Vorlesung
„Molekulare Analytik und Spektroskopie“

Röntgenbeugung und Massenspektroskopie

L. Grill, Sommersemester 2019

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Termine:

Mo 3.6.2019	8:15 – 10:00	HS E (TU)
Fr 7.6.2019	13:30 – 15:00	HS 10.11 (Uni)
Fr 14.6.2019	13:30 – 15:00	HS 10.11 (Uni)
Mo 24.6.2019	8:15 – 10:00	HS E (TU)

Vorlesungsunterlagen: https://chemie.uni-graz.at/de/pc-tc/lehre/

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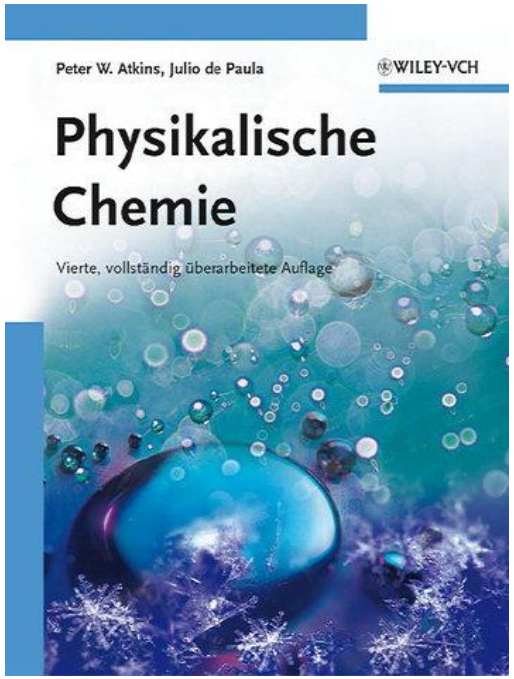
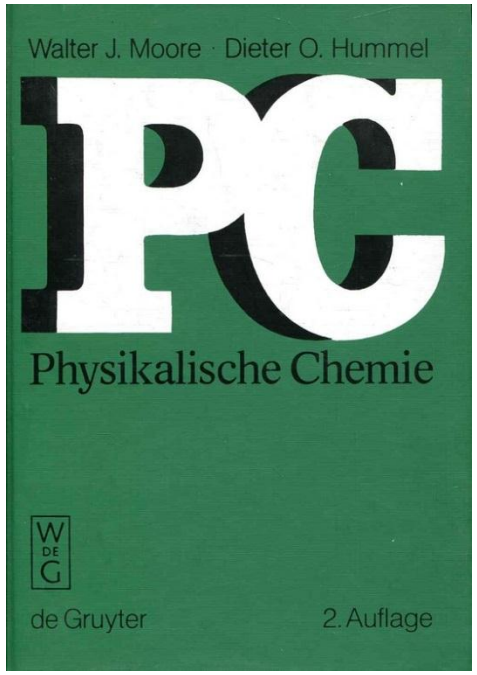
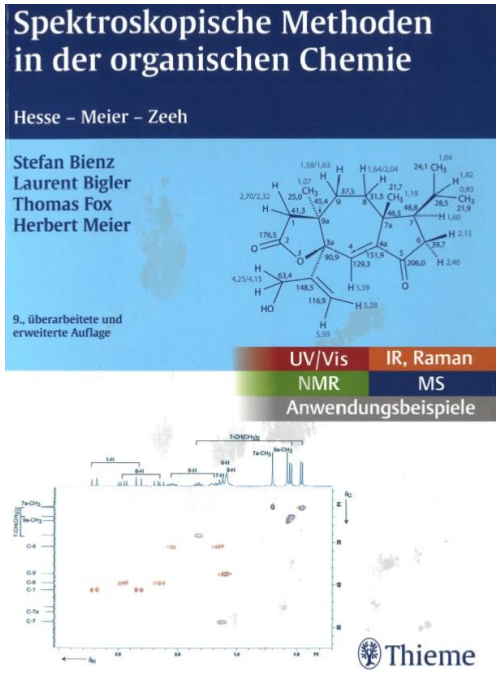
Literatur



