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Analysis of C_{60} Derivatives by Fast-atom Bombardment Mass Spectrometry as γ-Cyclodextrin Inclusion Complexes

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Many C_{60} derivatives form stable complexes with γ-cyclodextrin in a ratio of 1:2. These complexes can be easily analyzed by fast-atom bombardment mass spectrometry (FAB). Unlike the analysis of C_{60} derivatives directly by FAB, the spectra of these complexes were characterized by molecular ions with little or no fragmentation. The analysis of these complexes by FAB provides an easy and useful approach for the characterization of C_{60} derivatives. Most likely due to the size of the cavity, this approach is limited to C_{60} derivatives with molecular weights not significantly larger than that of C_{60} itself.

Since the discovery of fullerenes as the third allotrope of carbon, C_{60} and its derivatives have been one of the major foci in academic researches and practical applications. Many C_{60} derivatives, including those with great potentials in material science and medicine, have been synthesized.

Mass spectrometry has played a key role not only in the discovery of C_{60} but also in characterization of C_{60} derivatives.[1–14] A variety of ionization techniques, including electron impact (EI), chemical ionization, desorption chemical ionization (DCI), fast-atom bombardment (FAB), laser desorption and electrospray ionization, has been used to characterize C_{60} derivatives. The analysis of C_{60} derivatives appeared to be more difficult than C_{60} itself because many derivatives fragmented easily under most ionization conditions.

After its development in the early 1980s, FAB mass spectrometry has quickly become the method of choice for the analysis of nonvolatile compounds. The popularity of FAB is due mainly to the ease of operation and its ability to analyze many different types of compounds. Although FAB is considered one of the most popular methods, it is somewhat unfortunate to see that many C_{60} derivatives fragment extensively under FAB. The quality of the mass spectra is often much poorer than that obtained using desorption chemical ionization[6] and electrospray ionization.[11–13]

C_{60} and γ-cyclodextrin are reported to form a 1 to 2 complex.[14–17] This complex has been studied by FAB and proved to be stable in the gas phase.[14] We have studied the possibility of forming stable complexes between γ-cyclodextrin and C_{60} derivatives. In this paper the potential and limitations of analyzing C_{60} derivatives as γ-cyclodextrin complexes are reported.

EXPERIMENTAL

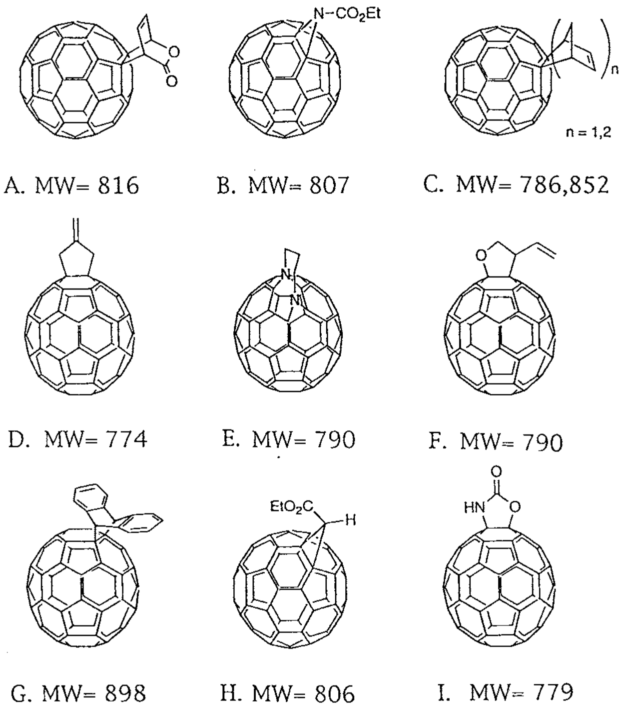
C_{60} was purchased from Materials Electrochemical Research Corporation (Tucson, AZ, USA). All C_{60} derivatives shown in Fig. 1 were synthesized as described in the literature.[18]

C_{60} and its derivatives were dissolved in toluene. The solution was then mixed with a γ-cyclodextrin water solution and stirred for two hours before drying with nitrogen. The solid sample of the complex containing excess γ-cyclodextrin was mixed with 1 microliter of matrix (magic bullet) on a FAB probe tip for subsequent mass spectrometric analysis. In the analysis of C_{60} derivatives directly by FAB, *m*-nitrobenzyl alcohol (NBA) instead of magic bullet was selected as the matrix for better mass spectral quality.

