Negative atomic halogens incident on argon and molecular nitrogen: electron detachment studies

Ginette Jalbert1, Aline Medina1, S D Magalhães1, Wania Wolff1, Ana L F de Barros2, P Carrilho1, A B Rocha3 and N V de Castro Faria1

1Instituto de Física, Universidade Federal do Rio de Janeiro, Caixa Postal 68528, Rio de Janeiro, 21941-972 RJ, Brazil
2Centro Federal de Educação Tecnológica Celso Suckow da Fonseca - CEFET-RJ, Rio de Janeiro, 20271-110 RJ, Brazil
3Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 21941-909 RJ, Brazil

E-mail: ginette@if.ufrj.br

Abstract. During the last years we have measured total detachment cross sections of atomic and cluster anions colliding with gases in the velocity range of 0.2 to 1.8 a.u.. In particular, we measured negative atomic halogens incident on argon and molecular nitrogen. These last data are for the first time analyzed using the simple semi-classical model that we have developed. For that purpose, the values of elastic plus inelastic cross sections for impact of free electrons on Ar and N2, the latter showing a shape resonance, convoluted with the anion's outermost electron momentum distribution yielded the overall shape of the anion cross sections. Inclusion of a velocity independent additive term, interpreted as an effective area of the collision region, led to accurate absolute cross section values. The high affinity of the halogens and the existence of a not well described resonance in the e-N2 collision, are characteristics that may be used to delimit the scope and validity of the model.

1. Introduction

Negative ions [1] can be accelerated by electric fields, deflected by electric and magnetic fields, and their outermost electrons are very weakly bound [2] and easily detachable. These facts make them suitable for applications where a fast neutral beam is required, for example, in the inertial confinement fusion [3]. Negative ions also possess dissimilar properties from the corresponding neutral and positive species, such as the existence of usually only one bound state [4]. As a consequence, they could be an interesting alternative to test theories and models usually developed for neutral and positive species.

During the last years we have systematically measured total electron detachment cross sections of atomic and cluster negative ions of elements of the second and third periods of the Periodic Table of Elements colliding with noble gases and nitrogen [5, 6] in the velocity range of 0.2 to 1.8 a.u.. Such study has been made possible because we developed a practical method of measuring these quantities by using a sputtering negative ion source and a standard tandem accelerator [5]. Until the development of our method, the experimental study of this kind of collisions suffered limitations due to the lack of appropriate apparatuses or perhaps
interest. Our interesting experimental studies have led us to devise different models, which have attained different degrees of success [6, 7]

Our experimental results exhibit some peculiar features. In all cases considered, namely atomic and cluster anions colliding with atoms (He, Ne and Ar) and a molecule (N₂), it is observed that for any given target the cross sections show similar velocity dependence, and also a maximum situated at almost the same velocity value. This value, however, differs for distinct targets. Even more astonishingly, the observed dependence on velocity shows a striking similarity to that reported in the literature for the elastic plus inelastic cross sections of free electrons, in collisions with the same targets used in our experiments. These interesting features are shown in Figure 1, where the three lines in (b) representing the anions results are normalized averages of a large number of measurements. In fact, for He and Ne targets the curves in (a) and (b) show a strong similarity. For the Ar target, the anions curve is broader than that for free electrons, but in both cases the maxima occur roughly around the same velocity. Finally, in the N₂ case shown in Figure 2, there are broad maxima at the same velocity for all the anions considered, and for free electrons the well known shape resonance occurs in its vicinity. So far this resonance did not show up in our results with anions, however experimental results not yet published hint that in some cases, namely anions of atoms with small affinities, it is observed but significantly broadened by the electron momentum distribution.

![Figure 1](image1.png)

**Figure 1.** (a)Total elastic plus inelastic cross sections of free electrons colliding with He, Ne and Ar; (b)Averaged normalized experimental detachment cross sections of different anions colliding with He, Ne and Ar, including F⁻ and Cl⁻.

