FRAGMENTATION OF SMALL CARBON CLUSTERS

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Introduction :

Small carbon clusters are present in various media, flames, plasmas as well as in the interstellar medium. They are building blocks of larger systems such as fullerenes and carbon nanotubes extensively studied for fundamental interest and potential applications. They have been observed, mostly as neutrals or cations, in the fragmentation of these large systems. Their structural properties have been the subject of numerous works [1]. Still, their stability properties with respect to a high degree of internal excitation and/or charge are largely unknown. Indeed, most of the fragmentation studies refer to the case of low excited states created by photofragmentation [2] or collision induced dissociation [3]. In these studies the ionic fragments only are detected so that a partial information is derived.

We present in this review fragmentation patterns of excited C_n^{q+} clusters created in C_n^+-He collisions in high velocity collisions ($n \leq 10$, $q \leq 4$). Thanks to recent experimental developments on the fragment detection system [4], all fragments neutral or charged are separately identified, allowing to resolve all fragmentation channels. Highly excited species are created in these experiments either by charge exchange (q=0), electronic excitation (q=1) or ionization (q=2,3,4). Using the results of a statistical fragmentation theory [5], it is possible to extract from the fragmentation patterns the energy deposited in the cluster by the various processes. This will bring new information on electronic processes in these complex atom-cluster collision systems.

Experimental set-up :

The experiments were done at the Tandem accelerator (Institut de physique Nucléaire, Orsay) with C_n^+ ionic carbon clusters (n≤10) of 2nMeV kinetic energy (constant velocity of 2.6 a.u). The experimental set-up has been described previously [6]. With seven silicium detectors operating in coincidence and suitably placed, all neutral, singly, doubly and triply charged fragments were intercepted. In standard operation of these detectors, charge signals are recorded, which provides the total kinetic energy of the fragments hitting the detector, that means, the total mass of the fragments. Recently, we showed that the analysis of the transient currents delivered by the detectors could be used to determine the *number* of fragments hitting the detector and *the mass of each fragment* [4]. This technique is illustrated in figure 1 for the case of neutral fragments emitted in C_{10}^+ -He collisions and all impinging on a single detector placed along the beam axis. This technique has been applied to all detectors of charged fragments as well, which allowed to measure all fragmentation channels [7].

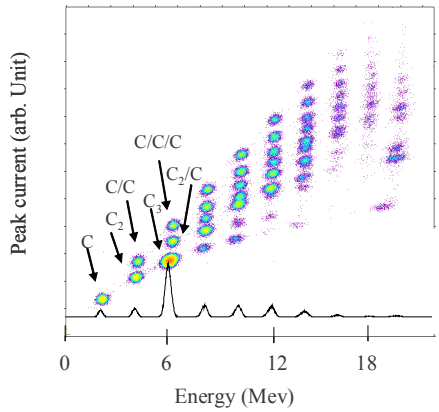


Figure 1: Two-dimensional representation of current signals for neutral clusters created in C_{10}^+ +He collisions. The integral of the current signal is given in abcissa and the peak amplitude in ordinate.

Fragmentation of neutral clusters:

In the figure 2 are presented the measured branching ratios of fragmentation of C_n clusters in a given number of fragments N_f (N_f=1 to n, n=5-10). Quite similar fragments distributions are obtained for all n values, in particular a dominance of two-fragments probability, in accordance with previous results on n=3,4 [6]. This indicates quite similar internal energy distributions of excited C_n, as discussed below. An odd-even oscillation is observed on dominant channels (see figure 3) that

may be explained by odd-even oscillations on the dissociation energies [5]. Inside a given number of fragments, branching ratios for the various channels are inversely proportional to the apparition energy of the channel (see figure 4).

