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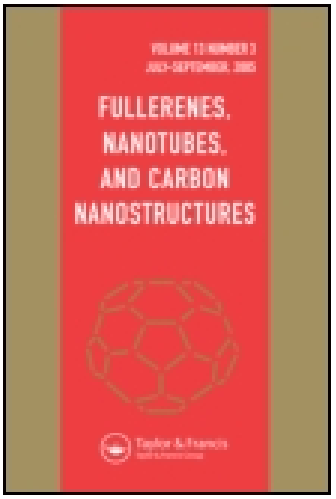

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Mass Spectrometric Transmutation of Fullerenes

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Mass Spectrometric Transmutation of Fullerenes

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MS/MS studies of the higher fullerenes C_n^+ (n = 60, 70, all even from 76-94) revealed that certain product ions were especially stable, and that these matched closely to the fullerenes that are particularly abundant in synthetic mixtures. All fullerenes fragmented by loss of C_2 molecules.

Keywords Mass spectrometry, laser desorption, fragmentation, fullerenes

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Introduction

In 2005, Cross and Saunders described the high temperature annealing of higher fullerenes (C_{70}, and various isomers of C_{76}, C_{78}, C_{84}) to form smaller fullerenes through loss of carbon atoms (1). C_{60} survived the passage through the ~1000°C oven without decomposition. The authors memorably described this transformation as the equivalent of turning gold into lead, given the price differential between pure samples of the higher versus lower fullerenes. The annealing process occurred in the gas phase in an argon flow, and the fullerenes resided in the oven for about 40 seconds. C_{76} decomposed to C_{70} and small amounts of C_{60}, and larger fullerenes also lost carbon atoms to form smaller fullerenes.

A MALDI-TOF/TOF mass spectrometer offers the opportunity to study this process from a different angle, and the MS/MS capability allows a mixture of fullerenes to be investigated, rather than having to laboriously separate the higher fullerenes. We analysed a commercially available mixture of fullerenes by tandem mass spectrometry without a matrix using a MALDI-TOF/TOF instrument and gathered decomposition information on the fullerenes C_{60}^+, C_{70}^+, and all C_n^+ (where n = even number) from C_{76-94}^+. All appear to decompose by sequential elimination of C_2 molecules, but certain fullerenes consistently dominate the suite of daughter ions. Experiments were run without a matrix, as we have found other inorganic cluster compounds to provide more intense spectra without a matrix (2).

The mass spectrometric study of fullerenes has a long and proud history (3), starting with the Nobel prize-winning discovery of C_{60} from mass spectrometric experiments on the laser vaporization of graphite (4). Smalley reported the photodissociation of C_{60}^+ in TOF/TOF experiments, he showed the primary fragmentation is C_2 loss and that the initial C_2 loss requires activation of 18 eV (5). High-energy collision-induced dissociation studies show a similar distribution of fragments, provided heavier target gases than He are used (e.g. O_2, N_2) (6). High-energy (150-1050 eV/molecule) surface impact fragmentation

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of C_{60}, C_{70}, C_{76}, C_{84}, and C_{94} on graphite generated even-numbered C_n species with abundances similar to those observed in fullerene synthesis (7). Cordero, Cornish, and Cotter conducted a MALDI-TOF/TOF investigation of C_{60}^+ and C_{70}^+, including collisional activation with He, Ar, Xe, and SF_6 (8). High-energy single collisions produced the best-resolved spectra, forming high mass C_{2n}^+ and low mass C_n^+ ions. Our study used solely Ar as the collision gas, and we examined a range of higher fullerenes in addition to C_{60}^+ and C_{70}^+.

Results and Discussion

The LDI-TOF mass spectrum of a commercial sample of mixed fullerenes is shown in Figure 1. It consists primarily of C_{60}, C_{70}, C_{76}, C_{78} and C_{84} with smaller amounts of higher fullerenes, all with an even number of carbon atoms, up to about C_{150} at which point the signal-to-noise ratio becomes very low. The intensity of the C_n^+ radical cations was good, with sample preparation involving simply evaporating a CS_2 solution onto an AnchorChip™ plate. The spectrum resembles that obtained of crude fullerene soot produced by resistive heating of graphite under an inert atmosphere (9).

