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ABSTRACT

The shape and position on the mass scale of the metastable peak at $M^*/q = 31.88$ in the mass spectrum of $n\text{-C}_4\text{H}_{10}$ has been calculated and compared with the observed peak. The calculation was made on the assumption that the ion beam width determined by the beam width of normal ions at the collector slit was widened by velocity components added to the fragments from kinetic energy released in the fragmentation process. The only adjustable parameter used was the total kinetic energy release in the fragmentation, T . A value of $T = 0.015 \pm 0.005$ eV gave the best fit of the observed peaks to the computed peaks. This value is compared with the literature values of T determined by different methods for this metastable dissociation.

I. INTRODUCTION

Attempts have been made to explain both the existence and the shape of peaks resulting from metastable ion dissociations in mass spectrometers of the Dempster type. Hipple¹ has shown why such peaks appear in such instruments. Coggeshall² investigated the question of the shape of normal metastable peaks; according to Coggeshall's analysis, the metastable peak should exhibit a sharp discontinuity at the calculated apparent mass M^* , and a tail toward higher masses. Experimentally this does not fit the observed fact that most metastable peaks are broad (compared with usual fragment peaks) and fairly symmetrical. Therefore the shape of metastable peaks has been reinvestigated in an attempt to resolve this difference between theory and experiment.

II. EXPERIMENTAL PROCEDURE

All data in this work were collected with a modified Consolidated Electrodynamics Corporation Model 21-103B mass spectrometer. The important parameters of this particular instrument are the radius of 12.70 cm; the ion-exit slit width, 0.152 mm; the collector slit width 0.533 mm (changed from 0.76 mm supplied by the manufacturer; and the outer radius of the analyzer tube, 13.97 cm.

For accurate determination of peak shapes in the region of mass 32, the mass range from $M/q = 28$ to $M/q = 34$ was scanned very slowly in a period of 2 to 3 minutes. During this period the accelerating voltage was monitored with a Rubicon Model 2730 potentiometer,³ and at each of several predetermined voltages a marker was placed on the record by flipping the galvanometer on-off switch. In this way, a curve for a mass versus chart distance was obtained from which each peak

profile could be accurately reproduced. During all scans the magnetic field was monitored with a Hall-effect probe, reading to ± 0.2 gauss, to assure that no drift in the magnetic field occurred during the scan. The estimated error in the mass scale is not more than ± 0.01 mass unit (mu).

III. RESULTS

The profiles of the metastable ion peak resulting from the dissociation

which should appear at $M^*/q = 31.88$, are shown in Fig. 1; they were scanned at accelerating voltages (V_A) of 3100, 1550, and 582 volts. Four features of these curves are significant: (a) The widths at half maximum of the peaks are abnormal and increase as an inverse function of the voltage. (b) The peaks have rounded tops. (c) The center of the peak is displaced about 0.08 mass units from the nominal value of $M^*/q = 31.88$.⁴ (d) The peak height varies with the square root of the accelerating voltage.

In Fig. 2 is shown the profile of a normal peak at $M/q = 32$, that of O_2^+ , which is a typical peak of ions having only thermal kinetic energy. The same three voltages were run as for $M^*/q = 31.88$ of n-butane. The O_2^+ peaks were almost identical, and the peak widths were independent of accelerating voltage (a small change of peak height occurs, the peak height decreasing as the accelerating voltage decreases).

Except for small differences due to possible mass discrimination in ion-collection efficiency at various points within the ion source, both O_2^+

and $n\text{-C}_4\text{H}_{10}^+$ should have the same thermal kinetic energy distribution. Hence the ion beam widths in the analyzing region for O_2^+ and $n\text{-C}_4\text{H}_{10}^+$ should be similar. A metastable dissociation of $n\text{-C}_4\text{H}_{10}^+$ in which the fragments receive no kinetic energy from the dissociation should not increase this beam width. Therefore if the kinetic energy release is zero, the beam from a metastable ion impinging on the collector slit should have the same shape as the O_2^+ beam, and the metastable peak should be distorted only by the change in apparent mass with distance beyond the ion source at which dissociation occurs.²

The observed metastable peaks are broader than the above considerations would predict, and it is a reasonable assumption that this increased width is due to velocity added to the fragment in the center-of-mass system of the accelerated $\text{C}_4\text{H}_{10}^+$ ion. The added velocity (positive or negative) arises from the kinetic energy released in the fragmentation process.

