An Anomalous "Metastable Peak" in the Mass Spectrum of Methanol

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A DETAILED study of the mass spectrum of methanol and its deuteriated analogues was recently undertaken using an M.S.9 double-focusing mass spectrometer in order to obtain information on the thermochemistry of the decomposition of the molecular ion.[1] The mass spectrum contains a number of "metastable peaks." Such peaks have often been used in order to obtain information on the accurate masses and elemental compositions of metastable and product ions,[2,3] the location of the "metastable peaks" being capable of measurement to about 250 p.p.m. in

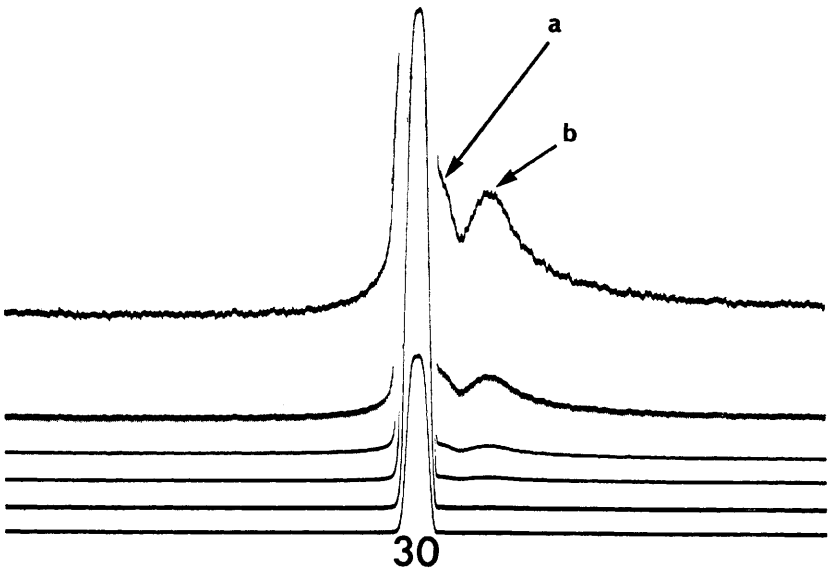

FIGURE. *The mass spectrum of methanol in the region of mass* 30.

mass, no deviation from the expected value ever having been reported. The mass spectrum of methanol in the region of mass 30 is shown in the Figure. The "metastable peak" corresponding to the transition

$$CH_4O^{+\cdot} \rightarrow CH_3O^+ + H\cdot$$

$$\text{or } 32{\cdot}026213 \rightarrow 31{\cdot}019388$$

should occur at an accurate mass of 30·042 which can be seen in the Figure partly resolved from the normal mass peak centred at 30·010563. Its position is indicated by the arrow 'a'. In addition, however, a second "metastable peak" is seen at an accurate mass of 30·122 (arrow 'b'). This peak appears in methanol spectra obtained on a single-focusing mass spectrometer[4] and the commercial machines M.S.12, CH4, and M.S.9 and seems to be produced in the decomposition of the molecular ion with loss of a hydrogen atom. This is evidenced by the fact that the anomalous peak is prominent in mass spectra taken using very low ionising energy (~10—11 ev) when *m/e* 31 and *m/e* 32 are the only ions detectable. Corresponding anomalous "metastable peaks" appear in the mass spectra of CH_3OD, CD_3OH, and CD_3OD.

Analogous compounds C_2H_5OH, HOH, CH_3NH_2, CH_3SH, and CH_3OCH_3 were examined but in no case was a corresponding anomalous peak seen. In the mass spectrum of hydroxylamine, however, two such anomalous peaks were observed corresponding to the reactions:

$$NH_3O^{+\cdot} \rightarrow NH_2O^+ \sim m/e\ 31{\cdot}15$$

$$\text{and } NH_2O^+ \rightarrow NHO^{+\cdot} \sim m/e\ 30{\cdot}10$$

The origin of all these peaks is currently being investigated in detail.[5] They provide the first examples of such peaks which do not appear exactly centred about the value $\frac{m_2^2}{m_1}$ where m_2 is the accurate mass of the product ion and m_1 that of the metastable ion.

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[5] J. H. Beynon, A. E. Fontaine, and G. R. Lester, to be published.