Each of these C_n^+ ions may be selected for MS/MS analysis, fragmentation being caused primarily by increasing the intensity of UV laser used for desorption. The excess energy deposited into the ions causes them to fragment *after* acceleration, and fragment ions are separated by the reflectron TOF. Ions decomposing in the first field-free region of the reflectron will appear at an m/z value different from that of the ion entering the reflectron, and such post-source decay (PSD) peaks appear broadened and at lower m/z values. Data were collected at three values of fragmentation energy for all fullerenes studied: (a) threshold laser power, (b) high laser power, and (c) high laser power with CID gas (Ar) switched on. The Bruker LIFT experiment was used for all MS/MS studies (10). Precursor ions are selected and fragmented in TOF-1 (the first of two co-linear time-of-flight mass analyzers). Fragment ions are selected to proceed to the source of TOF-2, where they are again accelerated and analyzed. Both sources allow control over acceleration and focusing of ions (11). Sufficient intensity for MS/MS studies were obtained for the fullerenes C_{60}, C_{70}, C_{76}, C_{78}, C_{80}, C_{82}, C_{84}, C_{86}, C_{88}, C_{90}, C_{92}, and C_{94}. The higher fullerenes provided MS/MS spectra that were too noisy for successful analysis. Mass spectra of C_{60}, C_{70}, C_{76}, C_{78}, C_{80}, and C_{82} are illustrated in Figure 2, while those for C_{84}, C_{86}, C_{90}, C_{92}, and C_{94} are shown in Figure 3.

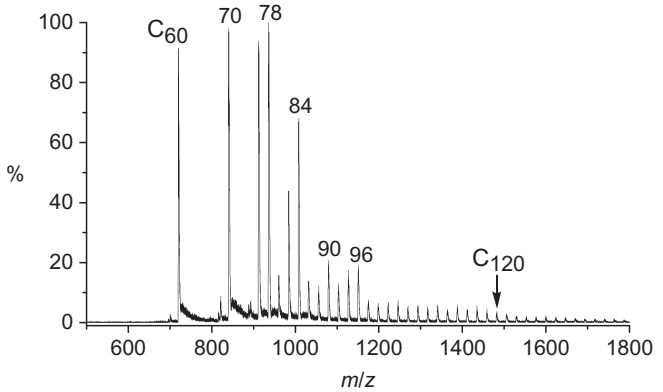

Figure 1. Positive-ion LDI-TOF mass spectrum of a commercial mixture of fullerenes.

