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## Multiple $h_3^+$ fragment production in single collision of fast $H_n^+$ clusters with He atoms

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### Abstract

The production of  $H_3^+$  ions resulting from single collisions of mass-selected ionic hydrogen clusters,  $H_n^+$  ( $n=9, 25, 31$ ), with helium at high velocity (1.55 times the Bohr velocity) has been studied. A strong double  $H_3^+$  ion production resulting from one incident cluster is observed. Moreover, evidence for a triple  $H_3^+$  fragment production is presented for  $n=25$  and 31. Thus, in this energy range, the collision gives rise to multifragmentation processes. The formation of  $H_3^+$  ions takes place in the fragmentation of the multicharged cluster resulting from the collision.

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## 1. Introduction

Fragmentation<sup>1-3</sup> is a relatively ubiquitous phenomenon that underlies processes such as polymer degradation, breakup of liquid droplets, the crushing of rocks, and the fragmentation of nuclei or atomic clusters. Fragmentation of mass-selected 60-keV/amu- $H_n^+$  induced by single collision with helium has been studied<sup>4</sup> for  $n = 9, 13, 21, 25$  and  $31$ . The deduced inclusive mass distributions of the fragments are strongly different from those obtained at lower energy<sup>5</sup> where molecular evaporation results from the collision. An important production of ionic fragments of masses which are intermediate between the masses of the evaporated dimers  $H_2$  and the ones of the resulting ionic fragments have been observed. First of these intermediate masses, the protonated hydrogen,  $H_3^+$ , is the simplest stable polyatomic system and then represents fundamental interest for experimental and theoretical studies<sup>5</sup>. Detailed ab-initio calculations had predicted the energy spectrum and the equilateral-triangular structure<sup>6</sup> which has been confirmed by foil-induced dissociation experiments<sup>7</sup>. The first astronomical observation of  $H_3^+$  had shown rovibrational transitions in the active degenerate infrared-band<sup>8</sup>. Since this observation,  $H_3^+$  infrared emission has been detected in many astronomical objects. Because of a great reactivity and its large amount in nature,  $H_3^+$  is assumed to play a central role in the chemical evolution of interstellar molecular clouds<sup>8</sup>. This  $H_3^+$  abundance is usually explained by the efficient exothermic reaction  $H_2^+ + H_2 \rightarrow H_3^+ + H$ .

In this paper, we report on the first experimental observation of multiple  $H_3^+$  production after fragmentation of mass-selected 60-keV/amu ionic hydrogen clusters,  $H_n^+$  ( $n=9, 25, 31$ ), induced by single collision with helium.

## 2. Experimental apparatus

The experiment was performed at the high-energy cluster-beam facility at the Institut de Physique Nucléaire de Lyon<sup>9</sup>. The clusters are formed in a cryogenic source and then ionized by

electron impact. Cluster ion beams of 0.54 to 1.86 MeV energies are formed by the new radiofrequency (RF) quadrupole post accelerator associated to the Cockroft Walton accelerator. The beam is pulsed with a cycle combining the cluster source cycle and the RF power one. After momentum analysis by a magnetic field, the incident beam is defined by two collimating apertures which ensure an angular dispersion of  $\pm 0.8$  mrad. Before reaching the gas jet, the beam goes through two parallel plates. A voltage which depends on the energy of the beam can be applied or set to zero between these two plates with a fast voltage amplifier. Thus, a cluster burst can either be deviated in the monitoring surface barrier (SB) detector or reach the target. The intensity of the collimated incident cluster beam in a burst is about 1000 clusters per second. The target is a gas jet described in detail previously<sup>10</sup>. In short, it is formed by expansion of helium in vacuum through a thin capillary. A differential pumping system is able to maintain the residual gas pressure at a value lower than  $5 \cdot 10^{-7}$  Torr in the region closed to the gas jet and along the beam line. The produced  $H_3^+$  ions are magnetically analyzed one meter after the interaction which corresponds to a time of flight of 0.30  $\mu$ s. A SB detector is located at  $30^\circ$  with respect to the beam axis, in such manner that only the  $H_3^+$  fragments are detected. Care was taken to ensure a complete collection of these fragments. This detector is connected to a pulse height analyzer, the signal being proportionnal to the total energy of the detected  $H_3^+$  ion. The number of transmitted  $H_n^+$  clusters is also measured in the analysis chamber as a test of the monitoring system since we have previously measured the dissociation cross sections in the same conditions<sup>11</sup>.