Atkins, de Paula
Physikalische Chemie
Wiley



Moore
Physikalische Chemie
de Gruyter



Hesse, Meier, Zeeh
Spektroskopische Methoden in der organischen Chemie
Thieme

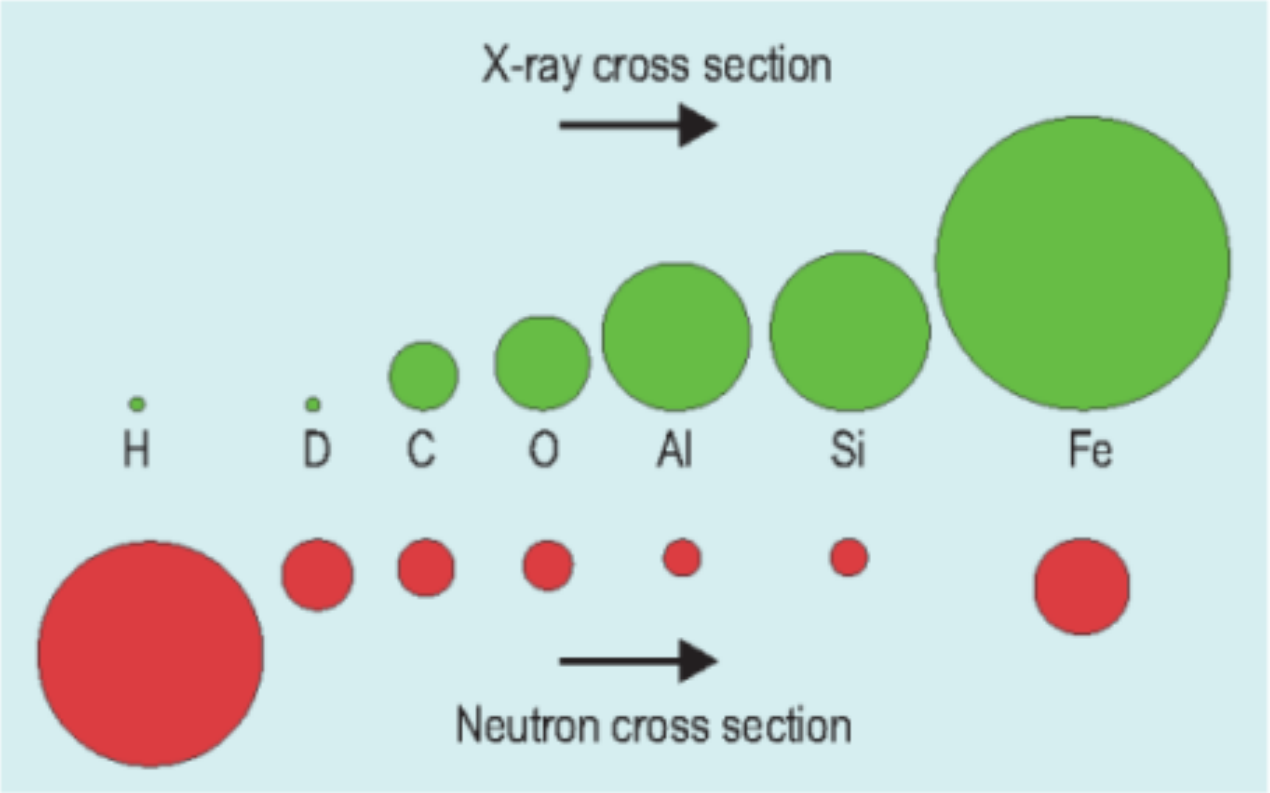
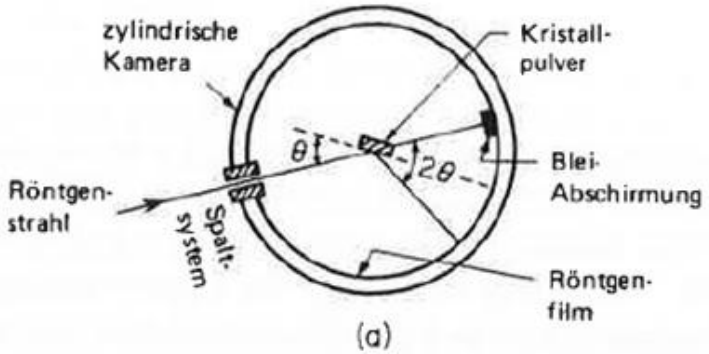
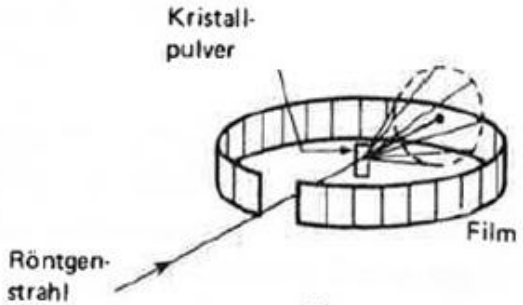


Fig. 2. Neutron and x-ray scattering cross-sections compared. Note that neutrons penetrate through Al much better than x rays do, yet are strongly scattered by hydrogen.

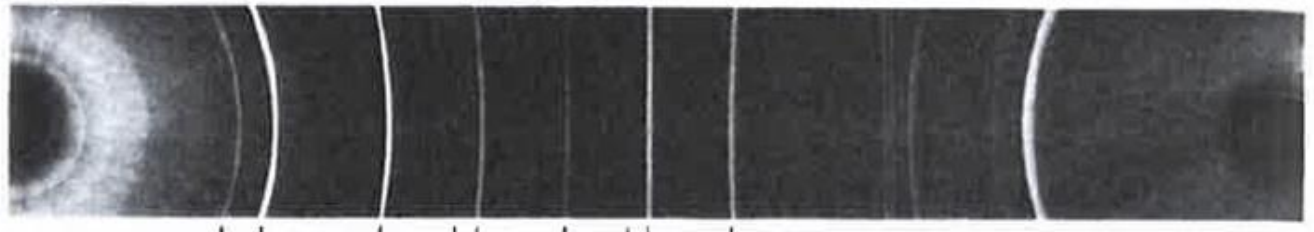
Quelle: Neutron Imaging Facility at BT-6, National Institute of Standards and Technology (NIST)



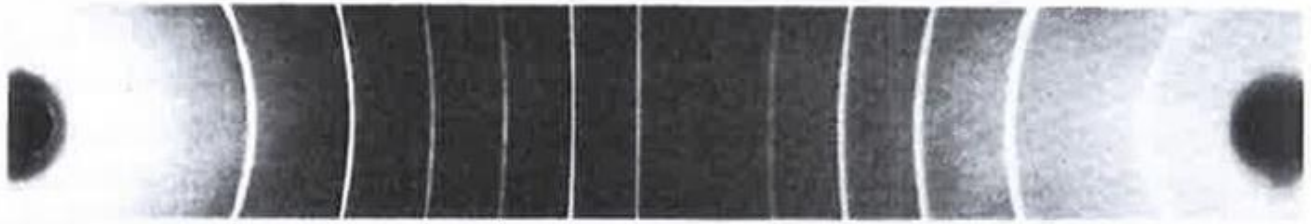
(a)



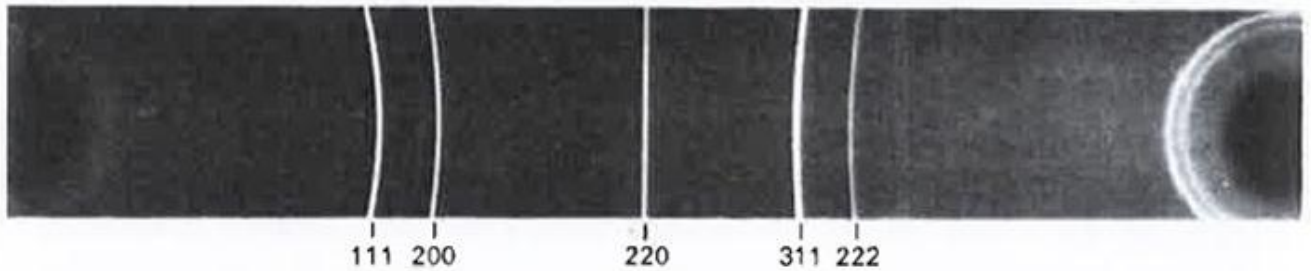
(b)



