Fission barriers for the emission of odd-numbered fragments from multicharged C_{60} prepared in Ar^{8+}-C_{60} collisions

S. Martin, L. Chen, J. Bernard, M. C. Buchet-Poulizac, B. Wei, and R. Brédy
Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard Lyon 1, UMR CNRS No. 5579
43 boulevard du 11 Novembre 1918-69622 Villeurbanne Cedex, France

(Received 11 February 2005; revised manuscript received 6 October 2005; published 10 January 2006)

We report on measurements of the branching ratios of emission of small C_n^+ fragments in asymmetrical fission of highly charged C_{60}^{r+} ions (r=4–6). For the channels corresponding to the emission of one fragment, only small fragments with an even number of carbon atoms are observed. For the channels with the emission of two fragments, successive emission of small fragments with an odd number of carbon atoms has been observed with a surprisingly high branching ratio (30%). In order to reproduce the experimental branching ratios in the framework of a statistical evaporation model, the height of fission barriers for the emission of one odd numbered fragment has to be reduced at higher temperature in order to allow the opening of these channels that are forbidden at lower temperature

DOI: 10.1103/PhysRevA.73.013204 PACS number(s): 36.40.Ei, 36.40.Qv, 36.40.Wa

The fragmentation of complex systems has been first studied both experimentally and theoretically using multicharged metallic clusters [1–3]. The repulsive Coulomb force is a source of instability for such systems leading to the so-called asymmetrical fission process; i.e., the relaxation of the cluster by the loss of one or several small charged fragments. For a given initial charge state, the asymmetrical fission barrier decreases with the decreasing sizes of the cluster. At the critical size, when the fission barrier is comparable to the dissociation energy for the emission of a neutral fragment, the asymmetrical fission competes with the evaporation process. The classical droplet model [4] has been used successfully to interpret qualitatively some trends observed in fission processes, for example, smaller parent clusters emit preferentially a smaller fragment.

Since its discovery, the C_{60} fullerene has been used as a model system for studying the dynamics of excitation and relaxation in complex systems with a large number of degrees of freedom. In spite of intense experimental and theoretical investigations carried out during the last decade on the fragmentation of C_{60}, the dissociation energy, the asymmetrical fission barriers and the critical charge state for different fragmentation schemes of C_{60} are still a matter of controversy [5–7]. The main difficulties in studying a relatively complex system in general such as clusters or large molecules arise from the determination of the excitation energy of the system. A theoretical investigation using molecular dynamics calculations has illustrated the existence of several phases of C_{60} as a function of the temperature [8]. At low temperature ($T<2400$ K), the C_{60} is in a solid phase and stays intact. In the range of $2400\ \text{K}<T<4000$ K, the C_{60} is in a flexible phase (the carbon pentagons and hexagons tilt easily) and forms during a short time a metastable state with two or more adjacent pentagons leading to the well-known emission of carbon dimers. Starting from $T\simeq6000$ K, the multifragmentation process, i.e., complete breakup of the fullerene cage, occurs resulting mainly in smaller ring and chain carbon fragments. Details of the structure of C_{60} at different temperatures can be found in a paper of Marcos *et al.* [9] from the molecular dynamics simulations. The calculations show that isomers with many dangling bounds exist in the range of $3500\ \text{K}<T<4500$ K from which the ejection of odd-numbered fragments like C_3 seems to be possible.

Up to now, few experimental works have been reported on fragmentation of C_{60} with selectively controlled excitation energy [10–12]. Commonly employed time of flight (TOF) spectra provide information on the fragmentation patterns of C_{60} with excitation energy in a large range leading to a variety of products from cool intact C_{60}, heavy fullerenes C_{60-2n}, to light fragments resulting from multifragmentation of hot C_{60}. This transformation of fragmentation patterns as a function of the excitation energy has been studied in detail and is now well established for neutral and singly charged fullerenes [10]. The series of C_{60-2n} fullerenes observed in the TOF spectra have been explained mainly by successive evaporation of C_2 neutrals and the number of observed fullerenes depends strongly on the initial temperature. More recent experiments [13–17] have shown that the commonly assumed dimer C_2 is not the only specie associated to fullerene partners C_{60-2n}. Larger fragments $C_{2n}^+(n>1)$ with an even number of carbons as well as fragments $C_{2n-1}^+(n\geqslant1)$ with an odd number of carbons have been observed in coincidence with charged fullerenes C_{60-2n}. In the above experiments, the temperature of C_{60} fullerenes is not really under well control and the fragmentation spectra are the result of various fragmentation channels due to a wide distribution of excitation energy. Fullerenes with an odd number of carbon atoms like C_{59} have been reported for particular collision systems like C_{60}^- on He [18], but the intensity of the corresponding peak is very weak.

