The Decomposition of Benzene and Deuterated Benzenes under Electron Impact

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Metastable transitions have been observed in the mass spectra of benzene, hexadeutero-benzene, 1,4-dideuterobenzene and 1,3,5-trideuterobenzene using a double-focusing mass spectrometer. Decomposition maps have been obtained for each substance and decomposition reactions leading to the production of all significant fragment ions have been suggested. Metastable transitions of several doubly-charged species were found. Loss if identity by the H and D atoms of the partly-deuterated benzenes was observed in metastable transitions in their mass spectra, indicating that rapid isomerization occurs before fragmentation.

The mass spectra of simple, unsubstituted aromatic hydrocarbons such as benzene and naphthalene are characterized by a very intense peak due to the molecular ion together with peaks of much lower intensity due to fragment ions [1]. Peaks arising from doubly-charged ions are much more abundant than in the mass spectra of aliphatic compounds and such ions account for a significant fraction of the total ionization in the mass spectra of many aromatic compounds. The most intense peaks due to fragment ions are frequently those arising from the loss of H or H_2 by the molecular ion, but in the case of benzene, peaks due to ions formed by the loss of C_2H_2 and C_3H_3 are also of moderate intensity.

Attempts to determine the routes by which fragment ions are formed from the molecular ions are hampered by the apparently complete randomization of H and D atoms in partially-deuterated compounds [2] together with very little knowledge of the structure (linear or cyclic) of some of the ions undergoing decomposition. Conclusions based on the cracking pattern produced by 70 V electrons could be in error if a fragment ion is formed by more than one route. More precise information on decomposition processes can be obtained from observations of metastable transitions which allow one to build up a decomposition map for the substance under investigation. Preliminary observations on the metastable transitions in the mass spectrum of benzene [3] have been extended and similar observations on the metastable transitions in the mass spectra of 1,4-dideuterobenzene, 1,3,5-trideuterobenzene and hexadeuterobenzene are now reported.

Experimental

All observations were made on an MS 9 double-focusing mass spectrometer (Associated Electrical Industries Ltd.) using 70 V electrons unless otherwise stated and with a trap current of 90 μA. The source temperature was typically 250 °C and the indicated pressure in the source pumping line was 2×10^{-6} mm Hg although the pressure in the ionization chamber was probably an order of magnitude greater than this. The indicated analyser tube pressure was 8×10^{-7} mm Hg.

Metastable transitions which occur in the field-free region between the electrostatic analyser and the magnetic analyser give rise to peaks which can be observed under normal operating conditions. If $m_1^+ \rightarrow m_2^+$ in this region, a diffuse peak is observed at $m/e = m_2^2/m_1$; if $m_1^{++} \rightarrow m_2^+$, the peak occurs at $m/e = 2\,m_2^2/m_1$ and stretches over a small range of m/e values owing to the release of kinetic energy [4, 5]. These peaks are frequently of low intensity and may be masked by peaks given by normal fragment ions. Most of the observations were therefore made using the field-free region between the source and the electrostatic analyser. If $m_1^+ \rightarrow m_2^+$ in this region, m_2^+ ions are transmitted by the electrostatic analyser only if the accelerating voltage V_0 is increased to $m_1 V_0/m_2$; if $m_1^{++} \rightarrow m_2^+$, V_0 must be altered to approximately $m_1 V_0/2\,m_2$, the m_2^+ ions being transmitted over a small range of voltages owing to the release of kinetic energy [6]. The field across the electrostatic analyser is constant so that the mass

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[1] M. E. Wacks and V. H. Dibeler, J. Chem. Phys. **31**, 1557 [1959].

[2] H. E. Grubb and S. Meyerson, Ch. 10 in "Mass Spectrometry of Organic Ions", Ed. F. W. McLafferty, Academic Press, New York 1963.

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scale is unchanged. Under these conditions, normal fragment ions are not transmitted and so do not interfere; since the observations are made immediately after the ions have been accelerated, this method of observing metastable transitions is extremely sensitive. The range of accelerating voltages which could be applied without breakdown in the source required that

$$m_1^+ < 4\, m_2^+ \quad \text{and} \quad m_1^{++} < 8\, m_2^+ .$$

Benzene ("AnalaR" grade) and hexadeuterobenzene (Ciba Laboratories) were used without further purification. Samples of partly deuterated benzenes were kindly supplied by Professor ALLAN MACCOLL, University College, London.

