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Fragmentation of small neutral carbon clusters

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Abstract

We report on theoretical and experimental efforts designed to understand the fragmentation of small neutral carbon clusters. Theoretically, the dissociation dynamics of C_n has been investigated using a statistical model based on the microcanonical Metropolis Monte Carlo method. In this model various structural quantities (geometries, dissociation energies, harmonic frequencies...) are required for both the parent cluster and the fragments. They have been obtained from quantum chemistry calculations for C_n up to $n=9$. Experimentally, a new detection system for high velocity fragments has been recently developed allowing the fragmentation of high velocity clusters to be totally recorded. Results for the branching ratios of deexcitation of C_n with $5 \leq n \leq 9$ formed by electron capture in high velocity C_n^+–He collisions are presented. In all cases, the agreement between theory and experiment is reasonably good provided that the theoretical branching ratios are convoluted with a C_n energy distribution centered at around 10 eV.

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1. Introduction

Charge transfer and fragmentation have been thoroughly investigated in atomic and molecular systems since the early days of collision physics. In contrast, the study of these processes in clusters has received much less attention. In the case of carbon clusters, most studies have concentrated on positively-charged species. In particular, the unimolecular decay of C_n^+ formed in a direct vaporization source has been studied by Radi et al. [1–3]. Photofragmentation experiments of jet-cooled cationic clusters have been performed by Geusic et al. [4–6] and by Bouyer et al. [7]. Fragmentation of C_n^+ clusters has been also investigated in collision induced dissociation (CID) experiments [8,9] and through mass-analyzed ion kinetic energy spectra (MIKES) [10–12]. In addition, fragmentation of negatively charged C_n^- clusters has been studied in CID [13] and in Surface-Induced Dissociation (SID) experiments [14].

The experimental information for fragmentation of neutral carbon clusters is much scarcer. Choi et al. [15] have studied photodissociation of linear neutral carbon clusters. Chabot et al. [16] have performed experiments in which excited neutral clusters C_n are produced by electron capture in collisions of fast positively charged C_n^+ clusters with He targets. In the latter experiments, the decay of the excited neutral cluster proceeds through a large number of fragmentation channels. In this paper, we present a detailed comparison between theory and experiment for the fragmentation of excited neutral C_n clusters ($5 \leq n \leq 9$) produced in such collisions. Since the collision time is much shorter than the time required for the cluster nuclei to move, the excitation energy will be redistributed among the

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cluster vibrational degrees of freedom well after the electronic excitation has occurred. Consequently, one can treat cluster fragmentation as a post-collisional process that is entirely controlled by the amount of energy that has been deposited in the C_n cluster during the collision (for short, this energy will be hereafter called, excitation energy or energy deposit).

Theoretical predictions and experimental results for C_5, C_7 and C_9 (i.e., neutral carbon clusters with odd number of atoms) have been already published in Refs. [17,18]. In order to complete these former studies, we present new experimental and theoretical results obtained for clusters having even number of atoms, namely C_6 and C_8. For the sake of completeness, a detailed analysis of the fragmentation of the odd-number clusters is also presented. In particular, we will show that the combination of experimental and theoretical branching ratios allows us to extract the energy deposited during the collision by charge transfer. This information is not available neither from a theoretical point of view nor from the experimental one.

The paper is organized as follows. In Section 2, a summary of the theoretical methods is given. In Section 3, the experimental set-up and the principle of the fragmentation analysis are briefly recalled. All the results are presented and discussed in Section 4. Finally, the conclusions and prospects of this work are given in Section 5.

2. Theoretical models

The traditional way to study the fragmentation of atomic clusters is to describe the time evolution of the excited clusters by means of molecular dynamics methods [19]. In these methods one follows the classical Newtonian equation of motion of the interacting many-atom system. A critical aspect is the description of the atom–atom interactions that govern the nuclear dynamics. This can be done by means of simple analytical two-body interaction potentials or by ab initio interaction potentials calculated on the "fly" [20]. The latter possibility is limited to small clusters due to its high computational cost.