The fragmentation scheme of a cluster is also determined by its initial charge state. By analogy with the critical size of metallic clusters at a given charge, a critical charge around 4+ has been already observed for the C_{60} [17]. For C_{60} with a charge higher than 4+, the asymmetrical fission dominates with respect to the evaporation process. Dynamical information on fragmentation processes has been obtained by studying the asymmetrical fission of C_{60}^{5+}. Fission channels with the emission of two small charged fragments have been observed. It offered the opportunity to study the relaxation of systems for which all fragmentation products could be analyzed. Direct experimental evidences for the successive emission of small fragments have been provided without ambiguity [16].

The relaxation of internal excitation energy of C_{60} by the evaporation of C_2 has been well described using the statistical model based on the Ruderman-Kittel-Kasuya (RRK) theory [19]. Three parameters are needed to calculate the decay rate of a specific channel by this model: the preexponential factor, the dissociation energy or the fission barrier for the decay channel, and the excitation energy of the parent. In recent works of Aarhus group [20], the preexponential factor has been determined precisely for neutral and monocharged fullerene. Combining this model and experimental branching ratios of different fission channels for a given parent ion C_{60}^{r+}, it is possible to determine one of the other two parameters: the asymmetrical fission barrier in a specific channel, $C_{60}^{r+} \rightarrow C_{60-m}^{(r-1)+} + C_m^+$, or the initial excitation energy [14,17]. In general, the fission barrier for a given decay channel is considered as a parameter independent of the excitation energy.

In this paper, we attempt to apply the RRK model to fission processes of highly charged C_{60}^{5+} and C_{60}^{6+} ions produced in collisions with Ar^{8+}. The puzzling point here is the observation of the successive emission of two small odd-numbered fragments with high abundance, while the channel for the emission of one odd-numbered fragment is forbidden. It is then a challenging work to reproduce experimental branching ratios in the framework of a multicascade model combined with the statistical evaporation model RRK. In order to explain the fact that the channel for the emission of an odd-numbered small fragment from a charged C_{60} is forbidden at lower temperature but is opened at higher temperature, reduced effective fission barriers will be discussed when the excitation energy of C_{60} parents is high enough. The estimated effective fission barriers will be compared to those obtained with a quasidroplet model.

The experimental setup is similar to that used in our previous coincidence studies [14]. A C_{60} powder is evaporated in an oven at a temperature of $\sim 500\ °C$. The C_{60} neutral jet interacts with the beam of Ar^{8+} (about 100 pA). The charged reaction products are extracted from the interaction zone by means of a high extraction field of 800 V over 8 mm ($E = 1000$ V/cm) to ensure a good collection efficiency for ions and electrons. The C_{60} ions and fragments are analyzed with a time of flight tube of 320 mm in length. The particles are post accelerated with a voltage of 5 kV towards a detector equipped with two multichannel plates and a multianode of 61 pixels linked to 61 individual discriminators. This device is useful for detecting two identical ions (for instance, C^+ and C^+) arriving at the same time on the detector but at different positions. The ejected electrons coming from the extraction region are detected with a semiconductor detector. The electron signal pulse height analysis provides the number n of emitted electrons in a collision event. Outgoing projectiles Ar^{6+} with two stabilized electrons are selected with an electrostatic analyzer. The charge of the target C_{60}^{r+} after the collision and before fragmentation is estimated by the relation $r = n + 2$ according to the electron number conservation law. Multicoincidence measurements are performed in an event-by-event mode.