Results

1. Singly-Charged Ions

a) Benzene

Metastable transitions leading to the formation of all fragment ions found in the mass spectrum of C_6H_6 were investigated, and those giving $C_3 - C_6$ fragment ions as products are summarized in the "decomposition map" shown in Fig. 1. Decompositions leading to C_2 fragment ions are very weak and diffuse, and no decomposition of a singly-charged ion to give CH_3^+ could be detected. Although the direct formation of CH_3^+ from $C_6H_6^+$ could not be ruled out owing to the limited range of accelerating voltages which could be applied, no peak at $m/e = 2.9$ arising from this decomposition was observed under normal operating conditions.

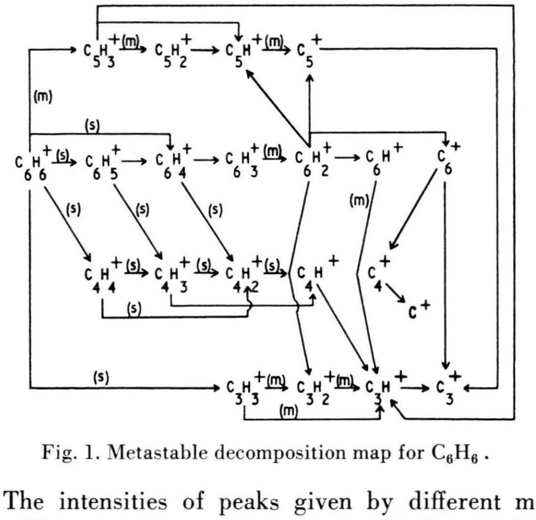

Fig. 1. Metastable decomposition map for C_6H_6.

The intensities of peaks given by different metastable transitions covered a range of about 10^4:1, but since the tuning of the source varies with changes in the accelerating voltage, the relative intensities of these peaks when given by decompositions which occur in the first field-free region are of semi-quantitative significance only. Transitions giving strong (s) and moderately strong (m) signals are shown in Fig. 1, the remaining signals being relatively weak. Peaks observed under normal operating conditions due to decompositions which occur between the two analysers will more nearly reflect the relative intensities of the signals arising from the different transitions, providing that there is no contribution from interfering metastable transitions.

b) Benzene-d_6

A similar investigation was carried out of all metastable transitions leading to fragment ions in the mass spectrum of C_6D_6 and, as expected, these were entirely analogous to those given by C_6H_6. Since the loss of a deuterium atom is more easily detected than the loss of a hydrogen atom because of the lower resolution required, these observations provided useful confirmation of the occurrence of the processes shown in Fig. 1.

c) 1,4-Benzene-d_2

The more prominent metastable transitions in the mass spectrum of this compound were investigated. The expected losses of H, H_2 and D, and HD by various $C_3 - C_6$ ions were observed, but a moderately strong signal was obtained for the process $80^+ \rightarrow 76^+$, indicating that the molecular ion can lose a D_2 molecule. When transitions leading to C_4 fragment ions were investigated using the first field-free region, losses of 26 and 27 amu by C_6 fragment ions and the molecular ion were observed, due to the loss of C_2H_2 and C_2HD molecules. A moderately strong signal was obtained for the process $80^+ \rightarrow 52^+$, indicating that the molecular ion can also lose a C_2D_2 molecule. Metastable transitions which were observed in the range $m/e = 32$ to $m/e = 37$ under normal operating conditions are shown in Fig. 2; the most intense peak is that at $m/e = 35.1$ given by the loss of a C_2HD molecule by the molecular ion, followed closely by that at $m/e = 36.45$ due to the loss of C_2H_2, together with the much weaker peak at $m/e = 33.8$ due to the loss of C_2D_2. Other peaks arise from the loss of acetylene molecules by various C_6 fragment ions or from the loss of H_2, HD and D_2 by C_3 fragment ions.

