

Strukturaufklärung in der molekularen anorganischen Chemie

14. Massenspektrometrie

Prinzip

Prinzip der Massenspektrometrie:

Trennung schneller gasförmiger Ionen nach Masse und Ladung

Informationen aus der MS:

- Molekülmasse
- Elementarzusammensetzung (Summenformel)
- Strukturinformationen

MS ist keine spektroskopische Methode! (→ Massenspektrometrie)

- beruht nicht auf der WW von elektromagnetischer Strahlung mit Materie
- elektromagnetische Strahlung ist nicht die Informationsquelle
- ist „nicht-konservativ“ (Probe wird bei der Messung zerstört)

Massenspektrometrie

Wechselwirkung mit Strahlung:

- (Optische/Radio) Spektroskopie
- Streuung/Diffraktion
- Resonanzmethode
- Elektrische Methode
- Ionisation

Probe Beeinflussung:

- Destruktiv
- Nicht destruktiv

Anwendung:

- Identifizierung/Sauberkeit
- Elementaranalyse
- Chemische Gruppen
- Chemische Konnektivität
- Konformations-Eigenschaften
- Symmetrie
- Geometrie (Längen, Winkel)
- Schwingungen
- Elektronische Struktur (/Dichte)
- (Elektrische) Dipolmomente

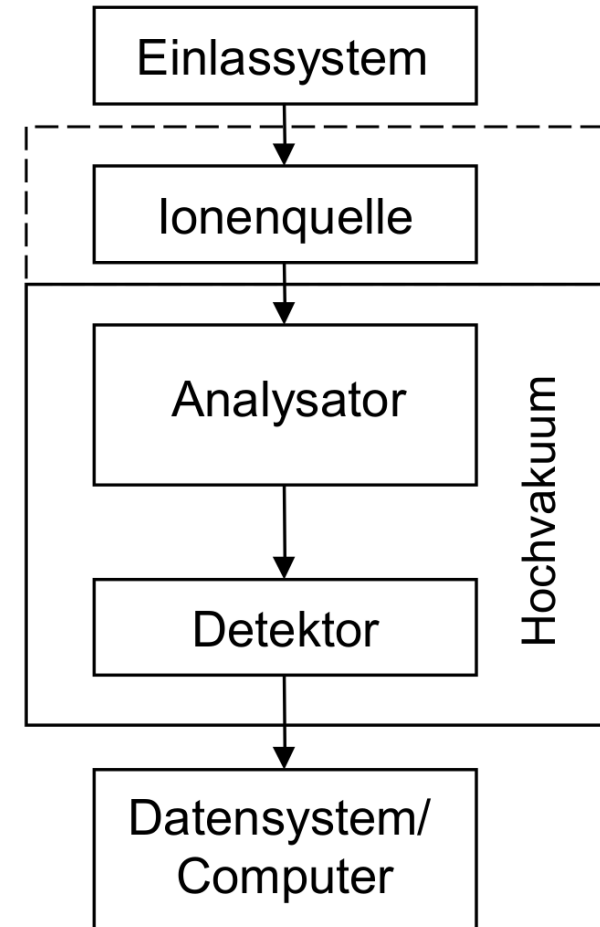
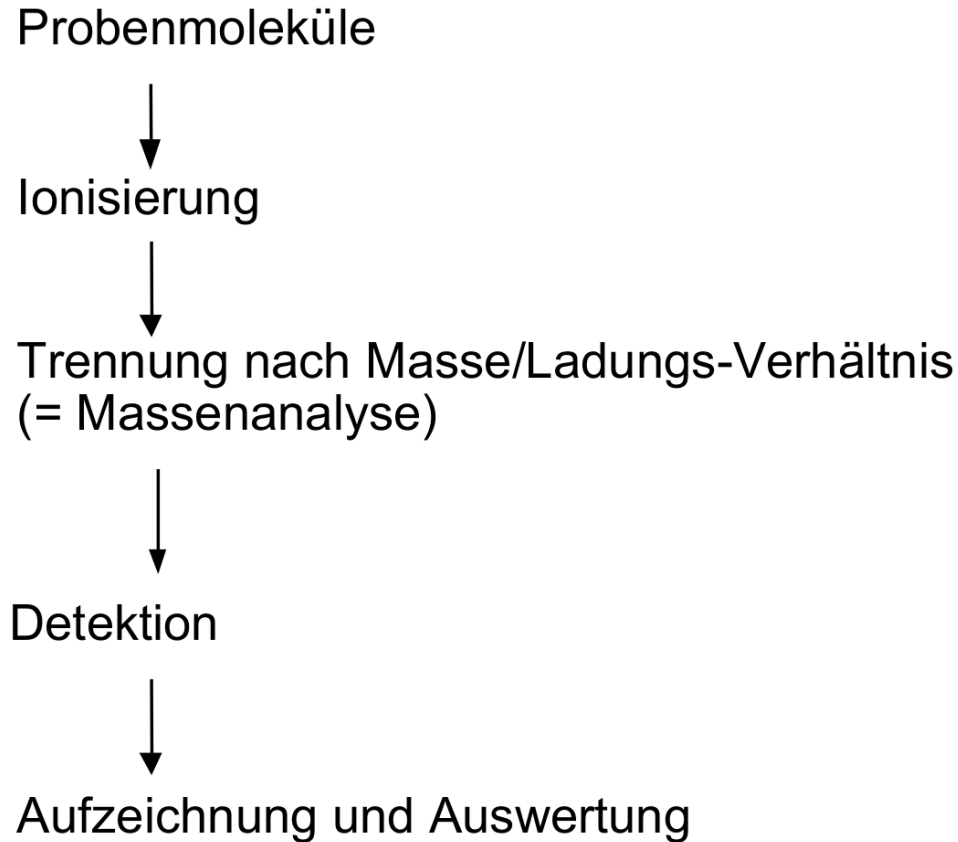
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