Table I gives the measured event counts and the relative branching ratios R_b associated to fission channels involving one light fragment, $C_{60}^{r+} \rightarrow C_{60-m}^{(r-1)+} + C_m^+$ ($r = 4-7$; $m = 2,4,6,8,10$) and two light fragments $C_{60}^{r+} \rightarrow C_{60-m}^{(r-2)+} + C_{n1}^+ + C_{n2}^+$ ($r = 6,5$; $m = 2,4,6,8,10$; $m = n_1 + n_2$; n_1 from 1 to $(m-1)$; $n_2 = m - n_1$). They are referred in the following as one-step and two-step fission channels respectively. Details about the data analysis can be found in the paper [14]. Two-step fission populations associated to C_{60}^{7+} and C_{60}^{4+} parent ions are not given here because of the low statistics for C_{60}^{7+} and a dominant evaporation process on the second step for C_{60}^{4+} ions. The branching ratios for the emission of doubly charged light fragments are very low for these charge states and can be neglected in this study. The population distributions of fission processes with successive ejection of three charged fragments are not presented here and will be given in a forthcoming paper. The ratio of event counts for all two-step channels over the total count number including one-step and two-step channels has been estimated to be 42% and 26% for C_{60}^{6+} and C_{60}^{5+} parent ions, respectively. One-step fission channels involving a light fragment with an odd number of carbon atoms is not observed at all. However, the branching ratio of events with two odd-numbered light fragments over the total event number of two-step channels is found to be surprisingly high, around 30% for C_{60}^{5+} and C_{60}^{6+} ions.

The measured branching ratios R_b for one-step channels, noted in the following by R_m, are plotted in Fig. 1 as a function of the number m of carbon atoms in the light fragment C_m^+ for C_{60}^{r+} parent ions ($r = 4-7$). A population shift towards lighter fragment C_2^+ is noted as the charge of the C_{60}^{r+} parent ions increases. Following the same method as in papers [14,17], the theoretical relative population distribution as a function of m has been estimated using the RRK model. The fission barrier for each reaction channel is calculated from the energy difference Δ_m^r of the initial and final states of the reaction. The atomization energies of the fullerene and the light fragments are estimated using the density functional theory (DFT) (see paper [14] for details). Knowing all fission barriers, the excitation energy remains the only adjusted parameter in order to match the theoretical and experimental branching ratios. The agreement between the theoretical branching ratios obtained with this model and the experimental distributions (Fig. 1) is rather nice. The obtained excitation energy of around 45 ± 5 eV corresponds to a temperature of about 2400 K, which is considered here as a low temperature.

It is noteworthy that due to the instability of fullerenes with an odd number of carbon atoms, the atomization energy of an odd-numbered fullerene is lower than the neighboring even-numbered fullerenes. Higher fission barriers are therefore found for fission channels with the ejection of an odd-numbered light fragment. As an example, the fission barrier for the ejection of a C^+ is about 3 eV higher than the one for the ejection of a C_2^+ [$B(C_2^+) = 8.4$ eV and $B(C^+) = 11.1$ eV for C_{60}^{6+}]. The theoretical branching ratios for the emission of one

TABLE I. Measured event count numbers for fission channels involving the emission of one and two light monocharged fragments and the branching ratio R_b for each fission channel. The charge of the parent ion C_{60}^{r+} ranges from $r=4$ to 7.

	C_{60}^{4+}		C_{60}^{5+}		C_{60}^{6+}		C_{60}^{7+}	
Fission channels	Counts	R_m	Counts	R_m	Counts	R_m	Counts	R_m
$C_{58}^{r-1}+C_2^+$	9237	0.338	16305	0.573	1820	0.654	62	0.795
$C_{56}^{r-1}+C_4^+$	14078	0.516	9360	0.329	833	0.299	16	0.205
$C_{54}^{r-1}+C_6^+$	3105	0.114	2195	0.077	131	0.047	0	0.000
$C_{52}^{r-1}+C_8^+$	726	0.027	485	0.017		0.000		
$C_{50}^{r-1}+C_{10}^+$	163	0.006	113	0.004				
$C_{58}^{r-2}+C^++C^+$			207	0.020	189	0.080		
$C_{56}^{r-2}+C_3^++C^+$			1087	0.104	284	0.121		
$C_{56}^{r-2}+C_2^++C_2^+$			1234	0.118	633	0.269		
$C_{54}^{r-2}+C_2^++C_4^+$			2803	0.269	590	0.251		
$C_{54}^{r-2}+C_3^++C_3^+$			574	0.055	47	0.020		
$C_{54}^{r-2}+C^++C_5^+$			257	0.025	86	0.037		
$C_{52}^{r-2}+C_4^++C_4^+$			1183	0.113	181	0.077		
$C_{52}^{r-2}+C_2^++C_6^+$			1038	0.099	140	0.060		
$C_{52}^{r-2}+C_5^++C_3^+$			375	0.036	41	0.017		
$C_{52}^{r-2}+C^++C_7^+$			101	0.010	20	0.009		
$C_{50}^{r-2}+C_5^++C_5^+$			65	0.006	4	0.002		
$C_{50}^{r-2}+C_4^++C_6^+$			949	0.091	105	0.045		
$C_{50}^{r-2}+C_7^++C_3^+$			250	0.024	14	0.006		
$C_{50}^{r-2}+C_2^++C_8^+$			285	0.027	18	0.007		