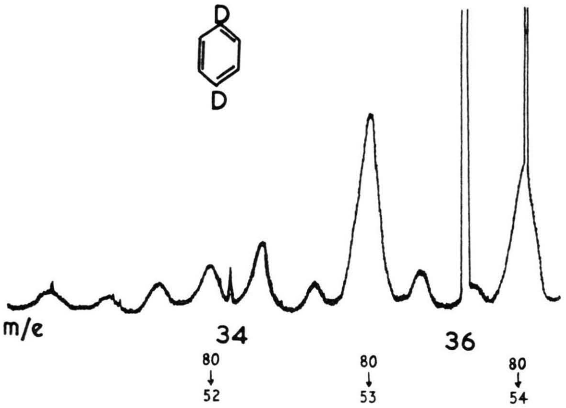

Fig. 2. Metastable transitions in the mass spectrum of 1,4-dideuterobenzene.

Peaks at $m/e = 19.0$, 20.0 and 21.0 were observed under normal operating conditions, arising from the loss of C_3HD_2, C_3H_2D and C_3H_3 respectively by the molecular ion. The intensities of these peaks were in the approximate ratio 1:3:1, and did not vary with the energy of electrons down to 18 V, the lowest energy at which they were studied.

d) 1,3,5-Benzene-d_3

Similar metastable transitions in the mass spectrum of this compound were investigated and the loss of C_2H_2, C_2HD and C_2D_2 by the molecular ion was again observed. The metastable transitions which were observed in the range $m/e = 32$ to $m/e = 38$ under normal operating conditions are shown in Fig. 3. Peaks at $m/e = 37.35$, 36.00 and 34.68 arise from the loss of C_2H_2, C_2HD and C_2D_2 respectively by the molecular ion, that at $m/e = 36.00$ being approximately three times as intense as the other two peaks. Other peaks are again due to the loss of acetylene molecules by various C_6 fragment ions and to the loss of H_2, HD and D_2 by C_3 fragment ions. Under normal operating conditions, further metastable peaks were observed at $m/e = 21.75$, 20.75, 19.77 and 18.80, which arise from the loss of C_3H_3, C_3H_2D, C_3HD_2 and C_3D_3 respectively by the molecular ion. The two central peaks were of equal intensity and were very much more intense than the peaks at $m/e = 21.75$ and 18.80.

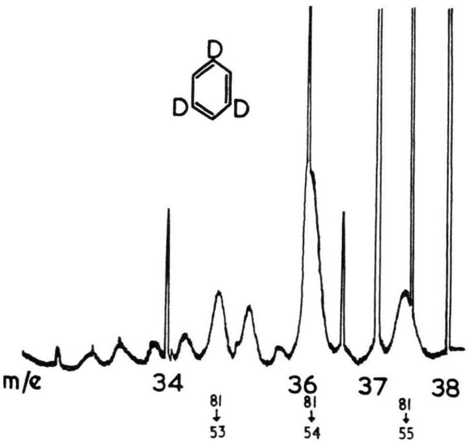

Fig. 3. Metastable transitions in the mass spectrum of 1,3,5-trideuterobenzene.

2. Doubly-Charged Ions

Metastable transitions of doubly-charged ions are of two types:

$$\text{(A)} \quad m_1^{++} \rightarrow m_2^{++} + (m_1 - m_2) \ ,$$

$$\text{(B)} \quad m_1^{++} \rightarrow m_2^{+} + (m_1 - m_2)^{+} \ .$$

Under normal operating conditions, type (A) transitions give rise to GAUSSIAN peaks at $m/e = m_2^2/2\,m_1$, and in some instances, these can be mistaken for peaks arising from metastable transitions of singly-charged ions of mass $m_1^{+}/2$. By making use of the region between the source and electrostatic analyser, evidence was obtained for the occurrence of the transitions

$$C_6H_6^{++} \rightarrow C_6H_5^{++} + H \ , \qquad (1)$$

$$C_6H_5^{++} \rightarrow C_6H_4^{++} + H \ , \qquad (2)$$

$$C_6H_4^{++} \rightarrow C_6H_3^{++} + H \qquad (3)$$

and it seems probable that part of the intensity ascribed to the reaction

$$C_3H_3^{+} \rightarrow C_3H_2^{+} + H \qquad (4)$$

results from the reaction

$$C_6H_6^{++} \rightarrow C_6H_4^{++} + H_2 \ . \qquad (5)$$

However, this transition could still be observed using 15 V electrons, confirming that (4) contributes.

