H_2 and N_2 ionization and dissociative ionization by C^- and O^- ions at intermediate velocities: Direct and electron loss channels

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Cross sections for single ionization and dissociative ionization of molecular targets under the impact of atomic anions were measured. Three systems were investigated, a H_2 target with C^- and O^- projectiles, and a N_2 target with O^- projectiles. The velocity range was 1.07–2.14 a.u. Recoil ions originated from the target (H_2^+, H^+, N_2^+, N^+, and N^{2+}) were measured in coincidence with projectiles in several final charge states ($q=-1$, 0, +1, and +2). These states, negative, neutral, and positive, respectively, correspond to direct, single, and multiple electron loss channels. Target ionization is mostly due to the projectile single electron loss and direct processes, while target fragmentation is dominated by the projectile double electron loss. These results point to both target ionization and projectile direct or single electron loss processes being dominated by large impact parameters, while fragmentation and multiple electron loss are associated to small impact parameters.

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I. INTRODUCTION

Negative ions (anions), and especially their collision processes with molecules, play an important role on a number of areas. For instance, collision processes associated to the Cl^- anion were found to be responsible for the depletion of the Earth ozone layer. The electrical conductivity of gases, the chemical and ionic composition of planetary upper atmospheres, the light emission in glow discharges, and the opacity of the solar atmosphere at red and infrared wavelengths, are all influenced by the presence of even small concentrations of anions [1,2]. The important, and sometimes unexpected, properties of these anions have been recently reviewed [3].

Systematic cross section measurements were undertaken by our group for several processes and universal scaling rules were found. A method for measuring total electron detachment cross sections was employed for atomic anions belonging to the second and the third periods of the Periodic Table, for He, Ne, and Ar targets [4]. In short, these anions, although presenting a wide range of electron affinities, had cross sections with nearly the same velocity dependence, differing only by multiplicative factors. The velocity dependence of these cross sections was similar to the one presented by the electron total (elastic plus inelastic) cross sections for the same target [5]. Thus, at least for collision studies at intermediate velocities, the extra electron of the anion behaved as a quasifree particle, and detachment was associated to the scattering of this electron.

Collisional destruction processes of small anionic clusters by noble gases [6] and by molecular nitrogen [7] were also studied. These experiments, using molecules either as target or as projectile, displayed the same trends as the previous anion-atom experiments, i.e., the cross sections were essentially a target-dependent curve multiplied by projectile-dependent factors.

Another set of experiments reported measurements of detachment cross sections for atomic halogen anions colliding with a molecular nitrogen target [8]. A simple geometric scaling was successfully proposed, based on the definition of halogen anion radii r_p [9,10] and on modelling the nitrogen molecule as two nitrogen atoms with radii equal to its average Hartree-Fock value r_t [11]. When the electron detachment cross sections of the halogen anions by N_2 were scaled by the factors $\pi(r_p+r_t)^2$ the F^-, Cl^-, Br^-, and I^- curves coincide with each other. Besides that, the velocity dependence of the total scattering cross section for electrons was also verified to be nearly identical to the detachment cross sections for halogen and hydrogen anions.

All these results motivated us to more detailed experiments and, in a subsequent work, cross sections were measured for B, C, and O anions colliding with He atoms [12]. A time-of-flight system and the coincident detection of the recoil ions and the projectile allowed measuring cross sections for several helium ionization channels, direct ionization (DI), i.e., no projectile electron loss, single (SL) and double (DL) electron loss. Similar orders of magnitude of the DI, SL, and DL cross sections were found.

The present paper uses the same experimental methods of Ref. [12], but now with molecular targets, studying their ionization and fragmentation. Cross sections were measured for the collision of C^- and O^- anions with H_2 molecules, and for O^- colliding with N_2.

The introduction of molecular targets serves, as one of its goals, to test the geometric character of these collisions, already discussed for the total detachment cross sections of anionic clusters in noble gases [6] and halogen atomic anions in molecular nitrogen [8].

Also, the double-to-single ionization ratio of hydrogen molecules, essentially identical to the ratio of the H^+ and the H_2^+ production cross sections [13], have been measured for a variety of projectiles [13]. Nevertheless, as far as the authors

TABLE I. H_2^+ and H^+ production cross sections (10^{-16} cm^2), under C^- impact, for direct ($\sigma_d^{ion}, \sigma_d^+$) and single electron loss ($\sigma_{sl}^{ion}, \sigma_{sl}^+$) collision processes. The superscripts ion and + stand, respectively, for molecule ionization and production of atomic singly charged fragments.

