($1.5v_0$, 60 keV/u). While the electron-capture cross section decreases from the H^+ ion to the H_3^+ one, the cluster electron-capture cross section is found to be independent of the cluster size and nearly equal to the capture cross section of the H_3^+ ion. The electron capture by hydrogen clusters on a helium atom is a process involving only the H_3^+ core of the cluster where the positive charge is localized. It appears that this very localized electron capture is not disturbed by the presence of molecules, up to 16, around the H_3^+ core. [S1050-2947(98)09511-0]

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I. INTRODUCTION

Hydrogen is by far the most abundant element in the universe and molecular hydrogen H_2 is known to dominate in cool regions. Otherwise, as observed in Jupiter's atmosphere, H_3^+ is supposed to have an important role in the interstellar medium as an initiator of chains of chemical reactions [1]. Recent quantum Monte Carlo simulation [2] and quantum chemical calculations [3] have investigated the effect of protonation of pure hydrogen clusters $(H_2)_n$ at low temperature. It was shown that the added proton gets trapped as a very localized H_3^+ impurity in the cluster and is surrounded by stable shells of solvating H_2 molecules. In recent years, research in cluster physics has expanded from the study of the isolated species in the gas phase to the interactions of atomic or molecular clusters with atoms, molecules, and other clusters [4]. When a beam of molecular or cluster ions collides with a gas target, there occur several competing reactions involving dissociation, electron capture, ionization, etc. In particular, electron-capture processes in ion-atom collisions play an important role in astrophysics, atmospheric physics, and plasma physics. Then, studies of electron-capture cross sections by protons [5] and molecular hydrogen ions on different targets [6] have been pursued by many investigators due also to the inherent importance of this fundamental process. In this paper, we deal with the collisional interaction of the H_n^+ mass-selected cluster ions with the helium atom where various types of elastic, inelastic, and charge-transfer processes may occur.

To our knowledge, no result on cluster electron capture is available for various cluster sizes at the same velocity. Low-velocity collisions of K_n^+ and Na_n^+ cluster ions of different sizes with a cesium vapor have been studied at a fixed energy laboratory (few keV) [7]. Total charge-exchange cross sections are measured and the resulting neutral products are shown to conserve the parent mass or evaporate by at most either one atom or dimer. Especially, cross sections for Na_n^+ clusters ranging from the monomer to the 21-mer lie between 40 and 10 Å^2, decreasing slowly with increasing size. Nevertheless, in this experiment, the electron-capture cross sections are shown to exhibit a strong dependence on cluster velocity [7]. Collisions involving fullerene ions at collision energies varying from a few eV to 100 keV in the laboratory frame have also been studied [8–10]. The electron-capture cross sections are measured for fullerenes and rare-gas atom targets. Recently, the capture cross section of 10 MeV C_5^+ clusters colliding with helium atoms have been measured [11].

In the present work, we report on a study of charge exchange between mass-selected swift hydrogen clusters ions H_n^+ and atomic helium,

$$H_n^+ + He \rightarrow H_n^* + He^+,$$

in a large size range ($3 \leqslant n \leqslant 35$) at the same velocity of $1.55v_0$ (60 keV/u), where v_0 is the Bohr velocity (fast cluster-ion/atom collision regime).

II. EXPERIMENT

Experiments have been performed at the cluster facility of the Institut de Physique Nucléaire de Lyon [12]. The schematic experimental setup (Fig. 1) has been described in detail elsewhere [13]. Briefly, swift mass-selected ionized hydrogen clusters H_n^+ are produced and sent to the collision chamber. Before entering the chamber, the beam is collimated by two apertures giving an angular divergence equal to 0.16 mrad. The beam then crosses a gaseous jet formed into a vertical cylindrical capillary tube. Measurements at various input pressures are made in order to check the single-

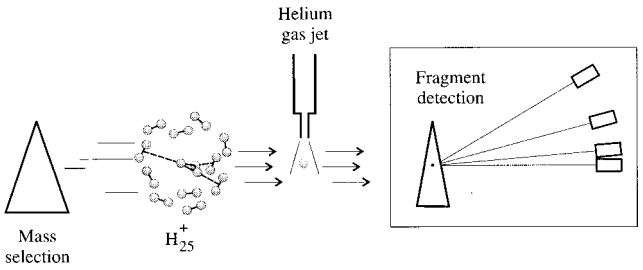

FIG. 1. The schematic experimental setup.

collision conditions. According to previous studies on the target thickness [14], absolute cross sections are deduced from the measurements. A magnetic analyzer is then used to deflect the H_p^{q+} ions according to the q/p ratio. Those are either nondissociated clusters ($p=n$) or fragments resulting from dissociation ($p<n$). Only neutral or singly charged fragments ($q=-1$, 0, or $+1$) are observed. The detection is made with silicon solid-state detectors intercepting the various q/p trajectories.