odd-numbered fragment is then found three orders of magnitude lower than the channels with an even numbered fragment. It is consistent with the fact that the experimental branching ratios of these channels are negligible.

Figure 2 presents the experimental and calculated branching ratios for the two-step fission channels of C_{60}^{6+} and C_{60}^{5+} parent ions. In this figure, the two numbers associated to each point represent the number of C atoms in the emitted fragments. Let us start by analyzing the even-even channels, i.e., asymmetrical fission channels involving two even-numbered light fragments. The dominant channels are the 2-2 and 2-4 emission for C_{60}^{6+} and the 2-4 emission for C_{60}^{5+}. To ensure the successive emission of two fragments, higher initial temperature of the C_{60} parent ions is needed which is estimated to be about 3800 K. Calculated branching ratios $R_{n1,n2}$ for the emission of C_{n1}^+ and C_{n2}^+ are obtained with a multicascade model corresponding to the successive fission processes. Although the theoretical decay rates vary with the temperature after the RRK model, the relative branching ratios remain nearly constant in the present energy range (2400–3800 K). The experimental branching ratios R_{n1} and R_{n2} measured for one-step channels $C_{60}^{r+}\rightarrow C_{60-n1}^{(r-1)+}+C_{n1}^+$ and $C_{60}^{(r-1)+}\rightarrow C_{60-n2}^{(r-2)+}+C_{n2}^+$ are therefore used in the calculation. A careful analysis of Fig. 2 shows that all experimental branching ratios of even-even channels are not well reproduced by the calculation, especially for 2-6, 4-6, and 2-8 channels. It is explained by the fact that for the second step, the parent ion is $C_{60-n1}^{(r-1)+}$ instead of $C_{60}^{(r-1)+}$. The fission barrier for the ejection of a fragment C_{n2}^+ from a lighter fullerene $C_{60-n1}^{(r-1)+}$ parent ion should be slightly different from that of a fullerene $C_{60}^{(r-1)+}$. The one-step branching ratio R_{n2} used in the calculation is then an approximation as poor as the value n_1 is large.

For fission processes involving two odd-numbered light fragments, the dominant channels are the 1-1 and 1-3 channels for C_{60}^{6+} and 1-3 and 3-3 channels for C_{60}^{5+}. Generally, the channels involving heavier light fragments like 5-3 and 7-3 from C_{60}^{5+} ions have higher branching ratios than those from C_{60}^{6+} parent ions. The possibility that the parent C_{60}^{r+} decays by emission of an excited doubly charged fragment, which itself undergoes a fragmentation into two singly charged fragments is excluded for two reasons. Firstly, the barrier for the ejection of a doubly charged fragment is comparable to that for the ejection of a singly charged odd numbered fragment; consequently its emission probability should be as low as that for one odd-numbered fragment. Secondly, experimental evidences have been provided for the fast successive ejection of two odd-numbered fragments by analyzing the velocity correlation between the two light fragments in the fragmentation of C_{60}^{5+} [16]. Therefore, in the following, the odd-odd channels are also considered as a successive emission process as in the cases of even-even channels. However, using the negligible one-step branching ratios, $R_1=R_3=R_5\approx 0$, it was not possible to reproduce the experimental branching ratios for odd-odd channels in a successive emission model, for example, $R_{1,3}=0.1$ in the case of $C_{60}^{5+}\rightarrow C_{56}^{3+}+C^++C_3^+$. In fact, the very low branching ratio for the ejection of the first