Beynon, Saunders, and Williams⁵ have shown that for the general metastable dissociation process shown in Eq. (2), for a dissociation in which total kinetic energy, T , is given to the fragments, the apparent mass at which the metastable ion, M_1^* , will appear is given by

$$M_1^* = \frac{M_1^2}{M_0} \left(1 + \frac{M_2 T}{M_1 \text{ eV}_A} \right) \pm 2 \frac{M_1^2}{M_0} \left(\frac{M_2 T}{M_1 \text{ eV}_A} \right)^{1/2} \quad (3)$$

As shown in Eq. (4), the maximum width, d , of the mass peak is given by twice the last term in Eq. (3):

$$d = \frac{M_1^2}{M_0} \left(\frac{M_2 T}{M_1 eV_A} \right)^{1/2} \quad (4)$$

Eqs. (3) and (4) were derived with the implicit assumption of zero beam width at a collector with zero slit width. Therefore, d , in a practical case, will represent the increase in beam width of the metastable ion beam, in comparison with the beam width of a normal peak.

In Eqs. (3) and (4), only those contributions from molecules which dissociate with the fragments emitted along the beam axis are considered. Flowers⁶ has discussed the effect of an isotropic distribution of the angle of dissociation with respect to the beam axis in which there is a cosine distribution of added velocity components. This effect leads to a double maximum in the resulting metastable peak.

To evaluate the maximum kinetic energy release, T , only the maximum spread need be considered, and at small values of T , normal collector slit widths, and normal ion-beam widths, the effect of a double maximum is average over most of the peak. It has not, therefore, been considered in the discussion to follow.

If, for the peaks shown in Fig. 1, the widths at various fractions of the peak height are plotted against $V_A^{-1/2}$, as shown in Fig. 3, a series of straight lines of various slopes results. The slope of each line is a measure of T , and it is obvious that the apparent kinetic energy release is a function of how the peak width is measured. In Fig. 4 the values of T calculated from these respective changes in peak width with voltage are plotted on a logarithmic scale against the fractions of peak height at which the width was measured. It is seen from this plot that the actual value of T

must lie between the limits 0.04 and 0.002 eV.

There is also a slight shift in the mass center of a metastable peak formed by a dissociation in which kinetic energy is released. This is given in the second term of Eq. (3), and for a shift in center of 0.08 mu, even at $V_A = 582$ volts where the shift should be largest, T would be 4.2 eV, completely outside the possible range of values shown in Fig. 4. For $T = 0.05$ eV, the shift of the center at $V_A = 582$ volts would be less than 0.001 mu. Therefore the shift in the peak position cannot be attributed to this term in Eq. (3).

There is one other feature of metastable peaks in Dempster-type instruments to which attention is called. The focus adjustment for maximizing the $M/q = 31.88$ peak of n-butane is different from that for maximizing a normal peak. By slightly decreasing the inner focus electrode potential (or conversely, increasing the outer), the height of the metastable peak is increased, whereas normal peaks are decreased in height. This must mean that under normal operating conditions with the focus potentials adjusted for normal peaks, when V_A would focus $M/q = 31.88$ the mass-58 ion beam is being partially blocked by the ion-source exit slit. It is to be noted, however, that no obvious change occurs in shape of the $M/q = 31.88$ peak when it is maximized with the focus slits.

IV. DISCUSSION

Coggeshall² has analyzed the factors determining the change in apparent mass at which a metastable ion appears as a function of distance beyond the ion source exit slit at which the parent ion dissociates. For clarity in the discussion to follow, the basic results of Coggeshall's analysis are reproduced here with the relevant equations, some of which have been put into a more useful form for this discussion.