However, the neutral fragments are not analyzed with respect to their mass. For each dissociated cluster, the information given by the detection of the neutral fragments is the sum of their masses. A typical example (H_{13}^+ incident clusters) is given in Fig. 2(a). This spectrum has been obtained for a given number of incident clusters ($\sim 1.1\times 10^5$) and for a target thickness of 1.41×10^{14} at/cm^2 for which the single-collision conditions are fulfilled (20% of dissociated clusters). It shows 13 separate peaks and the number S_N associated with each peak corresponds to the value of the sum of the mass numbers of all the neutral fragments coming from the dissociation of a cluster. In this paper, we deal with the last peak ($S_N=13$), which corresponds to the following fragmentation channel where all the fragments are neutral:

$$H_{13}^+ + He \rightarrow \sum \mu_i H_i + He^+, \text{ with } \sum (\mu_i i) = 13,$$

where μ_i is the number of fragments H_i.

This channel corresponds to the capture of a target electron by the H_{13}^+ cluster ion. The electron capture is followed by the dissociation of the excited neutral cluster produced. Indeed, measurements of the angular distributions of the neutral fragments have been performed and a first analysis of these data indicates that neutral fragments are mainly atomic and molecular hydrogen.

Figure 2(b) displays the spectrum obtained without a helium gas target for the same number of incident clusters as in Fig. 2(a). These events are due to collisions with the residual gas. In the last peak corresponding to the electron-capture process, the number of these spurious events corresponds to 8% of the peak ($S_N=13$) in Fig. 2(a) (about 0.07% of the number of incident clusters). These spectra [Figs. 2(a) and 2(b)] have been measured for all the cluster sizes varying from 5 to 35, odd values, and also for the H_2^+ and H_3^+ molecular ions.

III. DATA ANALYSIS

The absolute electron-capture cross section can be deduced from the measurements by two different methods, the

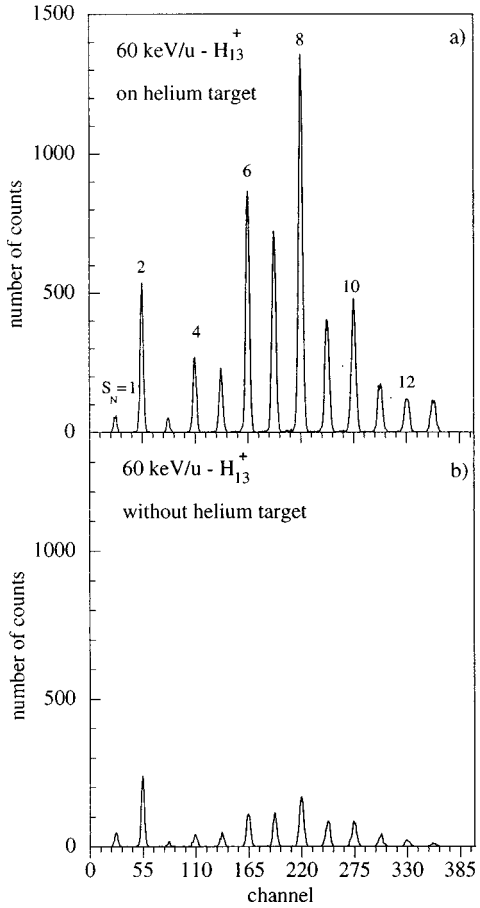

FIG. 2. (a) Detection of the neutral fragments for a given number of H_{13}^+ incident clusters ($\approx 1.1\times 10^5$) for a target thickness of (1.41×10^{14}) at/cm^2. In the spectrum, each peak corresponds to a value of the sum of the mass numbers for all the neutral fragments coming from one H_{13}^+ dissociated cluster (S_N). (b) The same as (a) without the helium target.

growth-rate method and the branching-ratio method. The use of these two methods could provide an evaluation of the uncertainty over the measured cross sections. The growth-rate method consists in the measurement of the number of events in the peak associated with electron capture ($S_N=n$) in the spectrum of detection of the neutral fragments for various target thicknesses ε and for a given number of incident clusters. Then, we deduce the fraction $F_c^n(\varepsilon)$ of electron capture events versus the target thickness ε. In a single-collision regime, the fraction depends on the target thickness as follows:

$$F_c^n(\varepsilon) = F_c^n(0) + \sigma_c^n \varepsilon, \tag{1}$$

where σ_c^n is the electron-capture cross section and $F_c^n(0)$ corresponds to the fraction of electron-capture events without a gas target (interaction with the residual gas).

