Electron-detachment cross section for CN^- and O_2^- incident on N_2 at intermediate velocities

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The electron-detachment cross section was measured for the molecular negative ions CN^- and O_2^- incident on N_2, in the 0.08–1.2 a.u. velocity region. Our setup uses the gas stripper of a tandem accelerator as a gas chamber. All cross sections present a maximum near 0.4 a.u., a velocity corresponding to the well-known shape-resonance that appears in the electron-N_2 collisions. A semiclassical model is employed to analyze the data. The role of this shape resonance is discussed in this article.

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I. INTRODUCTION

The process of anion electron loss in collisions with N_2 may pose interesting questions in the basic physics of ion-molecule collisions, whereby one may investigate what is the role played by the $^2\Pi_g$ shape resonance [1–3] on anion-N_2 electron-detachment processes. The effects of the shape resonance in anions colliding with N_2 were first observed by Risley, when measuring the detached-electron energy spectrum of H^-+N_2 collisions [4]. Afterwards other anion-N_2 collision systems were studied, among them F^--N_2 [5]. A theoretical model [6] predicted that the maximum charge exchange into the shape resonance occurs when the translational energy of the quasifree anion electron equals the N_2^- ($^2\Pi_g$) resonance energy of 2.2 eV. This maximum in the cross sections appears when the projectile velocity around 0.4 a.u.

On the other hand, we have already studied collisions of negative atomic, molecular and cluster ions, with several target atoms and molecules (see, for example, Refs. [7–9] and references therein), in the range from intermediate to high impact velocities. In fact, we developed a method of measuring cross sections of electron detachment in the case of atomic anions and destruction cross sections in the case of molecular or cluster anions. The method requires a stable source of negative ions of only a few tens of keV, in our case a SNICS ("Source of Negative Ions of Cesium Sputtering"), and also a tandem accelerator with a gaseous stripper fed from an external reservoir.

In order to interpret the behavior of the anion electron loss in collision with N_2 as a function of the relative velocity, we perform an extension of a simple model already proposed and employed by our group for atomic anions (see, for example, Ref. [9]), where the outermost electron is considered in a quasifree state with a momentum distribution and the electron-loss process is governed by the free-electron scattering cross section, which can be obtained from the literature. The similarities between the experimental cross sections of anions and electrons, observed in the velocity range of 0.2 to 1.8 a.u., suggest that the anionic cross sections can be described by a convolution of the momentum distribution of the anions' outermost electron with the free-electron-impact cross sections, where the absolute values may be obtained by adding a constant value, associated with the neutral core of the anion.

In addition to the interest in the basic physics of ion-molecule collisions, the study of electron detachment of anions is of particular interest in astrophysics. For example, the negatively charged cyanide CN^- is the smallest molecular anion observed in the interstellar space medium [10]. Other small molecular anions like CH^-, C_2^-, and C_2H^-, which may also occur in other astrophysical environments [11], have been recently studied by our group [12]. In order to investigate these anions in conditions that simulate that of astrophysical media, experiments such as ion storage devices [13] need to be implemented. Since the number of anions in such devices decays with time due to electron-loss processes occurring in collisions between the anions and the residual gases, there has been a growing demand for reliable total electron-detachment cross sections of these anions colliding with common residual gases. In this direction, we measured the electron-detachment cross sections of CN^- incident on N_2. Besides, we also measured O_2^- incident on N_2 for comparison, as will be explained in the text.

II. EXPERIMENTAL ARRANGEMENT AND RESULTS

The experiments were performed in a 1.7 MV tandem accelerator and, as they are described in detail elsewhere (see Ref. [7], for example), only a brief description of the experimental method will be given here. A cesium sputtering ion source produces CN^- and O_2^- anions which are pre-accelerated to a kinetic energy E (in the 5–30 keV energy range) and undergo velocity selection by a Wien filter. Afterwards, the ions are accelerated through the first stage of the 5SDH Pelletron tandem accelerator, which ends at the central high-voltage terminal kept at a potential V, as high as 1.7 MV. It is thus with a final energy $E + eV$ that the negative ions reach the central terminal, where a gas target exists; the stripper. If a negative ion does not loose any electrons in the stripper, it is decelerated and leaves the machine as a

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negative ion, with its initial pre-acceleration energy (E). The low energy of the anions when leaving the accelerator, even though the collision being studied occurs at high energies, allows detecting heavy atomic or molecular anionic projectiles with electro-magnets presenting low or moderate magnetic fields.

