Analysis at High Mass-resolution of Metastable Transitions in Mass Spectrometry

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Summary When the accelerating and electric sector voltages of a Nier–Johnson mass spectrometer are simultaneously varied to produce a spectrum of daughter ions derived from a selected metastable parent ion, the spetrum contains peaks which are not diffuse, so that precise mass measurement is facilitated and peaks due to isobaric daughter ions may be resolved.

THE apparent masses of diffuse 'metastable peaks' accompanying sharper normal peaks in mass spectra recorded on magnetic sector instruments have been measured previously under conditions of high mass-resolution.[1] The technique is of limited value for establishing the elemental compositions of metastable ions and their fragmentation products because the diffuse character of the metastable peaks persists at high resolution, and is often sufficient to cause significant overlap with adjacent normal or metastable peaks.

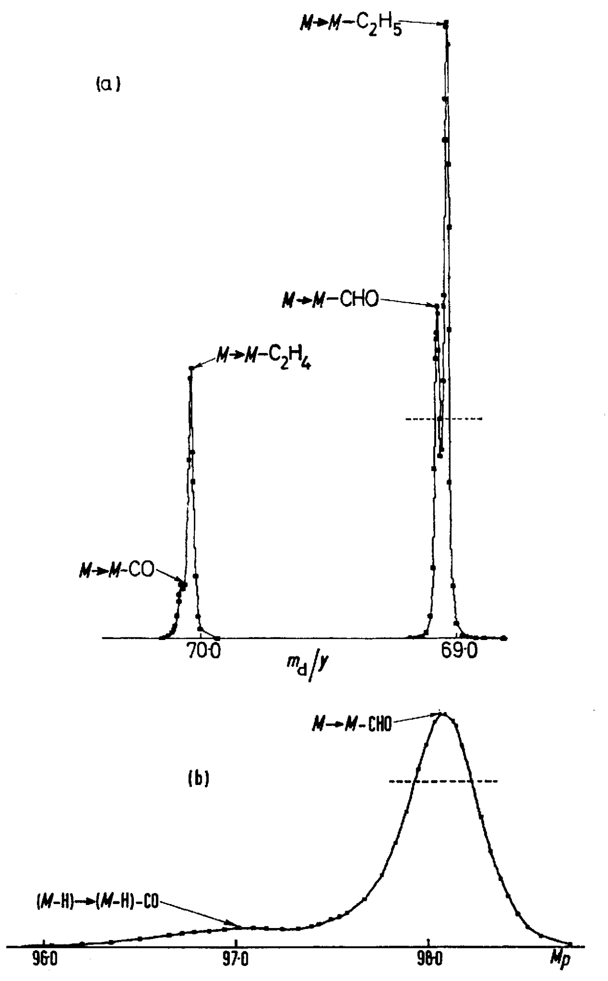

FIGURE 1. Peaks due to daughter ions from fragmentation of metastable molecular ions of cyclohexanone, measured on an AEI MS902 with V = 7760–8000V. The static resolution for normal ions was 2700 (10% valley). The level of the contour in Figure 2 is indicated by horizontal lines. (a) Combined V, E scans, parent: molecular ion (M_p = 98·073); (b) V scan, daughter: M – CHO (m_d = 69·070).

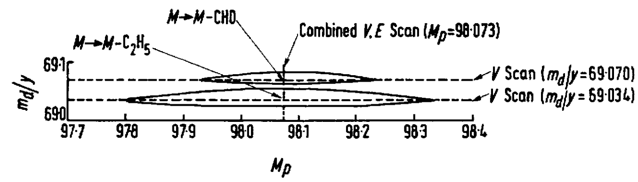

FIGURE 2. Schematic map of contour at a selected intensity level for part of the three dimensional metastable transition surface for cyclohexanone.

By operating a mass spectrometer of conventional Nier–Johnson geometry at constant magnetic field while the electric sector voltage (E) is varied, and the accelerating voltage (V) is kept proportional to E^2, a scan through daughter ions arising from a selected metastable parent ion fragmenting in the instrument's first field-free region (FF1) may be achieved.[2] We report that the above (combined V, E scan) technique produces a *mass* spectrum of the daughter ions, and that the peaks in it lack the diffuseness which characterises 'metastable peaks' recorded by commonly used methods.