Fortunately, the dynamics of interacting many-body systems is often ergodic and, therefore, it is mainly controlled by the structure of the accessible *N*-body phase space. This means that one can try microcanonical thermodynamics [21] with the hope that such a statistical treatment may explain the outcome of the fragmentation reactions. This is particularly important for large systems, since statistical methods are computationally much cheaper than molecular dynamics methods. In this work, we have used a microcanonical Metropolis Monte Carlo (MMMC) method that takes into account all possible fragmentation channels of a given system. This method was originally developed to study fragmentation of hot metal clusters [22–24]. More recently, it has been extended to study fragmentation of highly excited small neutral carbon clusters [17,18].

Since the MMMC method has been explained at length in reference [18], here we briefly summarize its main features. In this method, the size of the accessible phase space is restricted by the conservation of the global parameters: mass, charge, total energy, total linear momentum and total angular momentum (microcanonical ensemble). The main issue of Metropolis importance sampling is to find the region in the accessible phase space with maximum statistical weight (i.e., with maximum entropy). One does this along a diffusive path through the phase space called the Metropolis path. Then, a physical observable is evaluated as a statistical average in this region of maximum probability. The statistical weight measures the number of physically accessible states under the global conservation laws and is entirely determined by the microscopic properties of the fragments. Thus, the basic ingredients of this statistical model are binding energies, geometries, vibrational frequencies, and rotational constants of any possible fragment. To avoid inconsistencies these microscopic quantities must be obtained for all possible fragments at the same level of theory.

Geometries, harmonic frequencies, rotational constants and binding energies have been obtained from standard quantum chemistry calculations. In a first step, we have applied the density functional theory (DFT) with the B3LYP functional for exchange and correlation. This functional combines the Becke's three parameter nonlocal hybrid exchange potential [25] with the nonlocal correlation functional of Lee, Yang and Parr [26]. The geometries have been optimized by using the 6-311 + G(3df) basis set (B3LYP/6-311 + G(3df)). The B3LYP functional and the 6-311 + G(3df) basis set have been proved to be a good choice for the description of carbon clusters (see [27] and references therein). In the case of small carbon clusters, the calculated geometries and the vibrational frequencies are very close to those obtained at higher levels of calculations [28–30]. In a second step, more accurate values of electronic and binding energies have been obtained with the coupled cluster theory CCSD(T)/6-311 + G(3df) (which includes all single and double excitations, as well as triple excitations in a perturbative way [31]), using the B3LYP optimized geometries obtained in the first step. The electronic energies obtained at this level of theory have been corrected with the zero point energy (ZPE) obtained from DFT vibrational analysis. All structure calculations have been performed with the Gaussian-98 program package [32].

3. Experimental set-up

The experiments were done at the Tandem accelerator (Institut de Physique Nucléaire, Orsay) with C_n^+ ionic carbon clusters ($n \leq 9$) of $2n$ MeV kinetic energy (constant velocity of 2.6 a.u). The experimental set-up has been described previously [33]. With seven silicon detectors operating in coincidence and suitably placed, all neutral and 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, i.e., the total mass of the fragments. Recently, we have shown that the analysis of the transient currents delivered by the detectors can also be used to determine the number of fragments hitting the detector and the mass of each fragment [16]. This technique is illustrated in Fig. 1 for the case of neutral fragments emitted in C_6^+–He collisions and all impinging on a single detector placed along the beam axis. The observed signals appear in six vertical columns according to their position on the *x*-axis. The first column ($p = 1$) contains information about channels leading to a single C atom, the