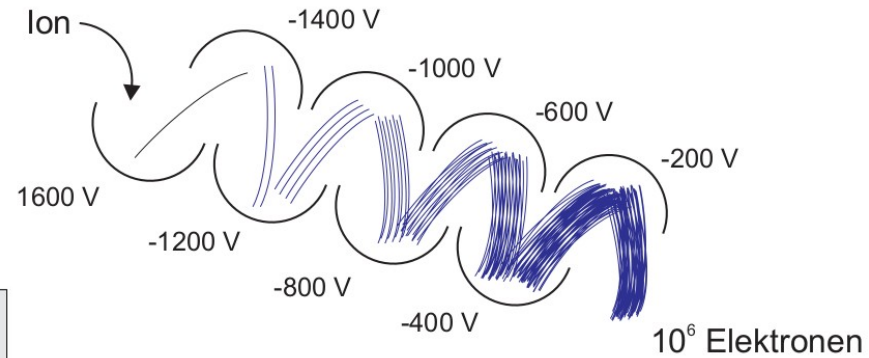
- Gas
- Flüssigkeit
- Feststoff

MS-Experiment



Sektorfeld-Massenspektrometer

Sekundärelektronen-Vervielfacher (SEV) →



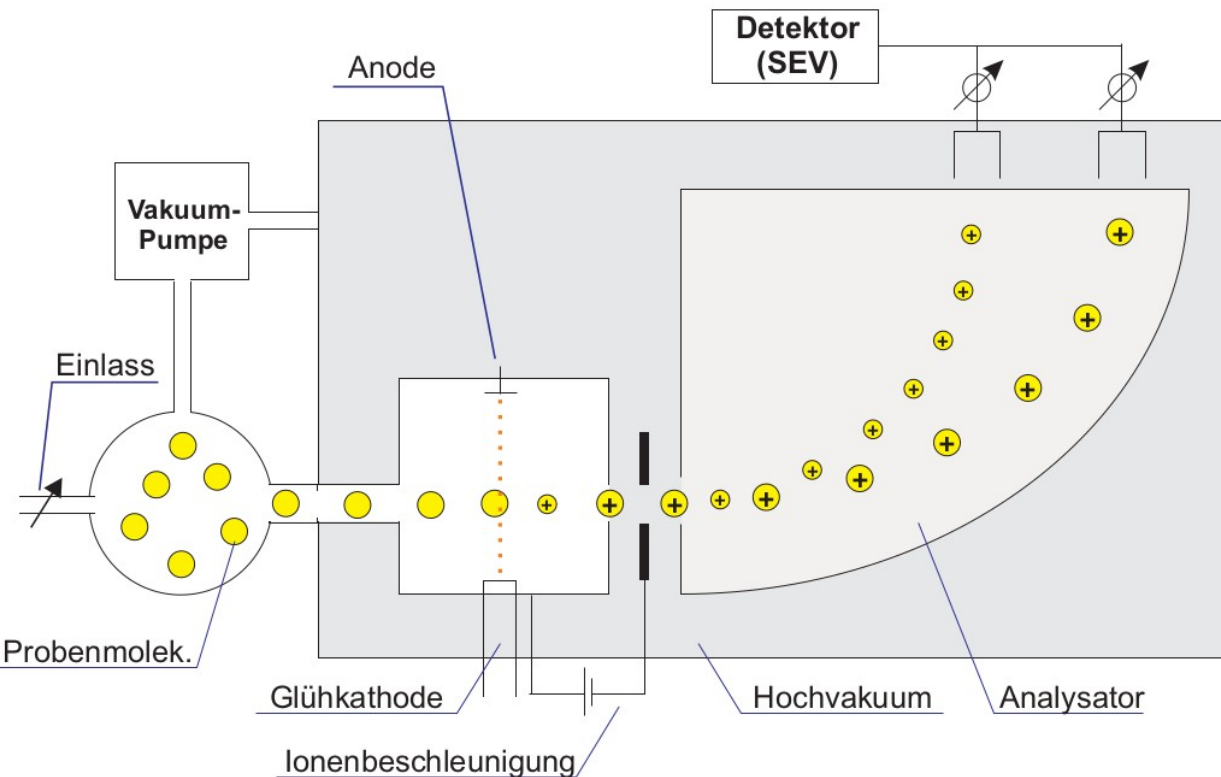
$$r = \sqrt{\frac{m}{z} \cdot \frac{2U_B}{B^2}}$$