The cross sections are extracted from exponential attenuation curves of the negative-ion current as a function of the target pressure, measured indirectly by measuring the pressure at one extremity of the accelerator, at ground potential. The absolute target density can be obtained by comparing the charged fraction yields coming from an auxiliary experiment with a hydrogen beam and from the analytical expressions of these fractions in terms of the well-known hydrogen charge-exchange cross sections [14]. The normalization procedure is simple and feasible due to the high stability of the accelerator beam current for time intervals of a some minutes. The exponential fitting analysis and the literature cross-section values used for the stripper pressure calibration are the major sources of uncertainties in the determination of the absolute cross sections. The results are presented in Table I.

Our experimental results are also presented in Fig. 1, together with the free-electron scattering cross section—elastic plus inelastic—with N_2 [$\sigma_{electron}(V)$] [15]. We have included the already measured data B_2^- and Al_2^- [16] in order to emphasize the huge resonance effect in the anions' cross sections. The error bars of the present measurements, CN^- and O_2^-, came from the exponential adjustment parameter and their systematic error component of calibration (≈10%) is not included in order to draw attention to the small random error; see Fig. 1. It is worth to mention that the systematic error is included in the B_2^- and Al_2^- data, which appear in Fig. 1.

TABLE I. Total-detachment cross sections of CN^- and O_2^- incident on N_2, in units of 10^{-16} cm^2 and the velocity in atomic units.

CN^-		O_2^-	
v(a.u.)	$\sigma \pm \Delta\sigma$	v(a.u.)	$\sigma \pm \Delta\sigma$
0.088	9.85 ± 0.20	0.194	16.66 ± 0.08
0.104	9.98 ± 0.15	0.224	17.23 ± 0.03
0.124	9.95 ± 0.30	0.250	17.4 ± 0.03
0.152	10.66 ± 0.41	0.274	17.55 ± 0.03
0.175	10.20 ± 0.40	0.296	17.87 ± 0.03
0.211	10.96 ± 0.03	0.316	17.89 ± 0.04
0.215	11.12 ± 0.50	0.335	18.12 ± 0.12
0.248	11.73 ± 0.07	0.354	17.78 ± 0.04
0.277	11.61 ± 0.06	0.371	17.80 ± 0.02
0.304	12.33 ± 0.03	0.387	17.88 ± 0.02
0.328	12.56 ± 0.05	0.403	17.86 ± 0.02
0.351	12.91 ± 0.04	0.418	17.84 ± 0.03
0.372	13.12 ± 0.04	0.433	17.68 ± 0.02
0.392	13.20 ± 0.03	0.447	17.55 ± 0.02
0.430	13.41 ± 0.03	0.461	17.78 ± 0.09
0.464	13.75 ± 0.06	0.474	17.87 ± 0.05
0.496	13.69 ± 0.06	0.487	17.74 ± 0.09
0.526	13.51 ± 0.04	0.501	17.77 ± 0.07
0.555	13.36 ± 0.05	0.512	17.62 ± 0.03
0.679	13.01 ± 0.08	0.559	17.39 ± 0.02
0.877	12.42 ± 0.02	0.612	17.10 ± 0.02
1.038	12.04 ± 0.03	0.661	16.91 ± 0.02
1.240	11.57 ± 0.05	0.707	16.84 ± 0.02
		0.791	16.64 ± 0.02
		0.935	16.41 ± 0.08
		1.061	16.34 ± 0.15
		1.173	16.20 ± 0.50

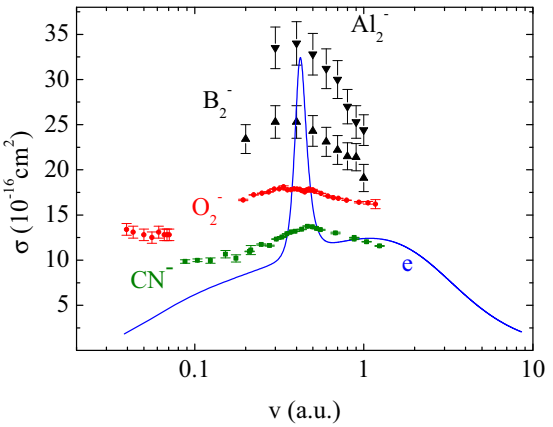

FIG. 1. (Color online) Electron-detachment cross sections for CN^-, O_2^-, Al_2^-, B_2^- and electron-scattering cross section—elastic plus inelastic—(full curve) colliding with N_2 [15], as function of velocity in atomic units. From bottom to top one first finds our present results of CN^-; the second set belongs to O_2^- and it consists of two parts: the one on the left refers to the data of Ref. [17] and the other on the right to our results; the third and fourth correspond to Al_2^- and B_2^- [16], respectively.