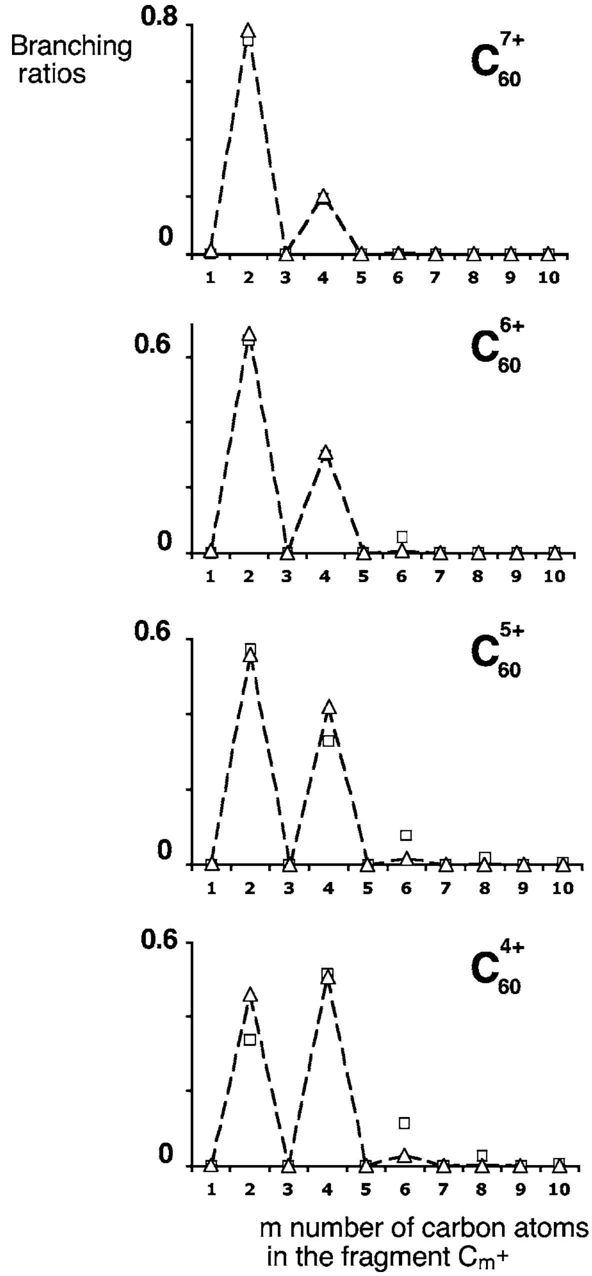

FIG. 1. Relative branching ratios (R_m) for one-step asymmetrical fission channels. m stands for the number of carbons in the small fragment. The parent ions are C_{60}^{4+}, C_{60}^{5+}, C_{60}^{6+}, and C_{60}^{7+}. Squares: Experimental values. Triangles: Theoretical values obtained using the RRK model. Branching ratios for channels with an odd number of m are negligible.

odd-numbered light fragment inhibits such fission channels.

To reproduce all experimental data including even-even and odd-odd channels in successive fission processes, we replace in the multicascade model, the negligible experimental branching ratios for the one-step emission of an odd-numbered fragment C_m^+ ($m=1,3,5,7$) from $C_{60}^{5,6+}$ by a set of adjustable branching ratios R'_m. By fitting all experimental two-step branching ratios $R_{n1,n2}$ as shown in Fig. 2, the adjusted branching ratios R'_m of one-step fission channels with an odd number of m for C_{60}^{4+}, C_{60}^{5+}, and C_{60}^{6+} parent ions have

