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Multi-ionization cross-sections of small ionic carbon clusters by particle impact as a tool to investigate their shapes

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Abstract. Single, double and triple ionization cross-sections of C_n^+ clusters in collisions with helium atoms at intermediate velocity (2.6 a.u.) have been measured ($n = 1 \rightarrow 5$). The relative multi-ionization cross-sections (double over single and triple over single) are first increasing with n, then decreasing when going from $n = 4$ to $n = 5$. We show, on the basis of an independent atom and electron collisional treatment, that this effect is attributable to a change in the cluster shape. The role of the cluster compactness on relative multi-ionization cross-sections is pointed out here for the first time.

PACS. 34.50.Fa Electronic excitation and ionization of atoms (including beam-foil excitation and ionization) – 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.) – 34.10.+x General theories and models of atomic and molecular collisions and interactions (including statistical theories, transition state, stochastic and trajectory models, etc.) – 36.40.Mr Spectroscopy and geometrical structure of custers

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As well-known, clusters are often predicted to have different shapes close in energy (isomers) [1]. The question of the actual shape or of the possible coexistence of various forms is thus an open problem which may depend on the experimental conditions of formation [2]. From an experimental point of view, some methods designed to get information on the shapes of free clusters of intermediate sizes have been developed. The gas phase ion chromatography (IC) has been shown to be useful for resolving the various shapes of large enough ionic species [3]. The coulomb explosion method was able to bring information on the shape of small size ionic clusters [4]. The chemical reactivity has been used as a tool to deduce information about the linear or closed form character of some reactants [5]. Also, it was shown that the optical absorption spectrum could often be used as a signature of the cluster shape [6]. In this work, we present another method, based on the measurement of the cluster multi-ionization cross-sections by particle impact. The sensitivity of the multi-ionization cross-sections to the atomic structure is understandable as follows: as the electronic cloud is around the nuclei, the more compact is the geometrical structure, the more probable it is for the incident particle to meet electrons and to eject a few. A similar argument was made for predicting increasing multi-ionization cross-sections for molecules aligned along the beam [7], an experimentally demonstrated result [8].

Experiments, performed at the Tandem facility in Orsay, refer to collisions of C_n^+ clusters ($n \leq 5$) with helium atoms at a constant impact velocity of 2.6 atomic units (a.u.). The experimental set-up has been described in previous papers, with all details concerning the extraction of the cluster ionization probabilities (single, double, triple...) given in reference [9] and those concerning the extraction of absolute cross-sections (beam-jet overlap determination) given in reference [10]. Interpretation of the experimental results will be done, as in the case of the already published $C_5^+ \rightarrow$ He case [9], within an independent atom and electron model involving $2s$ and $2p$ ionization. In spite of two severe approximations (the cluster is represented by a collection of independent atoms and the independent electron approximation is applied) this model proved to be reasonable in predicting single and multiple ionization cross-sections of C_5^+, probably for the following reasons: the "exact" initial orbitals are predominantly combinations of atomic $2s$ and $2p$ wavefunctions; the independent electron approximation is reasonable for

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Table 1. Calculated ground-state geometries of C_n^+ clusters ($n = 2 \rightarrow 5$), using gradient optimization within the CCD (Coupled Cluster) theory. In the case of C_4^+, two very close in energy isomers exist, with the rhombic form predicted to be more stable by 0.16 eV at the CCSD(T) level [12].

Cluster	Structure	Symmetry of states	Bond lengths (a.u.)	Bond angles (°)
C_2^+	linear	$^4\Sigma_g^-$	2.6511	
C_3^+	bent	$^2B_2$	2.4862	71.436
C_4^+	rhombic	$^2B_{1u}$	2.7174	108.692
C_4^+	linear	$^2\Pi_g$	$d_{12} = 2.5859$	
			$d_{23} = 2.3791$	
			$d_{34} = 2.5859$	
C_5^+	linear	$^2\Sigma^+$	$d_{12} = 2.3169$	
			$d_{23} = 2.4992$	
			$d_{34} = 2.3560$	
			$d_{45} = 2.5261$	

predicting total multi-ionization cross-sections in outer shells of low Z atoms [11]. Moreover multiple ionization in the cluster is found to occur predominantly, within the model, by ejection of electrons belonging to different atoms.

