Metastable Transitions of Triply-charged Ions

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THE importance of triply-charged ions in the mass spectra of certain aromatic compounds has recently been pointed out.[1] We now report that in a study of the decomposition of 9,10-diphenylanthracene under electron impact in an MS9 mass spectrometer (Associated Electrical Industries Ltd.), triply-charged ions down to $m/e = 83{\cdot}3$ [250^{3+} or $(M-80)^{3+}$] were observed and, by making use of the field-free region between the source and the electric sector, many metastable transitions of triply-charged species have been detected.

If the process $m_1^{3+} \rightarrow m_2^{2+} + m_3^{+}$ occurs with the release of T ev of kinetic energy, m_2^{2+} ions are transmitted by the electric sector when the normal accelerating voltage V_0 is adjusted to V such that where $\mu = m_3/m_2$, and e is the electronic charge.

$$V/V_0 = \frac{2m_2}{3m_1}\left[\frac{1}{1 \pm (\mu T/3Ve)^{\frac{1}{2}}}\right]^2 \qquad (1)$$

Since m_3^{+} is usually a very light ion such as CH_3^{+} or $C_2H_3^{+}$, $m_2 \gg m_3$ and μ is very small. This means that there is very little broadening of the peak due to m_2^{2+} as the accelerating voltage is scanned, so that $V/V_0 \approx 2m_2/3m_1$ and T cannot be evaluated. In the mass spectrum of 9,10-diphenylanthracene, the light fragment lost is usually

CH_3^+, $C_2H_3^+$, or $C_3H_3^+$ but a fairly strong signal is given by the transition:

$$C_{26}H_{18}^{3+} \rightarrow C_{20}H_{12}^{2+} + C_6H_6^+ \qquad (2)$$

This could be observed at several different accelerating voltages and, using a procedure previously described,[2] the kinetic energy released in this process was estimated to be 2·4 ± 0·3 ev. Similar observations were made on the corresponding decomposition of the doubly-charged molecular ion:

$$C_{26}H_{18}^{2+} \rightarrow C_{20}H_{12}^{+} + C_6H_6^+ \qquad (3)$$

and led to an estimate of 1·6 ± 0·2 ev for the kinetic energy released in this process. In terms of simple coulombic repulsion, this corresponds to a charge separation of just over 8 Å which corresponds fairly closely with the separation of the centres of the phenyl groups. No such simple picture can be invoked for the triply-charged ion.

The large numbers of metastable transitions of triply- and doubly-charged species observed in the mass spectrum of 9,10-diphenylanthracene suggests that many singly-charged ions are formed from multiply-charged precursors in such reaction sequences as

$$C_{26}H_{16}^{3+} \xrightarrow{-CH_3^+} C_{25}H_{13}^{2+} \xrightarrow{-C_2H_3^+} C_{23}H_{10}^{+} \qquad (4)$$

Since doubly-charged ions account for a considerable proportion of the total ionization in the 70 v mass spectra of condensed ring aromatic compounds,[3] our observations suggest that such spectra can only be interpreted if the formation of singly-charged fragment ions from doubly- and possibly triply-charged precursors is taken into account.

Note added in proof: A similar suggestion has recently been made to explain the occurrence of satellite peaks of singly- and doubly-charged ions observed in the 150v mass spectra of aliphatic hydrocarbons.[4]

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