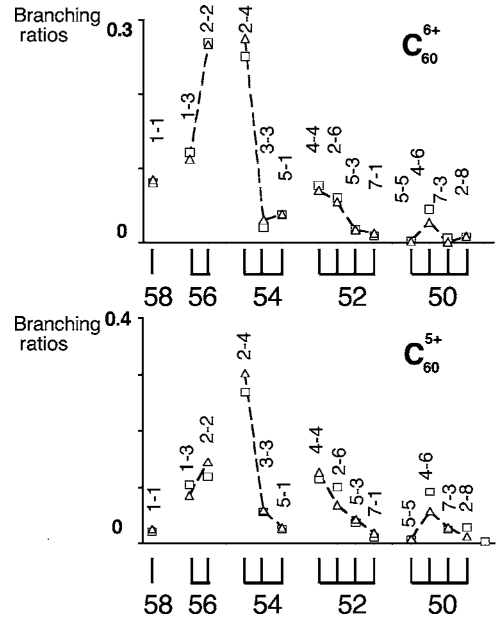

FIG. 2. Relative branching ratios ($R_{n1,n2}$) for two-step successive asymmetrical fission channels $C_{60}^{r+} \rightarrow C_{60-(n1+n2)}^{(r-2)+} + C_{n1}^+ + C_{n2}^+$ with $r=5$ and 6. The abscissa corresponds to the number of carbon atoms in the residual fullerene. The couple of numbers (n_1, n_2) associated to the two light fragments C_{n1}^+ and C_{n2}^+ are displayed above each point. Squares: Experimental values. Triangles: Values obtained with the multicascade model (see text).

been obtained and presented in Fig. 3. The experimental branching ratios R_m for one-step channels with an even number of m are renormalized including the contribution of R'_m and displayed in the same figure. Despite the large number of adjustable parameters used in the modeling, the solution is unique. This is due to the multiple constraints imposed by a large number of population equations necessary to describe the complex multicascade processes. The dominant odd-numbered fragment emission channels are the emission of C^+ from C_{60}^{6+}, C^+, and C_3^+ from C_{60}^{5+} and C_3^+ from C_{60}^{4+}. The respective dependences of R'_m and R_m versus m of odd-numbered and even-numbered light fragments have similar features. It is noteworthy that the maximum value of R'_m (0.2) for the emission of C^+ from C_{60}^{6+} is at least three orders of magnitude higher than the branching ratio R_1 estimated using the theoretical fission barrier. In the framework of the RRK model, a plausible interpretation is that the fission barriers for the emission of an odd numbered fragment is lower at higher temperature. Using the adjusted experimental branching ratios, the RRK model and a temperature of about 3800 K, the corresponding effective fission barriers have been estimated and presented in the Fig. 4 for parent ions C_{60}^{6+}. The reduction of the effective fission barriers for these odd numbered fragment emission channels with respect to the theoretical values based on the DFT model is indeed remarkable.

In order to interpret this unexpected reduction of fission barrier, we compare our effective fission barriers with the values estimated using a liquid droplet model [4]. The classical droplet model is modified to take into account the special structure of the fullerenes and the linear structure of the