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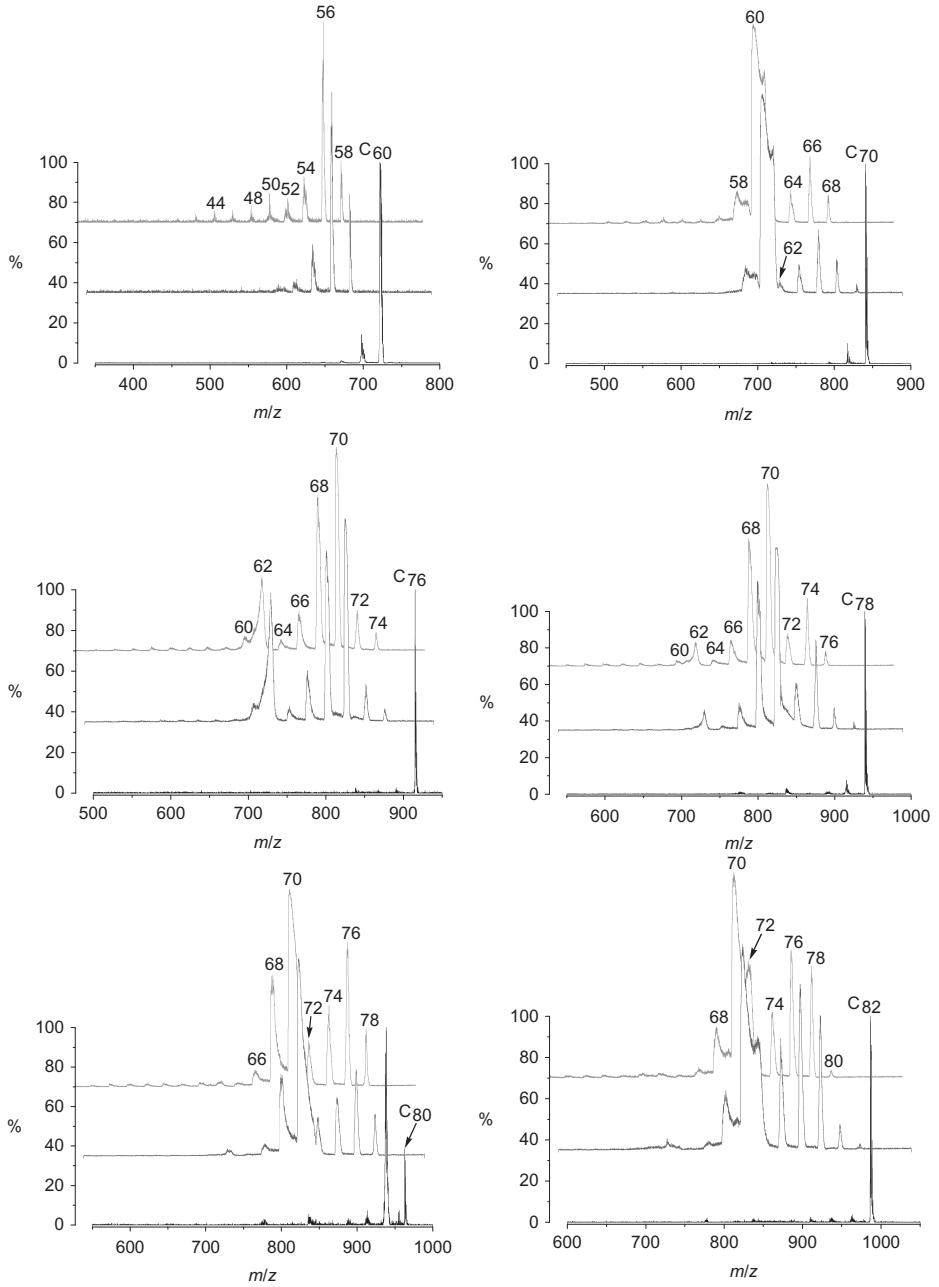

Figure 2. Positive-ion LDI-TOF/TOF mass spectra of C_{60}, C_{70}, C_{76}, C_{78}, C_{80}, and C_{82}. For each fullerene: threshold laser power (bottom), high laser power (middle), and high laser power and CID gas (Ar) switched on (top).

All data are summarized in Table 1. All fullerenes decompose by loss of even numbers of carbon atoms (2, 4, 6, . . . 16). No low-mass C_n^+ fragments were observed in our product ion spectra.