Velocity (a.u.)	$\sigma_d^{ion}(H_2^+)$	$\sigma_{sl}^{ion}(H_2^+)$	$\sigma_d^+(H^+)$	$\sigma_{sl}^+(H^+)$
1.24	0.84	0.98	0.55	0.63
1.75	0.62	0.77	0.38	0.42
2.14	0.45	0.52	0.27	0.28
2.74	0.21	0.34	0.14	

are aware, it has not been measured using anionic projectiles. Consequently a second goal of this paper was to obtain the ratios for direct ionization of H_2 by anions and compare with literature results when H_2 is ionized by electrons [14].

II. EXPERIMENTAL SETUP

The experiments were done in a 1.7 MV tandem accelerator. A negative ion source, based on the sputtering of material from a sample containing the element of interest, produces almost any atomic anion and can also produce molecular and cluster anions. These ions are accelerated to the high voltage terminal, at the center of the machine, where a gas target is placed. Three cases may happen. The anions lose two or more electrons, with the resulting positive ions being then accelerated another time in the second acceleration stage, between the high voltage terminal and the ground at the end of the system. The negative ions may lose just one electron, becoming neutral and leaving the accelerator with the same energy that they had in the high voltage terminal. Finally, negative ions not losing any electron in the stripper are decelerated and leave the machine with their initial preacceleration energy (a few keV).

In the present experiments the anions come from the neutral atoms obtained in the stripper. A fraction of these atoms capture electrons before the switching magnet and the anions are deflected to the beam line containing the collision setup. As this capture occurs when the neutral projectiles have their largest velocity and capture cross sections fall rapidly as the velocity rises, this technique limits the available velocities of the negative ion beams. The C^- anions may be produced in excited states which could in principle reach the collision region (4 m away from the switch) and alter the measured cross sections. Nevertheless large electric fields, such as the ones induced by the magnetic fields in the switch, are known to quench these excited states.

The experimental setup has been described elsewhere [12]. Briefly, the beam line has two double-slits 2 m apart, and in usual working conditions the beam cross section was a square of side 1 or 2 mm. The vacuum was in the range 10^{-7}–10^{-8} Torr, being maintained by turbo pumps, and by one cold finger at liquid nitrogen temperature. An electrostatic parallel plate analyzer, placed just before the entrance of the chamber, eliminated spurious beams produced between the magnet and the chamber.

The target is a conventional jet inside the scattering chamber differentially pumped by one large diffusion pump (600 l/s) and two other turbomolecular pumps (60 l/s). The charged particles leaving the target are analyzed in charge and mass by a time-of-flight spectrometer (TOF), orthogonal to the plane that contains the beam and the jet. The projectiles are again electrostatically analyzed after passing the target chamber.

The TOF allows measuring coincidences between the projectile and the target charged fragments, both in several possible charge states. Standard electronic modules were used, with the start being given by the projectiles. Neutral projectiles are detected by a surface barrier detector and charged projectiles by a channeltron. The positively charged target fragments, analyzed by the time-of-flight spectrometer, are also detected by a channeltron.

III. RESULTS AND DISCUSSION

Cross sections for ionization and fragmentation of molecular targets under the impact of atomic anions were measured for several projectile final charge states, the direct, single, double, and triple electron loss channels. Three systems were studied, a H_2 target with C^- and O^- projectiles, and a N_2 target with O^- projectiles. Recoil ions originated from the target ($H_2^+, H^+, N_2^+, N_2^{2+}, N^+, N^{2+}$, and N^{3+}) were measured in coincidence with the final charge state of the

TABLE II. H_2^+ and H^+ production cross sections (10^{-16} cm^2), under O^- impact, for direct and single electron loss (same symbols as in Table I).

Velocity (a.u.)	$\sigma_d^{ion}(H_2^+)$	$\sigma_{sl}^{ion}(H_2^+)$	$\sigma_d^+(H^+)$	$\sigma_{sl}^+(H^+)$
1.07	0.70	0.81	0.28	0.53
1.52	0.61	0.55	0.14	0.27
1.86	0.44	0.40	0.09	0.16
2.14	0.28	0.26	0.02	0.09

TABLE III. N_2 ionization cross sections (10^{-16} cm^2), under O^- impact, for direct (σ_d^{ion}) and single (σ_{sl}^{ion}), double (σ_{dl}^{ion}), and triple (σ_{tl}^{ion}) electron loss processes.

Velocity (a.u.)	σ_d^{ion}	σ_{sl}^{ion}	σ_{dl}^{ion}	σ_{tl}^{ion}
1.07	0.78		0.61	0.061
1.52	0.54	0.84	0.39	0.031
2.14	0.19		0.08	0.020

TABLE V. N^{2+} production cross sections (10^{-16} cm^2), under O^- impact, for direct (σ_d^{2+}) and single (σ_{sl}^{2+}), double (σ_{dl}^{2+}), and triple electron (σ_{tl}^{2+}) loss processes.