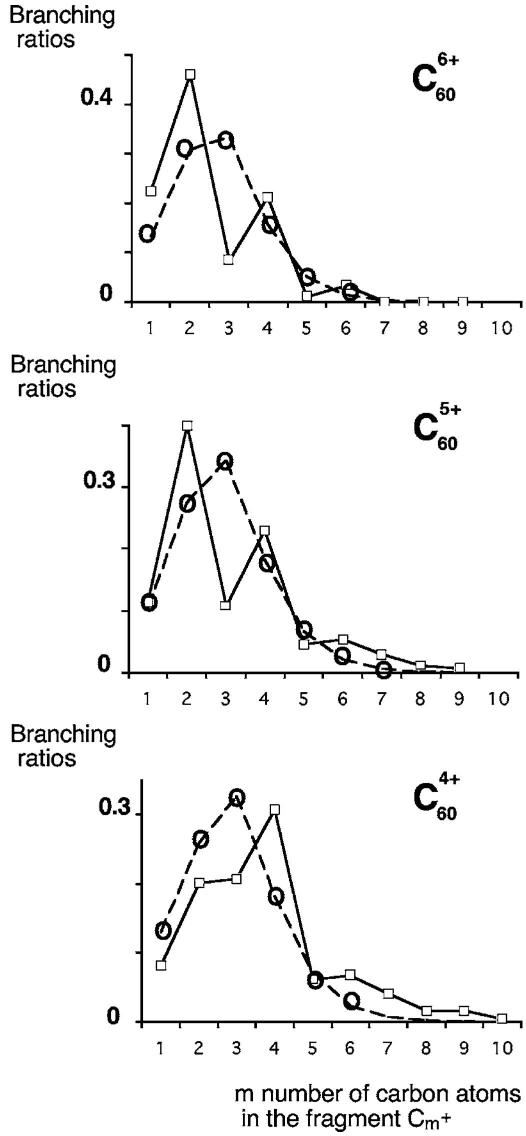

FIG. 3. Relative branching ratios for the first-step fission process $C_{60}^{r+} \rightarrow C_{60-m}^{(r-1)+} + C_m^+$ with a parent ion C_{60}^{6+}, C_{60}^{5+}, and C_{60}^{4+} at higher temperature (3800 K). For channels with an odd number of m, the branching ratios R_m' are adjusted using the multicascade model. For channels with an even number of m, the experimental branching ratios R_m in one-step fission processes are displayed. Squares: R_m and R_m' the solid lines are to guide the eyes. Dashed line: Relative branching ratios obtained with the RRK model which is combined with the quasidroplet model to estimate the fission barrier for each fission channel (see text).

light fragments. The atomization energies are calculated using the relation that reproduces relatively well the binding energies of C_m obtained with *ab initio* calculations [10]:

$$E_{\mathrm{at}}(C_m) = 6.06 - 0.0032m + 0.1m^{2/3} - \frac{6.14}{m} - 9.4 \times 10^5 m^2.$$

The coefficients in this relation cannot be easily related to the volume and surface energies like in the classical droplet model. Due to the smooth variation with m of the function E_{at}, the special even-odd alternation of the atomization energy of the fullerenes is not taken into account. The r-fold ionization potentials are calculated as follows:

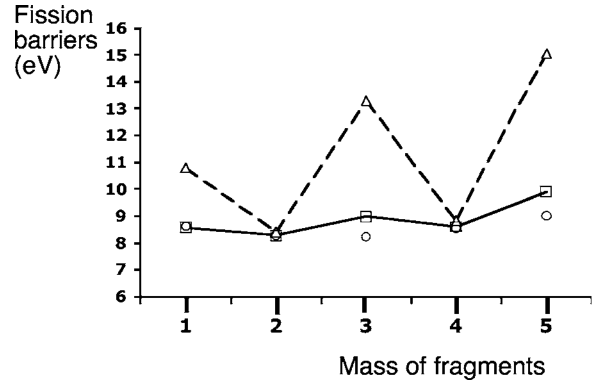

FIG. 4. Comparison of the fission barriers for the asymmetrical fission processes, $C_{60}^{6+} \rightarrow C_{60-m}^{5+} + C_m^+$. Squares: Fission barriers obtained with the RRK model using the experimental branching ratios for channels with an even number of m and the adjusted branching ratios R_m' for channels with an odd number of m. Triangles: Values calculated based on the DFT model. Circles: Values calculated with the quasidroplet model.

$$V_{\mathrm{ion}}(C_m^{r+}) = rW_\infty + \left(\frac{r^2}{2} - \frac{r}{8}\right)\frac{1}{a_s m^{1/3}},$$

where $W_\infty = 4$ eV and $a_s = 2.3$ a.u. are the work function and the Wigner Seitz radius, respectively. The fission barriers of C_{60}^{6+} calculated with this quasidroplet model are plotted in Fig. 4 and the corresponding branching ratios are shown in Fig. 3 (dashed lines).

The similarity between the effective barriers obtained with the adjusted branching ratios and the data from the quasidroplet model is notable. Therefore, based on this droplet model, a better description of the fragmentation of C_{60} is obtained for channels involving odd numbered fragments. This suggests that at higher temperature the fullerenes lose in some extent their rigid structure. The contrast between the relatively high stability of even numbered fullerenes and the instability of the odd numbered ones is strongly reduced, the energy needed for the escape of a C^+ and a C_2^+ is therefore very close. On the contrary, at lower temperature (about 2400 K), the strong even-odd oscillation of the fission barriers, calculated with the atomization energy of fullerenes obtained with DFT taking into account the even-odd alternation, is in good agreement with the experimental branching ratios. These results indicate that the structure of the C_{60} undergoes a transformation as a function of the temperature. Parameters such as the fission barriers calculated for C_{60} with a rigid structure are valid at low temperature (2400 K), but are not at a temperature around 3800 K, which is nevertheless still much lower than the temperature for the complete breakup of the fullerene.