### 3. Results and discussion

Typical spectra of  $H_3^+$  fragments obtained by collision of  $H_9^+$ ,  $H_{25}^+$ ,  $H_{31}^+$  incident clusters with helium atoms are displayed in Fig. 1. These spectra let appear two or three separated peaks at the energies of 180, 360, and 540 keV. The lower energy peak corresponds to single  $H_3^+$  detection events. Due to the magnetic selection of fragments with  $q/m$  ratio equal to  $1/3$ , the second peak corresponds to the simultaneous detection of two  $H_3^+$  ions. We have

checked that the branching ratio of the double  $H_3^+$  production over the single one is decreased by a small collimator set on the beam just before the analysis chamber. This effect is due to an angular distribution effect corresponding to the Coulomb repulsion between the fragments and confirms that two  $H_3^+$  ions are simultaneously detected. In the cases of  $H_{25}^+$  and  $H_{31}^+$  incident clusters, the spectra let appear a third peak at 540 keV. This third peak corresponds to the simultaneous detection of three  $H_3^+$  fragments.

As an example, in the  $H_{31}^+$  case the numbers of single, double, and triple  $H_3^+$  events correspond to  $\approx 9.4\%$ ,  $\approx 3.5\%$ , and  $\approx 0.15\%$  of the incident clusters, respectively. Pile up events of incident clusters in the monitoring detector have been measured and found to be less than 1%. Then, the simultaneous detection of  $H_3^+$  fragments coming from two different incident clusters is negligible ( $<10^{-4}$ ). Besides, we note that the proportion of  $D_2$  in the  $H_2$  gas of the source is less than 150 ppm. Moreover, it has been shown that deuterium appears mainly in even mass clusters<sup>12</sup>. Thus, the  $HD^+$  pollution is negligible ( $\ll 10^{-5}$ ).

For a given incident cluster size  $n$ , the single  $H_3^+$  production fraction  $F_{n,3}^S(x)$  (number of single  $H_3^+$  fragments per incident cluster) has been measured for various target thicknesses  $x$ . As shown in Fig. 2 for the  $H_{25}^+$  case, the fraction is linear versus the target thickness  $x$  in the target thickness range studied ( $x \leq 1.15 \cdot 10^{14}$  atoms/cm<sup>2</sup>). Double collision processes in the target are found negligible and the single-collision conditions are fulfilled for the single  $H_3^+$  production from  $H_{25}^+$  cluster in this target thickness range. In Fig. 3 the branching ratios,  $R_{D/S}$  and  $R_{T/S}$ , of the double  $H_3^+$  production fraction  $F_{n,3}^D(x)$  (number of double  $H_3^+$  events per incident cluster) and of the triple  $H_3^+$  production fraction  $F_{n,3}^T(x)$  (number of triple  $H_3^+$  events per incident cluster) to the single production fraction  $F_{n,3}^S(x)$  are reported versus the target thickness for  $H_{25}^+$ . They are found to be constant in the target thickness range studied. Thus, the single-collision conditions in the gas jet are also fulfilled for the double and triple production processes in the target thickness range  $x \leq 1.15 \cdot 10^{14}$  atoms/cm<sup>2</sup>. This target thickness range corresponds to the dissociation of at the most 30% of the  $H_{25}^+$

clusters in the gas jet <sup>12</sup> ( $\sigma^{\text{diss}} = (28.8 \pm 2.5) 10^{-16} \text{ cm}^2$ ). In fig 1 the spectra have been obtained in condition of single collision with the target thicknesses  $x = (3.0 \pm 0.3) 10^{14} \text{ atoms/cm}^2$ ,  $x = (0.95 \pm 0.09) 10^{14} \text{ atoms/cm}^2$ , and  $x = (0.73 \pm 0.08) 10^{14} \text{ atoms/cm}^2$  which correspond to the dissociation of 19%, 24%, and 24% of the  $\text{H}_9^+$ ,  $\text{H}_{25}^+$ , and  $\text{H}_{31}^+$  incident clusters, respectively.