$$\frac{m}{z} = \frac{r^2 B^2}{2U_B}$$

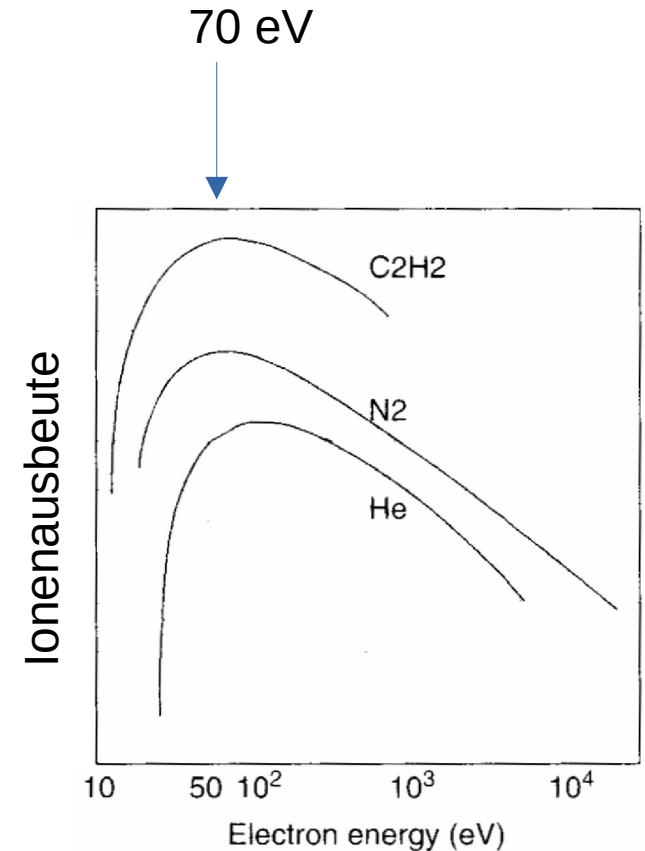
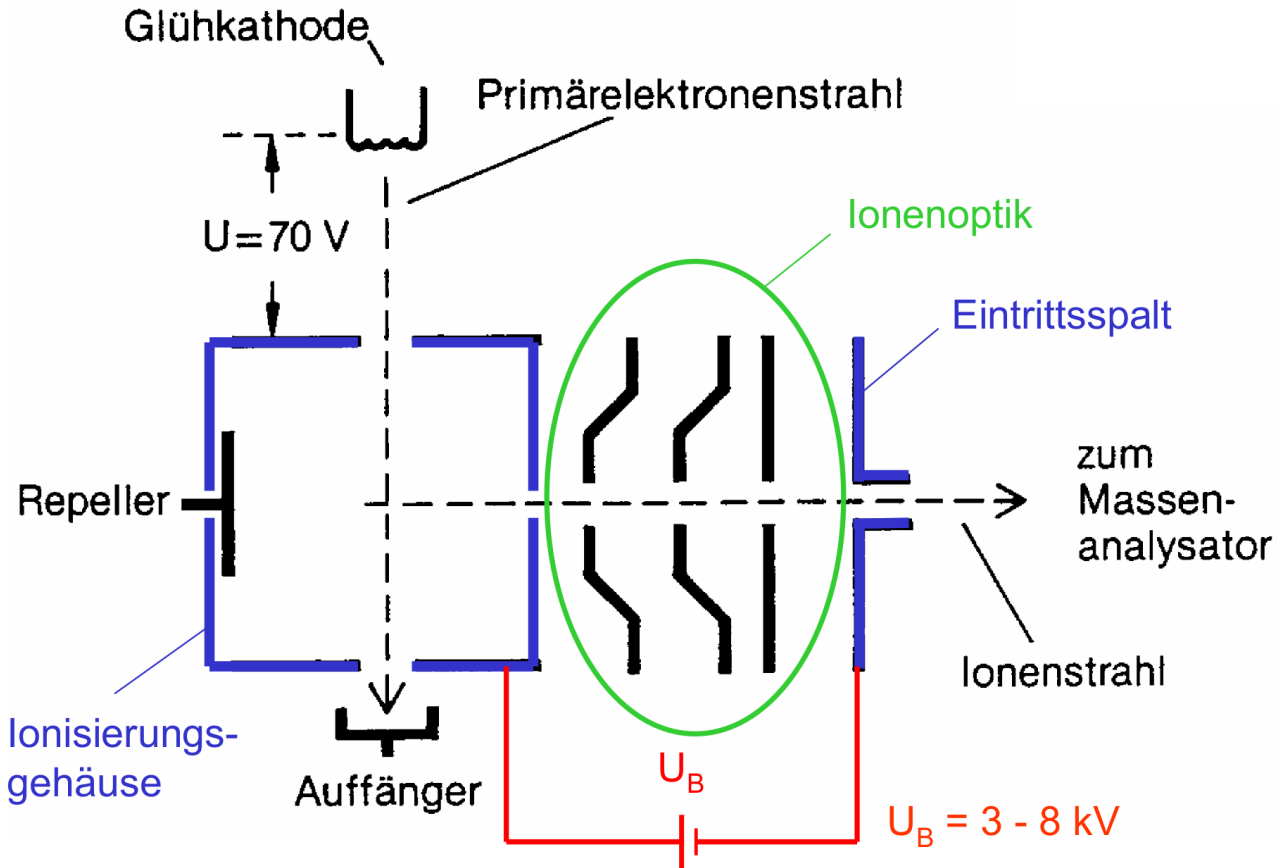
U_B – Beschleunigungsspannung

B – Magnetfeldstärke

r – Ablenkradius



Elektronenstoß-Ionisation



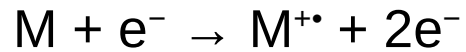
EI-MS

γ -ray	Hard X-ray	Soft X-ray	Vacuum UV	Near UV	Visible blue red	Near IR	Mid IR	Far IR	Sub-mmwave	mm-wave	Micro-wave	Radio-wave	
$\leftarrow < 0.1 \text{ \AA}$	5 \AA	100 \AA	2000 \AA			0.7 \mu m	2.5 \mu m	25 \mu m		1 mm		10 cm	$\rightarrow \lambda$
		10 nm	200 nm	400 nm	700 nm	2500 nm							
$> 10^9$	2×10^7	10^6	5×10^4	2.5×10^4	1.4×10^4	4000	400			10		0.1	$\tilde{\nu} / \text{cm}^{-1}$
1.2×10^7	2.4×10^5	1200	600	300	170	48	4.8			0.12		1.2×10^{-3}	$E / \text{kJ mol}^{-1}$
$120\,000$	2400	120	6	3	1.7	0.5	0.05			0.001		0.00001	E / eV
3×10^{19}	6×10^{17}	3×10^{16}	1.5×10^{15}	7.5×10^{14}	4×10^{14}	1.2×10^{14}	1.2×10^{13}			3×10^{11}		3×10^9	ν / Hz

