LYCEN 9434
Septembre 1994

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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To be published in Zeitschrift für Physik D. Atoms, Molecules and Clusters

1. Introduction

Fragmentation[1-3] 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[4] 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 [5] 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[5]. Detailed ab-initio calculations had predicted the energy spectrum and the equilateral-triangular structure[6] which has been confirmed by foil-induced dissociation experiments[7]. The first astronomical observation of H_3^+ had shown rovibrational transitions in the active degenerate infrared-band[8]. 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[8]. 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[9]. 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[10]. 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 5.10^{-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 µs. A SB detector is located at 30° 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[11].

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 ≈ 9.4%, ≈ 3.5%, and ≈ 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 negligeable ($<10^{-4}$). 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[12]. Thus, the HD^+ pollution is negligeable ($\ll 10^{-5}$).

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 ($x \leq 1.15\ 10^{14}$ atoms/cm^2). Double collision processes in the target are found negligeable 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 $x \leq 1.15\ 10^{14}$ atoms/cm^2. This target thickness range corresponds to the dissociation of at the most 30% of the H_{25}^+

clusters in the gas jet [12] ($\sigma^{diss} = (28.8 \pm 2.5)\ 10^{-16}\ cm^2$). In fig 1 the spectra have been obtained in condition of single collision with the target thicknesses x= (3.0±0.3) 10^{14} atoms/cm^2, x= (0.95±0.09) 10^{14} atoms/cm^2, and x= (0.73±0.08) 10^{14} atoms/cm^2 which correspond to the dissociation of 19%, 24%, and 24% of the H_9^+, H_{25}^+, and H_{31}^+ incident clusters, respectively.

However, the interaction of an incident cluster with the gas jet could produce a single H_3^+ ion and a H_p^+ fragment which could induce a single or a double 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

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

(I)

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

where $\sigma_{n,p}$ is the H_p^+ production cross section from the H_n^+ parent, $\sigma_{p,3}{}^{S}$ the single H_3^+ production cross section from an H_p^+ parent, $\sigma_{p,3}{}^{D}$ the double H_3^+ production cross section from an 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 H_{31}^+ incident clusters. The number of spurious single 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 ≈ 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[4]. 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 negligeable 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 ±10% to ±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 σ_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 $R_{D/S}$ (≥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 stationnary in the projectile frame(7). 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 :

$$(H_n^+)^* \rightarrow H_3^+ + (n-3)/2\, H_2$$

$$(H_n^{2+})^* \rightarrow H_3^+ + H_p^+ + \text{neutral fragments}$$

$$(H_n^{3+})^* \rightarrow H_3^+ + H_q^+ + H_p^+ + \text{neutral fragments}$$

etc...

with p=1,2,3,5,...odd, q=1,2,3,5,...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) (5,13). 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(14) 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 (15) 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 ≈ 4 Å (15). This impact parameter could be compared to the closed distances between the constituants 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 (16,17). For H_9^+, the typical distance between the H_2 molecules (17) (≈ 4 Å) is much greater than the distance between the H_2 molecules and the H_3^+ core (≈ 1.6 Å). 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 ≈ 3 Å 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.

The authors wish to thank M.C. Bacchus for hepfull discussions and R.Genre, J. Martin, R. Filliol, J.P. Lopez, H. Mathez for their expert technical assistance.

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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, and 31) on helium atoms (target thicknesses : 3.0, 0.95, and 0.73 10^{14} atoms/cm^2, 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}cm^2)	$\sigma_{n,3}^D$ (10^{-16}cm^2)	$\sigma_{n,3}^T$ (10^{-16}cm^2)
9	3.6 ± 0.4	0.20 ± 0.02	---
25	8.6 ± 0.9	4.12 ± 0.4	0.12± 0.15
31	13± 1.3	4.8± 0.5	0.21± 0.03

