produzierbar. Das Probengewicht änderte sich nie um mehr als 2 mp während eines Meßgangs. Sobald jedoch bei etwa 1940 °K der Schmelzpunkt erreicht wird, reagiert das Titan heftig mit dem Al_2O_3-Tiegel, in dem es sich während der Messung befindet. Über die Suszeptibilität des Titans im flüssigen Zustand kann deshalb keine Aussage gemacht werden, obwohl sich mit dem Molybdänofen etwa 2200 °K erreichen lassen. Eine Suszeptibilitätskurve des Reaktionsproduktes ist in willkürlichen Einheiten in Abb. 1 a mit eingezeichnet.

Das Vanadin besitzt – soweit bekannt – nur eine kubisch raumzentrierte Modifikation. Die Temperaturabhängigkeit der magnetischen Suszeptibilität dieses Metalls wurde in den letzten Jahren von verschiedenen Autoren in unterschiedlichen Temperaturbereichen untersucht: KRIESSMAN [7] (von 1150 bis 1970 °K); CHILDS, GARDNER und PENFOLD [8] (Proben verschiedener Reinheit mit je einem Meßwert bei 20, 77 und 293 °K); KOJIMA, TEBBLE und WILLIAMS [5] (von 293 bis 1620 °K); TANIGUCHI, TEBBLE und WILLIAMS [9] (von 293 bis 1620 °K); BURGER und TAYLOR [10] (von 100 bis 310 °K). Die hierbei mitgeteilten Absolutwerte bei Raumtemperatur weichen teilweise erheblich voneinander ab. Hierbei entsprechen offensichtlich die höheren Suszeptibilitätswerte dem reineren Vanadin. Abb. 1 b zeigt die eigenen Meßergebnisse an Vanadin 1 zusammen mit den Kurven von BURGER und TAYLOR [10], TANIGUCHI, TEBBLE und WILLIAMS [9] sowie der Untersuchung von KRIESSMAN [7]. Ab etwa 1450 °K weist die Messung von KRIESSMAN eine sehr große Streuung der Meßpunkte auf, die in der Abb. 1 b durch das Aufspalten der gezeichneten Kurve angedeutet wird.

Die magnetische Suszeptibilität des Vanadins fällt von Raumtemperatur bis etwa 1600 °K stetig ab, steigt dann aber nach einem langgestreckten Minimum wieder an. Oberhalb 2000 °K war dieser Anstieg noch steiler und zeigte eine Temperaturhysterese. Da jedoch oberhalb 2000 °K ein Apparatefehler vorerst nicht ausgeschlossen werden kann, sind diese Meßwerte nicht eingezeichnet. Bei etwa 320 °K zeigt sich eine Anomalie ähnlich derjenigen, die von BURGER und TAYLOR [10] bei 245 °K gefunden wurde.

Tab. 1 bringt die Suszeptibilitätswerte von Titan 1, Titan 2 und Vanadin 1 in dem gesamten durchgemessenen Temperaturbereich und die Raumtemperaturwerte von Titan 3 und Vanadin 2.

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Metastable Ion Intensities and Fragmentation Energies in Benzene

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The previously described new method [1, 2] of investigating metastable ions has been applied to benzene. A search was carried out for a number of metastable ion decompositions, of which twelve were found. They are summarized in Table 1. Other suspected processes which could not be detected were $78^{++} \rightarrow 77^{++} + 1$, $78^{+} \rightarrow 63^{+} + 15$, $77^{+} \rightarrow 76^{+} + 1$, $76^{+} \rightarrow 74^{+} + 2$, $73^{+} \rightarrow 72^{+} + 1$, $39^{+} \rightarrow 38^{+} + 1$, $38^{+} \rightarrow 37^{+} + 1$, and any processes leading to 27^{+} and 26^{+}. The detection sensitivity was generally of the order of 10^{-5} relative to the mass 78 intensity, but for $77^{+} \rightarrow 76^{+} + 1$ only 10^{-3} due to the background of $78^{+} \rightarrow 76^{+} + 2$.