Velocity (a.u.)	σ_{sl}^{2+}	σ_{dl}^{2+}	σ_{tl}^{2+}
1.52		0.28	0.15
1.86	0.023	0.06	0.04
2.14		0.01	0.08

projectile ($q=-1$, 0, +1, and +2). The time-of-flight method is not able to separate channels $H+H^+$ from H^++H^+, and N^+ from N_2^{2+}. However, from comparison of our results to those of Shah and Gilbody [15], it is inferred that the $H+H^+$ channel contributes with nearly 85% to H^+ production. Also, from estimates based on the data of Knudsen *et al.* [16] for CO_2 ionization and fragmentation, we can consider that the yield of N_2^{2+} is small, about 10%, compared to the N^+ yield.

For the C^--H_2 and the O^--H_2 collision systems we measured the production of H^+ and H_2^+. Both the direct and the single electron loss cases were studied. The velocity range was 1.24–2.74 a.u. for the C^- projectile and 1.07–2.14 a.u. for the O^-. For the N_2-O^- collision system we similarly measured the production of N^+ (N_2^{2+}), N^{2+}, and N_2^+, but now recording the direct, single, double, and triple electron loss cases. N^{3+} was not distinguishable from uncertainties. The velocity range was 1.07–2.14 a.u.

The normalization was done taking into account the beam current stability of our accelerator, better than 1% in 1 hour. Otherwise, we measured always the ionization by 1 MeV protons and normalized the data using averaged cross section values, coming from various experiments, 3.75×10^{-22} cm^2 for H_2 and 14.6×10^{-22} cm^2 for N_2 [17]. The experimental results are shown in Tables I and II for H_2 and Tables III–V for N_2, where the relative standard deviation of each value is 15%.

We begin the discussions with the projectile dependence of the H_2 results. Cross sections, for all measured combinations of the final projectile charge state and the recoil target ion, when compared at the same velocities are always larger for C^- than for O^- projectiles. For ionization the cross sections for C^- are higher, but within the same order of magnitude, than those for O^-. However, the difference increases in processes involving H^+ production (dissociative ionization) where cross section values for C^- can be up to 10 times larger, as can be seen in the two right columns of Tables I and II.

Looking now into dissociative ionization (H^+ production), the relative importance of the direct and the single loss cross sections presents a projectile dependence. While there are similar cross section values under the impact of C^- projectiles, for the O^- case the single loss values are a factor of 2 larger than the direct values. Likewise, the only measured value for N^+ production by O^- (Table IV) under single loss conditions is also a factor of 3 larger than the corresponding one for the direct process.

TABLE IV. N^+ production cross sections (10^{-16} cm^2), under O^- impact, for direct (σ_d^+) and single (σ_{sl}^+), double (σ_{dl}^+), and triple electron (σ_{tl}^+) loss processes.

Velocity (a.u.)	σ_d^+	σ_{sl}^+	σ_{dl}^+	σ_{tl}^+
1.07	0.27		1.96	0.56
1.52	0.11	0.33	0.48	0.22
2.14	0.05		0.20	0.11

Now we will compare the ionization and the charged atomic fragments production, first for the direct and then for the electron loss channels. For the direct channels, where the anion remains intact, ionization exceeds fragmentation in all three cases. This fact points to the idea that smaller impact parameters have a larger probability to fragment the molecule at the same time that the projectile increases its chance to lose electrons. The same holds true for single loss processes, as ionization always exceeds fragmentation for distinct projectiles and targets.

Considering now direct processes for O^-+H_2 and C^-+H_2 collisions, our present results for the ratio of the H^+ to the H_2^+ production cross sections are consistent with reported data by Hvelplund *et al.* [14] for p^-+H_2 collisions, presenting roughly the same values. O^- data present the same monotonic decrease as the antiproton data. Nevertheless C^- data is nearly constant, indicating that a more clear picture requires more measurements.

Considering the similarities of these anions, C^- and O^-, concerning sizes, electron affinities and ionization potentials we remark, as a possible explanation for the values of C^- cross sections being larger than those for O^-, the existence of metastable states in the capture of one electron by carbon [18–20].

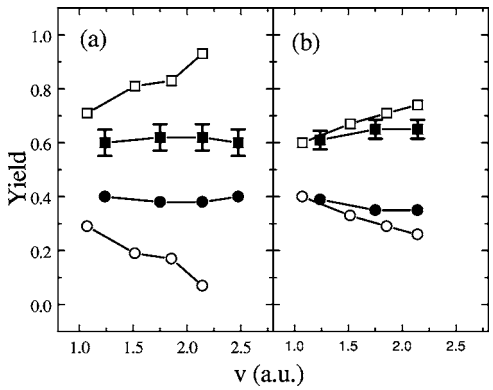

FIG. 1. Relative ion production of C^- (closed symbols) and O^- (open symbols) on H_2 targets, (a) direct processes and (b) single electron loss; circles, $\sigma_{H^+}/(\sigma_{H^+}+\sigma_{H_2^+})$; squares, $\sigma_{H_2^+}/(\sigma_{H^+}+\sigma_{H_2^+})$.

