Proton capture and loss in ion-molecule collisions

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Abstract.
We have measured proton distributions from the collision systems Ar+, Kr+ on CH4 molecular targets, searching for atom capture into the projectile continuum. Within the studied energy range (100 to 300 eV/u) we have not distinctive evidence of capture. A small contamination of ion beams with molecular ions as ArH+ or KrH+, have shown to be enough to produce peak shaped structures at the projectile velocity. We, therefore, concentrate our study on proton loss from molecular ions in collision with several targets.

Introduction
The dynamics of reactions involving atom capture and loss by ions interacting with H2 or hydrocarbons has been the object of several studies [1]. Proton capture produced by rare gas ions has been modelled and measured [1, 2] by using cross-beam techniques for chemical reactions. Cross sections and energy distributions of the resulting products have been well described by calculations based on the spectator stripping model [3].

Several works have been reported on the kinematics of such kind of reactions in plasmas, oriented mainly to obtain ion energy distributions, ion temperature and reaction factors for all the processes involved [4, 5, 6].

At energies as high as 200 eV/u, experimental evidence of Hydrogen capture to discrete states of H+ projectiles from CH4 was presented by Cook et al. [7]. Energy distributions of H2+ show a maximum at 45° with respect to the incident beam. The results were interpreted in terms of a two-step mechanism suggested by Thomas [8, 9]. Within this model, the angle of emission, θc, of the outgoing molecule is determined by the kinematics and it is independent of the type of interaction between the particles. Shakeshaft and Spruch made the quantum version of the classical model [10].

Experimental results were obtained later for the case of capture into the continuum induced by collisions of Ar+ and Kr+ on CH4 with energies between 100-300 eV/u [11]. Proton distributions showed a structure at an energy corresponding to the projectile velocity. A distinctive peak structure was observed when the acceptance angle was larger than the Thomas critical angle, θc = 1.3°. Such a structure was also reported with Kr+ as projectile and the energy dependence was found to be proportional to E−2.7±0.1.
Energy distributions of the fragments produced in collisions of ArH\(^+\) molecular ions with He and Ne have been also measured for energies about 40 keV [12]. Several structures around the projectile velocity were found.

In the present work we report on measurements of proton energy distributions in collisions of Ar\(^+\), Kr\(^+\) and ArH\(^+\) with atomic and molecular targets at energies between 70 eV/u and 1000 eV/u.

In the next section we describe our measurements of the proton energy distributions in an attempt to find evidence of atomic capture, and in section 2 we present proton emission from dissociation of incident ArH\(^+\) on atoms and molecules.

The experimental arrangement was described elsewhere [13, 14]. Briefly, ions are produced in a rf ion source, accelerated in a Cockcroft-Walton accelerator, and selected in a 90\(^\circ\) magnet with an horizontal exit. Base pressure in the accelerator is \(5 \times 10^{-7}\) Torr and increases up to \(8 \times 10^{-7}\) Torr during the measurements.

After the magnet selection the beam is collimated before entering the collision chamber. The gas target is provided by a needle located in such a way that the beam crosses the target at the focus of a cylindrical mirror analyzer. Pressure in the transport line and in the collision chamber were \(3 \times 10^{-7}\) Torr and \(6 \times 10^{-8}\) Torr, respectively.

1. Atom Capture
In reference [11], the proton energy distributions for Ar\(^+\) incident on CH\(_4\) show a structure centered at the beam direction, with a separate peak growing as the acceptance angle increases beyond the Thomas angle, \(\theta_c = 1.3^\circ\). The incident energy, \(E_o=6.06\) keV, corresponds to an equivalent proton energy of \(E_{eq}=151.5\) eV.

![Figure 1. Energy distributions of ions emitted in collisions for 4keV Ar\(^+\) with, a) CH\(_4\) target at three different emission angles, \(\theta = 0, 2\) and 4 degrees, b) He target (CH\(_4\) was added for comparison).](image-url)

We measured distributions of protons emitted in collisions of 4 keV Ar\(^+\) on CH\(_4\) (Figure 1). Our acceptance angle was \(\theta_0 = 2^\circ\) and the distributions were measured for different angles of emission. A structure is observed at the equivalent proton energy \(E_{eq}=100\) eV, decreasing for increasing emission angle.