In the model, the C_n^+ cluster is represented by $(n-1)$ carbon atoms and one C^+ ion, at some fixed positions during the collision. Positions of the nuclei have been calculated by three of us (Fossé, Rabilloud and Spiegelman) using gradient optimization within the CCD (Coupled Cluster) theory, as a part of a larger work on C_n^{q+} ($q \leq 2$) clusters to appear [12]. Total energies were finally calculated within the CCSD(T) approximation. All calculations were achieved using the GAUSSIAN 98 package [13]. Results for the lowest energy configurations are given in Table 1. In the case of C_4^+ two isomers are found to be very close in energy ($\sim$0.1 eV), with the rhombic form being more stable [12]. These results are in good agreement with calculations of other authors performed with various theories at a similar level of accuracy [1,14]. In the cluster-atom collisional treatment, performed within the impact parameter formalism, the knowledge of the atomic $2s$ and $2p$ ionization probabilities in the "reference" atomic collisions $C, C^+ \rightarrow He$ are required [9]. We started from one-electron impact parameter dependent ionization probabilities calculated by one of us (Maynard) within a Classical Trajectory Monte Carlo (CTMC) method with introduction of a parametric potential for the carbon ions and a frozen core for the helium atom [15]. On the other hand, it is known that the CTMC method yields reliable results for the total ionization probability but predicts distorted probability shapes because of the suppression of large impact parameters beyond a classical limit [16]. In order to correct this effect, we introduced a modified impact parameter dependent probability $P_m(b)$ written as $P_m(b) = N/\lambda^2 P(b/\lambda)$, where λ is an extension factor (λ greater than one) and N a normalization factor. These two parameters were then adjusted in order to reproduce our

Table 2. Measured single (σ_{SI}), double (σ_{DI}) and triple (σ_{TI}) ionization cross-sections for C_n^+ projectiles in collisions $C_n^+ \rightarrow$ He at 2.6 a.u. impact velocity.

	σ_{SI} (cm^2) (error bar)	σ_{DI} (cm^2) (error bar)	σ_{TI} (cm^2) (error bar)
C^+	1.00×10^{-16} (20%)	5.59×10^{-18} (29%)	
C_2^+	3.07×10^{-16} (19%)	5.20×10^{-17} (19%)	7.56×10^{-18} (22%)
C_3^+	3.93×10^{-16} (19%)	9.43×10^{-17} (19%)	1.74×10^{-17} (22%)
C_4^+	3.83×10^{-16} (21%)	1.08×10^{-16} (21%)	2.77×10^{-17} (24%)
C_5^+	5.46×10^{-16} (16%)	1.48×10^{-16} (18%)	3.69×10^{-17} (31%)

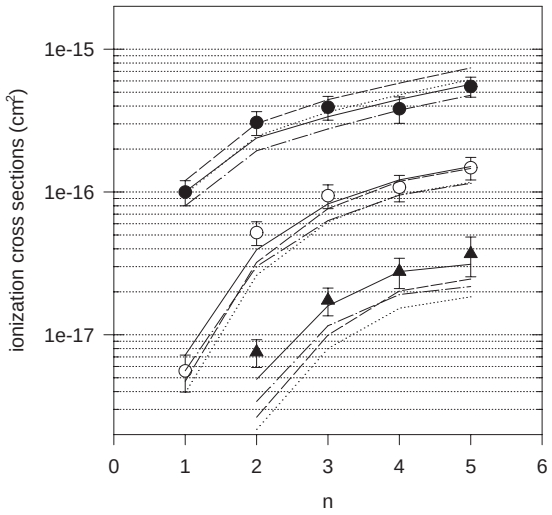

Fig. 1. Comparison between experimental single (filled circles), double (open circles) and triple (filled triangles) ionization cross-sections of C_n^+ projectiles (2.6 a.u. $C_n^+ \rightarrow$ He systems) and predictions of the independent atom and electron model (solid, dashed, dotted and dashed-dotted lines, see text).

experimental values of both single (SI) and double (DI) ionization cross-sections in the $C^+ \rightarrow$ He collision. Without correction ($N = \lambda = 1$), the gross ionization cross-section (SI plus twice DI) was in good agreement with the experimental value, but the ratio DI/SI was too large by roughly 40%.

Experimental single, double and triple ionization cross-sections of C_n^+ clusters are given in Table 2 and shown in Figure 1. In Figure 1 are also reported results of the independent atom and electron model, performed by introducing the lowest energy configurations of Table 1. Four theoretical curves are presented, corresponding to adjustment on extreme experimental values of SI and DI cross-sections in C^+; amongst those curves, two of them are obtained from slight modifications of $P(b)$ shapes (the dashed-dotted line with $N = 0.95$ and $\lambda = 1.12$ and the

