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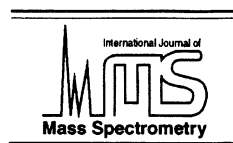
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Unimolecular ion dissociation and laser-induced coalescence of hydrogenated fullerenes

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Abstract

The ion-fragmentation behaviour of hydrogenated fullerenes has been investigated by tandem mass spectrometry applying sector instrumentation. In addition to the expected loss of hydrogen, unimolecular decay reactions are observed featuring cage rupture by the loss of hydrocarbon moieties. The findings are discussed in comparison with the behaviour of other fullerene derivatives. The gas-phase coalescence reactivity of C₆₀H₃₆ has been studied utilising laser desorption/ionization time-of-flight mass spectrometry. In contrast to pure fullerenes and certain organic fullerene derivatives, hydrogenated fullerenes do not readily undergo laser-induced fusion reactions. (Int J Mass Spectrom 195/196 (2000) 599–607) © 2000 Elsevier Science B.V.

Keywords: Hydrogenated fullerenes; C₆₀H₃₆; Unimolecular dissociation; Tandem mass spectrometry; Coalescence; Laser desorption/ionization

1. Introduction

Mass spectrometry of hydrogenated fullerenes has been almost exclusively concerned with providing a means for the analysis of synthetic products. A major goal has been to minimize fragmentation and chemical side reactions, in order that greater insight into the neutral sample composition may be obtained. Mass spectra which are practically free of fragmentation can be obtained by field desorption (FD) [1] and

matrix-assisted laser desorption ionization (MALDI), the latter applying a special matrix combination to allow for a “cooled” desorption/ionization event [2]. Valuable data can also be obtained by electron ionization (EI) of freshly prepared samples [3] albeit utilising a DCI probe tip (normally used for desorption chemical ionization).

Various synthetic approaches have been applied to the reduction of fullerenes and a variety of hydrogenated derivatives of varying hydrogen attainment can be obtained and characterised. The most prominent representative of this class of compounds is C₆₀H₃₆, which is readily produced via Birch reduction [4], radical induced hydrogenation [5], transfer hydroge-

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In memory of Professor Bob Squires.

nation of C_{60} by 9,10-dihydroanthracene [1], or Zn/HCl reduction [3]. The hydrogenation of fullerenes larger than C_{70} resulted in the efficient production of $C_{60}H_{36}$ by cage degradation, revealing this compound to be a true island of stability [6]. Thermolysis of $C_{60}H_{36}$ [3,7] led to $C_{60}H_{18}$ as a major product which can also be generated selectively by transfer hydrogenation [1]. Thus, there exists a close relationship in the “magic number” behaviour of hydrogenated and fluorinated fullerenes, as the fluorofullerenes $C_{60}F_{36}$ [8] and $C_{60}F_{18}$ [9] can be synthesized selectively from C_{60} utilising metal fluorides as fluorinating agents.

The understanding of how a particular modification of a pure fullerene can alter the material properties is of principal importance, paving the way for the tailor-made synthesis of compounds with the desired macroscopic features. This investigation focuses on two important aspects in fullerene gas-phase ion chemistry. First, applying EI and liquid-secondary ion mass spectrometry (LSIMS), the dissociation behaviour of hydrogenated C_{60} ions derived from $C_{60}H_{36}$ is studied by means of tandem mass spectrometry. These data reveal the influence of the hydrogen ligands on cage shrinkage reactions and allow direct comparison of pure and fluorinated fullerenes. Second, in laser desorption/ionization (LDI) experiments, the tendency of $C_{60}H_{36}$ to undergo gas-phase coalescence was investigated. Fullerenes were found to undergo laser-induced fusion reactions, readily forming large entities and certain derivatised fullerenes clearly showed an enhanced reactivity in these reactions. A fullerene with 36 σ -bonded (atomic) ligands attached represents an interesting case to be examined.