EI-MS: 10-300 eV

(Vgl. mit GED: elastische vs. inelastische Wechselwirkung)

Elektronenstoß-Ionisation



Ionisation



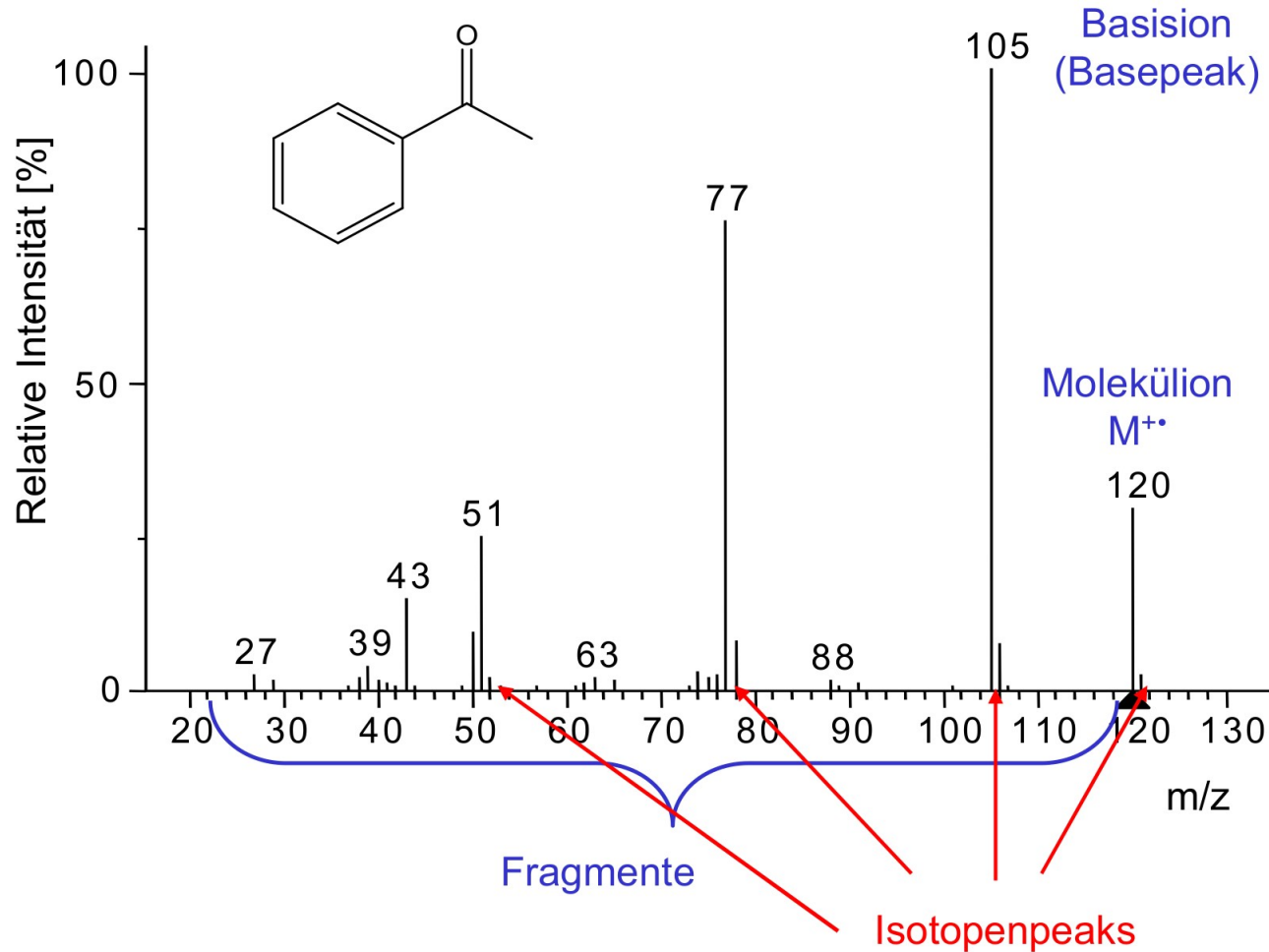
Fragmentierung in Ion und Radikal



Neutralverlust

A^+ und $C^{+\bullet}$ \rightarrow weitere Fragmentierungen

EI-Massenspektrum



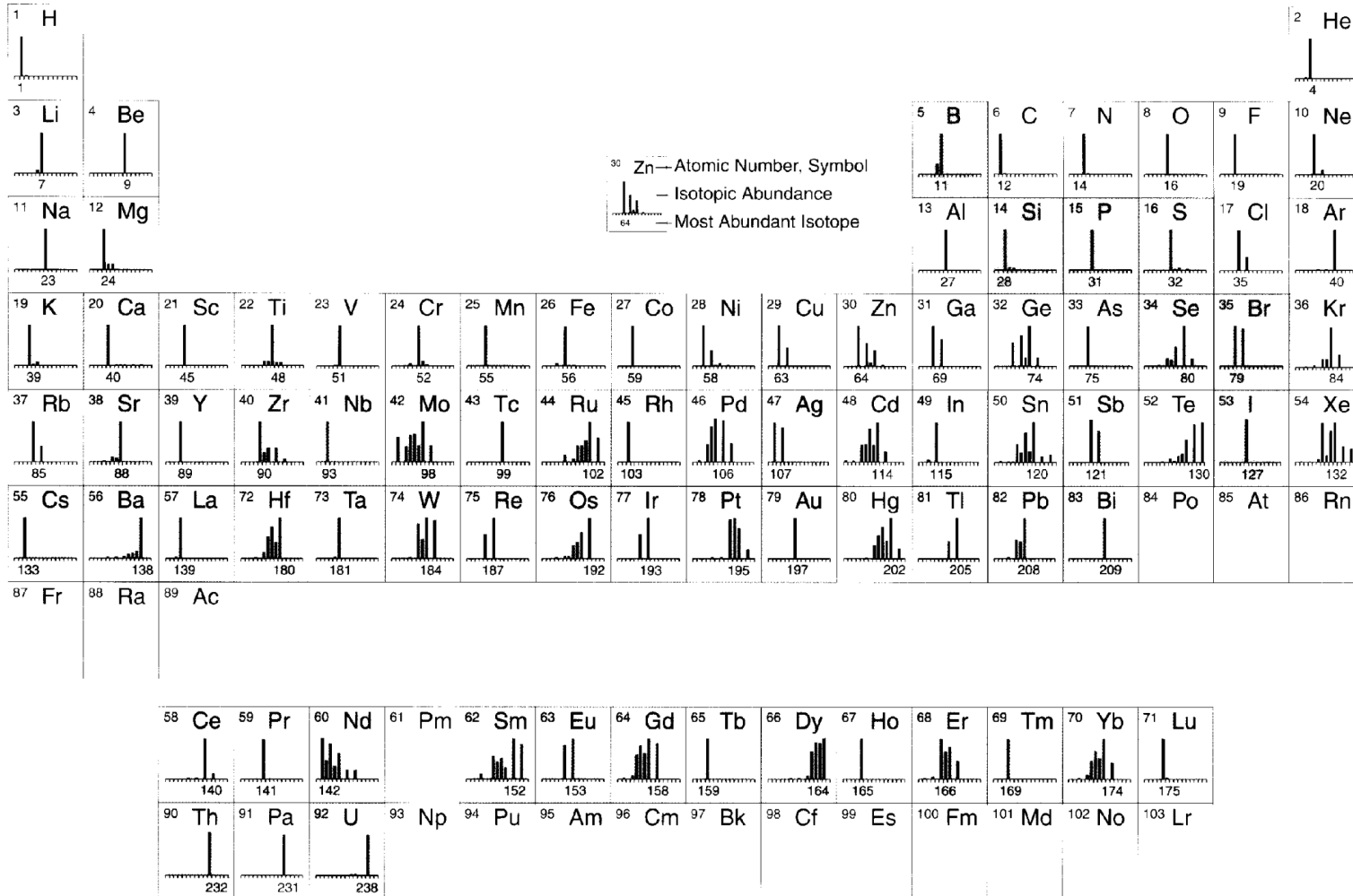
Acetophenon

C_8H_8O

$M = 120$

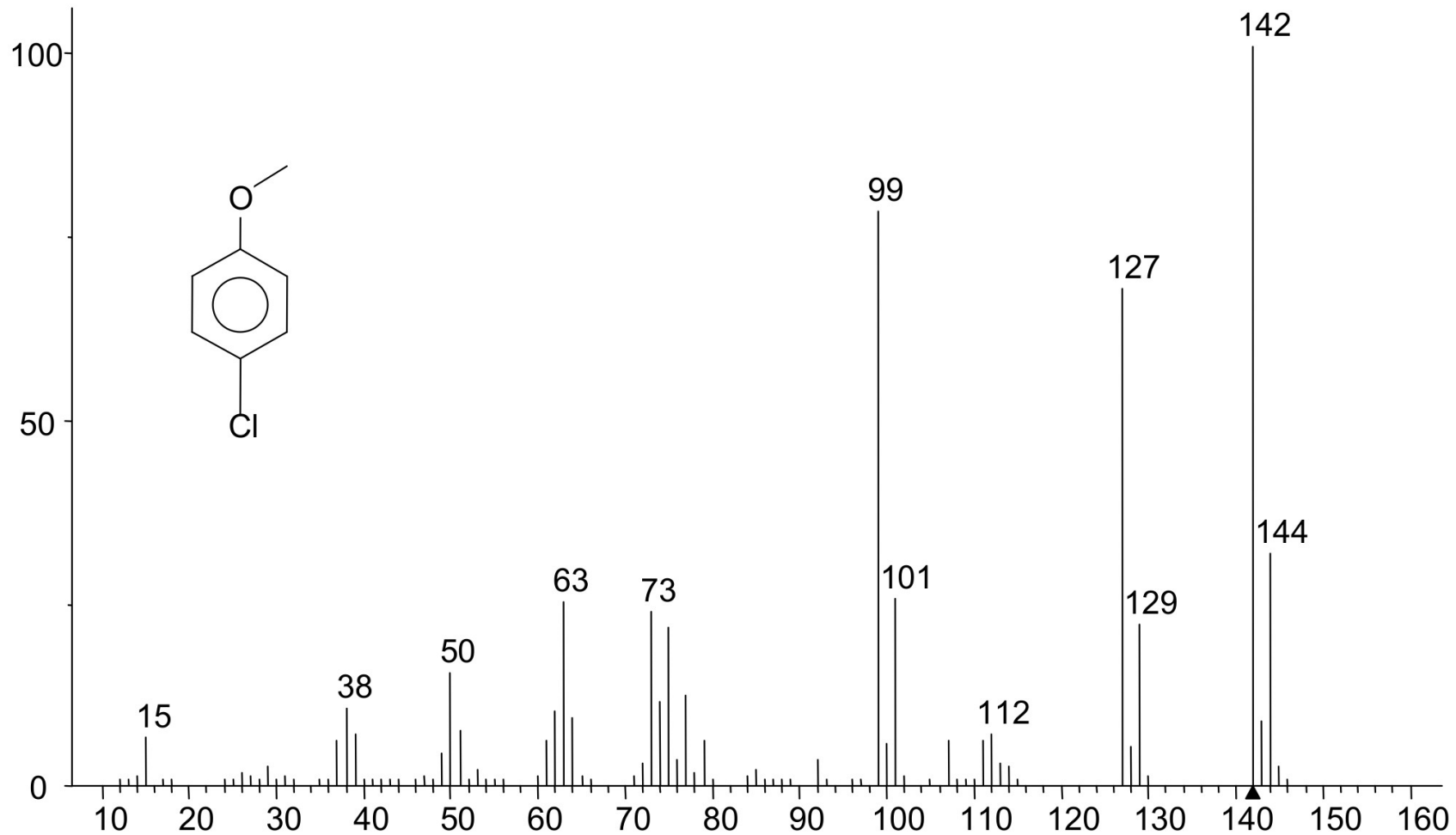
Spektreninterpretation

Isotopie der Elemente