We note that all cross sections shown present a very clear prominent peak-like structure around the velocity of 0.4 a.u. and that this peak also appears very prominently in the free-electron scattering cross section. The experimental results taken from Bennet *et al.* [17] for lower impact velocity are also shown in Fig. 1, showing that the peak around $v = 0.4$ a.u. is a local maximum even considering a broader velocity interval than measured by our group.

III. MODEL

Previous experimental results (see, for instance, Refs. [8,9]) have shown that the detachment mechanism has a simple underlying structure, both concerning the projectile and the target dependencies. In fact, it was shown that cross-section curves for electron scattering and negative ion detachment during collisions on rare gas or molecules present similar velocity dependencies. This observation is important because one could in principle use the electron scattering data to predict the behavior of detachment cross sections even where experimental data are not available. Another important point is that the curves for electron detachment are broader than the ones for a free-electron scattering. Also, our previous works have shown that the overall scale of the cross sections for electron detachment cannot be accounted for only by the pure electron scattering data, requiring additional information about

the geometrical size of the colliding partners; namely, the target atom and the neutral core of the colliding anion.

A semiclassical model was then proposed [9]. Here it will just be outlined. The model is based on considering the negative ion as a system formed by a single outermost electron plus a neutral core, each contributing to the detachment cross section and presenting a rather distinctive energy dependence.

The outermost electron contribution to the cross section is obtained by the convolution of its velocity distribution by the total electron scattering cross-section data. The momentum ($\vec{k}$) distribution is computed from the Fourier transform of the spatial wave function obtained from a Hartree-Fock level wave function, while the free-electron impact cross section for N_2 came from Ref. [15]. Identifying the momentum along the beam direction (k_z) as the velocity V expressed in atomic units, we then get the velocity distribution $g(V)$ of the outermost electron from the squared modulus of the Fourier transform of the electronic wave function integrated over the perpendicular directions to the beam direction (z). Thus, we define the outermost electron-detachment cross section (OED) by performing the convolution of the electron impact cross section on the target $\sigma_{\text{electron}}(V)$ with the velocity distribution of the outermost electron in the anion rest frame $[g(v - V)]$:

$$\sigma_{\text{OED}}^{\text{model}}(v) = \int \sigma_{\text{electron}}(V) g(v - V) dV. \qquad (1)$$

The neutral core detachment cross section $\sigma_{\text{NCD}}(v)$ contains the contribution from all electron detachment (single and multiple) except the outermost one. In the collisions between atomic species we have considered this contribution essentially constant [9]. The power of this approach resides in the fact that there was only one free parameter; namely, the geometrical contribution due to the neutral cores. Therefore, the total cross section $\sigma_{\text{TED}}^{\text{model}}$ was written as $\sigma_{\text{OED}}^{\text{model}}(v)$ plus a constant as a free parameter.

For the CN^- and O_2^- cases here studied, the above model was adopted in order to obtain the distribution velocity for the molecular case. For the outermost electron, a Hartree-Fock level wave function was calculated with the program GAMESS package (General Atomic and Molecular Electronic Structure System) [18]. This two-center wave function was then reduced to one center (corresponding to the center of mass of the molecule), giving an expansion similar to the one used for the atomic case except that we have to take into account the molecular symmetry. As this one-center function was written in the molecular frame a rotation needs to be performed in order to obtain a one-center function in the laboratory frame (LAB). In this frame, the velocity distribution corresponds to the squared modulus of the Fourier transform of the electronic wave function integrated over the Euler angles and over the perpendicular directions k_ρ to the beam direction (z).

