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Fragmentation of Highly Excited Small Neutral Carbon Clusters

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We present a combined experimental and theoretical study of fragmentation of small C_n clusters ($n = 5, 7, 9$) produced in charge transfer collisions of fast ($v = 2.6$ *a.u.*) singly charged $C_n{}^+$ clusters with He. Branching ratios for *all* possible fragmentation channels have been measured. Comparison with microcanonical Metropolis Monte Carlo simulations based on quantum chemistry calculations allows us to determine the energy distribution of the excited clusters just after the collision.

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Fragmentation is the natural escape door for carbon clusters excited above their stability thresholds [1,2]. Very often, the study of the dominant dissociation channels is used to obtain qualitative information on the cluster structure and stability (see [3,4] and references therein). More unusual is to analyze the excitation process that is responsible for the observed fragmentation. The analysis of the excitation dynamics is simple when the number of effective dissociation channels is small (see, e.g., Ref. [5] for the case of alkali clusters). But this is not the case for large excitation energies because many fragmentation channels are accessible and the energy distribution can be very broad. For example, for a cluster as small as C_9, there exist 30 different fragmentation states. Identification of all of them is an experimental challenge since it requires the detection and mass recognition of neutral fragments associated with different dissociation pathways. This can only be achieved by extensions of the usual grid or slit techniques [6,7].

The picture that consists of studying fragmentation separately from the process that has led to the excited parent cluster is valid when excitation is much faster than fragmentation [8]. Thus, it is valid for clusters excited by laser pulses, fast electrons or, as in this Letter, fast heavy particles. In the latter case, theoretical evaluation of the "collisional energy deposit" that leads to the excited cluster is difficult because one has to solve a dynamical problem that involves a large number of electronic and nuclear degrees of freedom. Consequently, the few theoretical attempts published so far have focused on small clusters [9,10] and on spherical or nearly spherical metal clusters that allow one to reduce the number of nuclear degrees of freedom during the collision [11–13]. The latter approximation has been shown to be very useful for alkali metal clusters at low impact velocities, i.e., small excitation energy. Extension of these methods to highly excited clusters and/or more complicated geometries is not easy. This leaves experiment as the only reliable source of information about excitation energies in this case.

In this Letter, we study fragmentation of highly excited C_5, C_7 and C_9 clusters produced in charge transfer collisions using a recently proposed experimental method that allows one to separate *all* possible dissociation channels. Determination of the cluster excitation energy from these measurements requires the knowledge of the geometries, dissociation energies, as well as rotational and vibrational properties of all possible fragments, including their various isomeric forms. We have obtained this information from *ab initio* quantum chemistry calculations using the *same* level of theory for all species. This is very important, e.g., to obtain consistent dissociation energies from the electronic energies of parent and daughter clusters. The information provided by previous accurate calculations [14–19] is basically restricted to electronic energies and vibrational frequencies of the most stable isomers. Our theoretical results have been used in Metropolis Monte Carlo simulations [20] to obtain fragmentation branching ratios for a given excitation energy. A comparison of the calculated branching ratios with the measured ones, allows us to deduce the energy distribution of the excited clusters that is responsible for the observed fragmentation. This can be done without any ambiguity because all dissociation channels are detected in the experiment.

The experiment has been performed at the Tandem accelerator in Orsay (France) using beams of $C_n{}^+$ clusters with a kinetic energy of $2n$ MeV (i.e., $v = 2.6$ a.u.), impinging on a helium gas. The experimental setup has been described elsewhere [21]. Briefly, it includes a collision chamber in which a gaseous jet is operating under single collision conditions, an electrostatic deflector for

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deviation of charged fragments according to their charge over mass ratios, and a detection chamber equipped with a special arrangement of eight semiconductor detectors that ensure full detection (100% efficiency) of all neutral, singly, and doubly charged fragments produced in the collision. We are only interested in neutral fragments formed in the charge transfer reaction $C_n{}^+ + He \rightarrow C_n{}^* + He^+ \rightarrow C_{n_1} + C_{n_2} + \ldots + He^+$. Therefore, we must discard neutral and charged fragments associated with the wrong type of collisions: dissociative excitation and ionization of the incident $C_n{}^+$ ions. To summarize, the main difficulties in the present experiment are (i) to identify events that are exclusively associated with charge transfer and (ii) to separate individual fragmentation channels. In contrast with usual methods based on the analysis of the total charge produced by the energetic fragments on the semiconductor detectors, our approach relies on the analysis of the shape of the transient *current* (see [22] for details).