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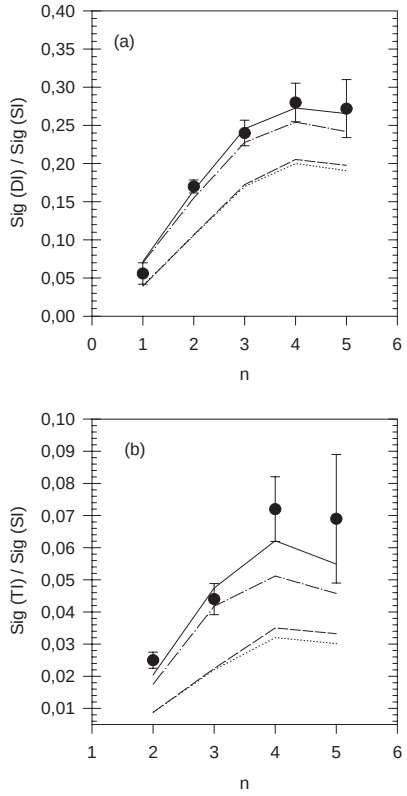

Fig. 2. Same as Figure 1 but for relative double over single ionization cross-sections (Fig. 2a) and triple over single ionization cross-sections (Fig. 2b).

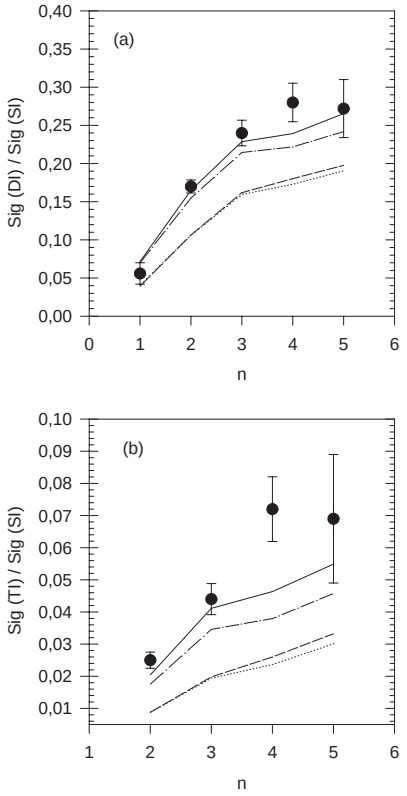

Fig. 3. Same as Figure 2 but calculations are done by assuming all clusters to be linear (see text).

solid line with $N = 1.20$ and $\lambda = 1.25$) and two of them from large modifications of the shapes (the dotted line with $N = 1.10$ and $\lambda = 1.55$ and the dashed line with $N = 1.35$ and $\lambda = 1.75$). It is seen that the solid line only occurs to predict quantitatively almost all experimental cross-sections whereas other curves mostly predict the n dependence of the cross-sections.

The situation is improved when looking at the relative cross-sections DI/SI (Fig. 2a) and TI/SI (Fig. 2b). Here, the two curves with the slightest modifications, both reproducing the largest experimental value for DI/SI in C^+, are in good agreement with all experimental DI/SI ratios and, in a lesser extent, TI/SI ratios. Remarkably, all simulations predict the decrease of the relative cross-sections when going from $n = 4$ to $n = 5$. We can show that this decrease is associated with a change in the cluster shape from the rhombic structure for $n = 4$ to the linear structure for $n = 5$. Indeed, if we assume all clusters to be linear, monotonic dependences of relative cross-sections with n are obtained as shown in Figures 3a and 3b. In these figures, C_3^+ has been assumed to be linear instead of bent as well as C_4^+ instead of rhombic. In the case of C_4^+, the distance between the atoms was shortened following results of our calculations for the linear isomer of C_4^+ (see Tab. 1). If we had kept the interatomic distances calculated in the rhombic C_4^+, we would have obtained ratios for DI/SI and TI/SI slightly lower (respectively 4% and 7%), that means, a larger shape effect. It is interesting to remark that plotting the relative cross-sections DI/SI and TI/SI emphasizes the role of the geometry. This is due to the fact that the n dependence of these quantities is governed by interatomic processes (multi-ionization by ejection of electrons belonging to different atoms, sensitive to the shape) although intraatomic processes (multi-ionization within an atom) lead to n-independent ratios. Experimental results clearly indicate that the C_4^+ ions were predominantly in a closed form in our experiment. Whereas the linear structure of C_5^+ had experimentally been inferred [3] as well as the bent structure of C_3^+ [4], no experimental evidence of a closed configuration for C_4^+ has been reported so far.

In conclusion, we have shown that the experimental size dependences of single, double and triple ionization cross-sections of C_n^+ clusters were reasonably well-reproduced by an independent atom and electron model. Within this model, a large increase of relative multi-ionization cross-sections (DI/SI and particularly TI/SI) is predicted when C_4^+ is in a rhombic form as compared to the linear form. This allowed to deduce that a dominant contribution of C_4^+ ions in the closed form was present in the experiment. This form is observed experimentally for the first time. In the future, we intend to pursue these measurements for clusters with larger sizes and to improve the accuracy of ionization cross-sections in the reference collision $C^+ \rightarrow He$ in order to constrain the model in a more stringent way. Theoretically, effects of delocalization and correlation in the simulation should also be estimated.

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