In summary, we have measured the branching ratios of fragmentation channels for two typical temperatures of C_{60} molecules characterized by the number of ejected fragments. The one-step emission corresponding to the ejection of one light fragment occurs at rather low temperature (about

2400 K). At this temperature, only the ejection of an even numbered fragment is possible. The residual part of the fragmentation is then an intact even numbered fullerene. The two-step channels are opened at higher temperature (about 3800 K) at which other isomers like isomers with dangling bounds can be populated. Under such conditions, fission barriers for the emission of a fragment with an odd number of carbons are drastically decreased and consequently the successive emission of two odd-numbered fragments becomes possible. Finally, the experimental branching ratios for two-step channels are relatively well reproduced using the fission barriers estimated with a quasidroplet model. As a conclusion, the statistical evaporation model RRK is suitable to describe the two-step fission processes of multiply charged fullerenes C_{60} as long as the fission barriers for the emission of odd numbered fragments is reduced in the corresponding excitation energy range.

For higher internal energies (>3800 K) leading to three- or four-step fission processes, other channels that are forbidden in the lower energy range could probably be opened. More experimental and theoretical investigations are necessary to understand such multistep processes, which could be helpful to understand the transition from the asymmetrical fragmentation regime at lower temperature to the multifragmentation regime at higher temperature.

This work has been supported by the Region Rhone-Alpes under Grant No. 97027-223 of the convention Recherche programme Emergence.

[1] P. Blaise, S. A. Blundell, C. Guet, and Rajendra R. Zope, Phys. Rev. Lett. **87**, 063401 (2001).
[2] C. Brechignac *et al.*, Phys. Rev. Lett. **81**, 4612 (1998).
[3] T. P. Martin *et al.*, Chem. Phys. Lett. **196**, 113 (1992).
[4] C. Brechignac, P. Cahuzac, F. Carlier, M. de Frutos, N. Kebaïli, J. Leygnier, A. Sarfati, and V. Akulin, in *Charge Clusters of Atoms and Molecules*, edited by T. P. Martin (Kluwer Academic, Dordrecht, The Netherlands, 1996), Vol. 313, p. 315.
[5] A. Daniel Boese and Gustovo E. Scuseria, Chem. Phys. Lett. **294**, 233 (1998).
[6] P. Scheier and T. M. Märk, Phys. Rev. Lett. **73**, 54 (1994).
[7] S. Tomita, J. U. Andersen, G. Gottrup, P. Hvelplund, and U. V. Pedersen, Phys. Rev. Lett. **87**, 073401 (2001).
[8] Seong Gon Kim and D. Tomanek, Phys. Rev. Lett. **72**, 2418 (1994).
[9] P. A. Marcos *et al.*, EPJdirect **6**, 221 (1999).
[10] E. E. B. Campbell, T. Raz, and R. D. Levine, Chem. Phys. Lett. **253**, 261 (1996); R. Ehlich, M. Westerburg, and E. E. B. Campbell, J. Chem. Phys. **104**, 5 (1996).
[11] A. Bordenave-Montesquieu *et al.*, J. Phys. B **34**, L137 (2001).
[12] O. Hadjar *et al.*, Phys. Rev. Lett. **84**, 4076 (2000).
[13] R. Vandenbosch, B. P. Henry, C. Cooper, M. L. Gardel, J. F. Liang, and D. I. Will, Phys. Rev. Lett. **81**, 1821 (1998).
[14] S. Martin, L. Chen, R. Brédy, M. C. Buchet-Poulizac, A. Allouche, and J. Désesquelles, Phys. Rev. A **66**, 063201 (2002).
[15] A. Reinköster, B. Siegmann, U. Werner, B. A. Huber, and H. O. Lutz, J. Phys. B **35**, 4989 (2002).
[16] L. Chen *et al.*, Phys. Rev. A **64**, 031201 (2001).
[17] L. Chen *et al.*, Phys. Rev. A **59**, 2827 (1999).
[18] M. C. Larsen *et al.*, Eur. Phys. J. D **5**, 283 (1999).
[19] K. S. Kassel, J. Phys. Chem. **32**, 225 (1928).
[20] S. Tomita *et al.*, Chem. Phys. Lett. **382**, 120 (2003).