In Fig. 5 is shown a schematic representation of metastable ion trajectories in Dempster-type instruments. Here R_1 , S_1 , and S_2 are respectively the ion source repellers, first slit, and exit slit; the ionizing electron beam (perpendicular to the plane of this diagram) is represented by the black dot. An ion of momentum equal to that of M^* , or the ion from the dissociation of M_0 at S_2 , will have a trajectory of radius r , the normal focal radius of the instrument. At this same focus condition, M_0 will have radius R defined by

$$R = r \left(\frac{M_0}{M^*} \right)^{1/2} \quad (5)$$

If, however, M_0 travels before dissociation through some distance defined by the angle θ and radius R , then the resulting ion, M_1 , will have an apparent radius r^* with a new center displaced a distance g from the normal center of focus:

$$r^* = \frac{(R-r)^2 + r^2 + R(2r-R) \cos \theta}{R + (2r-R) \cos \theta} \quad (6)$$

The new apparent mass, M_θ^* , defined by r^* in terms of $M_{\theta=0}^*$, is given by

$$M_{\theta}^* = M_{\theta=0}^* \frac{r^2}{(r^*)^2} = \frac{M_1^2}{M_0} \frac{r^2}{(r^*)^2} \quad (7)$$

The displacement, g , to the new center of r^* is given by

$$g^2 = (R-r)^2 + (R-r^*)^2 - 2(R-r)(R-r^*) \cos \theta. \quad (8)$$

This equation has not been reduced to eliminate r^* , hence it was solved point by point from values of r^* calculated from Eq. (6).

The ion beam of M_1^+ will strike the analyzer tube and be no longer collected when $g + r^*$ is equal to the outer radius of the analyzer tube; in the instrument used here, as in Coggeshall's instrument, this occurs at $\theta = 17$ deg.

The observed metastable peak should then be the sum of a manifold of peaks with constantly increasing mass centers as θ increases from 0 to 17 deg, the cutoff point. Also as θ increases, the number of metastable dissociations contributing to each peak in the manifold must decrease according to the half-life and the time of travel of the metastable ion. There are thus three parameters that must be considered at each point: (a) the beam shape, which determines the peak shape, (b) the kinetic energy release in the dissociation, which determines the width of the beam, (c) the half-life, which determines the height of the peak.

Consider first ion the beam distribution and shape as impinging on the collector slit. In Fig. 2, the O_2^+ peak can be reasonably approximated by a trapezoid, of which the sloping sides represent the beam width, about 0.034 mu, and flat top represents the slit width minus the beam width. The slit width corresponds to about 0.134 mu at $M/q = 32$. Using a trapezoidal

representation of the peak, one assumes a beam distribution which is of uniform intensity and which has a sharp cutoff on each side. The various peak shapes obtained as a function of beam width and slit width are shown schematically in Fig. 6. When the beam is wider than the slit, the peak, represented by a trapezoid, has sloping sides, the base of each equal to the slit width, and a flat top equal to the beam width minus the slit width. The beam width is assumed to be the normal O_2^+ beam width plus the width calculated from Eq. (4) for the kinetic energy release, T , of the dissociation. On the basis of the above model, the beam width will equal the slit width at $T = 0.0018$ eV, the lower limit of T from Fig. 4. Therefore the situation in Fig. 6C must apply, and the beam width must be greater than the slit width.

There have been two determinations of the half-lives involved in the metastable dissociation in Eq. (1). Hipple¹ found values of 1.6×10^{-6} sec or 2×10^{-6} sec, depending on the comparison standard used to normalize the intensity of the metastable peak. More recently, Coggeshall² has found three separate half-lives of 8.9×10^{-8} sec, 6.1×10^{-7} sec, and 2.7×10^{-6} sec. Under the conditions of our operation, the first of these can be neglected, as its intensity after a time equal to 7 to 10 half-lives as required for collection and acceleration, will be too low to contribute to the observed peak.

From Coggeshall's curves it is estimated that at 1550 V accelerating voltage and 1% average repellers (a collection plus acceleration time of 0.67 μ sec), the 0.61- and 2.7- μ sec components will contribute equally to the peak for those ions dissociating at the exit slit, S_2 . At 580 volts the ratio calculated from the half-lives and the above assumed ratio at 1550 volts is 0.7 part of the 0.61- μ sec component to 1 part of the 2.7- μ sec com-

ponent. This latter ratio does not agree with values from Coggeshall's curves; this is understandable, since Coggeshall made no subtraction of longer-lived components in estimating the shorter half-lives, and the true half-lives for the shorter-lived components must therefore be shorter than the values cited by Coggeshall. In the absence of better information, however, the half-lives cited by Coggeshall, and equal initial relative intensities of fragment ions at 1550 volts acceleration, have been assumed for calculating peak shapes. It is further assumed that both half-lives are associated with the same kinetic energy release in the dissociation process.