However, the interaction of an incident cluster with the gas jet could produce a single  $\text{H}_3^+$  ion and a  $\text{H}_p^+$  fragment which could induce a single or a double  $\text{H}_3^+$  production by collision with the atoms or molecules of the residual gas. The contributions of such two step processes have to be evaluated since they would also provide  $R_{D/S}$  and  $R_{T/S}$  ratios which do not depend on the target thickness. Their contribution can be estimated roughly from

$$\sum_{p=5, n-4 \text{ (odd)}} (\sigma_{n,p} x)(\sigma_{p,3^S} L/2) \text{ for the double production} \quad (\text{I})$$

$$\sum_{p=7, n-4 \text{ (odd)}} (\sigma_{n,p} x)(\sigma_{p,3^D} L/2) \text{ for the triple production}$$

where  $\sigma_{n,p}$  is the  $\text{H}_p^+$  production cross section from the  $\text{H}_n^+$  parent,  $\sigma_{p,3^S}$  the single  $\text{H}_3^+$  production cross section from an  $\text{H}_p^+$  parent,  $\sigma_{p,3^D}$  the double  $\text{H}_3^+$  production cross section from an  $\text{H}_p^+$  parent,  $x$  the target thickness,  $L$  the corresponding total residual-gas thickness and  $L/2$  the one after the gas target.

We give the details of this estimation in the case of  $\text{H}_{31}^+$  incident clusters. The number of spurious single  $\text{H}_3^+$  events ( $\sigma_{p,3^S} L/2$ ) produced in the residual gas from fragments of size  $p$  can be majored by ( $\sigma_{31,3^S} L/2$ ). The quantity ( $\sigma_{31,3^S} L$ ) has been measured and corresponds to  $\approx 1\%$  of the incident beam. In the same way, the number of spurious double events ( $\sigma_{p,3^D} L/2$ ) produced in the residual gas from fragment of size  $p$  can be estimated to be less than 0.3% of the incident beam. The fragment production yield ( $\sigma_{n,p} x$ ) is given by our previous data<sup>4</sup>. We have then deduced a contribution of 0.002% of the incident clusters for this two-step process for the triple production and 0.004 % for the double one.

The symmetrical process, production of a single  $H_3^+$  ion and a  $H_p^+$  fragment in the residual gas which induces a single or a double  $H_3^+$  production in the gas jet has been found to be of the same order of magnitude.

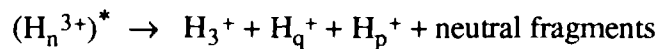
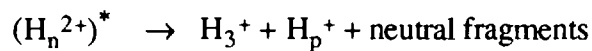
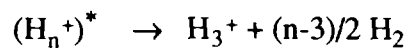
Expression (I) assumes that all the fragments of mass between 5 and 27 are produced simultaneously with an  $H_3^+$  ion. This is not realistic specially for the biggest fragments which are mainly produced by molecular evaporation. Therefore, we can estimate the contribution of these double collision processes to be much less than 0.002% of the incident cluster in the case of the triple production and 0.004 % in the double one case. Thus, these double step processes are negligible compared to the double  $H_3^+$  production (3.5%) and the triple one (0.15%). So, double and triple  $H_3^+$  events observed are resulting from a single collision of one  $H_{31}^+$  cluster with one helium atom.

A similar analysis leads to the same conclusion for the  $H_{25}^+$  and  $H_9^+$  cases.