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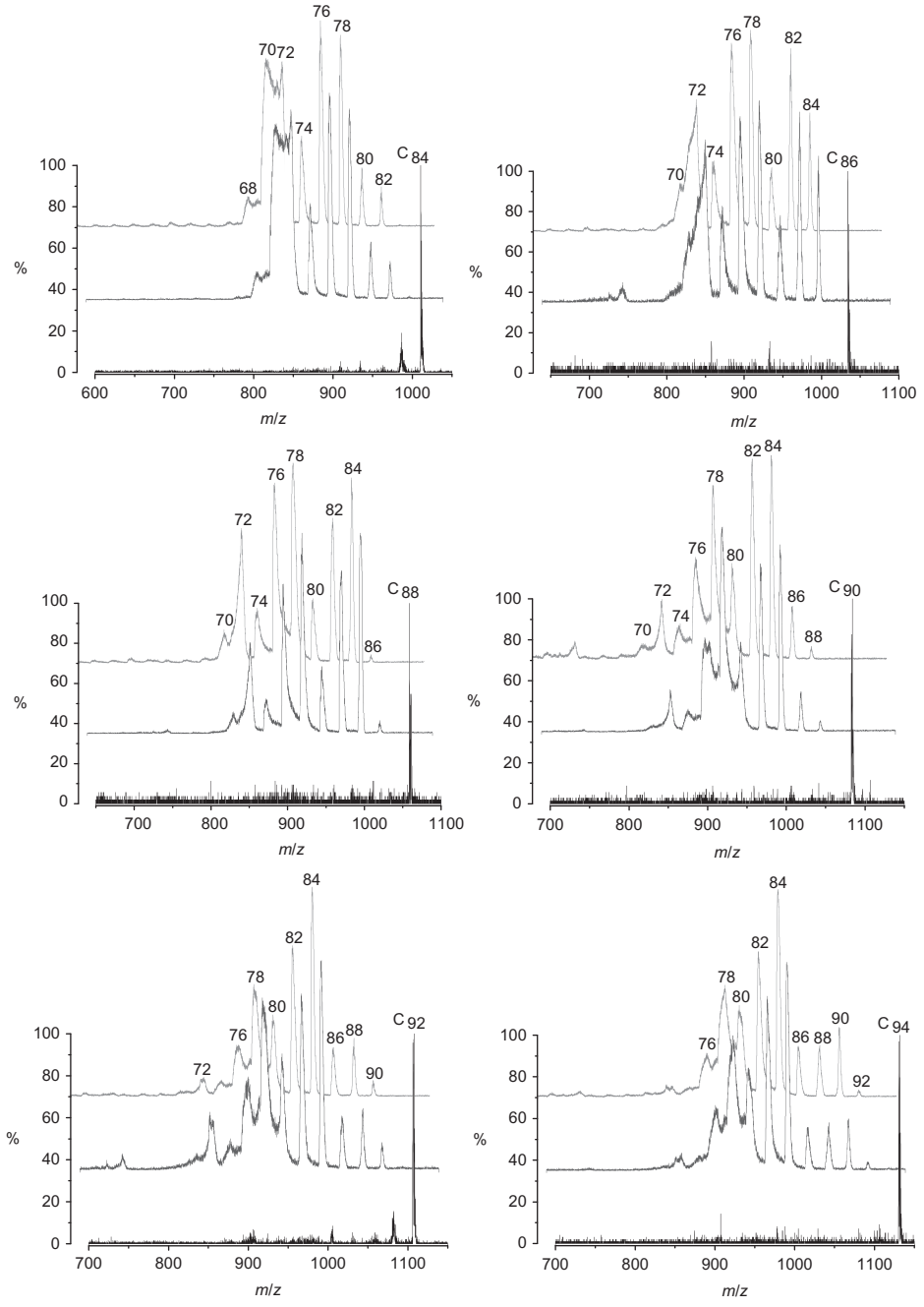

Figure 3. Positive-ion LDI-TOF/TOF mass spectra of C_{84}, C_{86}, C_{88}, C_{90}, C_{92}, and C_{94}. For each fullerene: threshold laser power (bottom), high laser power (middle), high laser power and CID gas (Ar) switched on (top). The effect of introducing Ar (under computer control, increasing the pressure to approximately 6×10^{-6} mbar) to act as a CID gas was minimal in these experiments, there was slightly more fragmentation for C_{60}^{+}, but for the higher fullerenes the effect was barely discernible.

Table 1
Peak intensities of fragment ions in the LDI-TOF/TOF of C_n^+.*

	Fullerene selected for MS/MS											
C_n^+	60	70	76	78	80	82	84	86	88	90	92	94
48	4							3	0 – 4 %			
50	7							8	5 – 9 %			
52	9							19	10 – 19%			
54	19							28	20 – 29 %			
56	50							33	30 – 39 %			
58	11	10						56	> 40 %			
60	⊛	70	7					⊛	Selected fullerene			
62		9	17	6								
64		4	3	3								
66		6	8	8	4							
68		2	26	28	19	11	6					
70		⊛	32	39	48	49	38	15	6	4		
72			6	7	6	16	20	20	16	8	4	
74			2	8	8	6	7	9	8	7	4	
76			⊛	2	11	10	13	20	23	19	15	11
78				⊛	4	7	11	15	20	22	24	26
80					⊛	1	3	5	5	10	12	15
82						⊛	2	10	10	15	16	16
84							⊛	6	10	13	17	18
86								⊛	1	3	5	4
88									⊛	1	4	4
90										⊛	1	4
92											⊛	1
94												⊛