As shown in Fig. 3, for the incident H_3^+ ions, the fraction $F_c^3(\varepsilon)$ is linear versus the target thickness in the range studied ($\varepsilon \leqslant 8\times 10^{14}$ at/cm^2). Double-collision processes are found negligible and the single-collision conditions are fulfilled. The single-electron-capture cross section σ_c^n is then deduced from the slope of the straight line (see Fig. 3).

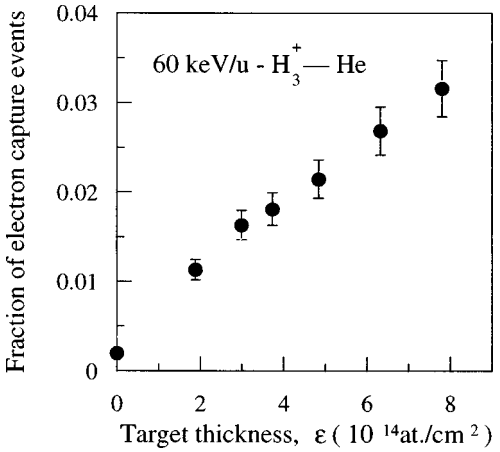

FIG. 3. The fraction $F_c^n(\varepsilon)$ of electron-capture events (see text) vs the target thickness ε for incident H_3^+ ions.

A second method, the branching-ratio method, has also been used to deduce the capture cross section from the data. From the spectra of the detection of the neutral fragments, like the ones shown in Fig. 2, we determine the branching ratio $R_{c/N}^n$ between the number of electron-capture events, peak $S_N=n$, over the total number of events in the total spectrum. The branching ratio is calculated after substraction of the spurious events. Thus, for a given target thickness for which the single-collision conditions are fulfilled, we can write

$$R_{c/N}^n=[N_c^{*n}(\varepsilon)-N_c^n(0)]/[N_N^n(\varepsilon)-N_N^n(0)], \qquad (2)$$

where $N_c^n(\varepsilon)$ and $N_N^n(\varepsilon)$ are the number of electron-capture events and the total number of events in all the spectrum, respectively, for a target thickness ε, and, $N_c^n(0)$ and $N_N^n(0)$ are those measured with no helium target. Besides, we measure by means of the growth-rate method the cross section σ_N^n of the production of at least one neutral fragment in the cluster fragmentation [15]. Then, σ_c^n is given by $\sigma_c^n = R_{c/N}^n \sigma_N^n$.

For the H_3^+ case discussed above, we obtain by this method a value for σ_c^n equal to $(3.8\pm0.4)\times10^{-17}$ cm^2 which is in good agreement with the one deduced by the growth-rate method [$(4.0\pm0.4)\times10^{-17}$ cm^2].

IV. RESULTS AND DISCUSSION

In Fig. 4(a) are reported the electron-capture cross sections as a function of the cluster size n. We also report the measured values for incident molecular ions, H_2^+ and H_3^+. The value for incident protons has been taken from the literature [4]. All the results have been obtained for the same velocity of the projectile, $1.55v_0$. It should be noted that the results have been extracted from several sets of measurements corresponding to different run times. The results displayed in Fig. 4(a) show the good reproductibility of the measurements. In Fig. 4(b) the mean value of the cross section for a given size σ_c^n is plotted versus the cluster size.

First, we observe a decrease of the electron-capture cross section from H^+ to H_3^+. Such a decrease of the electron capture has also been observed by Abraham, Nir, and Rosner [16] with D_2^+ and D_3^+ molecular incident ions colliding with argon at 100 keV/u. Besides, in the present work, for the cluster ions, i.e., $n\geqslant5$, the capture cross section is observed to be independent of the cluster size. The straight line plotted in Fig. 4(b) corresponds to an mean value $\langle\sigma_c^n\rangle$ of the cross sections over all the cluster sizes [$\langle\sigma_c^n\rangle=(4.4\pm0.4)\times10^{-17}$ cm^2]. The $\langle\sigma_c^n\rangle$ value is very close to the cross section obtained with the incident H_3^+ ion $(3.9\pm0.4)\times10^{-17}$ cm^2.