2. Experimental

The EI (Fig. 1) and mass-analysed ion kinetic energy (MIKE) [Fig. 2(a)–(c)] mass spectra were obtained utilising a double focusing sector instrument of reversed geometry (MAT-95, Finnigan, Bremen). Samples were spotted as toluene solutions onto the Pt wire of a DCI probe tip, dried, and then entered into

the ion source which was held at 260 °C. The Pt wire was heated for 2 min at a rate of 175 K/min and left at 350 °C for 1 min while the spectra were recorded. The electron emission was 1 mA and the electron energy was kept at 70 eV. The resulting ions were accelerated by 5 kV.

Low-energy collision-induced dissociations were carried out in the rf-only quadrupole (q) of a BEqQ hybrid instrument (ZAB-SEQ, VG Instruments, Manchester), where B = magnet, E = electrostatic sector and q/Q = reaction/detection quadrupole. $C_{60}H_{36}$ was ionized by LSIMS. The sample was freshly dissolved in a droplet of 3-nitrobenzyl alcohol (NBA) and bombarded with a beam of 30 keV Cs^+ ions. The resulting ions were accelerated to 8 keV and decelerated before entering the reaction quadrupole.

The coalescence experiments were conducted using a reflectron time-of-flight (ToF) mass spectrometer (Kompact MALDI IV, Kratos, Manchester) equipped with a nitrogen laser operating at 337 nm with a pulse length of 3 ns. Ions were accelerated into the analyser part by a static acceleration voltage of 20 kV. The spectra were obtained in the reflectron mode. In one experiment [insert Fig. 3(b)] a deflector electrode (ion gate) which is located further down the flight tube was used to separate ions of a selected mass range. As shown in previous experiments, this resulted in a more sensitive detection by minimising detector saturation effects [10]. The fullerene samples were deposited onto a stainless steel target slide in the form of a toluene solution and dried in a cold air stream before introduction into the ion source. Each individual ToF mass spectrum shown here represents the accumulation of 200 single-laser-shot spectra.

The hydrogenated fullerenes were prepared as previously described by the Birch reduction [4]. Both LSIMS and matrix-assisted LDI experiments revealed the occurrence of oxygenated analogues containing up to five oxygen atoms. Although it cannot be excluded that the gas-phase transfer is accompanied by oxygen uptake, it seems likely to assume that the sample oxidizes over time. However, none of the conclusions made in this report is affected by the presence of this impurity.

3. Results and discussion

3.1. Fragmentation of hydrogenated C_{60} cations

In contrast to the enormous wealth of information that has been gathered for the dissociation reactions of pure fullerenes, relatively little is known about the fragmentation behaviour of hydrogenated fullerene ions. Clearly, the extensive loss of hydrogen observed during the gas-phase transfer/ionization event has primarily led to efforts aimed at minimising the extent of fragmentation in order to allow a reliable product analysis. A more detailed look at the fragmentation pattern of $C_{60}H_{36}$ reveals that the loss of hydrogen is by no means the only dissociation channel accessible for this species.

A typical EI mass spectrum (70 eV, DCI probe) of $C_{60}H_{36}$ is shown in Fig. 1(a). It is worth noting that not only the doubly charged hydrogenated fullerenes (which were already observed in an earlier investigation [4]) are efficiently detected, but also the triply and quadruply charged counterparts. This ability to undergo multiple ionization under routine EI conditions more closely resembles the features observed for pure fullerenes [11]. The formation of dications has been established for fluorofullerenes [8], while any efficient multiple ionization of organic ligand bearing fullerenes has not been reported. The multiply charged ions were identified by the characteristic signal spacing of the ^{13}C isotopomers by 0.50, 0.33, and 0.25 Da for the doubly, triply, and quadruply charged ions, respectively. While $C_{60}H_{36}$ ions in the lower charge states are clearly observed, the greatest hydrogen content for ions carrying four charges was 28 hydrogen atoms. Within a given charge state, the relative abundance of ions with lower hydrogen content becomes more pronounced with increasing charge, and the relative intensity of the pure fullerene ion steadily increases as well. These findings strongly suggest that the ionization into higher charge states is accompanied by increasing degrees of fragmentation (in this case hydrogen losses) for which the pure fullerene represents a more stable product. However, the fragmentation behaviour of hydrogenated fullerene ions differs from that of most organic