FAB and linked scans at constant B/E were performed using a Jeol SX-102A double focusing mass spectrometer of reversed geometry (Jeol, Tokyo, Japan). The FAB gun was operated at 6 kV using xenon. Helium was used as the collision gas, at a pressure adjusted to reduce the ion beam intensity to half its initial value. The mass scale was calibrated with a mixture of alkali halides.[19]

RESULTS AND DISCUSSION

Despite the fact that FAB is often considered to be the easiest and the most often used mass spectrometric technique in the analysis of nonvolatile compounds,



A. MW= 816 B. MW= 807 C. MW= 786,852

D. MW= 774 E. MW= 790 F. MW= 790

G. MW= 898 H. MW= 806 I. MW= 779

Figure 1. Structures of fullerene derivatives.

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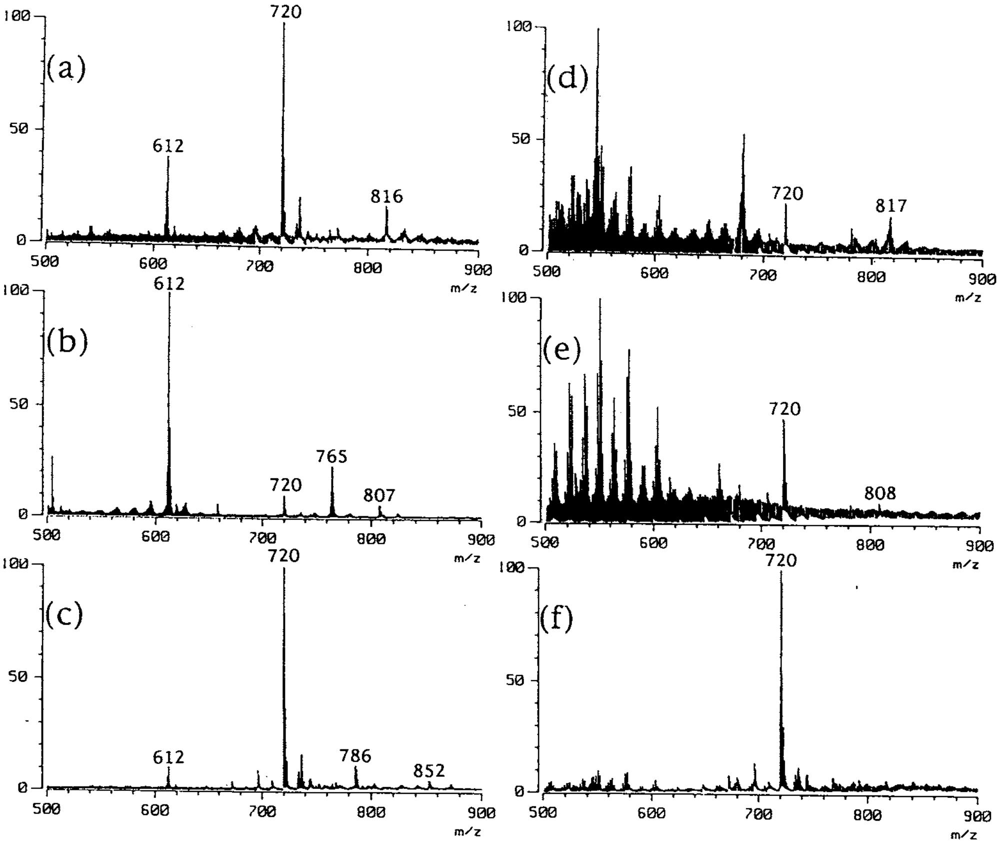

Figure 2. FAB mass spectra of compounds A, B and C in negative-ion mode (a, b, c) and positive-ion mode (d, e, f). The ions at *m/z* 612 (a, b, c) and *m/z* 765 (b) are matrix ions.