TABLE I **B. Farizon et al.**

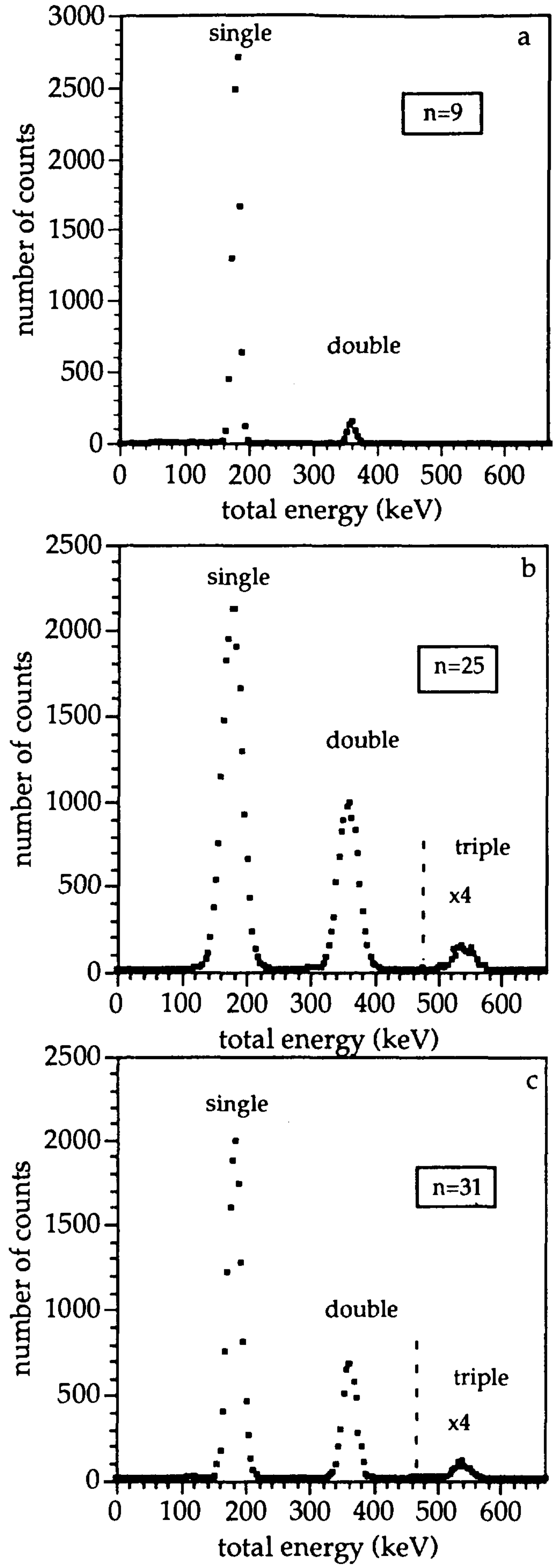

Fig. 1 , B. Farizon et al.

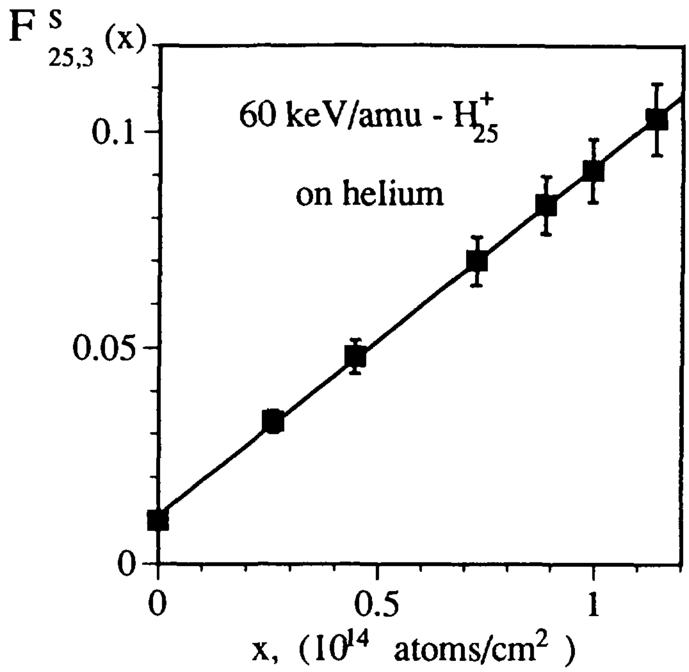

Fig. 2, B. Farizon et al.