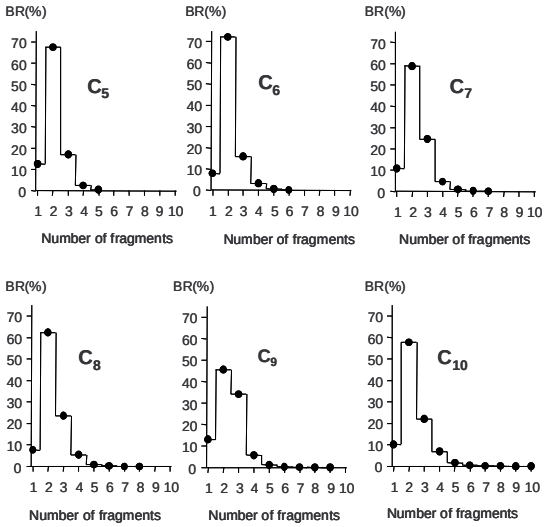


Figure 2: Measured distributions of fragmentation into a given number of fragments for neutral C_n clusters

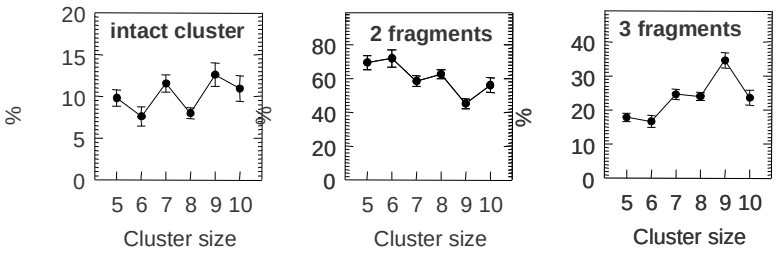


Figure 3: Evolution of the measured branching ratios with the cluster size for intact, two and three fragments emission.

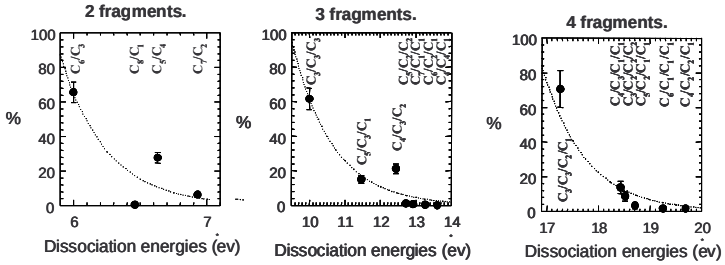


Figure 4 : Measured branching ratios for various channels of C_9 within a given number of fragments

This behaviour is compatible with statistical fragmentation approaches. The Microcanonical Metropolis Monte Carlo (MMMC) statistical fragmentation theory, based on quantum chemistry calculations, has been used to interpret these data. In the figure 5 are reported a example of calculated branching ratios as a function of the internal energy for C_9. As explained in [8], the fit of experimental branching ratios with the calculated branching ratios using relation (1) allowed to determine the energy distributions D(E) of C_n clusters after the collision. These energy distributions were found to be almost independent of n. We assumed a single energy distribution associated to the charge transfer process for n=5,7,9 that was derived from the best fit of all branching ratios $RB(N_f)$ following relation (2).