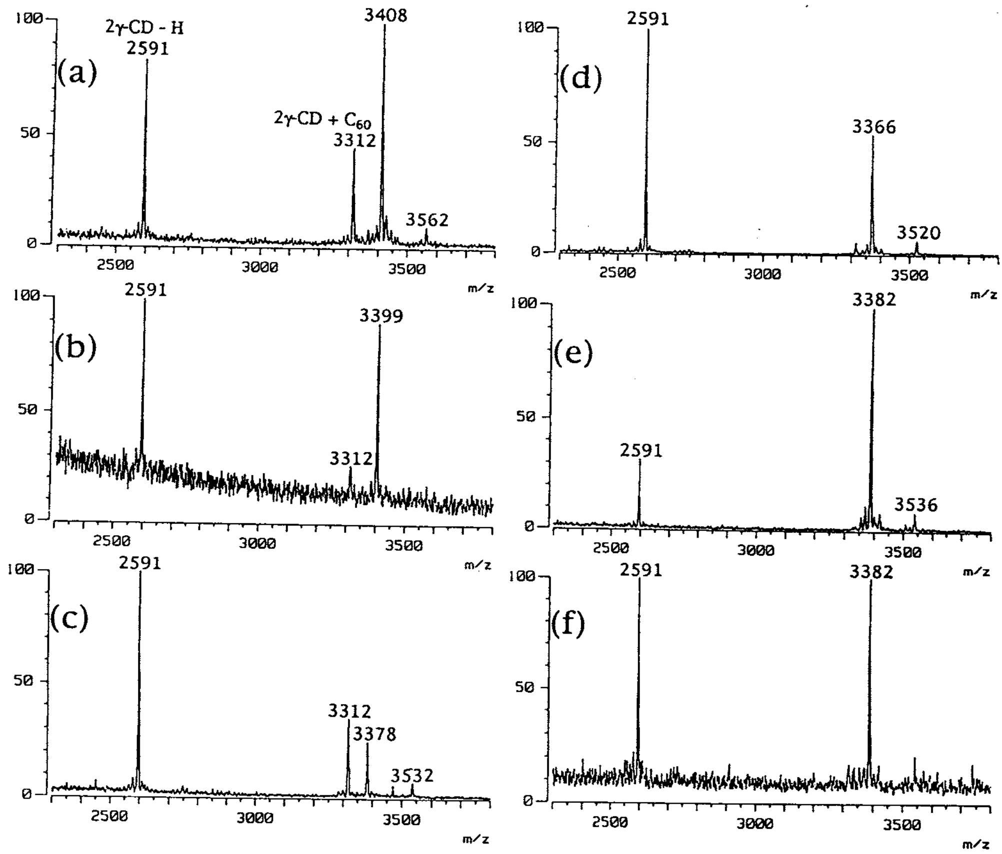

Figure 3. Negative-ion FAB mass spectra of the inclusion complexes of (a) compound A; (b) compound B; (c) compound C; (d) compound D; (e) compound E; (f) compound F. The ions at *m/z* 3562 (a), 3532 (c), 3520 (d) and 3536 (e) were interpreted in terms of addition of a matrix molecule to the molecular ions. All masses were labeled as nominal masses.