The absolute cross sections of single, double, and triple  $H_3^+$  production from the  $H_9^+$ ,  $H_{25}^+$ ,  $H_{31}^+$  incident clusters colliding with helium at 60 keV/amu are reported in table I. The errors in the absolute cross sections vary from  $\pm 10\%$  to  $\pm 15\%$ , taking into account the target thickness and statistical uncertainties. The determination of the target thickness  $x$  and tests of the absolute calibration are described in ref. 10. We observe an important  $H_3^+$  production even in the  $H_9^+$  case. The production cross section of at least one  $H_3^+$  is relatively high compared to the dissociation cross section  $\sigma_D$  ( $\sigma_{n,3}^S + \sigma_{n,3}^D + \sigma_{n,3}^T \approx 0.53\sigma_D$  for  $n=9$ ,  $\sigma_{n,3}^S + \sigma_{n,3}^D + \sigma_{n,3}^T \approx 0.45\sigma_D$  for  $n=25$ , and  $\sigma_{n,3}^S + \sigma_{n,3}^D + \sigma_{n,3}^T \approx 0.46\sigma_D$  for  $n=31$ ). The importance of the double production which is higher than 0.37 times the single one for the  $H_{25}^+$  and  $H_{31}^+$  has also to be noticed. The ratio of the double production over the single one is much smaller in the  $H_9^+$  case (0.055) and for this cluster the triple production is not observed. For the bigger size clusters where the triple production is observed, the ratio  $R_{T/S}$  (0.015) is much smaller than the ratio  $R_{D/S}$  ( $\geq 0.37$ ).

In the velocity range studied here (1.55 times the Bohr velocity), electronic excitations up to ionization of the incident cluster are involved in the collision. Moreover, the relative velocity of the projectile and the target atom is around or greater than the velocity of the electrons in the cluster. Then, the time for a typical collision with a target atom is short enough, compared to the typical time of the motion of the protons in the cluster, so that during the collision the protons can be considered to be stationary in the projectile frame<sup>(7)</sup>. Thus, processes such as ionization of the incident cluster followed by dissociation of the resulting unstable multicharged cluster can be involved. The observation of several charged fragments in coincidence shows that ionization of the incident cluster is involved.

Thus, the  $H_3^+$  production correspond to the following fragmentation channels of the unstable clusters :



etc...

with  $p=1,2,3,5,\dots\text{odd}$ ,  $q=1,2,3,5,\dots\text{odd}$ .

The first channel corresponds to the evaporation of all the molecules of the cluster. The others result from the ionization of the incident cluster.

The single  $H_3^+$  production could be connected to the total  $H_2$  evaporation of the cluster resulting from the energy transfer due to the collision. Such molecular evaporation has been observed after photon interaction or low energy collision (few eV/amu) <sup>(5,13)</sup>. Nevertheless, in these experiments, the evaporation of a great number of molecules is less probable than the evaporation of a small one. Taking into account the shape of the ionic fragment distributions previously measured, the contribution of the total molecular evaporation of the  $H_n^+$  to the single  $H_3^+$  production is probably small for the biggest cluster sizes.

Then, for  $H_{25}^+$  and  $H_{31}^+$ , the single  $H_3^+$  production mainly results from ionization and the quantities  $(\sigma_{n,3}^S + \sigma_{n,3}^D + \sigma_{n,3}^T) / \sigma_D \approx 0.45$  for  $n=25$  and  $(\sigma_{n,3}^S + \sigma_{n,3}^D + \sigma_{n,3}^T) / \sigma_D \approx 0.46$  for  $n=31$ ) are related to the ionization rate. Their high value show the importance of the ionization among the excitation processes and the  $H_3^+$  formation process appears to be an important

dissociation channel for the multicharged unstable cluster resulting from the collision.

If single  $H_3^+$  mainly result from ionization of the incident cluster, an other fragment can be expected in coincidence. This fragment could be an  $H^+$ ,  $H_2^+$ , another  $H_3^+$  or a bigger size fragment. Then, the double  $H_3^+$  production could result from a single ionization of the incident cluster. The question is : does single ionization of the incident cluster explain the entire double production? The importance of the intermediate mass fragment production observed previously and the existence of a triple  $H_3^+$  production lead to considere double and perhaps also triple ionization processes. Such ionization of the incident cluster can result from different excitation mechanisms. The double ionization of one molecule of the cluster can be proposed but the probably main mecanism is the ionization of two (or more) molecules in different sites of the cluster. The ionization produced by an emerging electron<sup>(14)</sup> after ionization inside the cluster could also contribute to the multiple ionization. These two last mechanisms depend on the impact parameter but also on the cluster size and the probability of multiple ionization should increase with the cluster size.