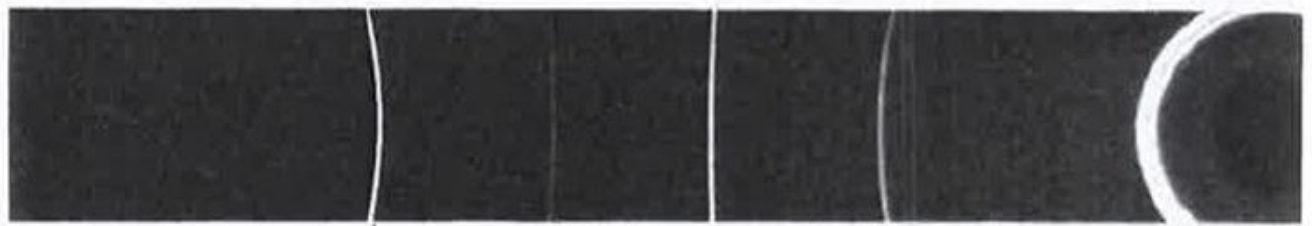
Natrium-chlorid



Kalium-chlorid



Kupfer



Eisen

Quelle: Physikalische Chemie (Moore)

equipment, and to Dr. G. E. R. Deacon and the captain and officers of R.R.S. *Discovery II* for their part in making the observations.

[1] Young, F. B., Gerrard, H., and Jevons, W., *Phil. Mag.*, **40**, 149 (1920).

[2] Longuet-Higgins, M. S., *Mon. Not. Roy. Astro. Soc., Geophys. Suppl.*, **5**, 285 (1949).

[3] Von Arx, W. S., Woods Hole Papers in Phys. Oceanog. Meteor., **11** (3) (1950).

[4] Ekman, V. W., *Arkiv. Mat. Astron. Fysik. (Stockholm)*, **2** (11) (1905).

MOLECULAR STRUCTURE OF NUCLEIC ACIDS

A Structure for Deoxyribose Nucleic Acid

We wish to suggest a structure for the salt of deoxyribose nucleic acid (D.N.A.). This structure has novel features which are of considerable biological interest.

A structure for nucleic acid has already been proposed by Pauling and Corey[1]. They kindly made their manuscript available to us in advance of publication. Their model consists of three intertwined chains, with the phosphates near the fibre axis, and the bases on the outside. In our opinion, this structure is unsatisfactory for two reasons: (1) We believe that the material which gives the X-ray diagrams is the salt, not the free acid. Without the acidic hydrogen atoms it is not clear what forces would hold the structure together, especially as the negatively charged phosphates near the axis will repel each other. (2) Some of the van der Waals distances appear to be too small.

Another three-chain structure has also been suggested by Fraser (in the press). In his model the phosphates are on the outside and the bases on the inside, linked together by hydrogen bonds. This structure as described is rather ill-defined, and for this reason we shall not comment on it.

This figure is purely diagrammatic. The two ribbons symbolize the two phosphate–sugar chains, and the horizontal rods the pairs of bases holding the chains together. The vertical line marks the fibre axis

We wish to put forward a radically different structure for the salt of deoxyribose nucleic acid. This structure has two helical chains each coiled round the same axis (see diagram). We have made the usual chemical assumptions, namely, that each chain consists of phosphate diester groups joining β-D-deoxyribofuranose residues with 3′,5′ linkages. The two chains (but not their bases) are related by a dyad perpendicular to the fibre axis. Both chains follow right-handed helices, but owing to the dyad the sequences of the atoms in the two chains run in opposite directions. Each chain loosely resembles Furberg's[2] model No. 1; that is, the bases are on the inside of the helix and the phosphates on the outside. The configuration of the sugar and the atoms near it is close to Furberg's 'standard configuration', the sugar being roughly perpendicular to the attached base. There is a residue on each chain every 3·4 A. in the z-direction. We have assumed an angle of 36° between adjacent residues in the same chain, so that the structure repeats after 10 residues on each chain, that is, after 34 A. The distance of a phosphorus atom from the fibre axis is 10 A. As the phosphates are on the outside, cations have easy access to them.

The structure is an open one, and its water content is rather high. At lower water contents we would expect the bases to tilt so that the structure could become more compact.

The novel feature of the structure is the manner in which the two chains are held together by the purine and pyrimidine bases. The planes of the bases are perpendicular to the fibre axis. They are joined together in pairs, a single base from one chain being hydrogen-bonded to a single base from the other chain, so that the two lie side by side with identical z-co-ordinates. One of the pair must be a purine and the other a pyrimidine for bonding to occur. The hydrogen bonds are made as follows: purine position 1 to pyrimidine position 1; purine position 6 to pyrimidine position 6.

If it is assumed that the bases only occur in the structure in the most plausible tautomeric forms (that is, with the keto rather than the enol configurations) it is found that only specific pairs of bases can bond together. These pairs are: adenine (purine) with thymine (pyrimidine), and guanine (purine) with cytosine (pyrimidine).

In other words, if an adenine forms one member of a pair, on either chain, then on these assumptions the other member must be thymine; similarly for guanine and cytosine. The sequence of bases on a single chain does not appear to be restricted in any way. However, if only specific pairs of bases can be formed, it follows that if the sequence of bases on one chain is given, then the sequence on the other chain is automatically determined.

It has been found experimentally[3,4] that the ratio of the amounts of adenine to thymine, and the ratio of guanine to cytosine, are always very close to unity for deoxyribose nucleic acid.

It is probably impossible to build this structure with a ribose sugar in place of the deoxyribose, as the extra oxygen atom would make too close a van der Waals contact.