With two parameters fixed--i.e., the half-lives and beam shape--the shape of the metastable peak has been calculated. Because the object of this investigation was to show that a reasonable representation of the metastable peak can be achieved with only one adjustable parameter, T , this is a relatively simple problem and computer calculations were not necessary. The time of travel of the $n\text{-C}_4\text{H}_{10}^+$ ion through the arc from $\theta = 0$ to $\theta = 17$ deg, the cutoff point, was divided into 10 equal time intervals, and the peak shape was numerically integrated by adding at each mass point the contribution from each of the trapezoids representing the appropriate time interval and corresponding apparent mass. One example of the integration schema is shown in Fig. 7. Using shorter time intervals, as might be done in a computer calculation, would not significantly alter the shapes obtained here.

The best results are shown in Fig. 8, where the peak shape calculated on the assumption $T = 0.015$ eV is compared with the observed peaks at accelerating voltages of 1550 and 582 volts respectively. A value of $T = 0.01$ eV

yields too narrow and a value $T = 0.02$ eV too broad a peak. Therefore it is concluded that the total kinetic energy released in the dissociation is $T = 0.015 \pm 0.005$ eV.

The calculated peak shown in Fig. 8a is a fair representation of the observed peak at 1550 volts in that the half width is about equal to that observed, the top is rounded (though slightly too narrow), and the calculated curve is a maximum at $M/q = 31.96$ as observed. The tails on the front and back of the peak are not reproduced, but neither are the tails on the O_2^+ peak included in our model peak.

In Fig. 8b, the calculated peak at 582 volts also has a rounded top and about the correct half width, but the top section is skewed toward the high-mass side and the maximum is displaced some 0.05 mu too high.

The value of T which was found to give the best fit for the width of the peak, namely $T = 0.015$ eV, is quite small. This can be interpreted as meaning that most of the internal energy of the molecule is distributed in vibrational and rotational energy states of the fragments before dissociation, as predicted by the quasi-equilibrium theory of mass spectra. The kinetic energy release is not zero, however, and calculations made assuming zero release of kinetic energy yield a very sharp, highly skewed peak. Such peaks are not the usual metastable peaks observed in Dempster-type instruments. On the other hand, even a value of $T = 0.05$ eV gives a quite broad peak, which is also a type rarely seen (however, some may be hidden under groups of normal peaks). It is therefore suggested that the value of T found here is not unusual, and that many metastable dissociations of singly-charged polyatomic molecule ions into polyatomic fragments are associated with values of T in the range of 0.01 to 0.05 eV.

There are two experimental results with which the value of T found for the metastable dissociation might be compared. Using the deflection method, Fuchs and Taubert⁷ measured the quasi-thermal energy distribution of ions from simple hydrocarbons, including $C_4H_{10}^+$ and $C_3H_7^+$, from n-butane. From this work, Taubert⁸ calculated $T = 0.10$ eV for the mean value of the kinetic energy release in the fast dissociation of $n-C_4H_{10}^+$ to $C_3H_7^+$ in the ion source of their instrument. Taubert cited no limit of error on this value. This value should not necessarily be compared directly with the value of T for the corresponding metastable dissociation. Ottinger⁹ has studied the kinetic energy release in fragmentation of metastable ions from heptane and n-butane by placing a velocity selector after the drift space in which the metastable ions decay and before the analyzing magnet. By comparing the energy widths of the parent peaks and fragment peaks, Ottinger obtained a value of $T = 0.04_1 \pm 0.01$ eV for the kinetic energy release in the metastable dissociation shown in Eq. (1). This value is stated to relate to the increase in peak width at half maximum peak height, and hence should be comparable to the value of $T = 0.015 \pm 0.005$ eV, which gave the best fit in the present work. Ottinger's value is quite close to the upper limit placed on T in Fig. 4. The two values, although in agreement on the order of magnitude of the kinetic energy, are not in agreement within the error limits cited. One possible source of error in this work lies in the assumed half-life of $2.7 \mu\text{sec}$ for the metastable ions contributing to the major fraction of the observed peak. If this half-life were too long, the effect would be to make the best-fitting energy too low.