The importance of the  $H_3^+$  production after dissociation of a multicharged hydrogen cluster could be related to the high efficiency of the  $H_2^+ + H_2$  reaction. It has been studied at low energy <sup>(15)</sup> and the relative contribution of the several competing channels are strongly dependent on the mass center collision energy (less than 5 eV) and the initial vibrationnal states. The  $H_3^+$  production predominates with impact parameter smaller than  $\approx 4 \text{ \AA}$  <sup>(15)</sup>. This impact parameter could be compared to the closed distances between the constituents of the cluster. An estimation of these distances can be deduced from the geometrical structures predicted for the ground state of these clusters which have been studied by ab initio calculations <sup>(16,17)</sup>. For  $H_9^+$ , the typical distance between the  $H_2$  molecules <sup>(17)</sup> ( $\approx 4 \text{ \AA}$ ) is much greater than the distance between the  $H_2$  molecules and the  $H_3^+$  core ( $\approx 1.6 \text{ \AA}$ ). The  $H_9^+$  cluster has been predicted to be the core (weakly deformed) of  $H_n^+$  ( $n \geq 11$ ). In these cases, additional  $H_2 - H_2$  distances such as  $\approx 3 \text{ \AA}$  are found in the structure of the ground state of  $n = 11, 13, 15$  clusters. All these internal distances correspond to impact parameter in the collision  $H_2^+ + H_2$  for which the  $H_3^+$  production is favoured. Nevertheless, the entire cluster is probably involved and the relative motion between the molecules (rotation and vibration) should play an important role in the definitive localisation



of the electron holes.

#### 4. Conclusion

In conclusion, a double and triple  $H_3^+$  production resulting from a single collision of  $H_n^+$  cluster of 60 keV/amu with helium is evidenced. A formation process of  $H_3^+$  ions takes place in the fragmentation after ionization of the incident cluster even for small species ( $n=9$ ), in this energy range. A multifragmentation process, the triple  $H_3^+$  production, is observed after at least a double ionization of the incident cluster. More exclusive data and further measurements such as fragment angular distribution measurements should uncover other cluster multifragmentation channels and give more information on the  $H_3^+$  production resulting from the multicharged cluster fragmentation.

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## Figure captions

**Figure 1** The spectra of  $H_3^+$  ions produced by collision of 60-keV/amu -  $H_n^+$  clusters ( $n=9, 25, \text{ and } 31$ ) on helium atoms (target thicknesses : 3.0, 0.95, and  $0.73 \cdot 10^{14}$  atoms/cm<sup>2</sup>, respectively). The peaks corresponding to the triple  $H_3^+$  events have been multiplied by 4.

**Figure 2** :  $F_{25,3}^S(x)$ , the number of single  $H_3^+$  fragments per incident cluster, versus  $x$ , the target thickness for the  $H_{25}^+$  incident cluster.

**Figure 3** : 60-keV/amu -  $H_{25}^+$  cluster : The branching ratio  $R_{D/S}$  of the double  $H_3^+$  production to the single one, and the branching ratio  $R_{T/S}$  of the triple  $H_3^+$  production to the single one both versus the target thickness.

**Table I** : The absolute cross sections of the single, double, and triple  $H_3^+$  production for the  $H_n^+$  incident clusters colliding with helium at 60 keV/amu are reported versus the cluster size.

n	$\sigma_{n,3}^S$ ( $10^{-16}\text{cm}^2$ )	$\sigma_{n,3}^D$ ( $10^{-16}\text{cm}^2$ )	$\sigma_{n,3}^T$ ( $10^{-16}\text{cm}^2$ )
9	$3.6 \pm 0.4$	$0.20 \pm 0.02$	---
25	$8.6 \pm 0.9$	$4.12 \pm 0.4$	$0.12 \pm 0.15$
31	$13 \pm 1.3$	$4.8 \pm 0.5$	$0.21 \pm 0.03$