The previously published X-ray data[5,6] on deoxyribose nucleic acid are insufficient for a rigorous test of our structure. So far as we can tell, it is roughly compatible with the experimental data, but it must be regarded as unproved until it has been checked against more exact results. Some of these are given in the following communications. We were not aware of the details of the results presented there when we devised our structure, which rests mainly though not entirely on published experimental data and stereochemical arguments.

It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material.

Full details of the structure, including the conditions assumed in building it, together with a set of co-ordinates for the atoms, will be published elsewhere.

We are much indebted to Dr. Jerry Donohue for constant advice and criticism, especially on interatomic distances. We have also been stimulated by a knowledge of the general nature of the unpublished experimental results and ideas of Dr. M. H. F. Wilkins, Dr. R. E. Franklin and their co-workers at King's College, London. One of us (J.D.W.) has been aided by a fellowship from the National Foundation for Infantile Paralysis.

J. D. Watson
F. H. C. Crick

Medical Research Council Unit for the Study of the Molecular Structure of Biological Systems,
Cavendish Laboratory, Cambridge.
April 2.

[1] Pauling, L., and Corey, R. B., *Nature*, **171**, 346 (1953); *Proc. U.S. Nat. Acad. Sci.*, **39**, 84 (1953).

[2] Furberg, S., *Acta Chem. Scand.*, **6**, 634 (1952).

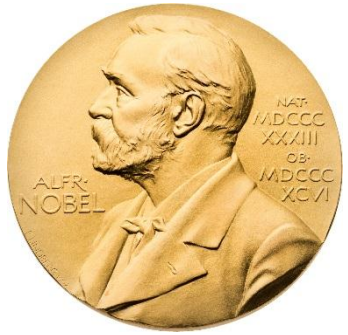
[3] Chargaff, E., for references see Zamenhof, S., Brawerman, G., and Chargaff, E., *Biochim. et Biophys. Acta*, **9**, 402 (1952).

[4] Wyatt, G. R., *J. Gen. Physiol.*, **36**, 201 (1952).

[5] Astbury, W. T., Symp. Soc. Exp. Biol. 1, Nucleic Acid, 66 (Camb. Univ. Press, 1947).

[6] Wilkins, M. H. F., and Randall, J. T., *Biochim. et Biophys. Acta*, **10**, 192 (1953).

The Nobel Prize in Physiology or Medicine 1962

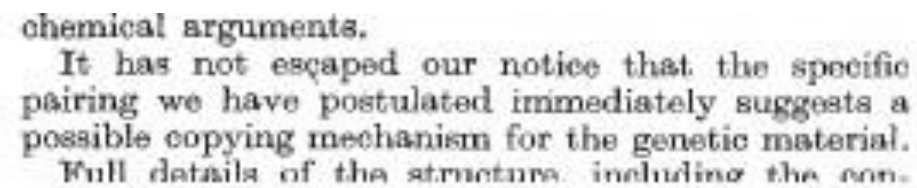


Francis Harry Compton Crick
Prize share: 1/3

James Dewey Watson
Prize share: 1/3

Maurice Hugh Frederick Wilkins
Prize share: 1/3

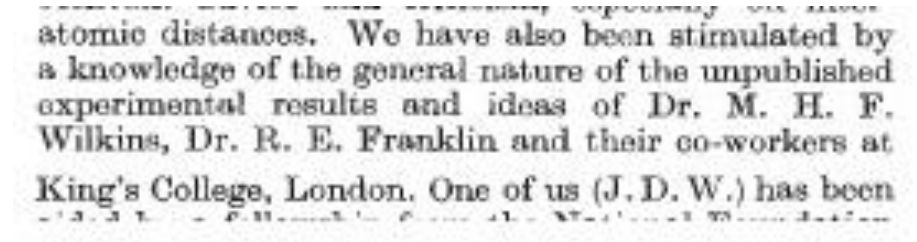
The Nobel Prize in Physiology or Medicine 1962 was awarded jointly to Francis Harry Compton Crick, James Dewey Watson and Maurice Hugh Frederick Wilkins *"for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material"*.



chemical arguments.

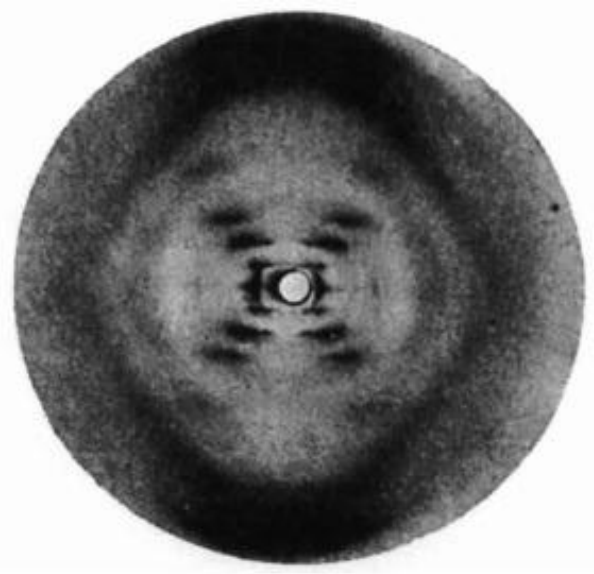
It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material.

