

## Kinetic Energy Loss in Collision-induced Fragmentations: Asymmetric Metastable Peaks in Mass Spectra

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*Summary* Conversion of part of the kinetic energy of an ion directly into internal energy when the ion interacts with a neutral gas molecule is established as the mechanism by which these ions are caused to decompose.

METASTABLE peaks† in mass spectra, once of use solely for establishing ionic fragmentation patterns, have recently been found to embody several more fundamental parameters.<sup>1-4</sup> We now report the observation of asymmetric

† It has become conventional to apply the designation "metastable peak" to the signal due to the product ion formed by any reaction (whether unimolecular or collision-induced) occurring in a field-free region in a mass spectrometer. We shall use the term in this paper without quotation marks.

composite metastable peaks (see Figure) and suggest a mechanism for their formation.

The unimolecular reaction  $\text{CH}_3\text{OCH}_3^+ \rightarrow \text{CH}_2=\overset{+}{\text{O}}-\text{CH}_3 + \text{H}\cdot$  can be examined in the first field-free region of a double-focussing mass spectrometer.<sup>5</sup> When this is done with a background pressure of  $2 \times 10^{-7}$  Torr in the field-free region a very narrow metastable peak [Figure (a)] is

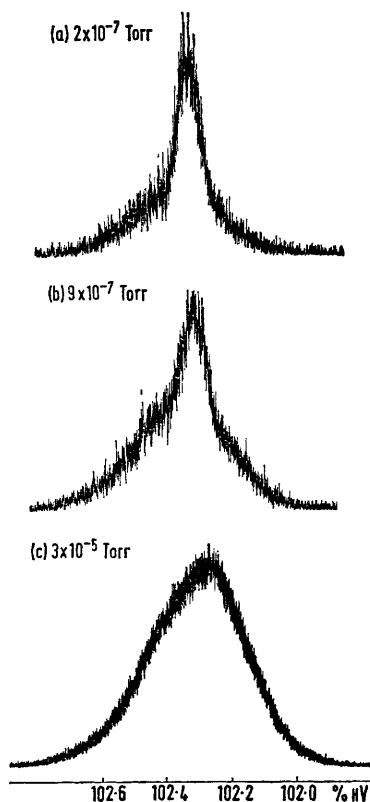


FIGURE. Asymmetric composite metastable peak due to the reaction,  $\text{CH}_3\text{OCH}_3^+ \rightarrow \text{CH}_2=\overset{+}{\text{O}}-\text{CH}_3 + \text{H}\cdot$ , at various collision gas pressures. Peak intensities increase in the order (c) > (b) > (a) and the scales have been adjusted in the inverse ratio, i.e., 10:8.5:1.

obtained. As air is admitted to the region a second, collision-induced peak which is both broader and shifted in position is evident and, at high pressures, it becomes dominant [Figure (b) and (c)]. The shift in position is directly proportional to the difference in kinetic energy of the reactant ions. In this case the dimethyl ether molecular ion loses, on average, 3.6 eV<sup>‡</sup> of kinetic energy when undergoing collision-induced fragmentation. This kinetic energy

loss must correspond in magnitude to the excitation energy transferred to the reactant. Calculating the kinetic energy release (T) upon separation of the products<sup>6</sup> one finds that the unimolecular  $(M-1)^+$  reaction releases 4 meV, and that the collision-induced process releases, on average, 150 meV. Furthermore, the shape of the latter peak indicates<sup>2b</sup> that a wide range of energies is released. We interpret these results as showing that glancing collisions undergone by high kinetic energy ions occur with measurable conversion of kinetic into internal energy. The resulting difference in vibrational and/or electronic energy is reflected in the shapes of the respective metastable peaks so that the energy content of the ions can be inferred.

The limited number of measurements done so far on the widths of collision-induced metastable peaks show that they are almost invariably broader than their unimolecular counterparts, in agreement with the idea that fragmentation occurs from the same electronic state having different amounts of vibrational/rotation energy. However, it is expected that isolated electronic states should also be accessible on collision and that fragmentation from such high energy states might result in less kinetic energy release than for unimolecular reaction (a smaller T value could for example, be the result of a smaller reverse activation energy due to formation of an electronically excited form of one of the products). This is apparently the case for the reaction

$\text{CH}_2=\overset{+}{\text{O}}\text{H} \rightarrow \text{CHO}^+ + \text{H}_2$  in methanol. Here the average kinetic energy release is ca. 50 meV<sup>§</sup> for the collision-induced reaction and 174 meV in the unimolecular process which also releases a much narrower range of kinetic energies. The most probable loss of ion kinetic energy upon collision as measured from the displacement of the metastable peak upon fragmentation is 12 eV. This methanol reaction was also examined in the second field-free region. In the presence of collision gas the metastable peak occurring in the mass spectrum was shifted to lower mass by 0.026u from the position (27.118 u) calculated for the reaction  $31.018^+ \rightarrow 29.003^+ + 2.016$ . This shift corresponds to a kinetic energy loss by the reactant ion of 11 eV, in good agreement with the value measured in the first field-free region.

Several other cases of kinetic energy loss accompanying collision-induced metastable fragmentations and related charge transfer processes<sup>7</sup> have been observed and will be discussed in detail elsewhere. The importance of the present observations seems to lie in the information they should provide on the higher electronic states of ions which are not normally accessible to experimental study.

All experiments were done using a modified RMH-2 mass spectrometer.

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<sup>‡</sup> The probable error in this and the other reported values for kinetic energy loss is less than 20%.

<sup>§</sup> It is implicit in this calculation that the neutral entity is assumed to be lost as  $\text{H}_2$  and not in two steps. The multistep situation is currently being investigated in collision-induced processes such as  $\text{CH}_4^+ \rightarrow \text{CH}^+ + 3\text{H}\cdot$ .

<sup>1</sup> J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.

<sup>2</sup> (a) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Internat. J. Mass Spectrometry Ion Phys.*, in the press; (b) E. G. Jones, J. H. Beynon, and R. G. Cooks, in preparation.

<sup>3</sup> J. H. Beynon, *Adv. Mass Spectrometry*, 1968, **4**, 123.

<sup>4</sup> (a) R. G. Cooks and J. H. Beynon, *Chem. Comm.*, 1971, 1282; (b) M. Bertrand, J. H. Beynon, and R. G. Cooks, in preparation.

<sup>5</sup> M. Barber and R. M. Elliott, presented at the 12th Annual Conference on Mass Spectrometry and Allied Topics, ASTM Committee E-14, Montreal, June 1964.

<sup>6</sup> J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrometry*, 1970, **3**, 661.

<sup>7</sup> R. G. Cooks, J. H. Beynon, and T. Ast, *J. Amer. Chem. Soc.*, in the press.