**TABLE I**

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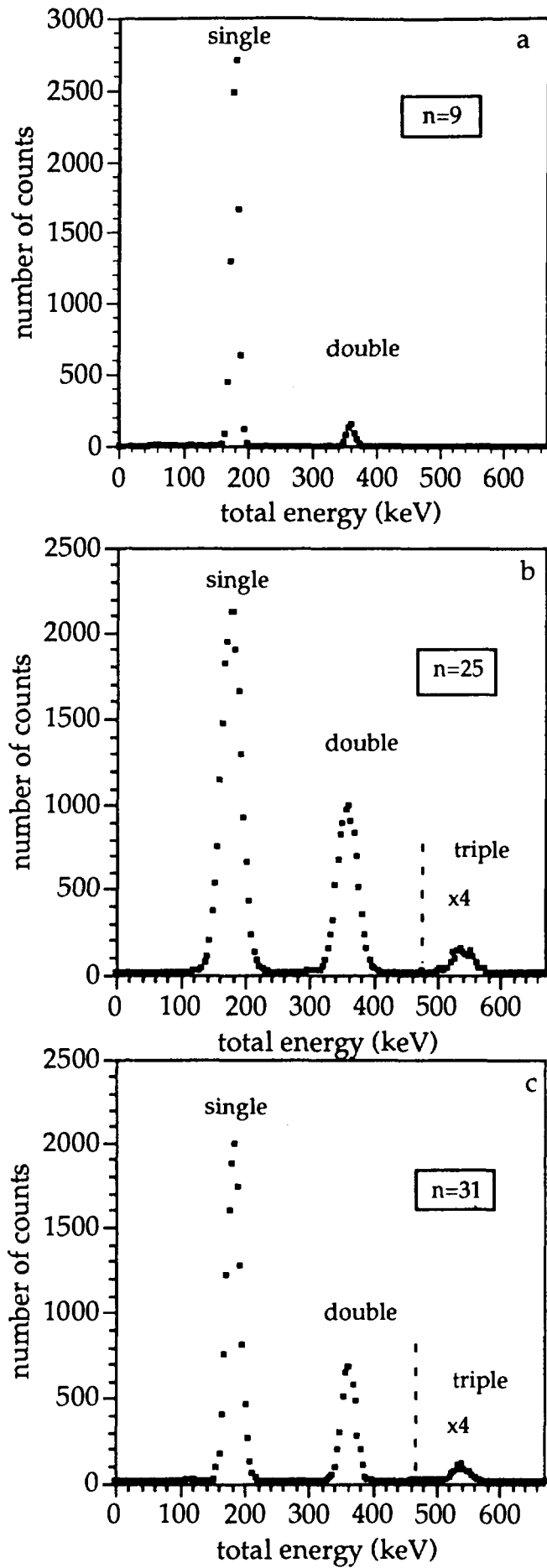


Fig. 1 , B. Farizon et al.

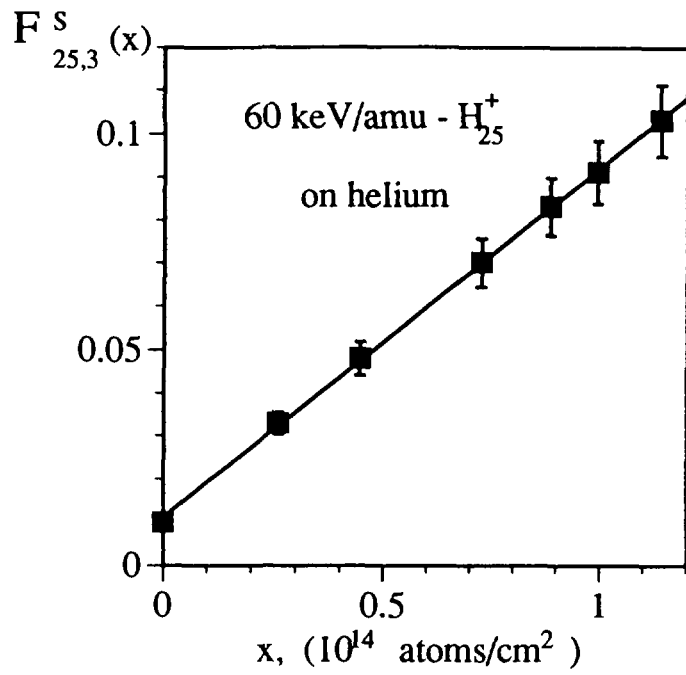


Fig. 2, B. Farizon et al.