Full details of the structure, including the con-

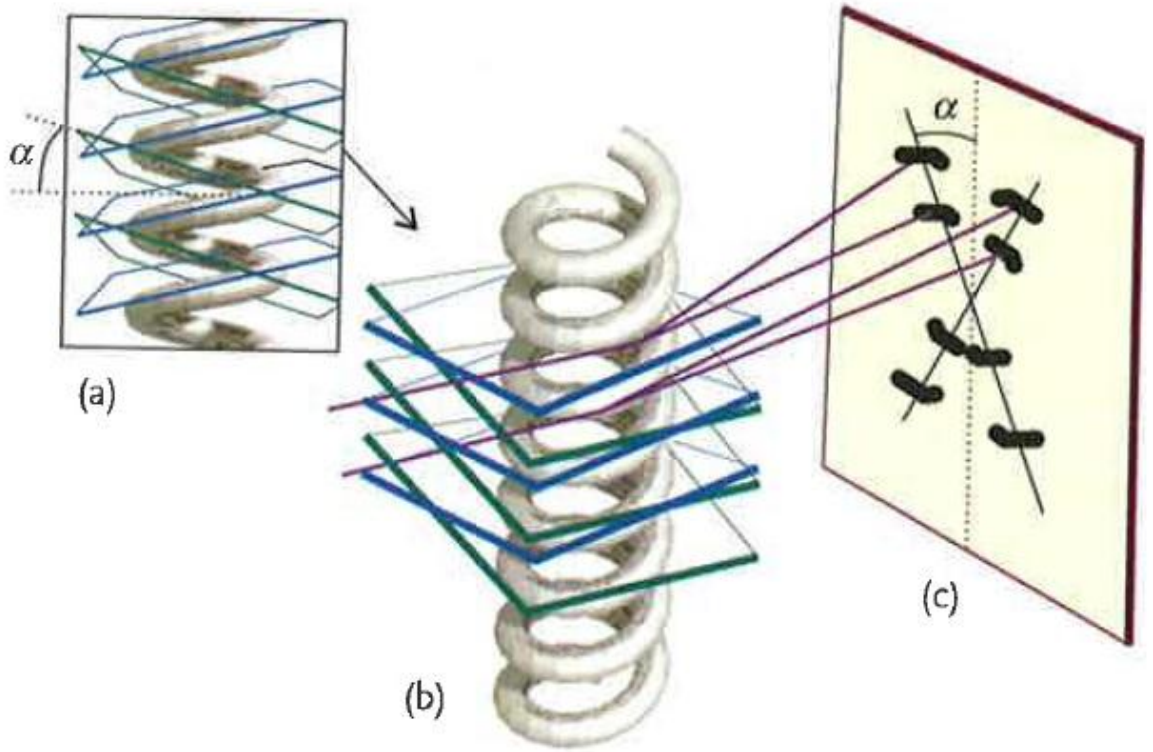


atomic distances. We have also been stimulated by a knowledge of the general nature of the unpublished experimental results and ideas of Dr. M. H. F. Wilkins, Dr. R. E. Franklin and their co-workers at King's College, London. One of us (J.D.W.) has been

DNA in Röntgenbeugung



R. E. Franklin and R. E. Gosling, Acta Cryst. 6, 672 (1953)



Source: Atkins/de Paula, Physikalische Chemie

Tab. 4.1 Atommassen einiger wichtiger Elemente, deren natürliche Isotope mit natürlicher Häufigkeit und exakten Massen, sowie Klassifizierung[1]

Element	Atommasse	nominale Masse	Isotopen	rel. Häufigkeit (%)	isotopische Massen	Klassifizierung
H	1.00794	1	^{1}H $^{2}H = D$	99.985 0.015	1.007825 2.0141102	X **X + 1**
Li	6.941	7	^{6}Li ^{7}Li	7.5 92.5	6.015123 7.016005	**X – 1** X
B	10.811	11	^{10}B ^{11}B	19.9 80.1	10.012938 11.009305	**X – 1** X
C	12.011	12	^{12}C ^{13}C	98.90 1.10	12.000000 13.003355	X **X + 1**
N	14.00674	14	^{14}N ^{15}N	99.634 0.366	14.003074 15.000109	X **X + 1**
O	15.9994	16	^{16}O ^{17}O ^{18}O	99.762 0.038 0.200	15.994915 16.999131 17.999159	X X + 1 **X + 2**
F	18.998403	19	^{19}F	100	18.998403	X
Na	22.989768	23	^{23}Na	100	22.989770	X
Si	28.0855	28	^{28}Si ^{29}Si ^{30}Si	92.23 4.67 3.10	27.976928 28.976496 29.973772	X X + 1 **X + 2**
P	30.973762	31	^{31}P	100	30.973763	X
S	32.066	32	^{32}S ^{33}S ^{34}S ^{35}S	95.02 0.75 4.21 0.02	31.972072 32.971459 33.967868 35.967079	X X + 1 **X + 2** X + 3
Cl	35.4527	35	^{35}Cl ^{37}Cl	75.77 24.23	34.968853 36.965903	X **X + 2**
Ar	39.948	40	^{36}Ar ^{38}Ar ^{40}Ar	0.337 0.063 99.600	35.967546 37.962732 39.962383	X – 4 X – 2 X
Fe	55.847	56	^{54}Fe ^{56}Fe ^{57}Fe ^{58}Fe	5.8 91.72 2.2 0.28	53.939612 55.934939 56.935396 57.933278	**X – 2** X X + 1 X + 2