**Under the harshest conditions attainable in the mass spectrometer, that is, 100% laser power, CID gas (Ar) switched on.*

C_{60}^+ itself seems particularly resistant to fragmentation, the most abundant fragment ion, C_{56}^+, represents the loss of only four carbon atoms (probably as 2 C_2 molecules). This observation is in stark contrast to the behaviour of the higher fullerenes under the same conditions, for which the most abundant daughter ions involve loss of between 6 (for $C_{76}^+ \rightarrow C_{70}^+$) and 16 (for $C_{94}^+ \rightarrow C_{78}^+$) carbon atoms in total. Particular product ions were especially prominent regardless of the precursor. C_{70}^+ readily lost five pairs of carbon atoms to form C_{60}^+, much in preference to loss of 1, 2, 3, 4, or 6. Similarly, C_{70}^+ itself was the most abundant product ion in the MS/MS spectra of C_{76}^+, C_{78}^+, C_{80}^+, C_{82}^+, and C_{84}^+. C_{76}^+ was the most prevalent in when fragmenting C_{86}^+ and C_{88}^+. C_{78}^+ is also especially prominent, appearing as the most common fragment from C_{88}^+, C_{90}^+, C_{92}^+, and C_{94}^+ precursor ions. Notably, these ions — C_{60}^+, C_{70}^+, C_{76}^+, and C_{78}^+ — are also those most abundant in the original mass spectrum of the mixture of higher fullerenes (Figure 1). There are also similarities with the high temperature annealing experiment of Cross and Saunders, in which C_{76} formed C_{70} and C_{60}, C_{78}A formed C_{78}B, C_{76}, C_{70} and C_{60}, and C_{78}B formed C_{78}A, C_{76}, C_{70} and C_{60}. Of course, our experiment is over much more quickly and thus captures many of the kinetic products of C_2 loss rather than the thermodynamic products accessed by the high temperature oven and extended exposure (~40 seconds). Hence we see all the same products—and they are generally the most abundant—but we also observe all the intermediate species as well. Kroto came up with a simple set of rules that predicted certain fullerenes should display special stability, including C_{60} and C_{70} (12).

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Early theoretical studies of C_{20} through C_{100} found C_{60}, C_{70} and C_{84} to be energetically more stable than their neighbors (13), and simple Huckel MO computations favoured $n =$ 60, 70, 76, 78, 84, and 90 (14).

Experimental

Mass spectrometric data were collected on a Bruker AutoflexII MALDI-TOF/TOF instrument. The fullerene mixture ("fullerite") was purchased from Aldrich and used without further purification. A saturated CS_2 solution of the fullerenes was prepared and single drops allowed to evaporate on an AnchorChip™ target (15). New spots were used for each experiment. MS/MS was performed using the LIFT experiment. The three spectra collected for each $C_n^{+\bullet}$ were recorded under conditions of (a) threshold laser power, (b) moderate laser power, and (c) high laser power with the introduction of argon gas for CID. These parameters allowed representative coverage of the fragmentation processes. Each LDI mass spectrum represents the accumulation of between 50 and 500 laser shots on the target, the stage was moved over the course of each experiment to expose fresh sample. Data were not processed (subtraction, smoothing, etc.) in any way. Table 1 was generated by integrating peak areas for each fullerene fragment ion and expressing the intensity as a percentage of the total ion current. This method is likely to slightly overestimate the intensity of the less abundant ions due to contributions from noise.

Conclusions

LDI-TOF/TOF mass spectrometry has been found to be a simple yet informative technique for probing the fragmentation pathways of higher fullerenes, without the necessity for tedious separations of the individual fullerene components. This methodology should be applicable for the investigation of other polyhedral inorganic clusters.

Acknowledgments

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