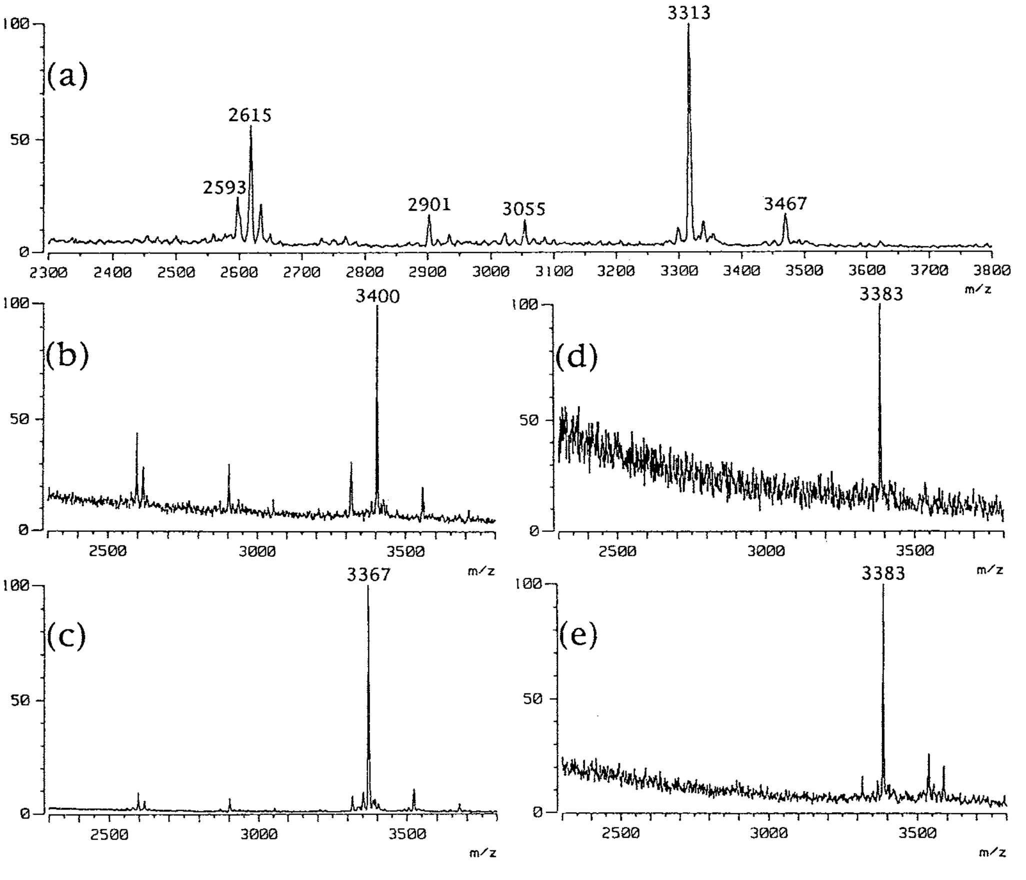

Figure 4. Positive-ion FAB mass spectra of the inclusion complexes of (a) C_{60}; (b) compound B; (c) compound D; (d) compound E; (e) compound F. The ions at *m/z* 2593 and 2615 were the protonated and sodiated γ-cyclodextrin dimers. The ions at *m/z* 2901 and 3055 correspond to the addition of two and three matrix molecules to the protonated γ-cyclodextrin dimer. The ions at *m/z* 3467 (a), 3554 (b), 3521(c) and 3537(e) were due to the addition of a matrix molecule to the molecular ion. All masses were labeled as nominal masses.

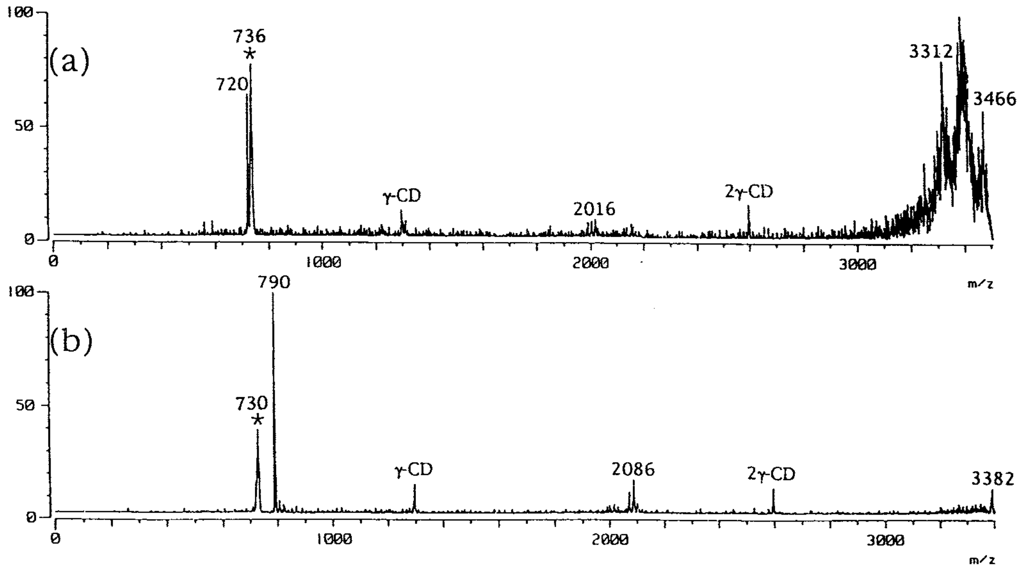

Figure 5. Product-ion mass spectra (negative-ion mode, linked scan at constant B/E) of (a) the matrix adduct ion of the C_{60}/γ-cyclodextrin inclusion complex (*m/z* 3466); (b) the molecular ion of the compound F inclusion complex. In (a), the reason for choosing the matrix adduct ion instead of the intact molecular ion (*m/z* 3312) is that an artifact peak in the B/E spectrum was superimposed on the C_{60}^{-} product ion if the molecular ion was selected as the precursor ion. The artifact peak arose from the transmission of a matrix ion (*m/z* 153) through the magnet, which then decomposed to *m/z* 34 ion in the second field-free region (FFR) prior to the electric field. The apparent masses of these artifact peaks were shifted to *m/z* 736 in (a) and *m/z* 730 in (b), respectively. ($736^2/3466 = 156.3$, $730^2/3382 = 157.6$; $34/153 = 736/3466 = 730/3382 = 0.2$).

desorption chemical ionization and electrospray ionization have appeared to be superior to FAB in the analysis of C_{60} derivatives. The FAB mass spectra of C_{60} derivatives are, in general, characterized by a C_{60} ion, with a very weak or even zero signal corresponding to the molecular ions (Fig. 2).

