Fine Structure in 'Metastable Peak' Shapes in Mass Spectra

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Summary: The 'metastable peak' due to the collision-induced reaction $H_3^+ \rightarrow H^+ + H_2$ shows fine structure which probably arises because of the formation of H_2 in several vibrational states while that due to $H_2^{+\bullet} \rightarrow H^+ + H^\bullet$ is composed of two separate peaks due to two different electronic transitions.

THE importance of observations on metastable processes in understanding the ion chemistry occurring in the mass spectrometer has grown remarkably. In addition to suggesting ionic fragmentation pathways and their use in kinetic studies and in testing theories of mass spectra, the recognition that metastable peaks can have a variety of shapes and the deduction of the relationships between shape and kinetic energy release[1] has provided a valuable new probe into the energetics of ionic reactions.

A relatively new feature of 'metastable peak' shapes has been the discovery of composite metastable peaks, *i.e.* superimposed peaks due to two processes occurring from the same ion.[2,3] A composite peak (Figure 1) results from the reaction $H_2^+ \rightarrow H^{+\bullet} + H$ in the mass spectrum of hydrogen: the width of the narrow component measured at half height corresponds to an energy release of 0.026 eV, that of the broad to release of 4.8 eV.† Transitions from the ground state of $H_2^{+\bullet}$ to the vibrational dissociation limit and to the first electronic excited state respectively account for these results. Of special note is the release of 15 eV at the extreme range of the transitions to the repulsive electronic state.

The mass spectrum of hydrogen also shows a 'metastable peak' corresponding to the transition $H_3^+ \rightarrow H^+ + H_2$, the study of which has led to the discovery of a further

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† The techniques used in measurements of this type are fully described in recent papers from this laboratory.[4]

degree of complexity in 'metastable peak' shapes, the existence of fine structure. When examined by changing the ratio of accelerating voltage to sector voltage to three times the normal value and scanning the accelerating voltage over a small range, this peak was observed to have the common Gaussian shape but it appeared to be more than usually broadened near the base line. In addition, the sides of the peak showed distinct steps (not due to instrumental factors). This fine structure could only just be resolved and in some scans one or more of the notches could not be distinguished. A typical scan of the metastable peak appears in Figure 2.

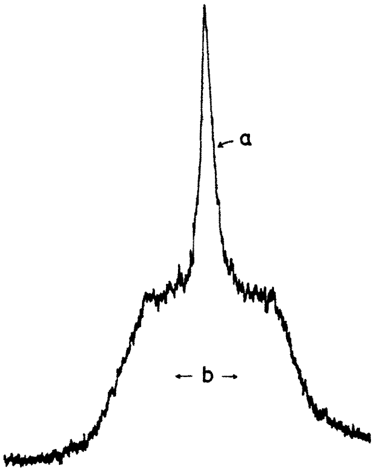

FIGURE 1. *The 'metastable peak' due to* $H_2^+ \rightarrow H^{+\cdot} + H^{\cdot}$. *Kinetic energy release, calculated at* a *and* b *and averaged over six scans was* 0·026 eV *and* 4·8 eV, *respectively.*

One interpretation of these observations is that the product H_2 is formed in a number of vibrational states. The centre of the peak corresponds to the formation of products having minimum kinetic and therefore maximum internal energy, in this case vibrational energy of H_2. Each notch on the peak represents product H_2 formed in a successively lower vibrational state. The data obtained fit this interpretation well, the known energy levels of H_2 require kinetic energy release down the series ν = 14, 13, 12, and 11 of 15, 77, 130, and 175 meV[5] and the observed energy release at each notch is 53, 102, 137, and 200 meV.

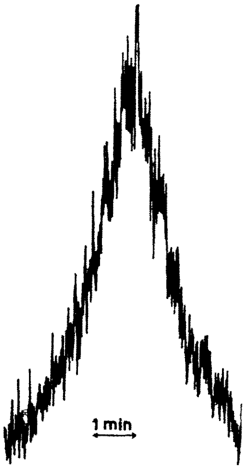

FIGURE 2. *The 'metastable peak' due to* $H_3^+ \rightarrow H^+ + H_2$, *illustrating the fine structure. The slow scan rate should be noted.*

The observed values have to be corrected for the small energy release not due to the vibrational effect. A value of 25 meV gives net values for ν = 14, 13, 12, and 11 of 28, 77, 112, and 175 meV. Repeated scans gave similar values. It should be noted that the effective resolution rapidly decreases as one moves away from the peak centre and the lower vibrational states are in fact not resolved. A further reason for this is that there appears to be a contribution from a process (or processes) which superimpose a much broader peak of lower abundance on the 'metastable peak' of interest.

A Perkin-Elmer–Hitachi RMH-2 mass spectrometer was used in this work.

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[1] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.

[2] J. H. Beynon, *Adv. Mass Spectrometry*, 1968, **4**, 123.

[3] D. Ioanoviciu and D. Ursu, *Rev. Roumaine Phys.*, 1967, **12**, 899 (*Chem. Abs.*, 1968, **69**, 31421).

[4] J. H. Beynon, *Analyt. Chem.*, 1970, **42**, 97A; J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrometry*, 1970, **3**, 455; J. H. Beynon, R. M. Caprioli, and T. Ast, *Org. Mass Spectrometry*, 1971, **5**, 229; J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Internat. J. Mass Spectrometry Ion Phys.*, 1969, **3**, 313.

[5] H. Beutler, *Z. phys. Chem.*, 1934, **B27**, 287.