The measurements were performed using a low accelerating field, $E = 100$ or 200 V/cm, so that the energy homogeneity of the ions leaving the ion source, as measured by the half-width $\Delta E'$ of the so-called "main peak" representing the profile of the molecular beam, was only a few volts. The so-called "satellite peak" originating from metastable ions was then scanned slowly at a rate of about 0.03 V/s

[1] CH. OTTINGER, Phys. Lett. **17**, 269 [1965].
[2] O. OSBERGHAUS and CH. OTTINGER, Phys. Lett. **16**, 121 [1965].

using a time constant of 7 seconds. The resulting peak width $\Delta E''$ was large compared to $\Delta E'$ due to a release of fragmentation energy E_f, which was calculated according to [1].

Column 3 of Table 1 gives the neutral fragment mass as calculated from the position of the satellite peak on the potential scale; it will be seen that the accuracy is always sufficient to identify the processes with certainty. In order to get a measure for the relative intensities of the decompositions, the product (satellite peak height) $\times \Delta E''$ was divided by (main peak height) $\times \Delta E'$, thus approximating the ratio of the peak areas. The measured metastable intensities are also influenced by the time of flight in the field-free region, which was between 2.86 and 4.15 μs, depending on the metastable ion mass m_0 and the ion energy U_c in the condenser. The quantity listed in column 5 is therefore the peak area ratio normalized to a time of flight of 1 μs. Because of the fact that the actual time of flight in the drift space covers different sections of the m_0^+-ion decay function, the entry into the drift space occuring between 1.26 and 1.98 μs after ionization, it is difficult to attach an immediate meaning to the figures in column 5, so that the used approximation for the area certainly suffices. Also the peak height measurements done on different days were only reproducible within about 30% due to slight temperature differences in the ion source. The intensities given are therefore only a rough guide.

In column 6 the intensities of column 5 were multiplied by the intensity ratio of ordinary ions, $I_m : I_{78}$ [3]. This provides a normalization of metastable intensities to $I_{78} = 100$ and a comparison with the metastable intensities from the literature in column 7.

1 No.	2 Process	3 Δm	4 E_f (eV)	5 Rel. Intensities per μs (%)	6 Metast. Int. norm. to $I_{78}=100$	7 Metast. Int. from literature
1 a	$C_6H_6^+ \rightarrow C_6H_5+H$ $78^+ \rightarrow 77^+ + 1$	0.93	0.072 ± 0.02	9.31	1.28	2.0–4.0 [4]; 0.1 [5]
1 b	$C_6H_4^+ \rightarrow C_6H_3^+ + H$ $76^+ \rightarrow 75^+ + 1$	1.09	0.096 ± 0.04	0.53	0.01	not reported
1 c	$C_6H_3^+ \rightarrow C_6H_2^+ + H$ $75^+ \rightarrow 74^+ + 1$	0.99	0.084 ± 0.03	1.51	0.07	not reported
1 d	$C_6H_2^+ \rightarrow C_6H^+ + H$ $74^+ \rightarrow 73^+ + 1$	0.99	0.044 ± 0.044	1.86	0.03	not reported
1 e	$C_4H_4^+ \rightarrow C_4H_3^+ + H$ $52^+ \rightarrow 51^+ + 1$	1.05	0.096 ± 0.03	0.40	0.08	not reported
1 f	$C_4H_3^+ \rightarrow C_4H_2^+ + H$ $51^+ \rightarrow 50^+ + 1$	0.93	0.066 ± 0.024	0.57	0.10	not reported
2 a	$C_6H_6^+ \rightarrow C_6H_4^+ + H_2$ $78^+ \rightarrow 76^+ + 2$	1.98	0.25 ± 0.04	4.68	0.23 *	0.35 [3] 0.1–0.4 [4]; 0.01 [5] 0.02 [3]
2 b	$C_4H_4^+ \rightarrow C_4H_2^+ + H_2$ $52^+ \rightarrow 50^+ + 2$	1.97	0.32 ± 0.11	0.64	0.11	0.09 [3] 0.01 [3]
3 a	$C_6H_6^+ \rightarrow C_4H_4^+ + C_2H_2$ $78^+ \rightarrow 52^+ + 26$	26.1	0.031 ± 0.005	1.91	0.36	0.11 [3] 0.05 [5] 0.10 [3]
3 b	$C_6H_5^+ \rightarrow C_4H_3^+ + C_2H_2$ $77^+ \rightarrow 51^+ + 26$	26.0	0.023 ± 0.005	1.17	0.24	[4], no intensity given
3 c	$C_6H_4^+ \rightarrow C_4H_2^+ + C_2H_2$ $76^+ \rightarrow 50^+ + 26$	26.1	0.027 ± 0.005	0.39	0.07	not reported
4	$C_6H_6^+ \rightarrow C_3H_3^+ + C_3H_3$ $78^+ \rightarrow 39^+ + 39$	39.6	0.038 ± 0.009	2.21	0.30	0.06 [5]

Table 1. Summary of metastable ions in benzene. * normal mass 76 intensity corrected for contribution from mass 76.01.