There are several reports on the formation of stable complexes of C_{60} with a variety of host molecules.[14–17, 20–22] Recently, Andersson *et al.*[14] reported a negative-ion FAB study of the C_{60}/γ-cyclodextrin complex; the complex proved to be stable in the gas phase. In the present work, several C_{60} derivatives were studied to investigate the possibility of forming stable complexes with γ-cyclodextrin dimer. The negative-ion FAB mass spectra of these samples (Fig. 3) showed that, like C_{60}, many C_{60} derivatives could form stable complexes with the dimer of γ-cyclodextrin. Moreover, it was gratifying to observe that the quality of the spectra is much better than that obtained in the analysis of C_{60} derivatives directly by FAB. As shown in Fig. 3, molecular ions of the 1:2 complexes were clearly observed. The observation of much better defined molecular ion signals suggested that the formation of a complex with two γ-cyclodextrins before FAB analysis could be a useful general method for the characterization of C_{60} derivatives. One possible reason for the good stability of the molecular ion is that, after the formation of a γ-cyclodextrin complex, the excess energy imparted to the sample could be delocalized throughout a molecule much larger than the C_{60} derivative thus reducing the chance of fragmentation. Furthermore, the C_{60} derivative is believed to be trapped inside the cavity of the γ-cyclodextrin dimer, and this arrangement may provide some protection for the guest molecule during ionization. The γ-cyclodextrin inclusion complexes of C_{60} and of C_{60} derivatives were also analyzed by positive-ion FAB. Besides the observation of more matrix-related ions, the positive-ion FAB spectra (Fig. 4) were similar to their negative analogs with clear signals corresponding to their molecular ions.

In the article of Andersson *et al.*,[14] a question was raised about whether the negative ion consists of C_{60}^- in the cavity of a γ-cyclodextrin dimer or a neutral C_{60} in the cavity of a deprotonated γ-cyclodextrin dimer. A tentative conclusion, based on a comparison of observed and calculated isotopic intensity distributions, was made about the relative importance of the two possibilities. This approach cannot reach a definite conclusion, mainly due to the overlapping of isotope peaks and the poor ion statistics of weak signals. More-direct evidence, however, can be obtained by a collision-induced dissociation (CID) study of C_{60}/γ-cyclodextrin complexes. The positive ion product-ion spectrum of the C_{60}/γ-cyclodextrin complex showed that the γ-cyclodextrin-related fragments were the major product ions. In contrast to positive ion CID, C_{60}^- was observed (Figure 5a) as the major product ion in the negative-ion CID. Similar results were obtained in the study of C_{60} derivatives/γ-cyclodextrin complexes by negative-ion CID (Fig. 5(b)). Based on these observations, it is more likely that the negative molecular ion consists of the C_{60}^- ion in the cavity of a γ-cyclodextrin dimer as the major species.

Although the present approach provided a simple and useful method for the characterization of many C_{60} derivatives, it was found that not all C_{60} derivatives could form stable complexes with γ-cyclodextrin dimer. C_{60} derivatives with molecular weight (or size) significantly larger than C_{60} were unable to form stable complexes with the dimer of γ-cyclodextrin. For example, in the analysis of a mixture consisting of C_{60}, $C_{60}(C_5H_6)$, and $C_{60}(C_5H_6)_2$, only C_{60} and $C_{60}(C_5H_6)$ were able to form stable complexes with γ-cyclodextrin (Fig. 3(c)). Ions corresponding to the $C_{60}(C_6H_5)_2$/γ-cyclodextrin inclusion complex were not detected. In another experiment, the ion corresponding to the complex of compound G and γ-cyclodextrin dimer was not detected in several attempts. These experiments suggest that there is a size limit for the guest molecule to form a stable complex with γ-cyclodextrin dimer. The limitation on the size of the C_{60} derivative is not surprising, considering the rather small size difference between C_{60} (7 Å diameter) and C_{70} (7 Å diameter at the equator, 8 Å between poles) which nonetheless precluded observation of a stable complex between C_{70} and γ-cyclodextrin.[16]

In conclusion, we have investigated the approach of analyzing C_{60} derivatives as γ-cyclodextrin complexes by FAB mass spectrometry. After the formation of γ-cyclodextrin complexes, most C_{60} derivatives studied in this report could be analyzed successfully by FAB. Considering the good quality of the FAB spectra, the availability of FAB, and the ease of sample preparation, this approach provides a simple and useful method for the characterization of C_{60} derivatives. Most likely due to the size of the cavity the approach is, however, limited to C_{60} derivatives with size not significantly larger than that of C_{60} itself. A search for host molecules with cavities larger than that of γ-cyclodextrin is needed for the full potential of this approach to be realized.

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