![Figure 2](image2.png)

**Figure 2.** (a)Total elastic plus inelastic cross sections of free electrons colliding with the molecule N₂; (b)Total experimental electron-detachment cross sections for F⁻ (∧), Cl⁻ (○), Br⁻ (△) and I⁻ (□) projectiles incident on N₂.
Why, in both Figures 1 and 2, do the two sets of curves (a) and (b) show these resemblances? The answer comes from the fact that the outermost electrons of the negative ions are very weakly bound. In other words, the transversal momentum needed to deflect an incident free electron, in the case of an incident anion is sufficient to detach its less bound electron. However, in the latter case, the not completely free electron has a velocity distribution around the anion’s velocity which makes, for example in the Ar case, the peak broader than in the free electron case. In fact, it is as if a beam of electrons with a poor energy resolution were incident on the target. In the He and Ne cases, this effect is less pronounced, because the free electron curve is more flat.

In order to gain insight into what happens in such complex collisions, a simplified description of the outermost electron and the others is needed. In [7], where clusters colliding with argon were studied, this was particularly the case. For the atomic outermost electrons, the velocity distributions were taken from a Fourier transform of the Hartree-Fock level wave functions calculated by Clementi and Roetti [8]. For the clusters outermost electrons, in some less complex systems, the velocity distributions were obtained from a Fourier transform of Hartree-Fock level wave functions calculated with the program Gamess. And finally, for the other electrons involved a geometrical approach was used in which the cross section is derived from an effective area of the collision region. That is a very complex case, because even in a single detachment event the electron can come from the core, and that can also be the case, for at least one of the electrons, in double or multiple detachment events. Such relatively large number of possibilities are thus probably the reason why the geometric approach works well. Another point in favor of our model is that core electrons demand small impact parameters to be detached. Anyway, a detailed calculation would be too complex. In fact, our method uses experimental or well established theoretical descriptions of the free electron scattering by atoms and molecules, together with the momentum distribution of the less bound electron of the anion, to reproduce the shape of the experimental curves.

2. Experimental results

The experiments that we analyze in this article were performed at the “Laboratário de Colisões Atômicas e Moleculares - LaCAM” of the “Universidade Federal do Rio de Janeiro-UFRJ”. Briefly, beams of atomic and cluster anions were produced by a source of negative ions by cesium vapor sputtering (SNICS-II). The ions were pre-accelerated to a kinetic energy $E_p$ and, after mass selection in a Wien filter, acquired an additional energy $V_e$ in the first stage of our laboratory’s 5SDH Pelletron accelerator, in which the potential $V$ may be as high as 1.7 MV. With that energy ($E_p + V_e$), they go through the gas stripper.

All our measurements of the total electron detachment cross sections were made using the stripper gas as target. This method is feasible because the pressure of the gas, which is introduced from outside through a pressurized insulating tube and regulated by an externally controllable valve, though not directly measurable, is nevertheless known. For each gas (He, Ne, Ar and N$_2$), published values of single-electron-loss cross sections of H$^-$ were used to make a correspondence between the stripper gas pressure and the readings of an ion gauge, placed at the grounded high-energy end of the accelerator.

The total, and absolute, detachment cross sections were extracted from exponential decay curves, obtained by varying the target pressure. Normalization was simple due to the stability of the accelerator beam current for time intervals of a few minutes. Uncertainties in the exponential fitting procedure and in the cross-section values used in the stripper pressure calibration are the main causes of uncertainty in the measured cross sections, estimated to be around 4 to 7 per cent.
Figure 3. Radial distribution functions for F\(^{-}\) (solid line) and Si\(^{-}\) (dashed line).