Concerning the results on H^+, H_2^+, and H_3^+ ions, one can observe that the number of exit channels associated with the electron-capture process increases with the ion size and could induce increasing curve crossing:

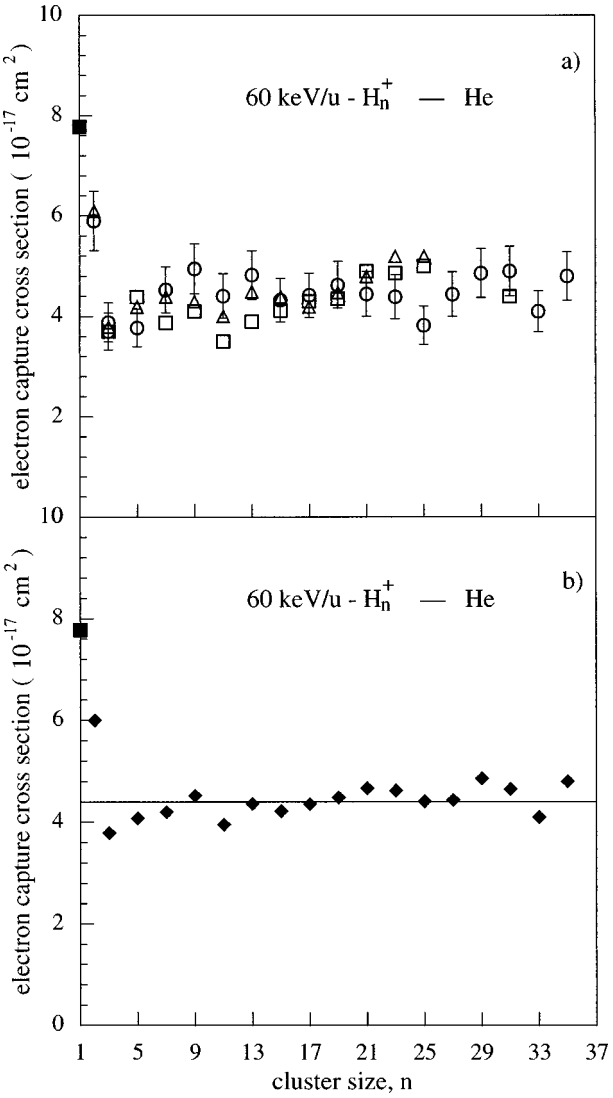

FIG. 4. The electron-capture cross section σ_c^n as a function of the cluster size n ($1\leqslant n\leqslant35$). The value for the incident protons (■) has been taken from literature [5]. All the results have been obtained for the same velocity of the projectile, $1.55v_0$. (a) Various symbols correspond to different sets of measurement. (b) The capture cross section σ_c^n (average value of the different experimental points for a given size) is plotted vs the cluster size n. The straight line corresponds to the mean value of all the cluster cross sections $\langle\sigma_c^n\rangle$, $n=5-35$, odd, [$(4.4\pm0.4)\times10^{-17}$ cm^2].

$$H^+ + He \rightarrow H + He^+,$$

$$H_2^+ + He \rightarrow H_2 + He^+$$

$$\rightarrow H + H + He^+,$$

$$H_3^+ + He \rightarrow H_3 + He^+$$

$$\rightarrow H_2 + H + He^+$$

$$\rightarrow H + H + H + He^+.$$

In our case, the time during the collision is short compared to the typical time of the motion of the protons in the molecular ion and the results obtained with the H_2^+ and H_3^+ molecular ions could be compared to the proton case with respect to the charge localization. The charge is not localized on a single proton but distributed over all the protons of the molecular ion. The most probable distance d(H-H) between the protons in the H_2^+ ions delivered by the accelerators [d(H-H)=1.2 Å] [17] and the one in the H_3^+ molecular ions [d(H-H)=1.1 Å] [18] could be compared with the largest impact parameter for capture by a proton, R_c^1. In a simple geometric model, R_c^1, the so-called capture distance, is deduced from the experimental value of the electron-capture cross section by protons (see Fig. 3 and Ref. [5]) (8×10^{-17} cm^2) as follows:

$$R_c^1 = (\sigma_c^1/\pi)^{1/2} = 0.5 \text{ Å}.$$

The most probable distance d(H-H) in the H_2^+ molecular ion is about twice as large as R_c^1 the capture distance deduced from the proton case. Yet, the electron of the projectile has to be taken into account and could screen the charge during the capture process. Moreover, due to the triangular structure of the H_3^+ ion, this screening effect could be stronger for H_3^+ than for H_2^+. Such screening effects connected to the delocalization of the positive charge in the molecular ion could explain the decrease of the electron-capture cross section observed in Fig. 4(b) from H^+ to H_3^+. Further experiments especially at various velocities should allow more insights into this result.