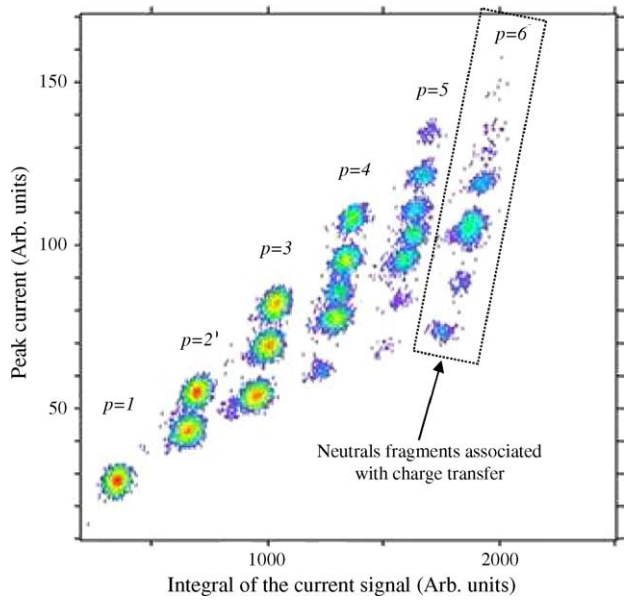

Fig. 1. Two-dimensional representation of current signals for neutral clusters created in C_6^+–He collisions. The integral of the current signal is given in abscissa and the peak amplitude in ordinate.

second one ($p=2$) contains two signals corresponding to C_2 and C/C, and so on. Neutrals signal associated with charge transfer appear in the last column ($p=6$). These signals only represent 5% of the total neutral production, which is due to the fact that charge transfer is much smaller than excitation and ionization at the impact velocity considered in this work.

4. Results

Dissociation energies of neutral carbon clusters obtained at the CCSD(T)//B3LYP/6-311 + G(3df) level of theory are presented in Fig. 2. Dissociation with emission of C (circles), C_2 (squares), C_3 (diamonds) and C_4 (triangles up) are shown. The channel with the lowest dissociation energy is C_{n-3}/C_3. It is worth noticing the alternation in the dissociation energy as a function of the cluster size. This oscillating behavior is more pronounced in the dissociation energy of channels corresponding to the evaporation of C and C_3, i.e., for fragment with odd number of atoms. Experimentally (see Fig. 6 below), the dominant fragmentation channels for C_8 are C_5/C_3 (55.4%), $C_3/C_3/C_2$ (17.5%), $C_4/C_3/C$ (4.8%) and C_4/C_4 (3.5%) followed by the evaporation channel C_7/C (1.8%). According to our structure calculations, the channel with the lowest dissociation energy is C_5/C_3 ($D_{8,3}=4.00$ eV), which is in agreement with the larger experimental branching ratio. However, in contrast with the experiment, the channels C_4/C_4 ($D_{8,4}=6.14$ eV) and C_7/C ($D_{8,1}=5.46$ eV) should present a larger branching ratio than the channels $C_3/C_3/C_2$ ($D_{8,3}+D_{5,2}=9.81$ eV) and $C_4/C_3/C$ ($D_{8,4}+D_{4,1}=10.96$ eV). Consequently, predictions solely based on energetic criteria are not sufficient to explain the measured branching ratios. It means that the fragmentation process is also controlled by entropic effects. For this reason we have applied the statistical method of microcanonical Metropolis Monte Carlo (MMMC) presented in full details in [18] to obtain a direct comparison with the experimental measurements.

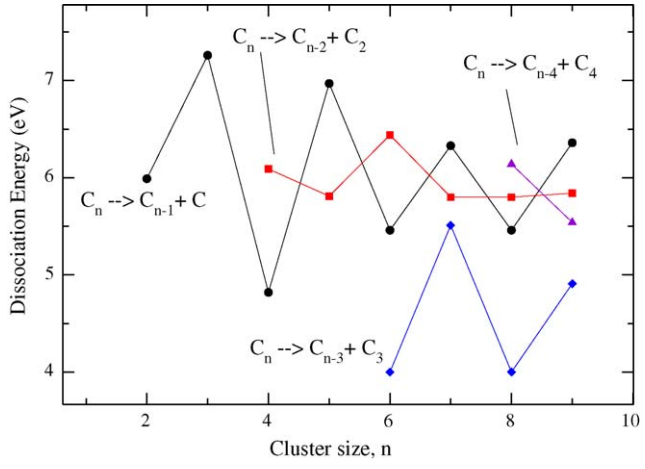

Fig. 2. Dissociation energies (in eV) of the process $C_n \rightarrow C_{n-x}+C_x$ evaluated at the CCSD (T) level of theory using geometries optimized at the B3LYP/6-311 + G(3df) level. $x=1$, $D_{n,1}$: circles; $x=2$, $D_{n,2}$: squares; $x=3$, $D_{n,3}$: diamonds; $x=4$, $D_{n,4}$: triangles up.