Type (B) transitions are difficult to observe under normal operating conditions since the peaks are usually of low intensity and are frequently masked by peaks due to normal fragment ions. In addition, they extend over several mass numbers owing to the release of kinetic energy, and have maxima at the "wings" of the peaks with a central minimum. If for any reason, only one "wing" of such a peak is observable, this may resemble a normal GAUSSIAN metastable peak and could therefore be wrongly assigned. In the mass spectrum of benzene, two such peaks have been observed at approximately $m/e = 5.8$ and 101.8 due to CH_3^+ and $C_5H_3^+$ ions formed in the process

$$C_6H_6^{++} \rightarrow C_5H_3^+ + CH_3^+ \qquad (6)$$

in which about 2.7 eV of kinetic energy are liberated[5]. By making use of the region between the source and electrostatic analyser, several other metastable transitions of this type have been observed. When the accelerating voltage was exactly $V_0/2$, benzene gave weak signals at $m/e = 74-78$, the most intense being at $m/e = 76$ and 78. These observations suggest that the species $C_6H_2^{++} - C_6H_6^{++}$ pick up an electron either from a slit edge or by a grazing collision in the gas-phase to give singly-charged species of the same mass. At a slightly higher accelerating voltage, $0.506\ V_e$, signals were obtained indicating the loss of H^+ by $C_6H_2^{++} - C_6H_6^{++}$ and $C_5H_2^{++}$, and at $0.509\ V_0$ the loss of H^+ by $C_4H_3^+$ was observed. No case of the loss of H_2^+ was definitely established, although very weak maxima in background signals were observed indicating that $C_6H_4^{++}$ and $C_6H_3^{++}$ may possibly lose H_2^+. Other metastable transitions of type (B) which were unequivocally identified were

$$C_6H_4^{++} \rightarrow C_5H^+ + CH_3^+ \ , \qquad (7)$$

$$C_6H^{++} \rightarrow C_5H^+ + C^+ \ , \qquad (8)$$

$$C_6H_5^{++} \rightarrow C_4H_2^+ + C_2H_3^+ \ . \qquad (9)$$

In addition, there is no doubt that the ions C_3H^+, $C_3H_2^+$ and $C_3H_3^+$ are also formed in the decomposition of C_6 doubly-charged species. Because of the very small change in mass/charge ratio, these ions are transmitted by the electrostatic analyser when the accelerating voltage is very close to that used for normal operation, V_0. The signal due to the $C_3H_3^+$ ion passes through a maximum at $V = 0.960\ V_0$, but a second maximum cannot be observed since the normal signal due to $C_3H_3^+$ ions will mask this. When V_0 is reduced from 8 kV to 4 kV, the maximum occurs at $V = 0.951\ V_0$, confirming that the signal is due to $C_3H_3^+$ ions formed from a doubly-charged species. Two maxima in each of the signals due to $C_3H_2^+$ and C_3H^+ ions are observed at similar voltages and show similar behaviour when V_0 is reduced from 8 kV to 4 kV, indicating that each ion is formed by the decomposition of at least two different doubly-charged species. If the two maxima were two "wings" of the same peak, their separation would increase as V_0 is decreased, whereas the separation remains almost constant and both maxima shift to lower voltage ratios. Attempts to assign the precursors on the basis of these observations were inconclusive.

Very weak signals were observed which could be interpreted as indicating that $C_6H_6^{++}$ decomposes to give $C_4H_4^+$ $(+C_2H_2^+)$ and $C_4H_3^+$ $(+C_2H_3^+)$ ions, but the peaks were very weak and broad and this assignment must be considered to be uncertain.

The loss of CH_3^+ and deuterated analogues by the doubly-charged molecular ions of the partly-deuterated benzenes was investigated. Under normal operating conditions, 1,4-benzene-d_2 gives metastable peaks due to the processes

$$\begin{aligned} C_6H_4D_2^{++} &\rightarrow C_5H_3^+ + CH\,D_2^+ \quad (m/e = 97.9 - 99.5) &(10)\\ &\rightarrow C_5H_2D^+ + CH_2D^+ \quad (m/e = 101.0 - 103.6) &(11)\\ &\rightarrow C_5HD_2^+ + CH_3^+ \quad (m/e = 104.4 - 106.9) &(12)\end{aligned}$$