fullerene derivatives, which would proceed by the loss of all attached ligands prior to the well-known shrinkage of the liberated carbon core by the loss of $C_{2n}/2C_n$. As can be deduced from Fig. 1(b), which gives an extension of the dication region, in between the signals expected for C_{60}^{2+} (m/z 360), C_{58}^{2+} (m/z 348), and C_{56}^{2+} (m/z 336), abundant peaks are observed on each expected m/z value. Assuming that these signals are predominantly caused by ion fragmentation, these can only result from either $C_{2n}/2C_n$ loss from ions still carrying hydrogen atoms and/or by the loss of hydrocarbonlike entities (loss of C_nH_x). In fact, the whole fragment ion region depicted in Fig. 1(b) shows an alternation of signal intensities below m/z 360 (predominantly C_{60}^{2+}) with relative maxima spaced by roughly 6 Da. On the basis of this regular pattern, it seems unlikely that these signals would represent a “magic number” behaviour of even-numbered carbon cores with preferred hydrogen attachments. Alternatively, this regular pattern could be caused by a difference of one carbon atom in the neutral moiety expelled from $C_{60}H_x^{n+}$ ions. This in turn would mean that not only hydrocarbonlike neutrals of even carbon content are lost, but also those with an uneven number of carbon atoms. These would formally correspond to species such as CH_x , C_3H_x , etc. and these have also been found as byproducts (C1 to C4 alkanes) besides the major decomposition product $C_{60}H_{18}$ when using thermolysis conditions [7].

In order to determine whether or not this type of fragmentation can occur, the unimolecular decay of several ions of varying hydrogen content and charge state was studied by tandem mass spectrometry. Figs. 2(a)–(c) represent the MIKE spectra recorded with a double focusing magnetic sector instrument (Finnigan MAT-95) of BE configuration (B = magnetic sector, E = electrostatic sector), using B for the precursor ion selection and an electric sector voltage scan for the daughter ion analysis. The precursor ions were generated by EI (DCI probe tip) and correspond to $C_{60}H_{36}^{+}$ for Fig. 2(a), $C_{60}H_{36}^{2+}$ for Fig. 2(b), and $C_{60}H_{18}^{+}$ for Fig. 2(c). The latter ion resulted from a sample for which the hydrogenation had resulted predominantly in $C_{60}H_{18}$. In all three spectra, the