$$RB_{th} = \int D(E) RB_{th}(E) dE \qquad (1)$$

$$RB(N_f)_{th} = \int D(E) RB_{th}(Nf/E) dE \qquad (2)$$

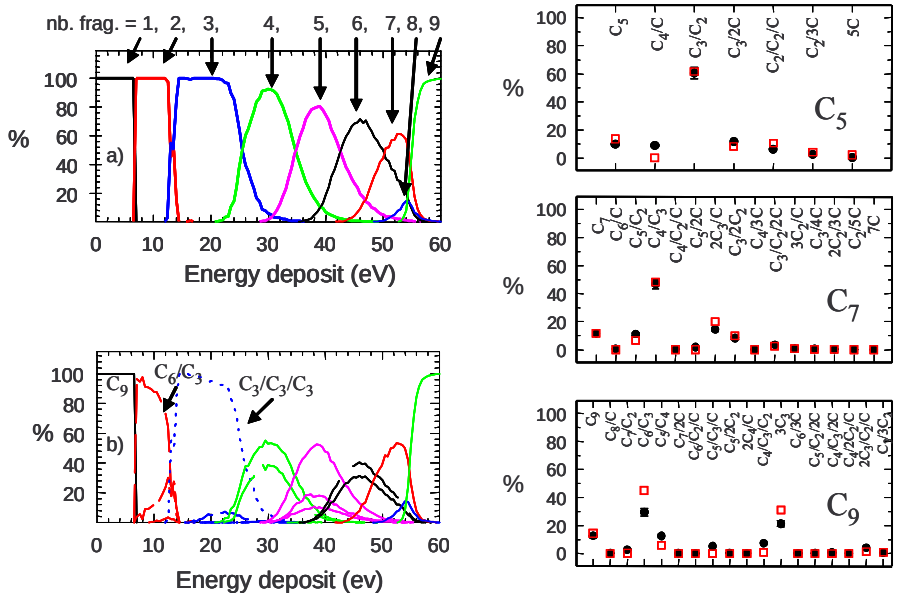


Figure 5 (left): Theoretical branching ratios as functions of the cluster excitation energy predicted by the MMMC theory for C_9. For all partitions (down), summed in number of fragments (up)

Figure 6 (right): Branching ratios for de-excitation of C_5, C_7, C_9. Full circles :experiment; open squares :convolution of the theoretical branching ratios (MMMC) with the energy distribution shown in figure 7.

In (2), D(E) is the sum of the cluster energy before the collision $D(E)_{ENT}$ (which is known, slightly increasing with n [7]) and the energy associated to the charge transfer process $D(E)_{CT}$. In the figure 6 is reported the comparison between

experimental and calculated branching ratios using the best fit of $D(E)_{CT}$, which is presented in the figure 7. It is seen that the agreement between experimental and calculated branching ratios is quite good. The $D(E)_{CT}$ distribution provides the energy deposited by charge transfer in C_n clusters. The component at higher energy is attributed to charge transfer process accompanied by electronic excitation. Indeed the position of the peak, as well as its relative intensity, both estimated using the IAE (Independent atom and electron model) supports this interpretation [9].

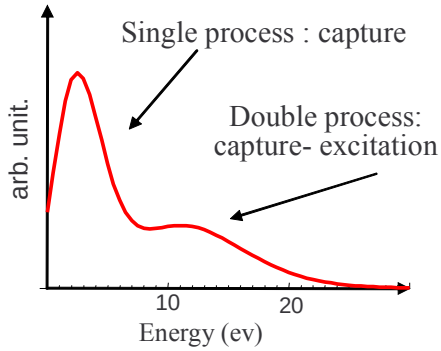


Figure 7: Energy distribution of excited C_n which fits the experimental branching ratios

Fragmentation of monocharged C_n^+ clusters:

In the figure 8 are presented the measured branching ratios of fragmentation of C_n^+ clusters in a given number of fragments N_f for n=5-10 and N_f=2 to n (only the dissociative part of electronic excitation is measured in the experiment). Contrary to the case of neutrals, we have a calculation of the energy deposited by electronic excitation which may be tested through the fragmentation pattern. The energy deposited by electronic excitation is calculated using the IAE model and the Classical trajectory Monte Carlo Method (CTMC) for the calculation of the energy deposited in individual carbon atoms [7,10]. In this model, the energy deposit is continuous, lower and higher limits for excitation of 2s and 2p electrons in carbon atoms corresponding to the energy of the first observed transitions an ionization potentials. Since first transitions [11] are above the dissociation energy of C_n^+ clusters, the whole calculated electronic excitation is dissociative, then comparable to the experiment. In the figure 9 is shown the internal energy of C_5^+ due to electronic excitation (IAE distribution convoluted with the energy of C_5^+ before the collision). The first peak (~14 eV) corresponds to excitation of 2p electrons, the second (~20 eV) to excitation of 2s electrons and the higher energy tail to double excitation processes. This energy distribution is superimposed to MMMC

breakdown curves calculated for C_5^+ that will be used, following equation (2), to derive theoretical branching ratios $RB_{th}(N_f)$.

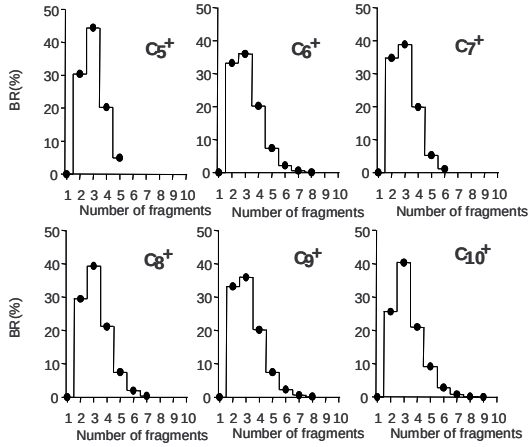
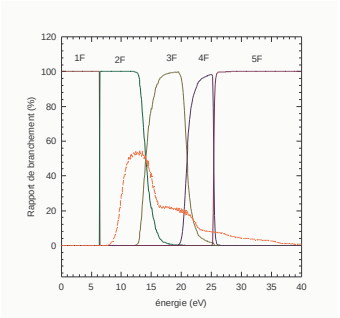