Turning now to the cluster ions, one of the most important features is the fact that the electron-capture cross section is found independent of the cluster size. No structure effect involving the geometric shells of H_2 seems to be present. Another important feature is the mean value of the capture cross sections of the clusters [see Fig. 3(b)], which is nearly equal to the H_3^+ value.

Quantum-chemical calculations have been focused on exploring the ground potential-energy surface of small H_n^+ clusters [2]. Such studies uncovered that the minimum energy structures correspond to a cluster formed by a three-center-bonded H_3^+ core with bond lengths on the order of 0.87 Å, solvated by essentially unperturbed H_2 molecules at distances of typically 1.6 Å in the first shell and more than 2 Å in the second shell. Going now to the cluster ions delivered by the cluster facility, previous experiments on hydrogen-cluster collisions with thin foils [19] allowed us to show that the H_3^+ core and the H_2 molecules are in their fundamental states. We can notice that the distance between the protons is smaller in the H_3^+ core of the clusters [d(H-H)=0.87 Å] than the most probable distance for the H_3^+ ion [d(H-H)=1.1 Å].

The absence of structure effect for the smaller sizes, as for example size 9, which is the first geometric shell of three molecules around the H_3^+ core, shows that the electron-capture process requires collisions at close distance to the H_3^+ core ion. Roughly, we can estimate that electron-capture occurs mainly below the impact parameter R_c^n deduced from the mean value of σ_c^n as follows:

$$R_c^n = (\langle \sigma_c^n \rangle / \pi)^{1/2} = 0.4 \text{ Å}.$$

This value has to be compared to the distance between the component of the cluster. The distance between the H_3^+ core and the added H_2 molecules in the H_9^+ cluster (1.6 Å) is four times larger than the maximum limit of the impact parameter R_c^n. Thus the capture process is localized near the H_3^+ core. Since the mean value of σ_c^n is nearly equal to the value of σ_c^3, the process of electron capture by hydrogen clusters on helium atoms seems to be the electron capture by the H_3^+ core of the cluster. That confirms the localization of the charge on the H_3^+ core in the clusters as suggested by theoretical works [2,3]. Nevertheless, the small difference observed between the mean value of σ_c^n and the value of σ_c^3 is not significant if we take into account the experimental uncertainties. But a difference could have been expected since the incident H_3^+ ions and the H_3^+ core of the incident clusters are not in the same vibrational state as explained before.

Another point has to be emphasized. Even for bigger sizes, such as $n=35$, the capture cross section is observed to be independent of the cluster size. The electron-capture process is not disturbed by the 16 H_2 molecules of the H_{35}^+ cluster. In fact, a decrease of the cross section when increasing size could be expected for large sizes due to a geometric screening of the H_3^+ core by the H_2 molecules. Indeed, the H_n^+-He collision should induce an ionization of H_2 before an electron capture, for example. The absence of geometric screening even with 16 H_2 molecules in the cluster is intriguing and should lead us to consider a kind of rather tubular structure for the hydrogen clusters with the H_2 molecules organized around an axis perpendicular to the triangular H_3^+ core.

V. CONCLUSION

We have measured the electron-capture cross section in collisions between mass-selected swift hydrogen-cluster ions H_n^+ and atomic helium, in a large size range ($3 \leqslant n \leqslant 35$) at a given velocity of $1.5v_0$ (60 keV/u).

The results obtained with the molecular ions show a decrease of the electron-capture cross section from H^+ to H_3^+. Such behavior can be connected with the relatively close distance between the helium and the projectile during the collision and to the delocalization of the charge on the molecular ion.

For the hydrogen clusters, the electron-capture cross section is independent of the cluster size. The mean value of the capture cross sections for clusters is nearly equal to the H_3^+ capture cross section. That shows that the electron capture by hydrogen clusters on a helium atom is a process involving mainly the H_3^+ core and confirms the localization of the

charge of the cluster on the H_3^+ core. An intriguing result is the fact that the cross section of this very localized electron-capture process is not disturbed by the presence of 16 molecules around the H_3^+ core. These experimental results should lead to further theoretical investigations on the geometric shells of H_2 molecules in ionized hydrogen clusters. Further experiments with other targets such as molecular targets should allow new investigations on the size dependence of the electron capture by a cluster.

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