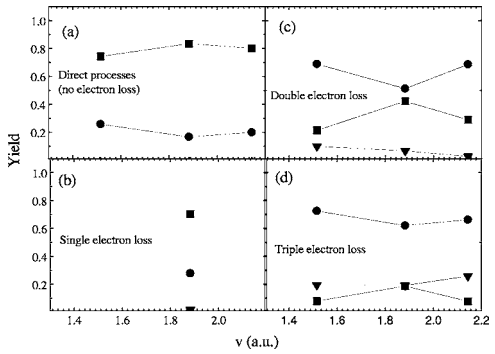

FIG. 2. Same as Fig. 1 for N_2 targets with O^- projectile, (a) direct ionization, (b) single loss, (c) double loss, and (d) triple loss; circles, $\sigma_{N^+}/(\sigma_{N^+}+\sigma_{N_2^+}+\sigma_{N^{2+}})$; squares, $\sigma_{N_2^+}/(\sigma_{N^+}+\sigma_{N_2^+}+\sigma_{N^{2+}})$; triangles, $\sigma_{N^{2+}}/(\sigma_{N^+}+\sigma_{N_2^+}+\sigma_{N^{2+}})$.

In the N_2 case and for direct processes (i.e., no anion electron loss), cross sections for molecule ionization are several times larger than the fragmentation ones, for the three measured velocities. These large cross section values suggest the dominance of large impact parameters, and indicate that our anion is seen by the target as a negative point charge. In other words, the condition for the anion to survive after the ionization of H_2 or N_2, given the small binding energy of its extra electron, is to behave as a point charge, i.e., either to have a small radius and/or to be far from the target. In fact, when compared with other values existing in the literature for positive ions, our values of direct ionization are only slightly different from the ionization of He by protons [17] and positive oxygen ions at velocities near 1.4 a.u. [18], for example.

Considering now the dissociative ionization of the molecular nitrogen target, it occurs mostly associated to the projectile double electron loss. It means that when the projectile collides with the target, the anion loses one or more electrons, while it breaks the target molecule. In this case, it could indicate that small impact parameters are responsible for these processes. It is worthwhile to mention that for impinging (10–100 keV) protons on N_2, the formation of N_2^+ ions dominates for both electron capture and ionization [17]. The N^{2+}/N^+ ratio is surprisingly larger for O^- than for protons, indicating an important contribution from projectile electrons to target fragmentation.

As a more clear way to discuss ionization and fragmentation, we show in Figs. 1 and 2 the yields for ion production in C^- and O^- interaction with H_2 and O^- with N_2, relative to the total. Figure 1, presenting the H_2^+ data, shows that the dominant effect is target single ionization. For direct processes, target ionization achieves yields in the 60%–70% range whereas fragmentation contributes with about 30%–40%. For the single electron loss case, target ionization presents distinct projectile behaviors, for O^- impact it decreases relative to the corresponding direct ionization values, while it remains nearly unaltered for the C^- case.

For the N_2 target there is a more complete picture, as we could also measure double and triple electron loss from the projectile. Figures 2(a)–2(d), respectively, present the N^+, N_2^+, and N^{2+} ion production yields for direct ionization and for single, double, and triple electron loss. We see that target ionization, i.e., N^{2+} ion production, is the dominant effect for direct ionization but becomes less dominant for single loss. For double electron loss, target ionization is less important than dissociative ionization leading to N^+ production. Target ionization becomes the less important of the three ion production channels for triple electron loss. We observe an evolution of each ion production as a function of the selected projectile charge state. Thus, N^{2+} production is nearly negligible for emerging O^- and grows up to 20% for triple loss, and the most noticeable case is that of N^+ production, which goes from 20% up to 60%. These results indicate, as noted before, that small impact parameters produce fragmentation with higher probabilities while the emerging projectile loses electrons. (See Ref. [20].)

As a first conclusion we mention that direct processes give an essential contribution to the ionization cross section of molecular targets, as already observed for noble gas targets [12], and a smaller one for the target fragmentation. Whereas the atomic fragment production is dominated by small impact parameter, and this reduces the survival probability for the incoming anion, direct ionization is dominated by large impact parameters, where the geometric character becomes evident. In other words, a very simple qualitative model can represent these two different regimes. A second conclusion is related to the comparison of the double-to-single ionization ratio of two-electron targets, such as H_2, under the impact of anions. Our preliminary results suggest an overall similarity with antiproton-impact data. Nevertheless a projectile dependence, verified when comparing C^- and O^- data, indicates that a more clear picture requires measurements with a wider spectrum of projectiles and velocities.

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