Angular distributions taken at the peak energy show that the center of the structure is located in the forward direction.

The structure is present, though it is washed-out, also for He targets at 4 keV, and more prominent at 6 keV. As a structure in the He case may arise from contamination with ArH\(^+\) coming with the projectile, we prepared a mixture of Ar and H\(_2\). Measurements done by selecting
Ar$^+$ at 6 keV ($E_{eq}=150$ eV) show a similar structure, centered at the equivalent energy of the projectile, which decreases with the emission angle.

If the magnet is set to select an ArH$^+$ beam, a sharp peak appears in the distribution, with a counting rate as high as that obtained with Ar$^+$ projectiles, though the beam current drops by a factor of 1000 for the case of ArH$^+$ ions.

Measurements with the H$_2$ and Ar mixture show proton emission with the projectile velocity for both the atomic Ar$^+$ and the molecular ArH$^+$ beams in collision with He targets.

So, even though the magnet is able to separate the maxima of Ar$^+$ and ArH$^+$ beams, small variations in the energy or the magnet current of the order of 1% are sufficient to mix the intensities of both beams. We then cannot determine whether the structure in the case of CH$_4$ comes from proton capture by Ar$^+$ projectiles, or whether it is due to proton loss from an ArH$^+$ beam produced in the ion source.

In order to have enough separation between the beam and the contamination while keeping the equivalent energy as low as possible, a Kr$^+$ beam was used. In this case several Kr isotopes were found. In table 1, the stable isotopes and their relative abundances are listed. To avoid contamination it may not be convenient to choose the most intense ion beam, $^{84}$Kr$^+$, because it will have a contribution of $^{83}$KrH$^+$. Therefore the alternatives are, $^{82}$Kr$^+$ and $^{86}$Kr$^+$ due to their abundances. Possible beam fluctuations in the magnetic selector system are smaller.

In figure 2 proton distributions for 6 keV Kr$^+$ projectiles on CH$_4$ are shown for the three different used isotopes $^{82}$Kr$^+$, $^{84}$Kr$^+$ and $^{86}$Kr$^+$. Clear peak structures are present for the three ion beams, but collisions with He targets also show such a structure, but centered at a slightly higher energy.

Distributions of protons emitted in collisions of $^{86}$Kr$^+$ ions for a higher incident energy, 21 keV ($E_{eq} \approx 250$ eV), show no structures for $^{82}$Kr$^+$ and $^{86}$Kr$^+$, while a clear distinctive peak is observed for $^{84}$Kr$^+$ ions (Figure 3). Though the equivalent energy is twice the value presented by Breinig et al. [11], the energy dependence reported by them for the proton yield, $\propto E^{-2.7}$,

### Table 1. Stable isotopes of Kr

| Isotope | Abundance (%) |
|---------|---------------|
| 78      | 0.35          |
| 80      | 2.27          |
| 82      | 11.6          |
| 83      | 11.5          |
| 84      | 57            |
| 86      | 17.3          |
should be applicable to our results. However, we do not observe a proton peak due to capture.

In conclusion, the identification of the process which produces the observed structures in proton distributions for Ar$^+$+CH$_4$ below 10 keV was not possible. The contribution of the proton loss from molecular ArH$^+$ ions, generated in the ion source due to contamination, masks the existence of the proton capture by Ar$^+$. Conditions of stability and resolution of the experimental system are quite demanding. Fluctuations in the beam energy should be much smaller than 1%. For high enough energies, when such conditions are fulfilled (250 eV/u Kr$^+$ ions), no proton capture was observed.

![Figure 3. Energy distributions of ions emitted in collisions for 21 keV $^m$Kr$^+$ with CH$_4$, with $m$=82, 84 and 86.](image)

2. Proton loss

While the proton capture cross section might be too low to be observed in our experiment, the proton loss process has a cross section at least three orders of magnitude higher.

To measure proton emission from molecular ion beams, a 50:50 mixture of Ar and H$_2$ was injected into the ion source. The discharge conditions were the same during the whole measurement. The angular acceptance was $\theta_0 = 1.5^\circ$, and the energy resolution, 0.8%.