the intensity ratio of the peaks being 1:3:1 within experimental error. Similarly, 1,3,5-benzene-d_3 gives metastable peaks due to the processes

$$\begin{aligned} C_6H_3D_3^{++} &\rightarrow C_5H_3^+ + CD_3^+ \quad (m/e = 96.6 - 99.0) &(13)\\ &\rightarrow C_5H_2D^+ + CHD_2^+ \quad (m/e = 99.8 - 102.45) &(14)\\ &\rightarrow C_5HD_2^+ + CH_2D^+ \quad (m/e = 102.95 - 105.65) &(15)\\ &\rightarrow C_5D_3^+ + CH_3^+ \quad (m/e = 106.2 - 108.8) &(16)\end{aligned}$$

the intensity ratio of the peaks being 1:9:9:1 within experimental error. The kinetic energy release in each case is close to 2.7 eV as found for benzene.

Discussion

The rate constant, k, for a given decomposition reaction increases in a complicated manner with increase in internal energy of the ion undergoing decomposition[7]. If the internal energy is such that

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$k = 10^5 - 10^6\ \text{sec}^{-1}$, decomposition occurs in the analyser tube and gives rise to a metastable transition. This internal energy lies within closely-defined limits and is the minimum energy leading to a decomposition which can be observed in a mass spectrometer under normal operating conditions. In certain cases, the minimum value of k exceeds $10^6\ \text{sec}^{-1}$ so that no metastable transition is observed. If no metastable transition can be observed for processes yielding a particular fragment ion, it is probable that such ions are formed in a single step from an excited molecular ion possibly formed in a repulsive state. In general, however, provided that the sensitivity is sufficiently high, a metastable transition should be observable for all decomposition reactions contributing to the overall fragmentation process.

The time between the formation and collection of an ion varies approximately as the square root of the mass of the ion so that the recorded mass spectrum is a measure of the relative abundances of different ions at different times after their formation. Similarly, as OTTINGER [8] has pointed out, the observed intensities of metastable transitions must be corrected for the different times taken by ions of different mass to traverse the field-free region. Since the relationship between the number of ions decomposing and the rate constant k characterising their decomposition is unknown, this correction is not readily made. This, together with uncertainties in intensities arising from slight variations in instrumental conditions, prohibits any precise quantitative interpretation of relative intensities of metastable transitions from being made. Even if corrections could be made, the intensities of different metastable transitions could not be simply related to the relative probabilities of different processes occurring in the source ($k > 10^6\ \text{sec}^{-1}$) since the relationships between population, k, and internal energies for different decomposition reactions are unknown.

Twelve metastable transitions in the mass spectrum of benzene were listed by OTTINGER [8], together with seven others which were suspected but could not be detected. The present work considerably extends the number of metastable transitions observed, and confirms the occurrence of five of the seven processes suspected by OTTINGER. In view of the great stability of the benzene molecular ion, it is unlikely that the minimum value of k will exceed $10^6\ \text{sec}^{-1}$ for any process, so that the decomposition map shown in Fig. 1, together with the decompositions of doubly-charged species, should provide a fairly complete picture of the way in which benzene breaks down under electron impact. The results confirm that the singly-charged molecular ion undergoes at least five decomposition reactions; since the appearance potentials of these fairly intense metastable transitions range from 5.1 – 7.4 eV [9], MELTON and ROSENSTOCK suggest [10] that the decompositions take place from isolated sets of electronic states between which radiationless transitions cannot occur.

In general, the strongest metastable transitions were those in which H, H_2 or C_2H_2 was the species lost; those in which a fragment containing an odd number of carbon atoms was lost were usually much weaker, with the exception of the loss of C_3H_3 by the molecular ion. Almost all ions decompose by two or more routes: the $C_6H_2^+$ ions is unusual since in addition to the expected loss of H and H_2, metastable transitions indicating the loss of CH, CH_2 and C_3 were also observed. Since only one route was observed leading to the formation of the $C_6H_2^+$ ion, it is unlikely that it is formed in several electronic states and the five decomposition reactions are presumably in competition with each other. Alternatively, two or more isomeric forms of the $C_6H_2^+$ ion may be formed and undergo different decomposition reactions. Four reactions were observed in which the species C_3 was lost, suggesting that this may be a fairly common process.