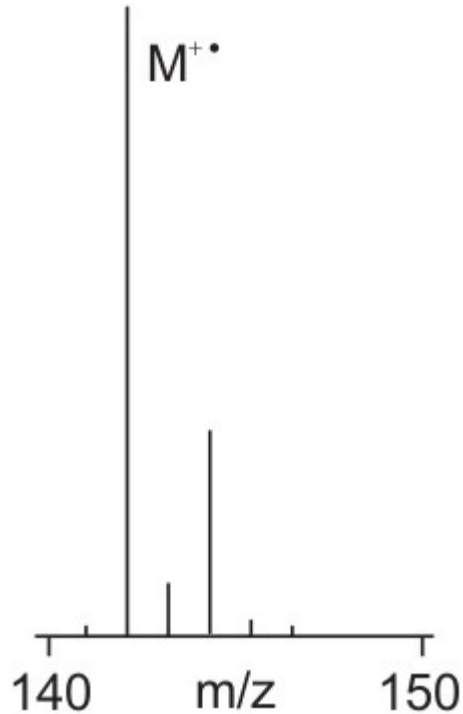


Element	Massenzahl	Rel. Häufigkeit in %	Exakte Masse [amu]	Chemisches Atomgewicht [g/mol]
H	1	99,99	1,007825	1,0079
D	2	0,01	2,014102	
C	12	98,93	12,000000	12,0107
	13	1,07	13,003355	
N	14	99,63	14,003074	14,0067
	15	0,37	15,000109	
O	16	99,76	15,994915	15,9994
	17	0,04	16,999132	
	18	0,21	17,999160	
F	19	100,00	18,998403	18,9984
Si	28	92,23	27,976927	28,0855
	29	4,68	28,976495	
	30	3,09	29,973770	