As an illustration, we present in Fig. 1 a two-dimensional representation of the current signals (peak amplitude vs time integral) for neutral fragments produced in collisions of C_7^+ with He. The observed signals appear in seven 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 second one ($p = 2$) contains two signals corresponding to C_2 and C/C, and so on. Neutral signals associated with charge transfer appear in the last column ($p = 7$). These signals only represent 3% 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 Letter. Detection and analysis of such a small contribution is one of the major achievements in the present experiment. After assignment of all signals, branching ratios are extracted. Their precision is only limited by the counting rate (~ 1500 counts for total charge transfer and for each n value) and the jet background subtraction, since we have found no ambiguity in the identification of the different signals. According to the jet-detector distance, any fragmentation occurring within a time window of [0-180] ns is totally detected and identified.

The measured branching ratios associated with each fragmentation channel are shown in Fig. 2. To understand these results, we have performed theoretical simulations using the microcanonical Metropolis Monte Carlo (MMMC) method as described in reference [20]. In this method, one moves in phase space until a region with maximum statistical weight is found. A physical observable is then evaluated as a statistical average in this region of maximum probability. In the present application, the phase space is defined by the number of fragments and the mass, spin multiplicity, electronic and nuclear angular momenta, geometry, position, orientation, linear momentum, and internal excitation energy of each fragment. The statistical weight measures the number of physically accessible states at a fixed energy and is entirely determined by the microscopic properties of the fragments. With our definition of phase space, evaluation of this weight requires knowledge of the ground state energies, harmonic frequencies, geometries, and moments of inertia of each fragment. These microscopic properties have been evaluated using standard quantum chemistry techniques fol-

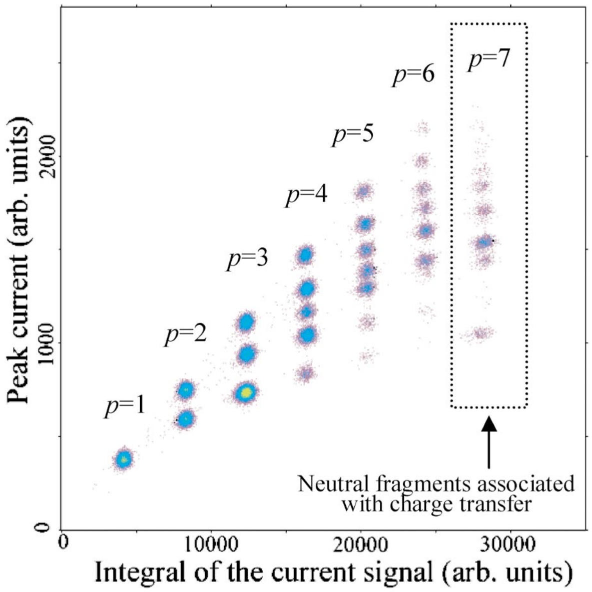

FIG. 1 (color online). Two-dimensional representation of current signals for neutral clusters created in $C_7{}^+$ + He collisions. The integral of the current signal is represented in abscissa and the peak current intensity in ordinate.