3. Model

In Figure 1(b) we illustrate our discussion of the model, presenting average normalized results of measured cross sections of atomic anions of the 2\(^{nd}\) and 3\(^{rd}\) periods of the Table of Elements, including F\(^{-}\) and Cl\(^{-}\). We show in figure 2(b) atomic halogen anions incident on N\(_2\). It is evident from the results shown in both figures, that each target (He, Ne, Ar and N\(_2\)) has shown a pattern, quite independent of the incident anion species. It will be shown that these differences reflect the wave function of the anion's outermost electron.

In our model the spatial wave functions of the least bound electrons \(\psi(\vec{r})\) are taken from wave functions tables of Clementi and Roetti [8]. They are given by a linear combination of Slater type orbitals \(\chi_i(\vec{r})\):

\[
\psi(\vec{r}) = \sum_{i=1}^{i=N} C_i \chi_i(\vec{r})
\]  

(1)

The basis functions are then factorized into a radial \(\psi(r)\) and an angular part. In Figure 3 are shown the radial distribution functions \(|\psi(r)|^2r^2\) of the fluorine and silicon ions, of large and small affinity, respectively. The square of the Fourier transform of the wave function of the valence electron, integrated over the perpendicular directions to the beam direction, \(|\Psi(k_z)|^2\), is shown in Figure 4 as a function of the momentum in the beam direction, for the same negative ions.
As already explained, in our model the contribution of the outermost electron to the total detachment cross section is obtained from the following convolution:

\[
\sigma_{\text{eleconv}}(v) = \int \sigma_{\text{electron}}(V) g(v - V) dV
\]

(2)

where \( g(v - V) \) is the velocity distribution of the anion’s outermost electron, i.e., the Fourier transform of the negative ion wave function in coordinate space; where, with \( k_z = V \) in atomic units,

\[
g(v - V) = |\Psi(v - V)|^2
\]

(3)

\( \sigma_{\text{electron}}(V) \) is the electron impact cross section for the gas; and \( \sigma_{\text{eleconv}}(v) \), the anion’s outermost electron detachment cross section.

It can be noticed that for silicon the width of the radial distribution function is about twice that for fluorine. Though the velocity distribution curves are symmetric, the free electron cross sections curves are not symmetric with respect to their maxima, thus shifting the maxima of the resulting anions outermost electron cross sections, obtained through convolution. Those displacements are also observed in the experimental results.

The role of the core electrons of the negative ions is more difficult to describe. In fact, as already stated, the complexity of the interaction of those electrons with the target electrons makes it difficult for a first principle description of the collision process. In fact, there are a large number of possibilities, i.e., the core electron can be detached in many different ways. For example, when one electron is detached it can come from the core. In the case of multiple detachment, surely at least one electron comes from the core. In our geometrical approach, the additive constant needed to reproduce the experimental results is defined as:

\[
b = \pi (R_{\text{core}} + R_{\text{target}})^2
\]

(4)

The core radius \( R_{\text{core}} \), the target atom radius \( R_{\text{target}} \), and more generally the size of an atom, are not precisely defined physical quantities. The value assigned to the radius of a particular atom will always depend on the definition chosen for “atomic radius”, and the more appropriate definition will depend on the physical situation under study. However, we can estimate the order of magnitude of the atomic radii. Knowing \( b \) and \( R_{\text{target}} \), we can extract \( R_{\text{core}} \) and compare it with the values existing in the literature.

4. Calculations
First, we present an analysis for \( F^{-} \) and \( Cl^{-} \) incident on \( Ar \). Figures 5(a) and 5(b) show the results of the convolution followed by the fitting of the additive constant, for \( Cl^{-} \), together with the experimental results. Although the agreement could be considered good, these results are not our best when compared with other calculations for atomic and cluster anions that we have already published [7]. In fact, halogens have high affinities when compared with the atoms of reference [7], which means they have more tightly bound outermost electrons. As a consequence, our free electron hypothesis is less valid.

The core radius that is obtained using expression (2), with \( R_{\text{target}}(v)=0.71\,\text{Å} \), is \( r_{\text{core}}(Cl)=0.5\,\text{Å} \), comparable to the value found in the literature, i.e., \( r(Cl)=0.79\,\text{Å} \). For \( F \), as shown in Figure 5(b), the free electron results are too near the \( F^{-} \) result to allow a radius to be extracted.