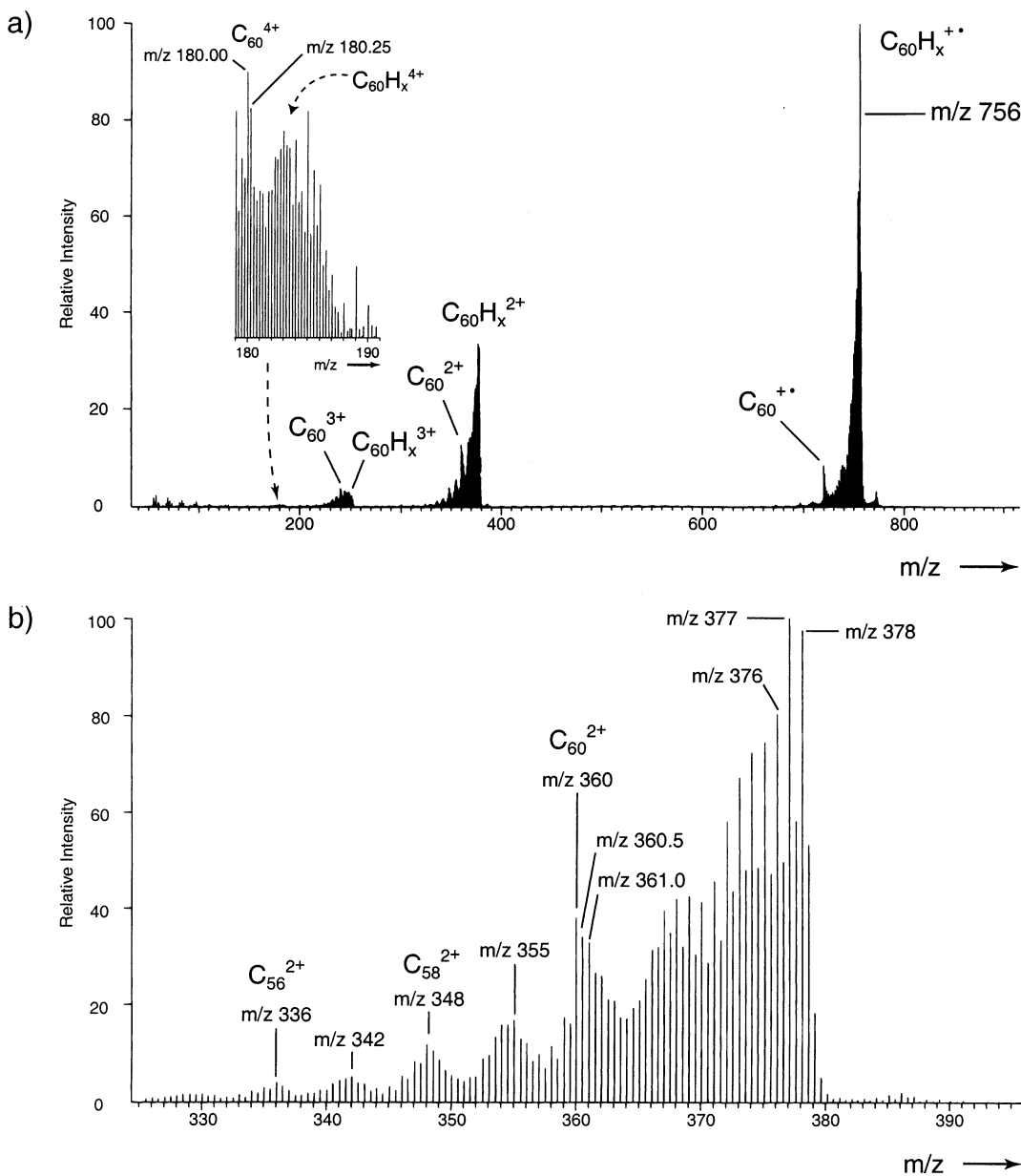


Fig. 1. (a) 70 eV EI mass spectrum of $C_{60}H_{36}$ applying a DCI probe; (b) enlarged dication region.

main beam region is off scale, accompanied by signals observed for the loss of up to four hydrogen atoms.

Three major signals were detected for the dissociation of $C_{60}H_{36}^{++}$ [Fig. 2(a)]. The most intense peak is approximately 5 Da broad and centered at a position

corresponding to the loss of 15 mass units, followed by signals centred at the loss of 28 mass units (6–7 Da broad) and a very low intense signal approximately centered at the loss of 42 mass units. Unlike the well-known C_2 losses from ionized C_{60} , neutrals such as CH_x , C_2H_x , and C_3H_x are lost from the hydroge-