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh

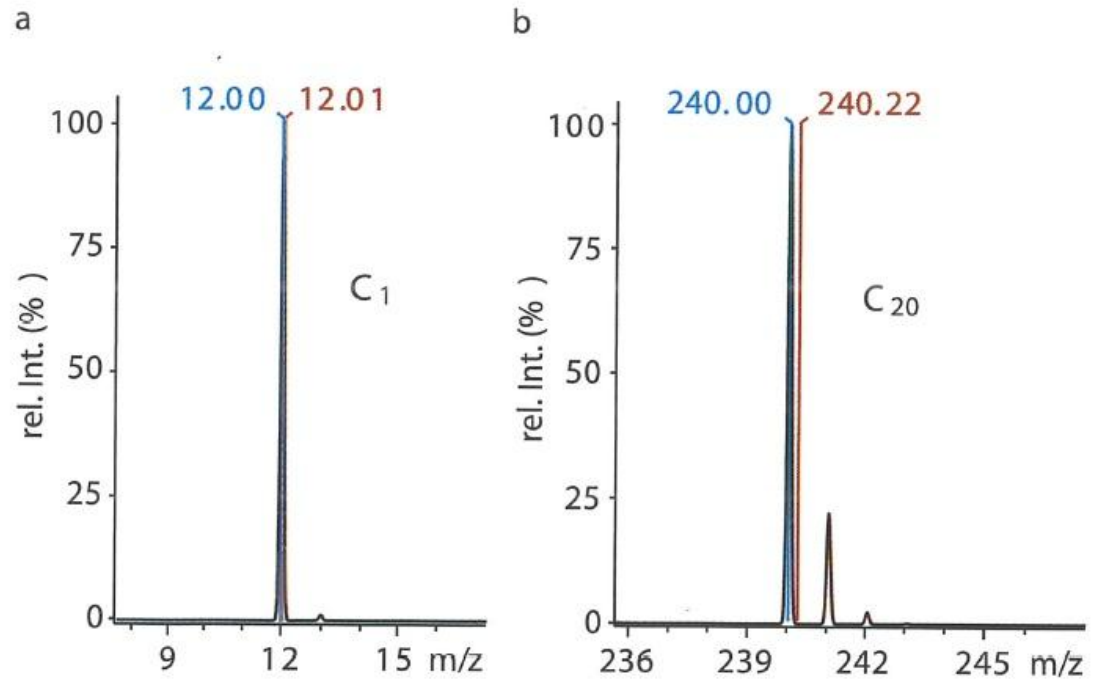


Abb. 4.8 Einfluss der Anzahl C-Atome auf die Isotopenverteilung bei großen Molekülen anhand der berechneten $M^{+\bullet}$ Spektren hypothetischer C_n-Verbindungen (blau: monoisotopische Masse, rot: Lage der Molmasse (M_R))

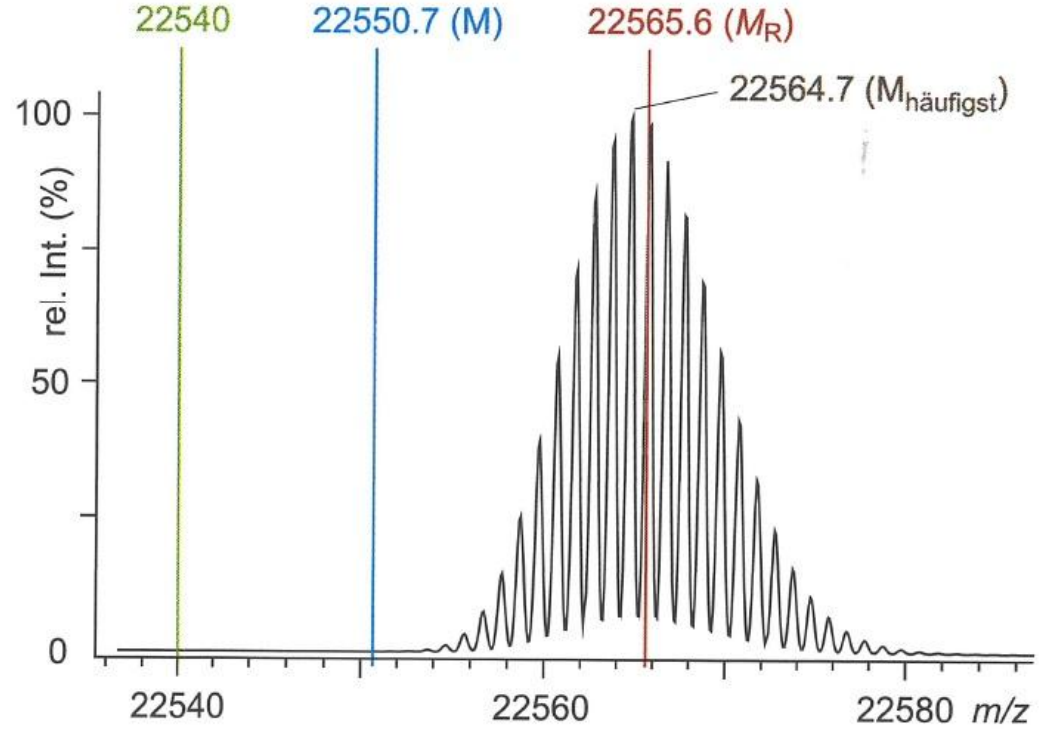


Abb. 4.9 Berechnete Isotopenverteilung für das Ion eines hypothetischen Biopolymers (Peptid) mit der Summenformel $C_{1000}H_{1500}N_{280}O_{290}S_{15}$ (blau: monoisotopische Masse (M), rot: Molmasse (M_R) die ungefähr der häufigsten Masse ($M_{häufigst}$) entspricht, grün: Nominalmasse