Second, an analysis of the total electron - nitrogen molecule scattering cross section is presented. Figure 2(a), from references [9, 10], shows a resonance near 0.5 a.u. and a broad maximum near 1.2 a.u.. In our calculations, for the region of velocities larger than approximately 0.5 a.u., we used experimental values of different authors [9]. In the vicinity of that resonance,
and also for low velocity values, where the incident electrons have energies less than 2 eV, we chose to use theoretical calculations [11, 12].

When we perform the convolution, although the resonance is roughly in the same position of the halogen anions maxima, the agreement is not so good as in the results of figure 5 and of reference [7]. This is due to the assumed e-N₂ input data for velocities lower than 0.5 a.u..

Figure 6 illustrates the results obtained for Cl⁻ and I⁻.

5. Conclusions
We had two main reasons to adopt a semi-empirical model to describe our experimental results. First, the fact that all detachment cross sections of atomic or clusters anions colliding with atoms and molecules present the typical behavior shown in figures 1(b) and 2(b), i.e., all have essentially the same shape, and a maximum at a target dependent position. Second, the fact that available experimental and theoretical results on electron-atom or electron-molecule collisions, systems that are much simpler than anions colliding with atoms and molecules, show a striking similarity to our results. The cross section maxima even occur at almost the same position.

Finally, the published electron collision results are supposed to be well known and accurate. In fact, when comparing the figures 1(a) and 2(a), the main and important difference comes from the shape resonance of the e-N₂ collisions shown in figure 2(a). The fact that the cross sections for the electron-noble gas collisions shown in figure 1(a) for He, Ne and Ar, are well known and smooth, is responsible for the good agreement between our model and the experimental values. In addition, the experimental and theoretical uncertainties in the resonance shape and, more important, the fact that the resonance is rather intense and too near the zero velocity, and
the electron velocity distribution of halogens too broad, puts a limit to the applicability of our model.

Acknowledgments
This work was partially supported by the Brazilian agencies CNPq, FUJB and FAPERJ.

References
[1] Earl W, McDaniel, Mitchell J B A and Rudd M E 1994 Negative Ions, Atomic Collisions: Heavy Particle Collisions (New York: Wiley-Interscience)
[2] Andersen T 2004 Phys. Rep. 394 157
[3] Sant’Anna M M, Zappa F, Santos A C F, de Barros A L F, Wolf W, Coelho L F S and de Castro Faria N V 2004 Plasma Phys. Control. Fusion 46 1009
[4] Andersen T, Haugen H K and H. Hotop 1999 J. Phys. Chem. Ref. Data 28 1511
[5] Luna H, Magalhães S D, Acquadro J C, Martins M H P, Santos W M S, Jalbert Ginette, Coelho L F S and de Castro Faria N V 2001 Phys. Rev. A 63 022705
[6] Zappa F, Jalbert Ginette, Coelho L F S, Rocha A B, Magalhães S D and de Castro Faria N V 2004 Phys. Rev. A 69 012703
[7] Jalbert Ginette, Silva Lívia, Wolff Wania, Magalhães S D, Medina Aline, Sant’Anna M M and de Castro Faria N V 2006 Phys. Rev. A 74 042703
[8] Clementi E and Roetti C 1977 At. Data Nucl. Data Tables 14 177
[9] Hoffman K R, Dababneh M S, Hsieh Y -F, Kauppila W E, Pol V, Smart J H and Stein T S 1982 Phys. Rev. A 25 1393
[10] Kennerly R E 1980 Phys. Rev. A 21 1876
[11] Dubé L and Herzenberg A 1979 Phys. Rev. A 20 194
[12] Gillan C J, Noble C J and Burke P G 1988 J. Phys. B At. Mol. Opt. Phys. 21 L-53