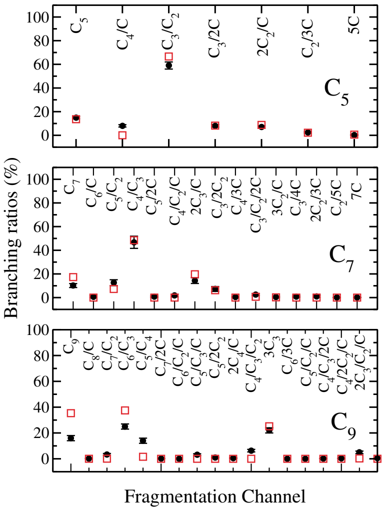

FIG. 2 (color online). Branching ratios for deexcitation of C_5, C_7, and C_9 clusters. Full circles: experiment; empty squares: convolution of the theoretical branching ratios with the energy distributions shown by dashed lines in Fig. 3. For C_9, the figure does not include channels leading to five or more fragments because the corresponding ratios are smaller than 1%.

lowing a procedure similar to that used in [23] for doubly charged carbon clusters. Briefly, we have optimized the geometries of the different species, from C_2 to C_9, using a density functional theory with a hybrid B3LYP functional for exchange and correlation [24,25]. These calculations have been performed using a quite flexible $6-311+G(3df)$ gaussian basis set. Harmonic vibrational frequencies have also been obtained at this level of theory. Electronic and dissociation energies have been evaluated using the coupled cluster method including all single and double excitations, as well as triple excitations in a perturbative way: CCSD(T)/$6-311+G(3df)$ [26]. For these calculations we have used the density-functional theory geometries obtained in the previous step. Our CCSD(T) energies differ by less than 0.2 eV with those reported previously [15,16,18] using CCSD(T) optimized geometries. All calculations have been performed with the GAUSSIAN-98 program [27].

In agreement with previous theoretical calculations [16], our results show that the global energy minima for C_3, C_5, C_7, and C_9 clusters correspond to linear geometries with singlet spin multiplicities. The relative stability of the different isomers for C_4, C_6, and C_8 is still a subject of controversy in the literature. The global energy minima that result from our CCSD(T) calculations for these species correspond to singlet cyclic isomers, in agreement with previous CCSD(T) calculations [17,18]. In contrast, multireference configuration interaction calculations have predicted that triplet linear isomers are the most stable ones [19]. In practice, these isomers are nearly degenerate (within 0.2 eV according to [19]), which implies that both linear and cyclic isomers may play an important role in the fragmentation process. The present MMMC simulations include both types of geometries as well as both singlet and triplet spin multiplicities for *all* fragments.

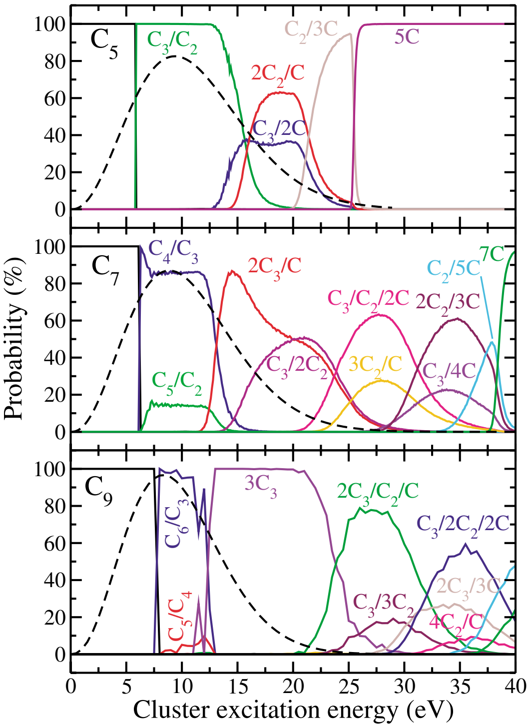

FIG. 3 (color online). Theoretical branching ratios as functions of the cluster excitation energy. Dashed lines: cluster energy distribution $f(E)$ multiplied by ten (see text).

Figure 3 shows the calculated branching ratios $R_i(E)$ as functions of the cluster excitation energy. The branching ratios exhibit abrupt variations when the excitation energy is close to the dissociation thresholds. The slope of the curves depend on the number and type of fragments. Figure 3 shows 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. The C_5, C_7, and C_9 clusters are totally broken into individual C atoms for energies above 26, 40 and 57 eV, respectively.