IV. DISCUSSION

In Fig. 2 appears the results of our analysis corresponding to CN^-. The outcome of Eq. (1) is presented in Fig. 2 by the *dotted* line. Observe that if we add a constant

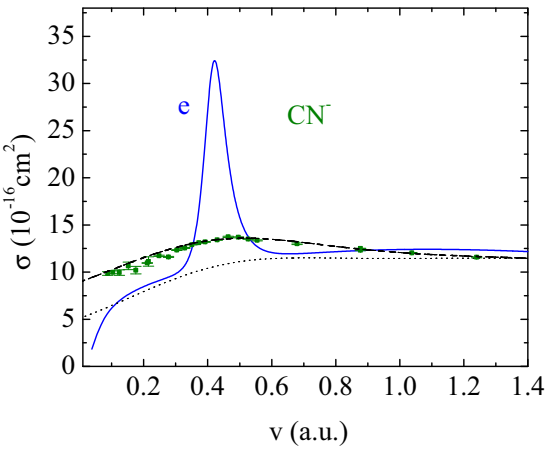

FIG. 2. (Color online) Our theoretical model along with the experimental results and the electron scattering cross section [15]—elastic plus inelastic—(full curve) colliding with N_2 for CN^-: dot for $\sigma_{\text{OED}}^{\text{model}}(v)$ and dash for $\sigma_{\text{TED}}^{\text{model}}(v)$.

($\approx$3.0) to the $\sigma_{\text{OED}}^{\text{model}}(v)$ curve, the result will be compatible with experimental data in the velocity interval from 0.1 to 0.5 a.u., whereas for higher velocities we observe a deviation from the experimental data when the same constant is added.

In Fig. 3 we now present the results of our analysis corresponding to O_2^-. The outcome of Eq. (1) corresponds to the *dotted* line. Unlike the CN^- case the shape of the experimental curve is not so well reproduced by our approach.

First, in the CN^- case, the contribution of the outermost electron for the cross section is more than 80% of the total one (see in Fig. 2 the *dotted* line). However, for O_2^- this contribution is less than 40% of the total cross section. As the dependency on the velocity of the cross section shape is given by the outermost electron contribution, the flat dependence dominates the O_2^- case. An equivalent way to understand the cross-section behavior is shown in Fig. 4, where we display the squared

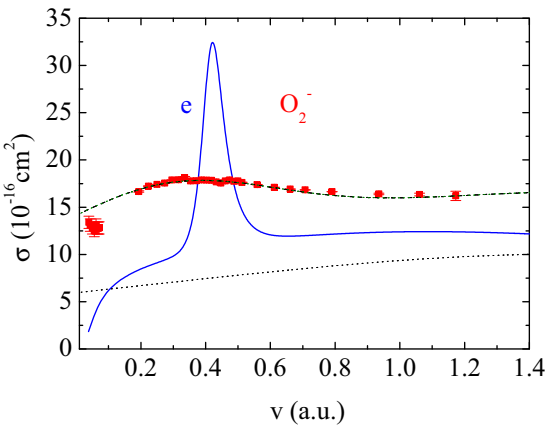

FIG. 3. (Color online) Our theoretical model along with the experimental results and the electron scattering cross section [15]—elastic plus inelastic—(full curve) colliding with N_2 for O_2^-: dot for $\sigma_{\text{OED}}^{\text{model}}(v)$ and dash for $\sigma_{\text{TED}}^{\text{model}}(v)$. Empty squares give experimental values of Ref. [17].

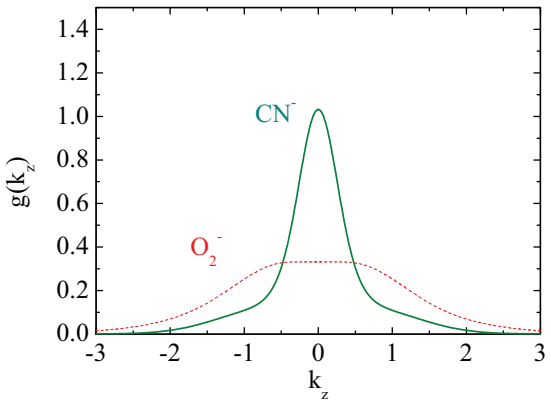

FIG. 4. (Color online) Squared modulus of the Fourier transform g as function of the momentum k_z along the beam direction. Full curve: CN^-, dash: O_2^-. See text for details.

modulus of the Fourier transform $g(k_z)$ of the electronic wave functions integrated over the perpendicular directions to the beam direction (z) for the two anions here considered. The flat behavior of the theoretical cross sections for O_2^- may be associated with the behavior of the Fourier transform of its wave function.