The MMMC predictions of the branching ratios as functions of the excitation energy for C_5, C_6, C_7, C_8 and C_9 are presented in Fig. 3. The branching ratios exhibit abrupt variations when the excitation energy is close to the dissociation thresholds. The slope of the curves depends on the number and type of fragments. This figure shows also that variations are more pronounced when the number of fragmentation channels that compete in the same energy region is small. As expected, the largest fragments appear at low excitation energies. As a common feature, Fig. 3 shows that dominant channels always involve C_3. In particular, for C_9, the $C_3/C_3/C_3$ channel has a remarkably large branching ratio. This is explained by the strong stability of C_3 compared to that of other carbon clusters. Moreover, in many experiments, the loss of neutral C_3 has been found to be the dominant dissociation process for both positively and negatively charged cluster ions. C_5, C_6, C_7, C_8 and C_9 clusters are totally broken into individual C atoms (vaporization) for energies above 26, 31, 40, 45 and 57 eV, respectively.

In Fig. 4, the theoretical branching ratios of fragmentation of C_n clusters in a given number of fragments N_f ($N_f=1$ to n, with $5 \leq n \leq 9$) are presented. This information is important for the comparison with the experimental data as discussed below. In the same figure we have also reported the effective temperatures as functions of the excitation energy [18]. This physical quantity is relevant for the study of phase transitions in atomic clusters. Indeed, the microcanonical first order phase transition in a finite system is associated with an S shape in the caloric curve $T(E)$. This shape implies that, in the transition region, the system decreases its temperature with increasing internal energy or, in other words, the system cools down while it absorbs energy [34]. Fig. 4 shows that the behavior of the calculated caloric curves is monotonous except in the regions where new decay channels are open (change of the number of fragments). The presence of *plateaux* and *oscillations* in the caloric curve can therefore be interpreted as the signature of first order phase transitions. In all cases, the phase transitions are more apparent when total

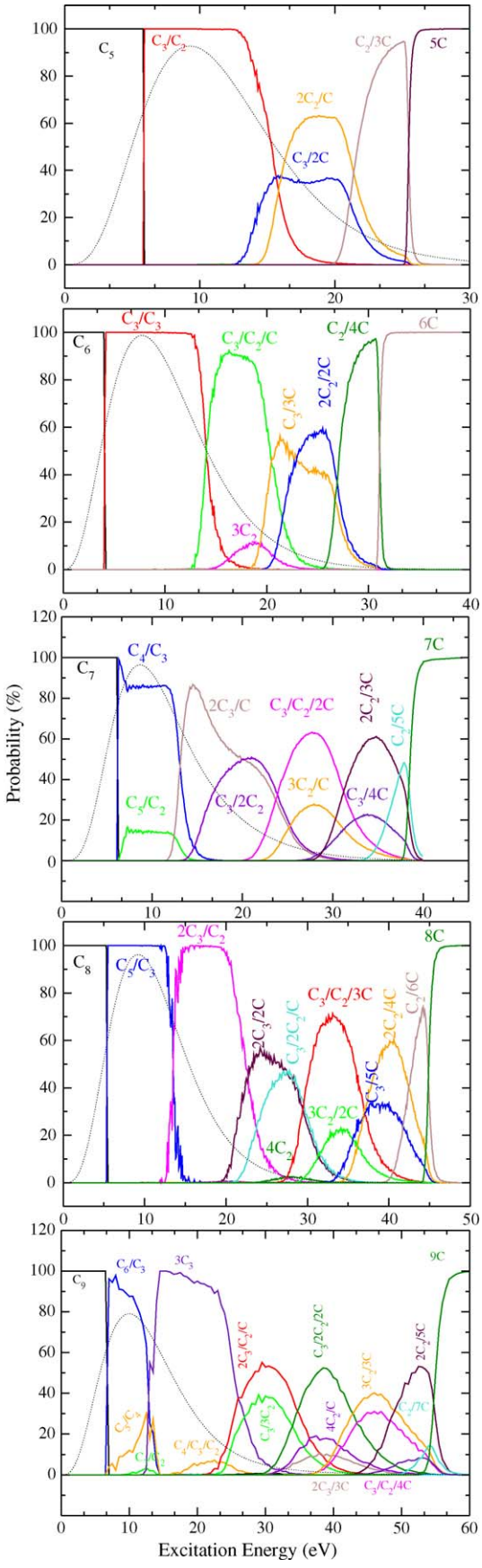

Fig. 3. Theoretical branching ratios as functions of the cluster excitation energy. Dashed lines: cluster energy distribution (re-scaled for a better visualization).