The results obtained for the decomposition of doubly-charged species show that high kinetic energy CH_3^+ ions are formed in the decomposition of both $C_6H_6^{++}$ and $C_6H_4^{++}$ ions, although in the latter case, the signal was too weak for the kinetic energy release to be measured. Although no processes yielding $C_2H_2^+$ or $C_2H_3^+$ ions from singly-charged species could be found, in agreement with OTTINGER's findings, the formation of $C_2H_3^+$ by the decomposition of $C_6H_5^{++}$ occurs and provides a route by which C_2 fragment ions may be formed. As BEYNON and FONTAINE [11] have pointed out, the liberation of about 2.7 eV in reaction (6) suggests that the $C_6H_6^{++}$ ion is a straight chain ion rather than a cyclic ion,

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although it is impossible to assign a detailed structure to the ion.

The fragmentation of partially-deuterated aromatic compounds appears to involve the more or less complete randomization of H and D atoms prior to fragmentation. McDonald and Shannon [12] have shown that the relative intensities of fragment ions in the mass spectrum of 1,2,3-trideuterobenzene are best explained on this basis. It is to be expected that randomization will decrease as the internal energy of the molecular ion decreases in which case the ions in which this is least likely to occur are those giving rise to metastable transitions. However, as the results given above for 1,4-dideuterobenzene and 1,3,5-trideuterobenzene show, randomization appears to occur even in these ions. The internal energies possessed by these ions are from about 5 – 7 eV and it seems probable that rapid isomerization processes may occur which randomize the H and D atoms, since the 4.5 eV available from a mercury resonance lamp is sufficient to isomerize benzene and many alkylbenzenes [13, 14]. Ionized forms of fulvene, prismane or "Dewar" benzene, or of the radical precursors recently postulated [15], could all be present in the ionization chamber and rapid 1,2- and 1,3-shifts could lead to loss of identity of individual H and D atoms.

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Untersuchungen zur Emission positiver Sekundärionen aus festen Targets. Die Brauchbarkeit der Ionenbeschuß-Ionenquelle in der Massenspektroskopie *

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If solids are bombarded by ions, positive secondary ions (SI) of all elements of the target material are emitted. The mass analysis of these SI permits conclusions to be drawn about the composition of the target material. An arrangement based upon this kind of ion production is called an ion-bombardment ion source.

In this paper it was investigated whether or not this ion source is suitable for quantitative analysis of solids by mass spectrometry. For this purpose the SI yield γ^+ of 27 elements was measured at constant bombardment conditions (12 keV A^+-ions, 45° incidence). γ^+ is approximately 1% for 10 elements — Si, Mn, Fe, Co, Ni, Rh, Ta, W, Os, and U. Aluminium shows the largest, gold the smallest SI yield. Yields differ by a factor of 1000 for different elements. The influence of the ionization energy on the SI yield is discussed. The yield is independent of the concentration in the range 0.02 – 20%.

Die Reinheitsforderungen der Festkörperphysik sind in den letzten 10 Jahren um Größenordnungen gestiegen. Neue Verfahren zur Herstellung ultrareiner Substanzen sowie Verfahren zum Nachweis der restlichen Verunreinigungen wurden entwickelt. Eines dieser empfindlichen Nachweisverfahren bedient sich der Massenspektroskopie.

Die Arbeitsweise dieses Verfahrens besteht darin, von der zu untersuchenden Probensubstanz Ionen zu erzeugen, diese mit Hilfe elektrischer und magnetischer Felder nach Massen zu trennen und die Ionen zur Bestimmung ihrer Masse und ihrer Häufigkeit nachzuweisen.

Die hauptsächliche Schwierigkeit dieses Analyseverfahrens liegt heute noch bei der Ionenerzeugung. Sie ist durch die Forderung gegeben, daß die Zusammensetzung des Ionenstrahls repräsentativ für die Zusammensetzung der untersuchten Probe sein soll. Zur Zeit sind alle kommerziellen Massenspektrographen für die Festkörperanalyse mit der Hoch-

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* Ergebnisse der Dissertation von H. E. Beske, Universität Mainz.

** Jetzt Kernforschungsanlage Jülich des Landes Nordrhein-Westfalen.