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh

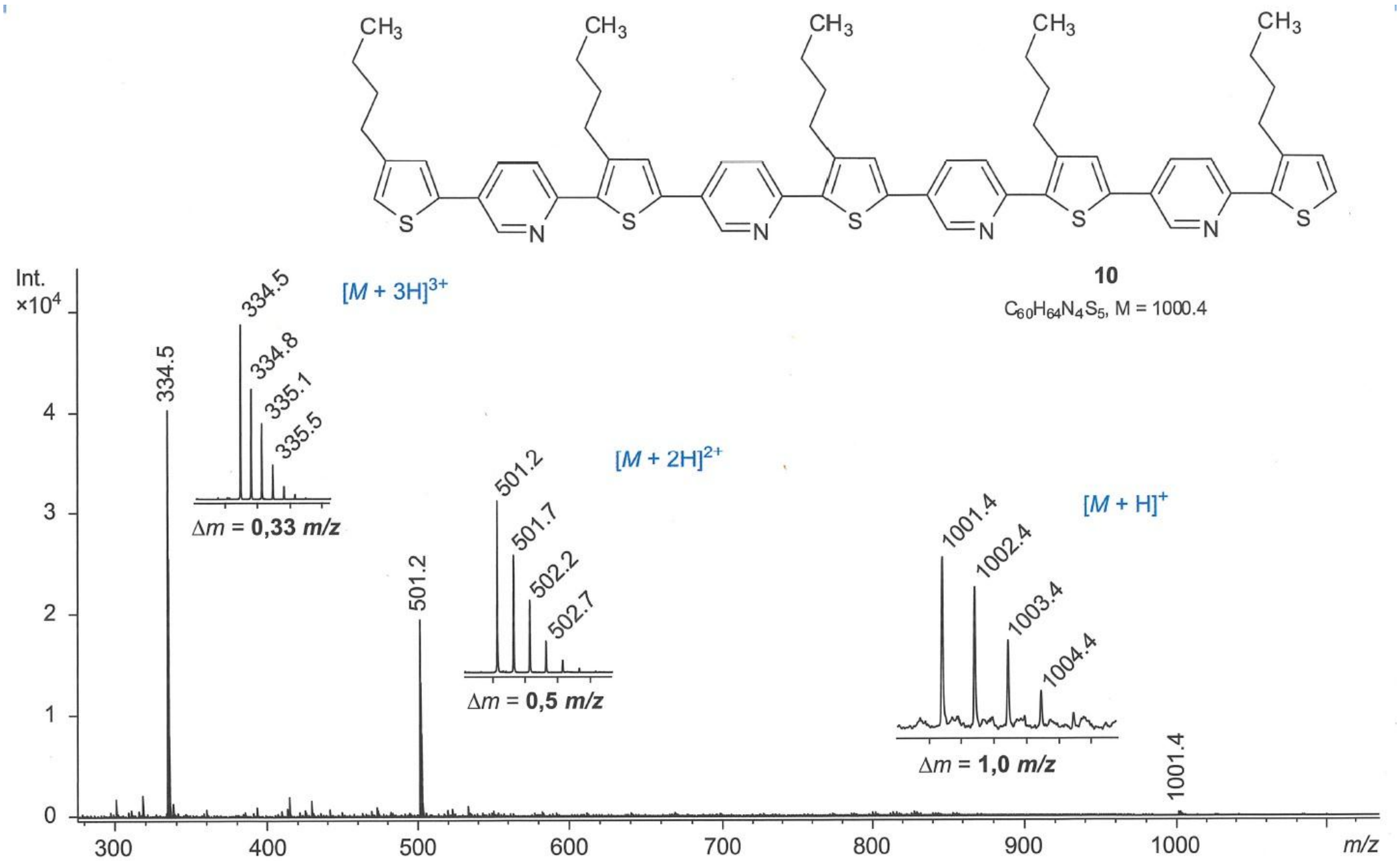
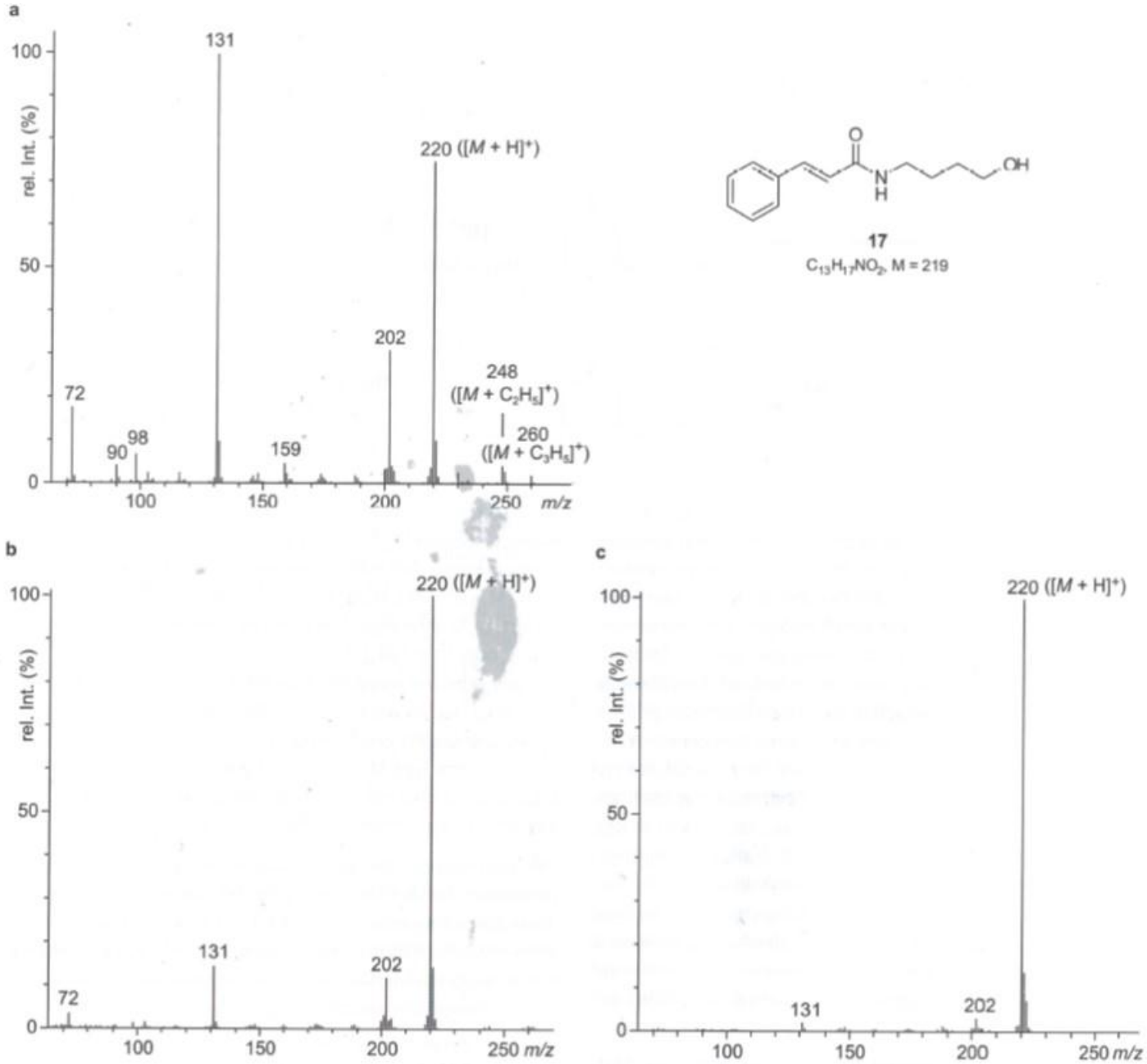