[3] Mass Spectral Data, Amer. Petroleum Institute Research Project 44 [1953].
[4] D. P. Stevenson, Structural Interpretation of Spectra, Technical Report No. 51–61 [1961].
[5] H. M. Rosenstock and M. Krauss, Advances in Mass Spectrometry Vol. 2, Oxford 1963, p. 257.

The electron energy in the molecular beam was usually around 20 eV, although other values between 15 and 55 eV were used occasionally. It had to be high enough to give sufficient intensity, but not so high that the region of direct ionization of the background gas beside the beam extended up to the satellite peak on the energy scale. As the distance between the main peak and the satellite peak is given by $(\Delta m/m) \cdot U_c$, the satellite peak could for small values of $\Delta m/m$ (e. g. $78 \rightarrow 77$) only be sufficiently resolved by use of a U_c as high as 1050 V. Other values for U_c were 670, 570 and 341 V. – The pressure during the runs was between 1.5 and $2.5 \cdot 10^{-7}$ torr.

From Table 1 it is apparent that the metastable intensities can be very high. For mass 77, about 25% of all observed fragment ions were formed between 1.97 and 5.65 μs, so that the satellite peak is very strong, as seen in figure 1. In fact, here the metastable intensity is so high that even the main peak is influenced, its left flank being rounded off to the right, and its right flank being drawn out into the tail. It could be shown that for this reason the center of the mass 77 main peak lies consistently at lower potentials than the mass 78 peak center, which accounts at least in part for the Δm being 7% too low for $78 \rightarrow 77$. Of all the Δm values this one is least influenced by statistical errors.

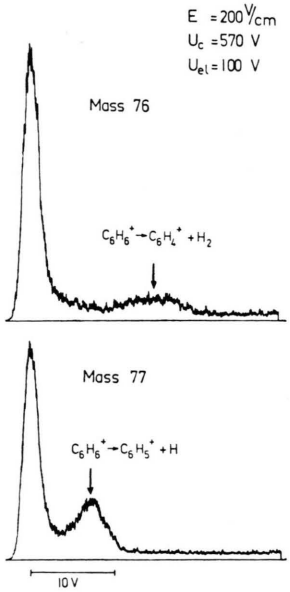

Fig. 1. Two typical satellite peaks showing large metastable intensities.

Considering that in an ordinary mass spectrometer the time of flight from which metastable decomposition fragments are collected is usually several μs long, a comparison of cols. 6 and 7 shows that the metastable intensities reported in the literature are generally too low, presumably due to discrimination as a result of fragmentation energy release [6]. It is conceivable that the present apparatus has much less discrimination of this kind, since between the molecular beam and the condenser entrance slit no ion focusing was applied, and the ion beam had a diameter of about 1 cm in this region.

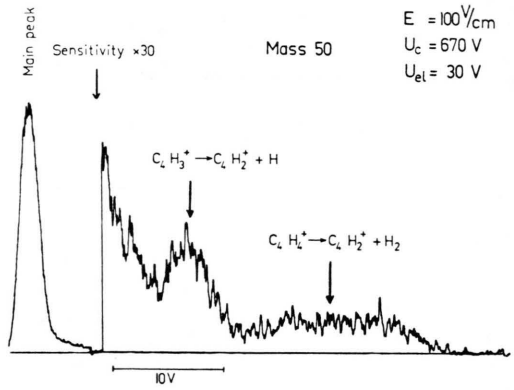

Fig. 2. Two satellite peaks with different fragmentation energy distributions.

According to Table 1, column 4, the fragmentation energies clearly fall into four groups which coincide with the four types of reaction: loss of H, H_2, C_2H_2, and C_3H_3. For the large E_f associated with H_2 loss it is apparent from the shape of the satellite peak that it is rather a crude simplification to describe the fragmentation energy by the single parameter E_f derived from the half-width. The two satellite peaks in figure 2 show qualitatively that large differences in the fragmentation energy distribution exist; the measurements were, however, not detailed enough for a determination of the energy distribution.

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[6] Ch. Ottinger, to be published.