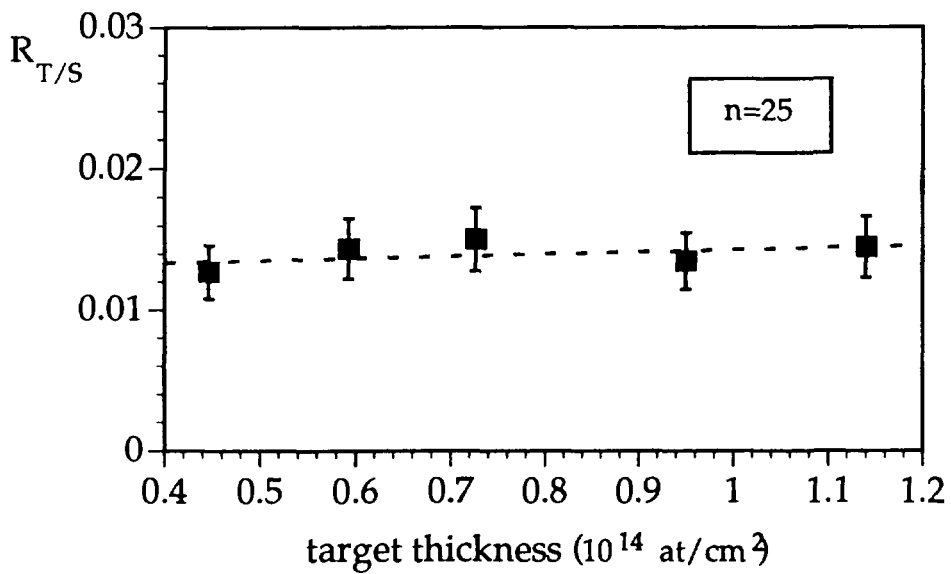
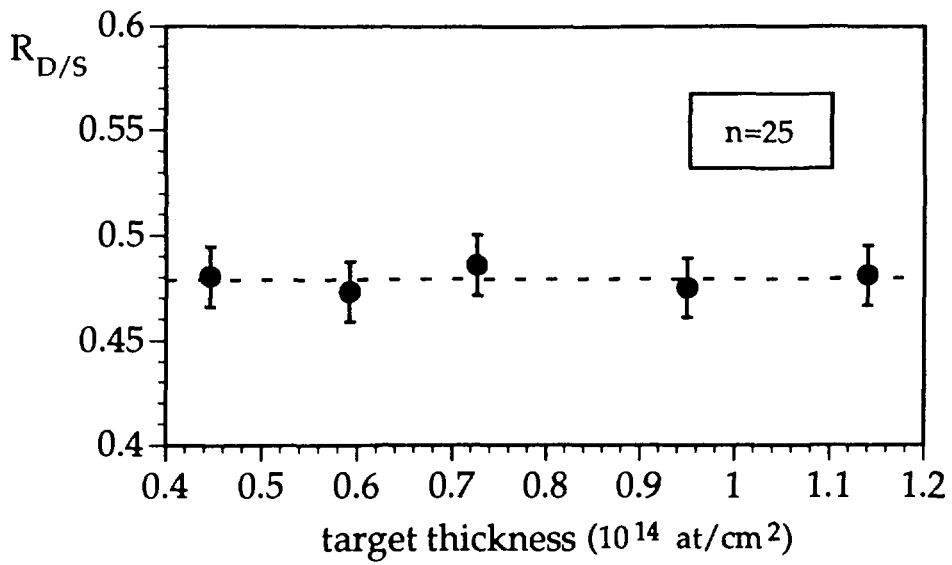


Fig. 3, B. Farizon et al.