Abb. 4.10 ESI-MS der Verbindung **10** mit Signalen für Ionen des Typs $[M + H]^+$, $[M + 2H]^{2+}$ und $[M + 3H]^{3+}$ (Probe von N. Finney, Universität Zürich)

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh



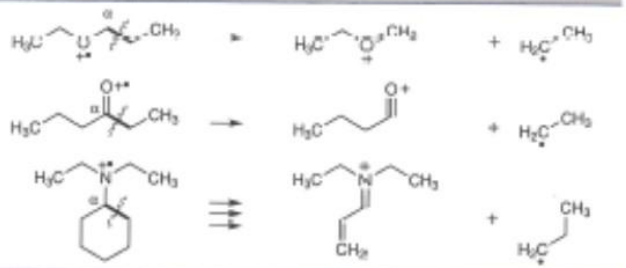
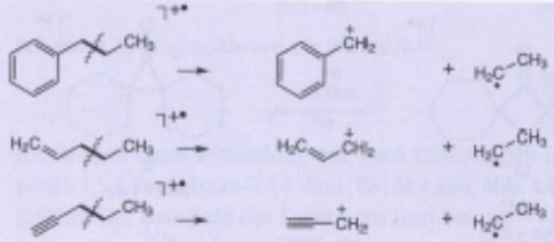
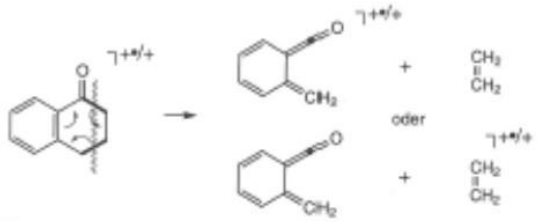
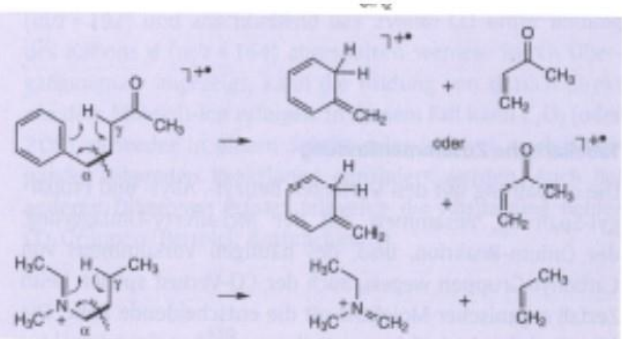
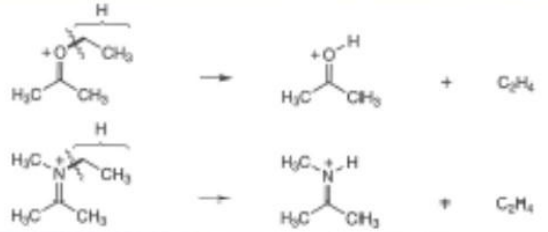
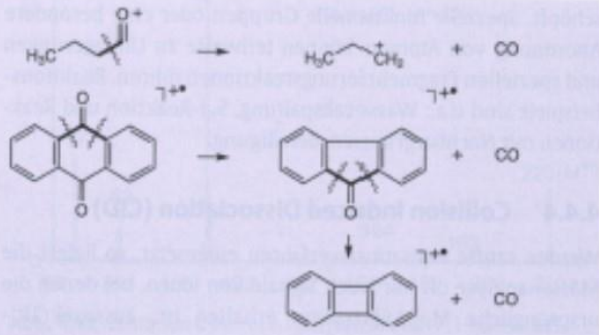
17

$C_{13}H_{17}NO_2$, M = 219

Abb. 4.21 CI-MS von *N*-Cinnamoyl-4-aminobutanol (**17**; Probe von M. Hesse, Universität Zürich) mit (a) CH_4, (b) Isobutan und (c) NH_3 als Reaktandgas

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh

Tab. 4.8 Zusammenfassung der Hauptfragmentierungsreaktionen in der EI-MS

Typ/Bezeichnung	Ausgangs-Ion	Wiederholung des gleichen Reaktionstyps	Beispiel
α-Spaltung Radikalprozess *Voraussetzung* Ein Radikalkation mit Lokalisierung des Radikals auf einem Heteroatom (N, O, S, seltener Halogen)	Molekül-Ion und radikalische Fragment-Ionen	nein	
Benzyl- und Allyl-Spaltung Radikalprozess *Voraussetzung* Ein Benzyl-, Allyl- oder Propargyl-gebundener Substituent	Molekül-Ion und radikalische Fragment-Ionen	nein	
retro-Diels-Alder-Reaktion (RDA) Neutralprozess *Voraussetzung* Ein 6-gliedriger alicyclischer oder heterocyclischer Ring mit mindestens einer Doppelbindung	Molekül- und Fragment-Ionen	ja	
McLafferty-Umlagerung Neutralprozess *Voraussetzung* Ein zu einer Doppelbindung γ-ständiges H-Atom	Molekül- und Fragment-Ionen	ja	
Onium-Reaktion Neutralprozess *Voraussetzung* Ein Alkyl-Substituent (außer Methyl) an einem die Ladung tragenden Heteroatom wie N (Immonium), O (Oxonium) etc.	Fragment-Ionen	ja	
CO-Verlust Neutralprozess *Voraussetzung* Cyclische Carbonyl-Verbindungen (Ketone, Chinone), Ketoformen cyclischen Enole, Phenolen; Metallcarbonyle; Carbonylhaltigen Fragmentionen (z.B. Acylium-Ionen aus α-Spaltung von Carbonyl- und Carboxyl-Verbindungen)	Molekül- und Fragment-Ionen	ja	

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh