FULLERENE IONISATION

Singly, doubly and triply charged C_{60}

QUADRUPOLE MASS SPECTROMETRY
EPIC APPLICATION NOTE 234-1

The measurements described in this note were carried out using a Hiden EPIC 1000 N instrument to examine the ionisation of Fullerene. Mass Spectra were acquired over a 1000 AMU mass range with peaks of interest observed at 720 AMU, 360 AMU and 240 AMU. The data include details of the ionisation potentials for singly, doubly and triply charged C_{60} and relative abundance data for the isotopes.

The experiments illustrate the sensitivity and resolution of the EPIC 1000N system across the 1000 AMU mass range.

Experiment Details

A Fullerene sample was introduced into the gas phase by the use of a heated ceramic crucible. The resulting gaseous sample was then analysed using an EPIC 1000 N system. During this analysis the quadrupole inlet and vacuum chamber were maintained at 120°C.

The spectra obtained displayed the presence of Fullerene based species at masses to over 700 amu, Fig.1. These species were observed to exist in 3 distinct series corresponding to the general formula $[C_{60}]^{q+}$, where q=1,2,3. The $[C_{60}]^{+}$ series showed the presence of up to n = 9 atoms of the 13C isotope of carbon.

The peaks due to $[C_{60}]^{2+}$ and $[C_{60}]^{3+}$ were observed to follow the same isotopic pattern, Fig 3 and Fig 4 respectively. The resulting spectra for these series can be seen to yield peaks that are a fraction of a mass unit wide due to the multiple charges present. These peaks could be fully resolved to give a 10% valley, demonstrating the high resolving power of the quadrupole filter.

The spectra obtained at high electron energies displayed the presence of extensive ranges of multiply charged fragments, Fig 5. These show the Fullerene to fragment by the loss of C_2 units, with the relative intensities of these species reflecting their relative stabilities.

The electron energy spectrum obtained for the $[C_{60}]^{q+}$ exhibit 3 distinct profiles reflecting their relative formation energies, Fig 6. The profile obtained for the formation of C^{+}_{60} shows an appearance potential of approximately 10eV and gives a maximum in the region of 40eV before decreasing in intensity. The electron energy spectrum for the $[C_{60}]^{2+}$ formation shows an appearance potential of about 15eV, with the intensity increasing to a plateau region above approximately 70eV electron energy. The $[C_{60}]^{3+}$ formation gave a similar appearance potential to the doubly charged ions, however the signal remains low until about 60eV before increasing to form a plateau at high electron energies. These electron energy profiles clearly demonstrate the energy dependence of the ionisation processes undertaken by Fullerene and the sequential nature by which multiply charged ions are formed.

FULLERENE : Results and Discussion

The main features of the Fullerene experiments are as follows:-

1. The EPIC 1000N mass range is 1000AMU with better than unit mass resolution (see figure 1).

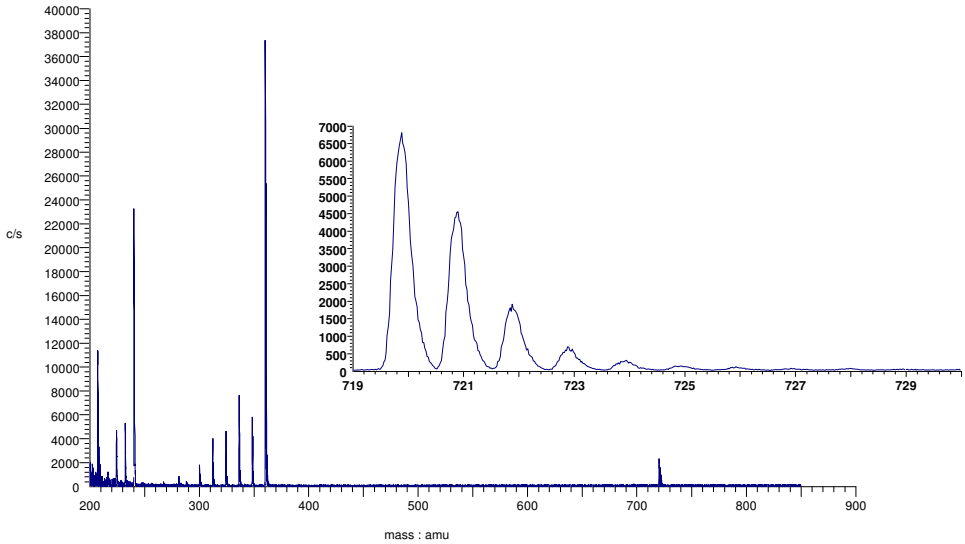


Fig. 1.The Fullerene mass spectrum displaying the isotopic series

2. The Fullerene sample had as its major constituent C_{60}.
3. The C_{60} was detected as
   i) singly charged ions of m/z = 720
   ii) doubly charged ions of m/z = 360
   iii) triply charged ions of m/z = 240

The parent ion (m/z = 720) (see figure 2) was found to be accompanied by isotopic ions with m/z = 721, 722, ..., 729. The intensity distribution of the isotopes is in satisfactory agreement with that predicted by the 'Isoform' program incorporated in the NIST database. The relative abundances of m/z >723 are, however, greater than those given by the program.

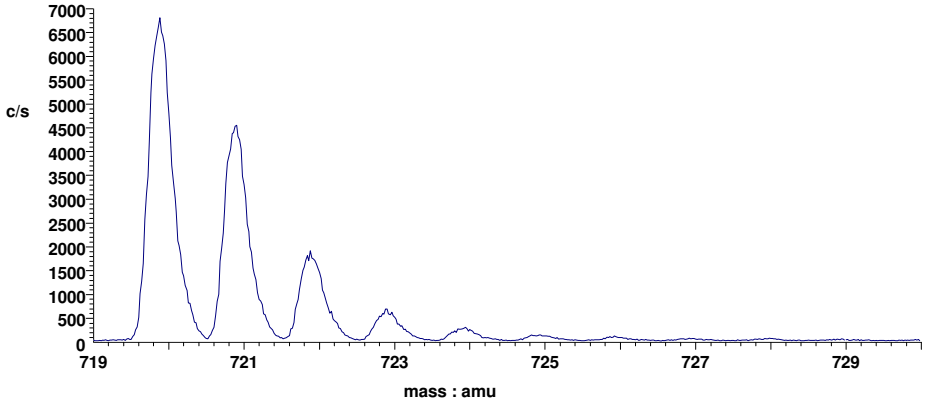


Fig. 2. The C60 isotope sequence

4. The C_{60}^{++} ions (see figure 3) were similarly accompanied by peaks at 360.5, 361, 361.5 .... which were taken to correspond to the isotopic masses 721, 722, 723....

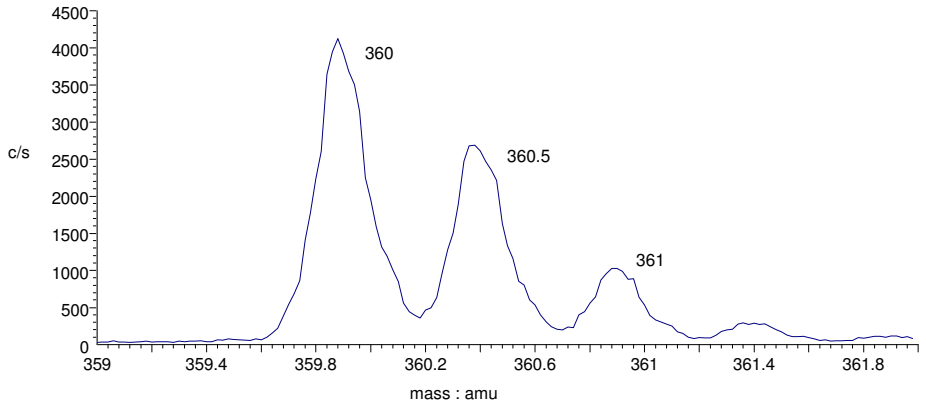


Fig. 3. The C60 doubly charged series

5. Again, the C_{60}^{+++} ions (see figure 4) had associated peaks at 240.3, 240.7, 241.00 ...

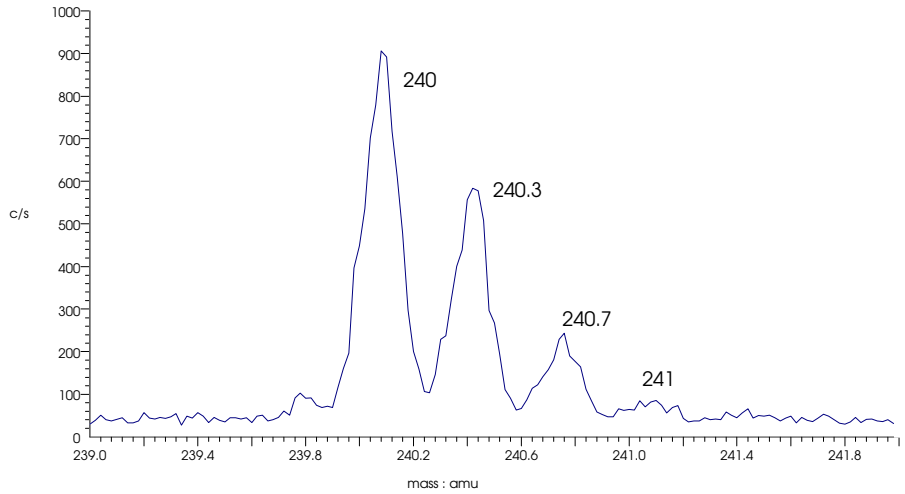


Fig. 4.The C60 triply charged series with 0.33 mass separation

6. The C_{60}^{+++} peaks at a m/z separation of 0.33 were well resolved.

7. A series of peaks (see figure 5) m/z = 360, 348, 336, 324, ... i.e. with an m/z interval of 12 were attributed to $(C_{60} - aC_2)^{++}$ where a = 0,1,2,3, ... i.e. to parent C_{60} molecules which had lost one or more carbon dimers, C_2. The intensities of the peaks can be related to the ease with which 1,2,3 ... dimers are ejected

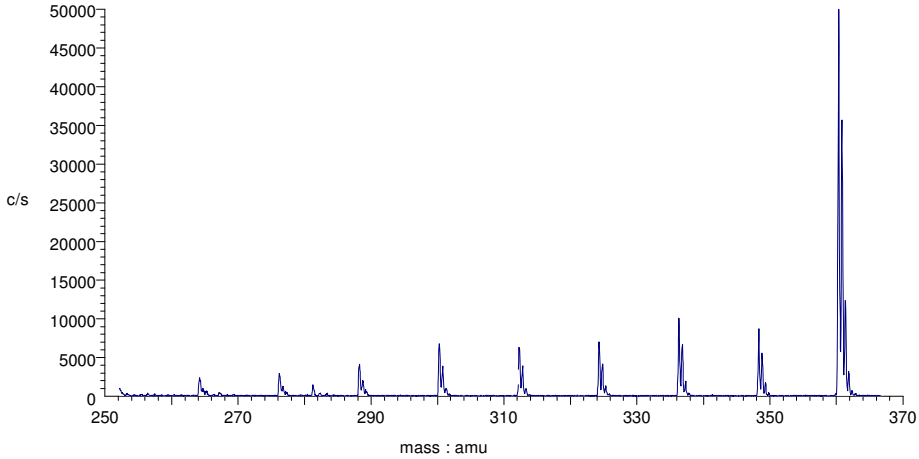


Fig. 5 C60 doubly charged with assoc. peaks from C60-aC2

8. The $(C_{60} - aC_2)$ molecules were also detected with a m/z interval of 8 (= 24/3) at 240, 232, 224, 216 from the triply charged isotope molecules. See figure 6.

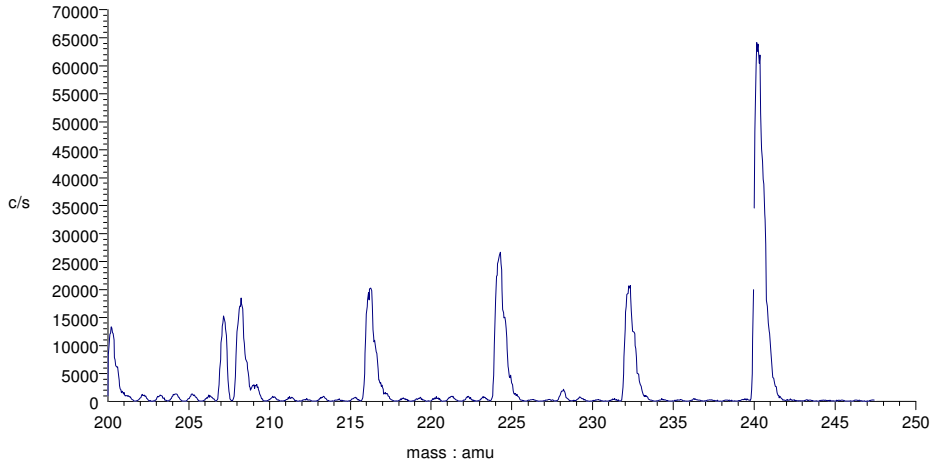
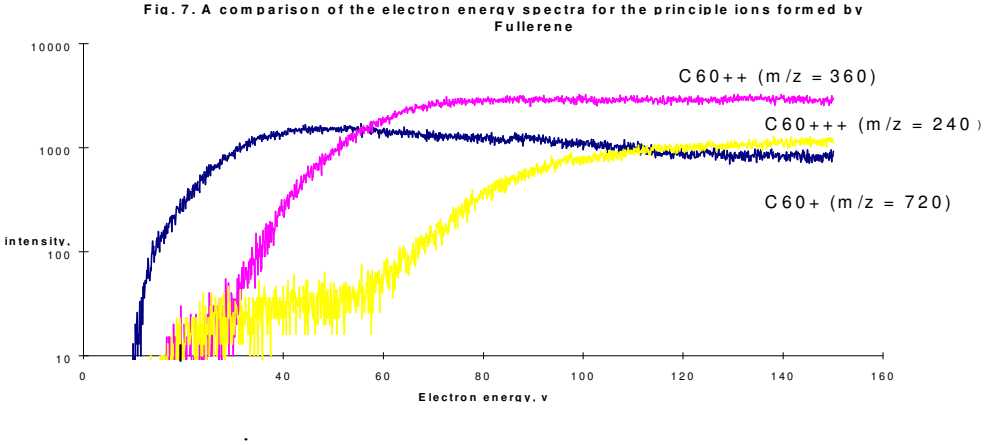


Fig. 6 C60 triply charged with assoc. peaks from C60-aC2

Electron energy scans (for electron energies of up to 150 eV) of all the major m/z peaks were carried out. The ionisation threshold for producing C_{60}^{+} ions was about 10eV while that for producing C_{60}^{++} and C_{60}^{+++} was about 15eV (see figure 7).



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