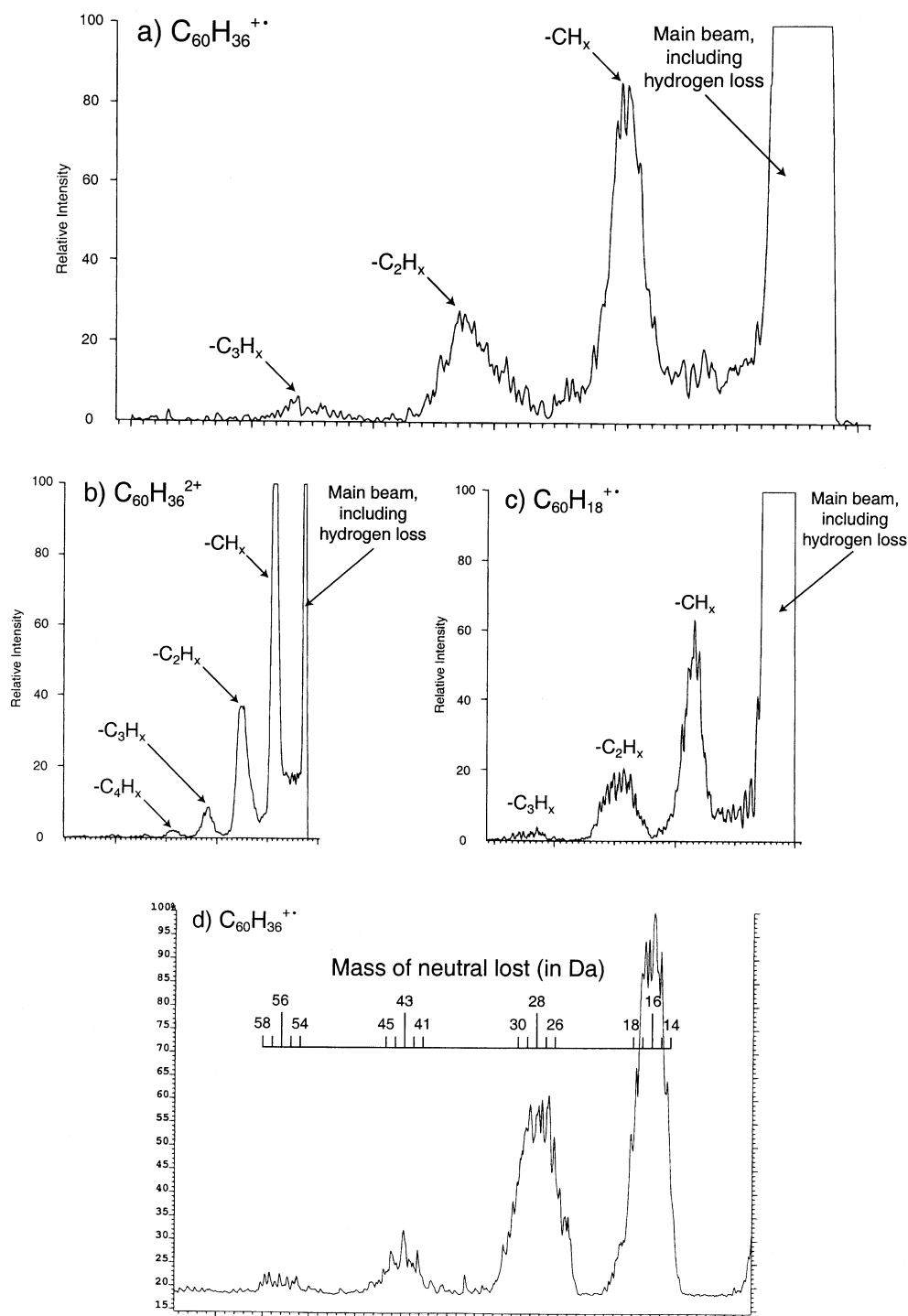


Fig. 2. Partial MIKE spectra of (a) $C_{60}H_{36}^{+\bullet}$, (b) $C_{60}H_{36}^{2+}$ (the CH_x -loss signals are off scale), (c) $C_{60}H_{18}^{+\bullet}$, (d) partial low-energy CID of $C_{60}H_{36}^{+\bullet}$. Note that in all spectra the signals due to hydrogen losses and the main beam are off scale.

nated counterparts. Unfortunately, the present experiments do not enable the establishment of the exact hydrogen content of the neutrals lost. One major reason for this is that the resolving power of the electric sector is not high enough to compensate for the broadening of the daughter ion signals due to kinetic energy release in the fragmentation. Another major concern which can hamper the unequivocal assignment of the daughter and parent ion may result from co-selected isobaric ions. Considering the relative abundances shown in Fig. 1(a), a considerable contribution from the ^{13}C isotopomers of C_{60}H_x with $x < 36$ can be expected for the ion beam selected at m/z 756 [Fig. 2(a)]. However, for statistical reasons, a loss of 16 mass units would still correspond predominantly to a $^{12}\text{CH}_4$ neutral, although the precursor ion would be of lower hydrogen attachment than $\text{C}_{60}\text{H}_{36}$. Unfortunately, the present experiments cannot compensate for these interferences. These considerations are also true for the signals derived from $\text{C}_{60}\text{H}_{36}^{2+}$ [Fig. 2(b)] and $\text{C}_{60}\text{H}_{18}^{++}$ [Fig. 2(c)] for which also the loss of C_nH_x with $n = 1, 2, \dots$ has been observed. This strongly suggests a similar fragmentation mechanism for the decay of the doubly charged analogue and a hydrogenated fullerene of considerably lower hydrogen content.