It is convenient to define a quantity M_p such that

$$M_p = (V/V_0)(E_0/E)^2 m_0.$$

V_0 and E_0 are values of V and E at which the main ion beam is transmitted by the electric sector, and m_0 is the mass of normal singly charged ions transmitted by the magnetic sector if V and E are set to V_0 and E_0 respectively. We note that ions of mass m_d carrying y charges will be transmitted by the magnetic sector if E is chosen so that

$$E/E_0 = (y/m_d)m_0.$$

If such ions are produced by fragmentation in FF1 of metastable parent ions of mass m_p carrying x charges, and no translational energy is released in the reaction, they will be transmitted by the electric sector also if V is chosen so that

$$M_p = m_p/x.$$

In practice translational energy generally is released and the daughter ions are transmitted over a range of M_p values centred on m_p/x. M_p may be regarded as an index of the ratio of the ion kinetic energy (IKE) of a metastable parent ion to that of its daughter, scaled in terms of the mass-to-charge ratio of the parent.

It may be seen that the combined V, E scan yields a mass spectrum of daughter ions derived from metastable parents characterised by constant M_p, in contrast to the commonly used V scan technique (V varied, E and m_0 constant) which gives an M_p spectrum† of metastable parent ions which fragment to daughters of constant mass-to-charge ratio and

IKE. The combined V,E scan may also be contrasted with the superficially similar MIKE scan (E varied, V and magnetic field constant) on instruments of reversed geometry,[3] which yields an IKE spectrum of daughter ions derived from metastable parents of constant mass-to-charge ratio and IKE.

Figure 1 shows narrow mass-resolved peaks obtained in combined V,E scans through daughters of metastable molecular ions of cyclohexanone. For comparison, broad IKE-resolved peaks obtained in a V scan under otherwise identical conditions are also shown. Peaks due to loss of ·CHO from the molecular ion appear in both scans.

Spectra from combined V,E scans may be considered as cross sections at constant M_p of a three-dimensional m_d/y, M_p, intensity surface. Spectra from V scans are then cross sections of the same surface, but at right angles to those of combined V,E scans. If the same value of m_0 is used, both techniques require the same values of V and E, and therefore yield the same intensity, at points where the cross sections intersect. Figure 2 shows contours at a selected intensity level for part of such a surface for cyclohexanone. Neglecting variation of intensity with V, the abundances of metastable ions are proportional to the volumes under peaks in the three-dimensional surface. As a single combined V,E scan through such a peak cannot reveal the extent to which it has been broadened in the M_p direction by energy release, or the extent of overlap with adjacent peaks in the M_p direction, the combined V,E scan is of limited value for comparison of abundances. At high mass-resolution the combined V,E scan may be used to reveal the extent to which peaks due to isobaric daughter ions derived from a common metastable parent have been resolved, and to obtain precise measurements of the masses of daughter ions from metastable transitions.

On instruments of reversed Nier–Johnson geometry it is possible to scan through metastable parent ions fragmenting in FF1 to daughters of fixed IKE by varying V at constant E and magnetic field. Spectra so produced should be mass-resolved, like those from the combined V,E scan above, and the technique should permit the resolution of peaks due to isobaric metastable parent ions which generate a common daughter ion.

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† Because E and m_0 are constant, this M_p spectrum is equivalent to an IKE spectrum.

[1] J. H. Beynon, J. A. Hopkinson, and A. E. Williams, *Org. Mass Spectrometry*, 1968, **1**, 169; A. Carrick and H. M. Paisley, *ibid.* 1974, **8**, 229.
[2] S. Evans and R. Graham, in 'Advances in Mass Spectrometry,' ed. A. R. West, The Institute of Petroleum, London, 1974, Vol. 6, p. 429; R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions," Elsevier, Amsterdam, 1973, p. 47.
[3] J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Y. Ridley, *Analyt. Chem.*, 1973, **45**, 1023A, and references therein.