The branching ratios observed in the experiment correspond to fragmentation of the parent cluster in a time interval 0–180 ns. In the MMMC method, one assumes that the system is in thermodynamic equilibrium and, therefore, that the system has an infinite time to relax the initial excitation energy among the different degrees of freedom. Thus, to check that the experimental conditions are compatible with the use of the MMMC method, we have chosen C_5 and performed time dependent fragmentation calculations in the framework of the Weisskopf formalism [13] including only the dominant fragmentation channels shown in Fig. 2. The results of this model show that the calculated branching ratios for $t = 180$ ns and $t = \infty$ are practically identical. To compare the results of the MMMC method with experiment, one has to convolute the calculated branching ratios with the collisional energy deposit distribution. As already discussed, this distribution is totally unknown. The impact velocity considered in this Letter (2.6 a.u.) lies in the region where charge transfer competes with excitation and ionization. This must be taken into account to obtain a reasonable form for the energy distribution. As is well known, at large impact velocities, perturbative models predict that excitation probabilities decrease monotonically as the excitation energy increases [28]. At low energies, however, excitation is restricted to a few states lying in a narrow region of the energy spectrum. This selectivity is due to a quasiresonant electron transfer from the target to the projectile (in other words, to the fact that the target-projectile system can be considered as a quasimolecule). At intermediate velocities, the energy distribution of the excited clusters should lie between these two limits. Thus, we have convoluted the calculated branching ratios with an energy distribution of the form

$$f(E) = NE^{a_1} \exp[-a_2(E - a_3)^{a_4}] \tag{1}$$

where the a_i's are fitting parameters and N is a normalization factor that ensures $\int dE f(E) = 1$. This form is flexible enough to qualitatively reproduce the change of the energy distribution when one goes from low to high impact velocities. For each cluster, the values of the a_i parameters have been determined by a least squares fit of the measured branching ratios. The results of the three fits are given in Fig. 2 and the form of the $f(E)$ function is shown by dashed lines in Fig. 3. It can be seen that, although the three fits have been performed independently, the resulting energy distribution is very similar in the three cases. This is reasonable because the collision velocity is the same for the three clusters. It also supports the form chosen for $f(E)$. We have performed additional fits using different analytical functions (combinations of Lorentzian and other exponential functions) and the quality of the fits is similar to that shown in Fig. 2. The energy distributions peak around 10-12 eV and have a width at half maximum of ~10 eV. The fits reproduce very well the measured branching ratios, especially for C_5 and C_7. The most significant discrepancy is the absolute value of the branching ratio corresponding to the C_9 and C_6/C_3 channels. More detailed calculations and experiments are necessary to understand this discrepancy, which might be due to the fact that fragmentation has not finished within the 180 ns of the present experiment. For the three clusters investigated here, the dominant fragmentation channel is C_3/C_{n-3} ($n = 5, 7, 9$). This channel appears in the same energy region as the C_5/C_2 one for C_7 and the C_5/C_4 and C_7/C_2 ones for C_9 (see Fig. 3). Therefore, energetic considerations cannot be used to explain all the observations. Figures 2 and 3 also show that prominent channels with more than three fragments always involve C_3. In particular, 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, which is confirmed by our CCSD(T) calculations and previous photodissociation and collision induced dissociation experiments [29–31].

In conclusion, we have studied dissociation of excited C_5, C_7, and C_9 clusters using a recently proposed experimental method that provides unambiguous information about *all* fragmentation channels. The excited clusters have been produced in collisions of ${C_5}^+$, ${C_7}^+$, and ${C_9}^+$ with He at an impact velocity of 2.6 a.u.. Branching ratios for all fragmentation channels have been measured. We have also performed MMMC simulations that make use of structure parameters obtained from quantum chemistry calculations. A comparison with the experimental measurements has allowed us to determine the energy distribution of the excited clusters just after the collision. The energy distribution is practically the same for the three systems, which supports the validity of the model. The present combination of theory and experiment opens the door for precise determinations of the energy distribution of highly excited clusters with a large number of fragmentation channels.

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