A further point of concern relates to interferences due to dissociations occurring in front of the ion-selecting magnet. As can be seen in Fig. 1(a), the $\text{C}_{60}\text{H}_{36}$ sample contains trace amounts of species higher in mass, such as the oxygenated analogue for instance. In principle, these species could fragment in front of the magnet and produce a daughter ion of similar momentum to $\text{C}_{60}\text{H}_{36}^{++}$, so that the daughter ion would pass the magnet, and appear as a supposed fragment ion in the MIKE spectrum of $\text{C}_{60}\text{H}_{36}^{++}$ [12] due to the daughter ions' lower translational energy. To prove the authenticity of the origin of the observed daughter ions, $\text{C}_{60}\text{H}_{36}^{++}$ was dissociated in an rf-only quadrupole of a BEqQ hybrid instrument following momentum and energy selection by B and E, respectively. In this manner, the type of interfering ions outlined above cannot contribute to the daughter ion spectrum for which the important region is shown in

Fig. 2(d). A reasonable daughter ion intensity could only be achieved at relatively low resolution and the fragmentation had to be promoted by collisions with Ar at a pressure of 5×10^{-7} mbar at a laboratory collision energy of 170 eV. In the depicted region [Fig. 2(d)], four signals were obtained, centered at m/z values corresponding to the loss of 16, 28, 43, and 56 mass units. Again, the broadening of the signals (5–7 Da broad) prevented the establishment of the hydrogen content, but clear evidence has been provided for the C_nH_x loss from $\text{C}_{60}\text{H}_{36}^{++}$. For instrumental reasons, LSIMS was used for the ionization in this experiment [Fig. 2(d)], which prevented an analogous investigation of the dication, as it was not observed under these conditions and, also, the $\text{C}_{60}\text{H}_{18}$ sample was not available for these experiments.

The observation that hydrogenated fullerene ions undergo cage shrinkage by the loss of hydrocarbonic entities involving the cage carbon atoms differs from that of most organic ligand bearing fullerenes. Besides a few exceptions, such as the CO loss from fullerene oxides, cage dissociations are observed in general only after the attached ligands are released from the cage. However, a close relationship exists between the fragmentation behaviour of highly fluorinated fullerenes and that of highly hydrogenated fullerenes [13]. In addition to the loss of F^\cdot , ionized fluorofullerenes were found to undergo efficient dissociations by loss of perfluoroalkyl radicals, for which a chainlike transition structure was postulated. Although the exact nature of the neutral lost could not be established in our experiments, the observed loss of C_nH_x entities from hydrogenated C_{60} ions closely resembles the fluorofullerene behaviour under similar conditions.

3.2. Laser-induced coalescence

The activation of fullerenes by laser desorption/ionization can lead to the efficient formation of larger carbon clusters [14]. These so-called coalescence reactions are believed to take place in the plume that rapidly expands into the gas-phase upon laser ablation of the fullerene target. The product distribution ob-

tained in these experiments provides important insight into the composition and reactivity of the particles present in the plume. The products of coalescence of pure fullerenes are centred around the multiples of the precursor fullerene, possessing a giant fullerene structure rather than a dumbbell geometry [14], and the peaks are spaced by C_2 . In Fig. 3(a), the corresponding positive-ion LDI mass spectrum of [60]fullerene is given. Mechanistically, coalescence involves the aggregation of fullerenes accompanied by C_2 loss fragmentation and C_2 uptake and incorporation into the cage [14,15]. It is a tempting thought to direct the coalescence reactivity by the deliberate modification of the carbon core and, indeed, remarkable findings could be derived utilising derivatised fullerenes as precursor materials [16–18]. Oxides of the [60]fullerene [16] and certain ligand bearing derivatives [17] exhibited a clearly enhanced coalescence reactivity, and in some cases carbon atoms from the attached ligands were involved in the formation of products which did not exclusively possess a giant fullerene structure [18]. In recent experiments fullerene oxides could be fused intact into dimeric forms, albeit applying softer conditions than in the present experiments [19,20].