Second, there are few anions which are not bound at the Hartree-Fock level. Their existence is entirely due to correlation effects. Other anions are predicted to exist at the Hartree-Fock (HF) level but their quantitative description are only achieved by considering the correlation energy. In both cases, the attachment energy of the electron is commonly small. On the other hand, there are some anions, such as CN^-, which are considerably stable and can be satisfactorily described at the HF level. In the CN^- case, this stabilization can be rationalized based on the fact that this system is iso-electronic with CO, which is a quite stable molecule. In the O_2^-, there is no corresponding iso-electronic molecule which is stable.

We must stress that for other target systems, e.g., He, Ne, Ar, our model provides an excellent agreement with the experimental total detachment cross sections for various anion projectiles [8,9]. As noted in the present work, the same is not true for the case of N_2 and this may be associated with the fact that we are not able to account completely for the effect of the N_2 shape resonance. In addition, there does not exist in the literature a simple expression to describe the loss of at least one electron from a neutral molecule colliding with another neutral one, in particular with the presence of an important resonance, as it is the case of the nitrogen molecule. Thus, in order to take into account the effect of the shape resonance, we have tried an empirical expression for σ_{NCD} with reasonable velocity dependence such that, when properly weighted and added to the $\sigma_{\mathrm{OED}}^{\mathrm{model}}(v)$, is able to reproduce the experimental data. We mean that the total cross section will be given by

$$\sigma_{\mathrm{TED}}(v) = A\sigma_{\mathrm{OED}}^{\mathrm{model}}(v) + \sigma_{\mathrm{NCD}}(v), \tag{2}$$

where

$$\sigma_{\mathrm{NCD}}(v) = Be^{-a(v-b)^2} \tag{3}$$

is our trial expression with three parameters (a, b, and B). It is evident that this approach looses the beauty of having only one free parameter.

We have performed a fitting of the above expression with the experimental data in order to find the best-four free parameters (A, B, a, and b) for each case. In Figs. 2 and 3 are displayed the fitting for the CN^- and O_2^- cases. They are represented by the *dashed* lines and correspond to the sets ($A = 0.99$, $B = 3.9$, $a = 1.7$, $b = 0.01$) and ($A = 1.65$, $B = 6$, $a = 4.5$, $b = 0.27$) for the CN^- and O_2^-, respectively. We observe that our choice for the function representing the contribution of the core combined with the outermost electron contribution [$\sigma_{\mathrm{OED}}^{\mathrm{model}}(v)$] properly weighted leads to a good agreement with the experimental data in all of the velocity range for CN^-. Concerning O_2^-, we also reproduce well the experimental data over a wide range of velocities; the exception regards the data of Bennett *et al.* [17] whose experimental methods employed were different from ours and could explain such kind of discrepancy.

Seeking an interpretation for the function chosen to depict the role of the collision between two neutral molecules, we can say that, as the degree of penetration in the core-molecule collisions should be more sensitive to the collision velocity, the velocity dependence will be more relevant in collisions between molecular anions and molecular targets than in collisions between atomic anions and atomic targets. This fact would explain why in the latter case we only need to add a constant to the $\sigma_{\mathrm{OED}}^{\mathrm{model}}(v)$ to fit the experimental data whereas in the former this is not possible. Finally, as in the literature one does not find an expression to describe this kind of collision, we have chosen a Gaussian function inspired in the profile of the shape resonance.

V. CONCLUSION

In conclusion, we measured the total electron detachment of the CN^- and O_2^- molecular anions impacting on molecular nitrogen. An important qualitative and interesting find is that the electron-detachment cross section curve of CN^- and O_2^- as a function of the relative velocities confirms the existence of maxima corresponding to the resonance $^2\Pi_g$ of the free-electron-N_2 collisions, a fact already predicted by Vu Ngoc Tuan *et al.* [5].

Different from what has been obtained earlier [8,9] in order to describe electron detachment in collisions between atoms with atomic and molecular anions, the quantitative agreement between the theoretical cross sections and the experimental ones does not occur when a constant contribution coming from the core is added. However, we have reproduced satisfactorily well the experimental results for CN^- and O_2^- with an adapted model from the previous ones.

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