Figure 8: : Measured distributions of fragmentation into a given number of fragments for monocharged C_n^+ clusters

A comparison between measured and calculated branching ratios is presented in the figure 10. The agreement is not good, but a slight shift of the IAE distribution towards higher energy (+2eV) allows the dominant channels to be well reproduced. Nevertheless, there is still a lack of probability in the calculated energy distribution in the four fragments region. This result points out the occurrence of higher energy transitions in the cluster, due to more bounded molecular states (for instance the 2s binding energy is 19 eV in the carbon atom as compared to a 22-28eV band for σ electrons in C_5 [12]) which are not present in the atomic model.



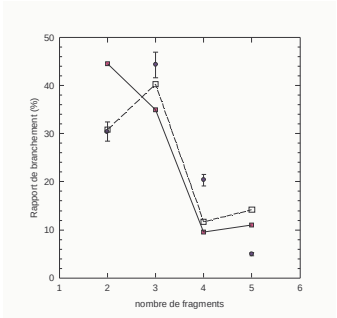


Figure 9 (left): Calculated energy distribution following electronic excitation in C_5^+(red) superimposed on MMMC breakdown curves (see text).

Figure 10 (right) : Comparison between measured branching ratios of dissociation of C_5^+ and results of the IAE-MMMC model: brut results (full squares, solid line), results obtained by shifting the IAE distribution by +2eV (open squares, dotted line).

Fragmentation of multicharged C_n^{q+} clusters (q≥2):

In the figure 11 is reported a two-dimensional representation of measured branching ratios of C_n^{q+} clusters for n=5-10. We see that the distributions are very similar for n=7-10 with a dominance of respectively, two, four/five and seven fragments for q=2,3,4. As dissociation energies are slightly increasing with n (case of doubly ionised clusters [13]), this would indicate a slightly higher internal energy for higher n clusters due, for a part, to ionization in deeper bound inner valence σ states. For the case of n=5,6 there is a limitation at 5 and 6 of the number of emitted fragments and it would be necessary to look at the kinetic energy of the fragments to have a complete energetical balance. Calculations of molecular dynamics, taking into account the coulombic energy barriers and currently performed on those systems [14], will help to interpret these data.

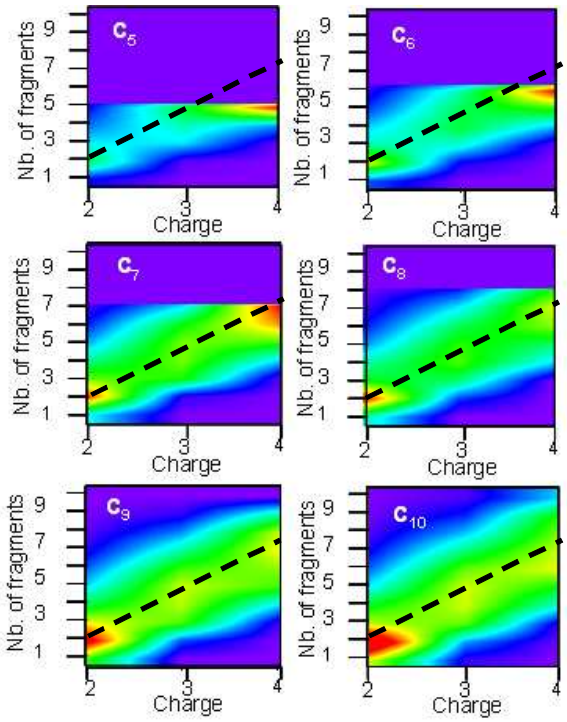


Figure 11: Two-dimensional representation of measured branching ratios in a given number of fragments (ordinate) as a function of the charge q (abscissa) for C_n^{q+} clusters, n=5 to 10.

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