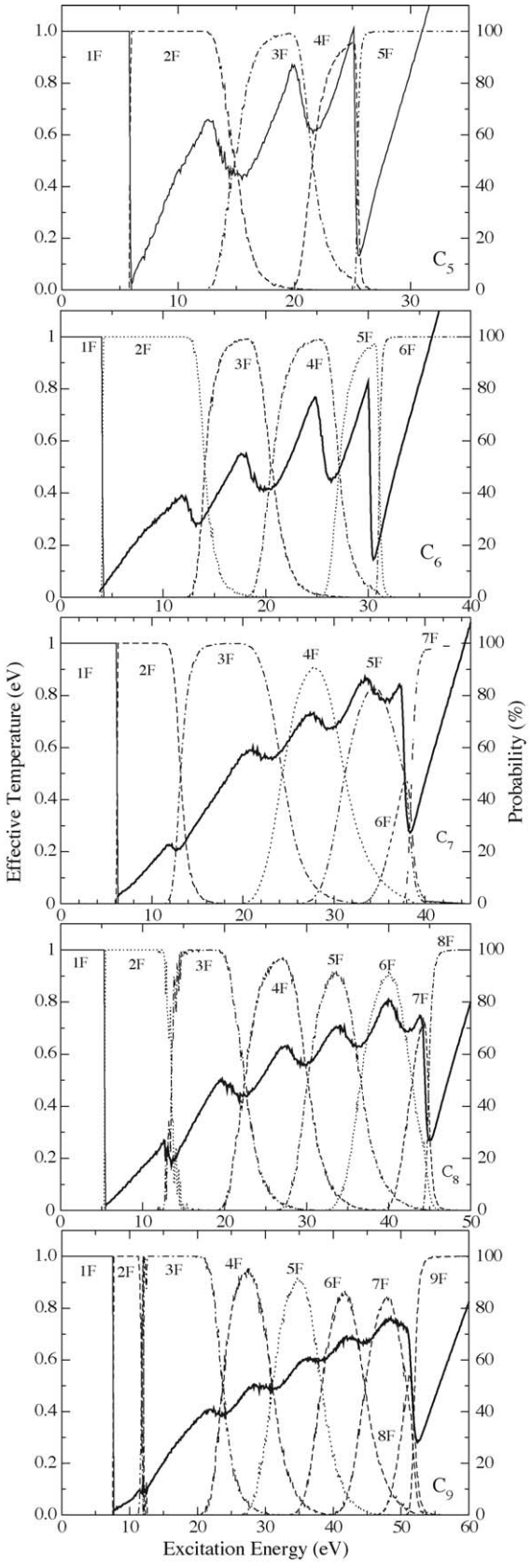

Fig. 4. Theoretical branching ratios summed in number of fragments (right axis) and effective temperatures (left axis and solid line) as functions of the cluster excitation energy predicted by the MMMC model.

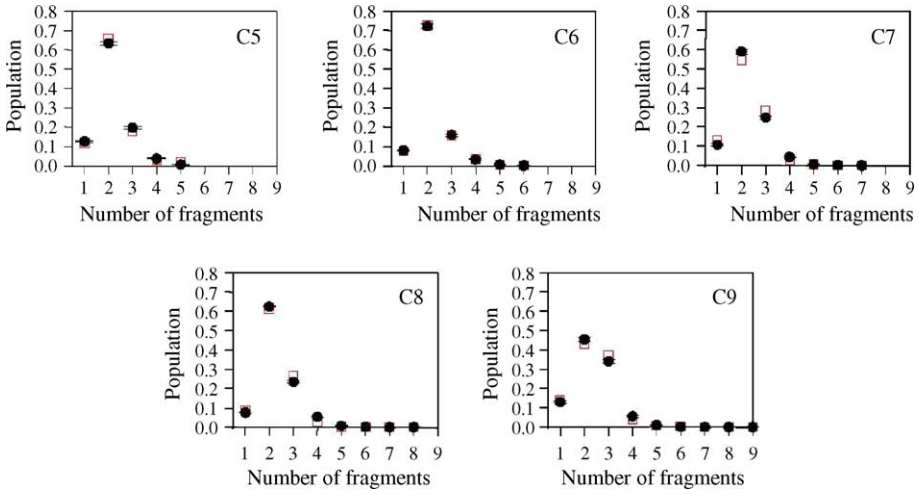

Fig. 5. Measured (full circles with error bars) and predicted (open squares) distributions of fragmentation into a given number of fragments (see text).

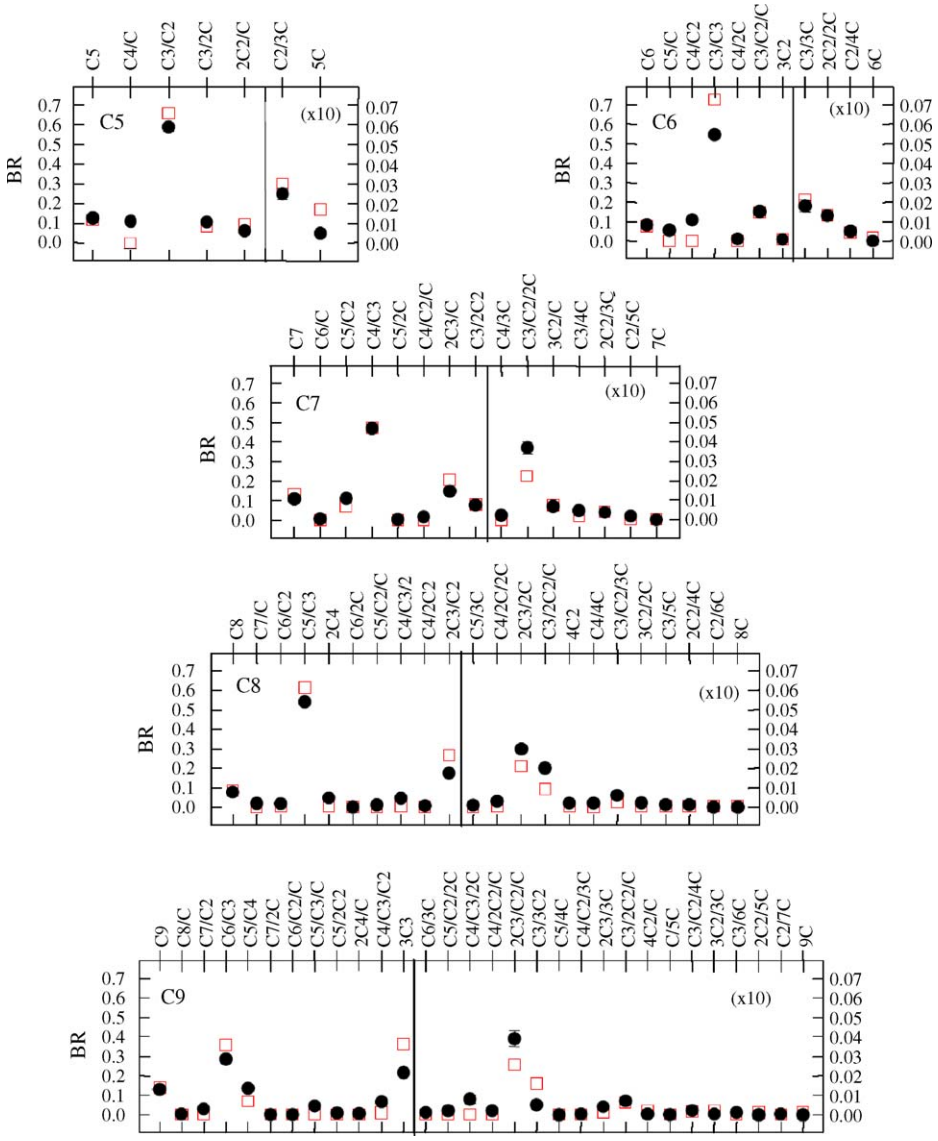

Fig. 6. Branching ratios for fragmentation of C_5, C_6, C_7, C_8 and C_9 clusters. Full circles with error bars: experiment; open squares: convolution of the theoretical branching ratios with the energy distributions shown by dashed lines in Fig. 3. Dissociation channels with very small branching ratio (right *y*-axis) are shown on the right hand side of the figures using an enlarged scale.

vaporization of the parent cluster occurs. The latter process takes place around $T = 0.4$ eV, which is close to the boiling temperature of macroscopic liquid carbon: $T_b = 0.44$ eV.

In Fig. 5 the measured branching ratios of fragmentation of C_n clusters in a given number of fragments N_f ($N_f = 1$ to n, with $5 \leq n \leq 9$) are shown. Quite similar fragments distributions are obtained for all n values, in particular, a dominance of two-fragments probability, in agreement with previous results on $n = 3$, 4 [33]. This suggests that the energy distributions of excited C_n are very similar (see also the discussion below).

To compare theoretical and experimental branching ratios, the former must be convoluted with the energy distribution of the neutral C_n cluster formed in the collision. In a previous work [17], we used an energy distribution with a well defined analytical form that contains a few adjustable parameters (the use of this particular analytical form was justified on physical arguments [17]). For each cluster, the values of the parameters were determined by least-squares fits of the calculated branching ratios to the measured ones for each individual fragmentation channel. The resulting energy distributions were found to be almost independent of n. An alternative procedure to determine the cluster energy distribution just after the collision is to use the sum of branching ratios associated with a given number of fragments (as given in Fig. 4), instead of using the individual branching ratios. The results of the fits are given in Fig. 5 and the form of the energy distributions is shown by dashed lines in Fig. 3. It can be seen that, although the five fits have been performed independently, the resulting energy distributions are very similar in the five cases. In other words, the resulting energy distributions are almost independent of n. This is reasonable because the collision velocity is the same for the five clusters and, consequently, the energy deposited in the collision should be very similar. More importantly, as can be seen in Fig. 5, the agreement between experimental and calculated branching ratios is very good.

We have used the energy distributions given in Fig. 3 to convolute the individual MMMC branching ratios. The results of such convolutions are compared in Fig. 6 with the experimental results for each individual fragmentation channel. As can be seen, the general agreement is good. Although the procedure used to obtain the energy distributions is slightly different to that used in [17,18], the convoluted branching ratios are close to those reported in that work for C_5, C_7 and C_9. In the case of C_9, for which there is a large number of fragmentation channels, channels with five or more fragments (not given in [17] because the corresponding branching ratios are smaller than 1%) are also shown in Fig. 6. Even for these channels, the agreement between theory and experiment is good.

5. Conclusions and perspectives

In conclusion, new results concerning the fragmentation of C_6 and C_8 clusters have been presented, with measurements and theoretical predictions of branching ratios for all possible fragmentation channels. These results are an extension of former studies on neutral carbon clusters with odd number of atoms up to $n = 9$. We have shown that a statistical model based on the microcanonical Metropolis Monte Carlo method combined with structure information obtained from ab initio quantum chemistry calculations allows us to study the fragmentation dynamics of excited C_n.

The combination of experimental results and MMMC predictions for the branching ratios enables us to estimate the energy deposited during the collision. In all cases, we have found that a C_n energy distribution centered at around 10 eV leads to a good agreement between theoretical and experimental branching ratios.

Using the same methodology, we plan to study in a systematic way, fragmentation of excited singly charged carbon clusters formed by electronic excitation in high velocity C_n^+–He collisions. This process leads to higher energy deposits and a comparison with available experimental data will provide another stringent test of the theory used in this work. Finally, application of the present fragmentation model to larger carbon clusters, such as C_{60}, will be also considered in the near future.

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