In this context, $C_{60}H_{36}$ possessing a fullerene core to which 36 σ -bonded atoms are attached represents an interesting target material. Considering this structure [21], a fusion of pure fullerenes, following the efficient evaporation of hydrogen, appears as plausible as a scenario in which certain single bonds between the hydrogenated carbon atoms are broken to initiate the aggregation into larger hydrogen-containing clusters. The positive-ion LDI mass spectrum derived from $C_{60}H_{36}$ is shown in Fig. 3(b) and is characterised by the abundant formation of hydrogenated C_{60} ions. As reported earlier, C_{60} ions containing an uneven hydrogen content appear enhanced [2,22]. Two types of fragment ions are produced. In addition to carbon clusters with less than 60 carbon atoms and which still contain hydrogen, there are pure fullerene ions abundantly formed as well. The direct comparison with the LDI spectrum of C_{60} [Fig. 3(a)] reveals that the species derived from the $C_{60}H_{36}$ target

barely undergo coalescence at all. Although larger clusters were formed, their abundance was at such a low level, that an ion gate had to be utilised to enhance their detection efficiency. The ion gate was used to allow only a well-defined range of ions to pass on to the detector which resulted in the more sensitive registration of these ions by preventing saturation effects. The result of such an experiment is shown as the insert in Fig. 3(b). Moreover, a higher laser power had to be applied to obtain the signals shown in the insert. Due to the different experimental parameters, it is difficult to quantify the relative abundance of these coalescence products, but roughly estimated, their abundance is at least two orders of magnitude lower compared to the hydrogenated C_{60} ions in Fig. 3(b). The low intensities make accurate mass assignment difficult, but these signals are spaced by 24 mass units and are close to the expected m/z value for pure carbon cluster ions. A possible hydrogen attachment to the coalesced carbon clusters cannot be excluded, but has to be of minor extent as the signals are clearly separated from each other. Therefore, fusion products of large hydrogen content were not observed, which makes the involvement of the initially hydrogenated [60] fullerene rather unlikely. The overall distribution of the coalescence products observed [the insert in Fig. 3(b) shows only a fraction of it] features monotonically decreasing intensities with increasing size or mass. The enhancement at multiple masses of the fullerene core, which is so characteristic for the fusion of pure fullerenes [14], is also not observed. While the low mass region clearly shows that pure fullerenes are formed, there is no evidence for a fullerene/fullerene aggregation. The distribution of the coalesced product resembles more a scenario in which smaller fragments are incorporated into a fullerene core leading to larger clusters without the formation of products of particularly enhanced stability. In summary, $C_{60}H_{36}$ shows a strikingly different reactivity pattern in comparison to other fullerene derivatives. In contrast to the efficient coalescence of pure carbon clusters and certain fullerene derivatives, the substitution of the majority of π bonds by hydrogen has an adverse effect on the laser-induced fusion towards larger clusters.