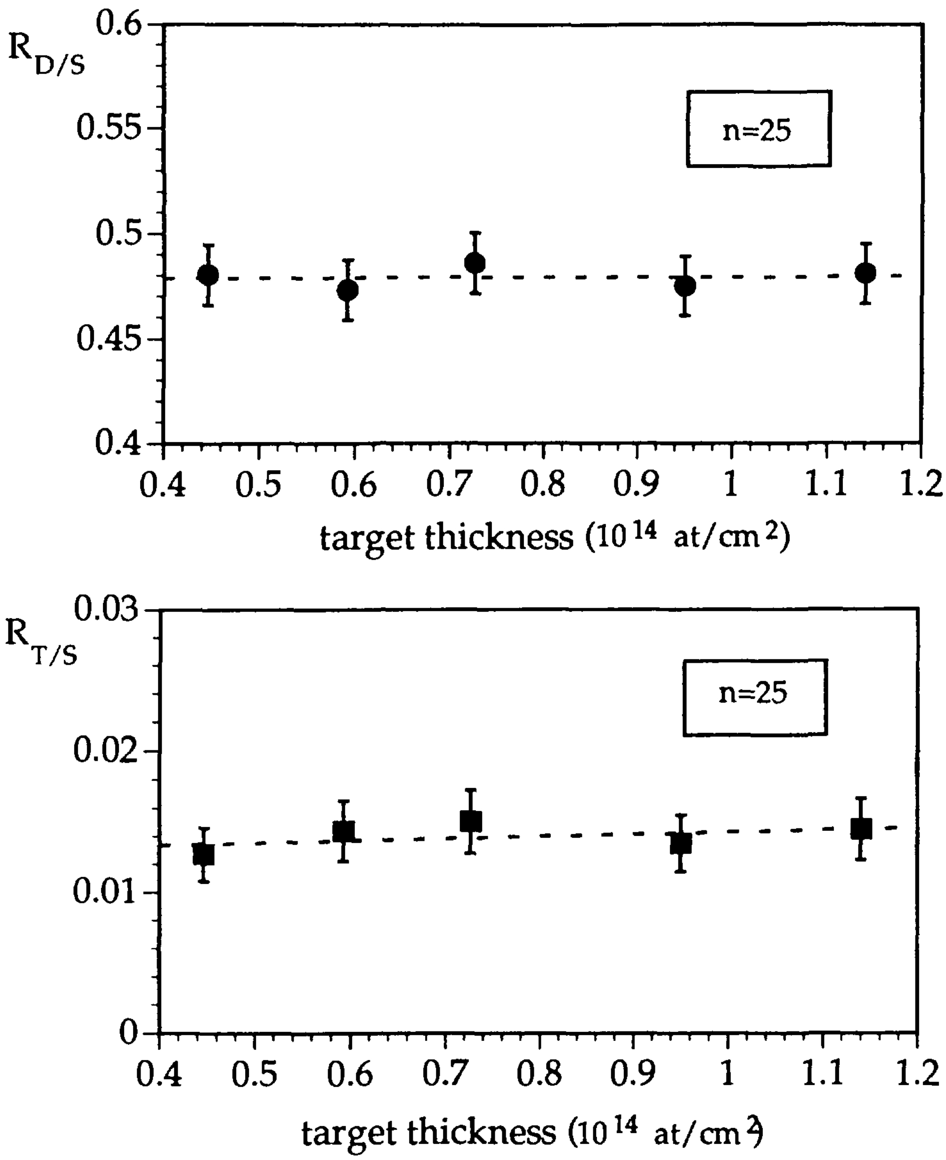

Fig. 3, B. Farizon et al.