Proton energy distributions for 21 keV ArH$^+$ projectiles incident on He for emission angles between $\theta = 0^\circ$ and $\theta = 15^\circ$ are shown in figure 4. It is evident that the cross section decreases rapidly with the emission angle, being 200 times smaller at $\theta = 15^\circ$ with respect to that resulting for the beam direction. Similar distributions were measured before by Breinig and collaborators [12].

The central peak in the distribution is located at 511 eV and four peaks are symmetrically located at 55 and 110 eV around the central peak. As the emission angle increases, the lateral peaks seem to hide in the main structure while the central peak becomes smaller.

The origin of the proton loss structure is attributed to dissociation of the ArH$^+$ due to excitation to continuum vibrational states. As the molecule is moving, the emission of the fragments will be centered at the projectile velocity and the angular distribution will depend on the initial orientation of the molecule.

The interaction time between the projectile and atom was estimated to be $4.0 \times 10^{-15}$ sec, which is small compared to the vibrational period of the molecule, $10^{-14}$ sec, and rotational period, $10^{-13}$ sec [15, 16, 17]. Within this conditions, the Franck-Condon principle will be used in the following interpretation.

The contribution to the central peak should come from dissociation from the $X^1\Sigma^+$ state, the ground state of the molecule, which ends up in separate Ar and H$^+$ [16, 17]. The other two peaks have their origin in dissociation from excited electronic states.

From ArH$^+$ potential curves in [16] we consider only those excited states which dissociate in a neutral Ar and a proton. According to the Franck-Condon principle, vertical electron
transitions take the electron to an excited state, which may be in the region of the continuum of the vibrational states, and then dissociate with a kinetic energy given by the difference between the energy of the excited state and the one of the separate atoms in the asymptotical region.

When the transformation to the projectile system of reference is done, the lateral peaks are centered at 1.5 and 6 eV approximately. Similar values were obtained in [12]. When the energy of 6 eV is projected onto the states which dissociate into a proton, the classical turning point for all the electronic states results in vertical transitions from excited vibrational states of $X^1\Sigma^+$. In the case of the structure centered at 1.5 eV, the initial states correspond also to excited vibrational states. However, there is also a probability of transition from the vibrationless ground state, but this state should dissociate by tunnelling through a ridge in the potential curves at higher internuclear separation.

In conclusion, the observed proton distributions are consistent with a molecule with a certain distribution of vibrational states produced in the RF ion source.

**Figure 5.** Energy distributions for protons emitted at $\theta = 0^\circ$ for different projectile energies as indicated in the figures.

**Figure 6.** Proton energy distributions emitted in collisions of 22 keV ArH$^+$ incident on different targets ($E_{eq}=535$ eV). The distribution for CH$_4$ is divided by 2.
Distributions of protons emitted from dissociation in the beam direction as a function of the projectile energy are shown in figure 5. The cross sections increase as \( E_0 \) varies from 10 keV to 40 keV. The shape of the distributions changes significantly. While for the higher energies the central peak is lower than the lateral peaks, its relative contribution grows as the energy decreases and becomes the dominant structure at 10 keV. The lateral peaks relative contributions become then small, and they are hardly distinctive for energies lower than 10 keV.

The intensity and the shape of the structures may also be compared for different targets, (Figure 6). All the distributions show a central peak located at the proton equivalent energy and the symmetrical structures around them. These structures, hardly observed for CH\(_4\), are clearly distinctive for He. The central peak is the main contribution for all the targets considered, being the biggest for CH\(_4\), while the lowest is due to He. As the characteristic impact parameter to dissociate the target becomes smaller with the target size, the probability of excitation may increase.

3. Conclusions
In summary, we have found no evidence for H capture at the energies where no contamination effects were present. A better mass separation is necessary to avoid beam contamination with molecular species.

We obtained, in addition, proton distributions from dissociation of rare-gas-hydride molecules in collision with atoms and molecules.

We have shown that the observed structures, located at velocities close to that of the projectile, depend on the target species and the projectile energy. A central peak, identified as dissociation from the ground state, conforms the main contribution at lower energies, while lateral peak-shape structures symmetrically distributed around the central one become observable at higher energies. These structures correspond to isotropic proton emission from dissociative states produced by electronic excitation to continuum vibrational states.

Excited vibrational states of the molecular ions, populated in the RF ion source, appear to be necessary to interpret the observed structures.

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