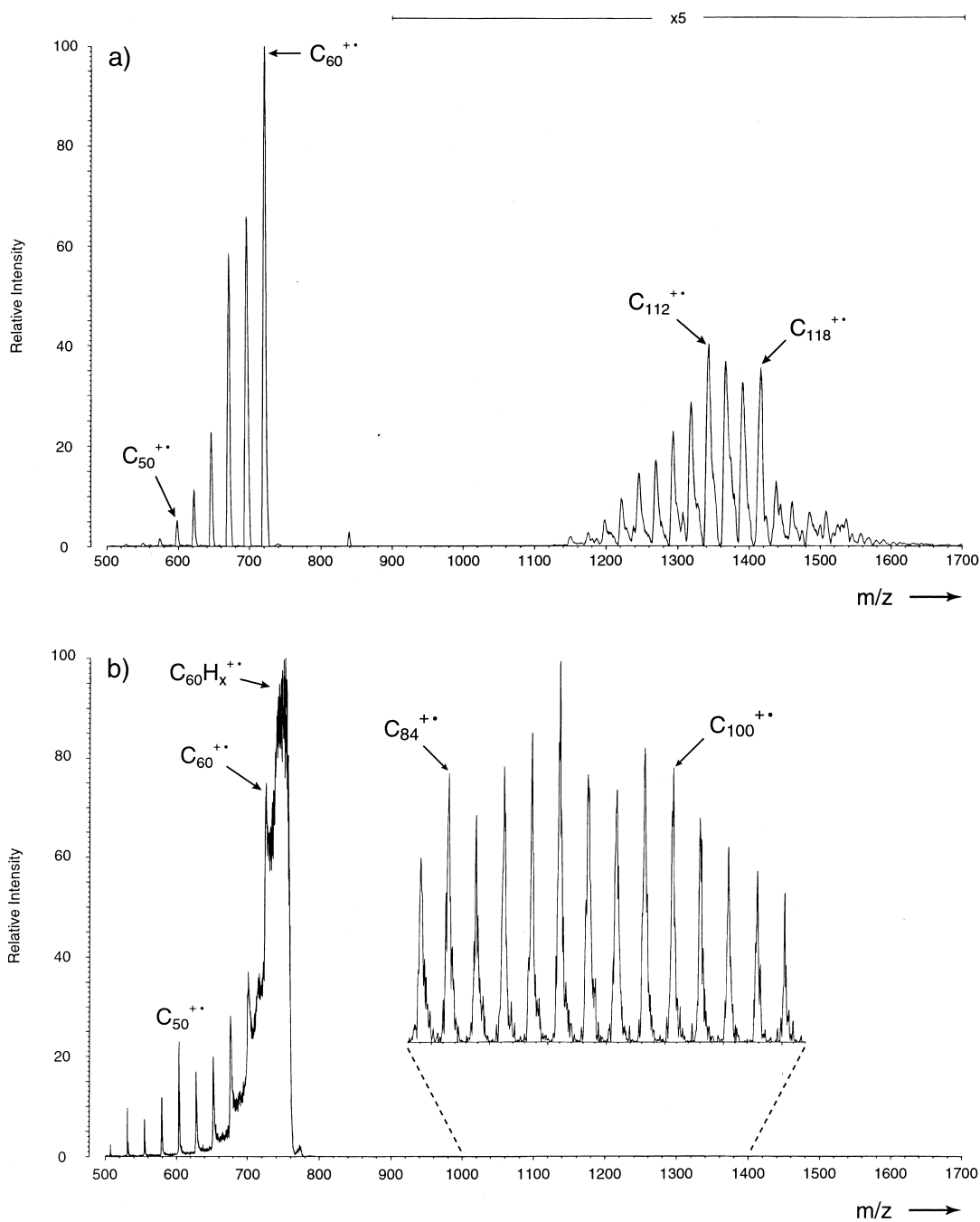


Fig. 3. (a) Positive-ion LDI mass spectrum of C_{60} , (b) positive-ion LDI mass spectrum of $C_{60}H_{36}$. The insert was obtained by using an ion gate selecting the ions detected.

4. Conclusion

Hydrogenated fullerene ions undergo unimolecular cage shrinkage reactions via the loss of hydrocarbon-like neutrals. Although the exact hydrogen distribution of the fragments could not be established, this behaviour reveals similarities to the fragmentation behaviour of fluorofullerenes, rather than to pure or organic ligand bearing fullerenes. This underlines the close link between these two classes of derivatives which has been already established for certain structural features. Furthermore, hydrogenated fullerenes show a drastically reduced tendency to undergo laser-induced coalescence reaction to form larger entities. Again, this is in striking contrast to the performance of pure fullerenes and certain ligated derivatives. It seems likely to assume that steric hindrance and/or the lack of a sufficient amount of suitably positioned double bonds might have an adverse effect in these reactions.

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