It is to be noted that a computer program could be set up to systematically vary these parameters: the beam shape, the half-lives, the relative

intensity of each half-life, and the value of T associated with each half-life. Optimizing these parameters--of which there are six if there are two contributing half-lives, each with its own value of T --might lead to a better fit to the observed peak shapes, but would not necessarily lead to the correct values of half-lives and kinetic energies. For this reason the investigation here has been limited to the use of measured parameters and of an idealized model of the beam shape with only T as an adjustable parameter, to show that the peak shapes observed in the mass spectrometer are not the result of instrumental artifacts.

The model used above to calculate the peak shape is obviously quite simplified, hence may not explain all ramifications of metastable ion behavior in all types of mass spectrometers. For example according to the model used, one would expect the metastable peak at $M/q = 31.88$ in *n*-butane to be flat topped in a sector-type instrument (or to have a double-peaked distribution according to Flowers⁵), with the center not significantly displaced from the calculated value. As shown by Stevenson and Schissler,¹⁰ the peak in their 90 deg sector instrument is quite similar to that observed in Dempster-type instruments. Flowers has observed that metastable peaks in double-focusing instruments are not displaced from the calculated position. One interpretation of these observations is that instead of there being a single value of T , there is a continuous distribution of kinetic energies, and the energy found here ($T = 0.015$ eV) represents some average of this distribution. Under this assumption the beam distribution function would be a Gaussian. Such an assumption would not modify the general shape of the calculated peak for Dempster-type instruments, but details of the structure would be modified.

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FOOTNOTES AND REFERENCES

* This work was performed under the auspices of the Atomic Energy Commission.

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FIGURE CAPTIONS

Fig. 1. Profiles of $M/q = 31.88$ peak from the metastable dissociation $n\text{-C}_4\text{H}_{10}^+ \rightarrow \text{C}_3\text{H}_7^+ + \text{CH}_3$. Accelerating voltage, V_A , for curve A, 3100 V; curve B, $V_A = 1550$ V; and curve C, $V_A = 582$ V. Mass scale assumes $M/q = 28 (\text{C}_2\text{H}_4^+) = 28.00$.

Fig. 2. Profile of O_2^+ peak of oxygen at $V_A = 3100$ V.

Solid line, observed profile

Dashed line, trapezoidal representation of peak.

Fig. 3. Peak widths in mass units of the $M/q = 31.88$ peak in $n\text{-C}_4\text{H}_{10}$ at various percentages of the total peak height plotted against the inverse square root of accelerating voltage.

Fig. 4. Apparent dissociation energy of metastable $\text{C}_4\text{H}_{10}^+ \rightarrow \text{C}_3\text{H}_7^+ + \text{CH}_3$ as measured by the change in peak width with accelerating voltage, plotted as a function of percentage of peak height at which widths were measured.

Fig. 5. Schematic representation of metastable ion trajectories in a Dempster-type mass spectrometer.

Fig. 6. Models used for peak shapes at various beam widths impinging on the collector slit.

Fig. 7. Schema for integrating mass peak $M^* = 31.88$ in mass spectrum of $n\text{-C}_4\text{H}_{10}$. $V_A = 1550$ V. The zero point is counted at $1/2$ value because dissociations before slit S_2 do not contribute and therefore the time interval is $1/2$ the other time intervals. Peak shapes based on assumption of $T = 0.015$ eV. Peak heights based on assumption of equal parts of $0.61\text{-}\mu\text{sec}$ and $2.7\text{-}\mu\text{sec}$ half-lives present at emergence of beam from S_2 .

FIGURE CAPTIONS (Cont'd)

Fig. 8. Comparison of the calculated with the observed shape for $M/q = 31.88$
peak in $n\text{-C}_4\text{H}_{10}$.

(a) $V_A = 1550 \text{ V.}$

(b) $V_A = 582 \text{ V.}$

Fig. 1

MUR-0522

Fig. 2

MUB-0527

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Fig. 3

Fig. 4

MUB-8524

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Fig. 5

MUB-8526

Fig. 6

Fig. 7

MUB-8525

Fig. 8

MUB-8523

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