P	31	100,00	30,973762	30,9738
S	32	94,93	31,972071	32,0660
	33	0,76	32,971459	
	34	4,29	33,967867	
	36	0,02	35,967081	
Cl	35	75,78	34,968853	35,4527
	37	24,22	36,965903	
Br	79	50,69	78,918338	79,9040
	81	49,31	80,916291	
I	127	100,00	126,904468	126,9045

EI-MS von p-Chloranisol

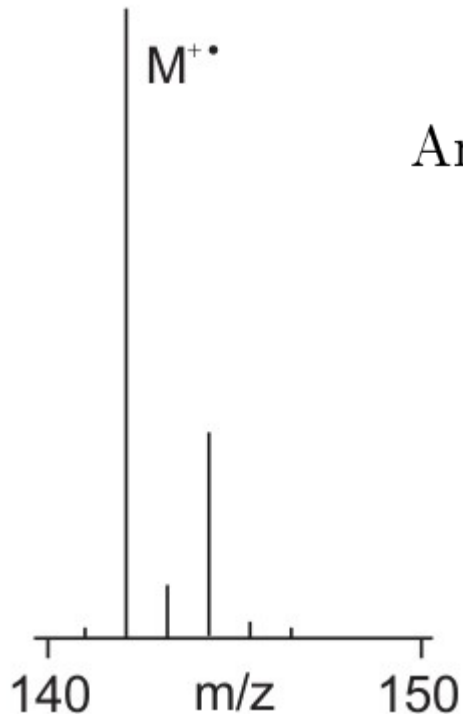


EI-MS von p-Chloranisol



	Summenformel	m/z	Masse
(1)	$^{12}C_7 ^1H_7 ^{35}Cl ^{16}O$	142	142.0185400
(2)	$^{12}C_6 ^{13}C ^1H_7 ^{35}Cl ^{16}O$	143	143.0219000
(3)	$^{12}C_7 ^1H_7 ^{35}Cl ^{17}O$	143	143.0227700
(4)	$^{12}C_7 ^1H_6 ^2H ^{35}Cl ^{16}O$	143	143.0248300
(5)	$^{12}C_7 ^1H_7 ^{37}Cl ^{16}O$	144	144.0155900
(6)	$^{12}C_7 ^1H_6 ^2H ^{35}Cl ^{17}O$	144	144.0290400
(7)	$^{12}C_5 ^{13}C_2 ^1H_7 ^{35}Cl ^{16}O$	144	144.0252500
(8)	$^{12}C_6 ^{13}C ^1H_7 ^{37}Cl ^{16}O$	145	145.0189500
(9)	$^{12}C_4 ^{13}C_3 ^1H_7 ^{35}Cl ^{16}O$	145	145.0286100

P-Chloranisol: ^{13}C -Peak

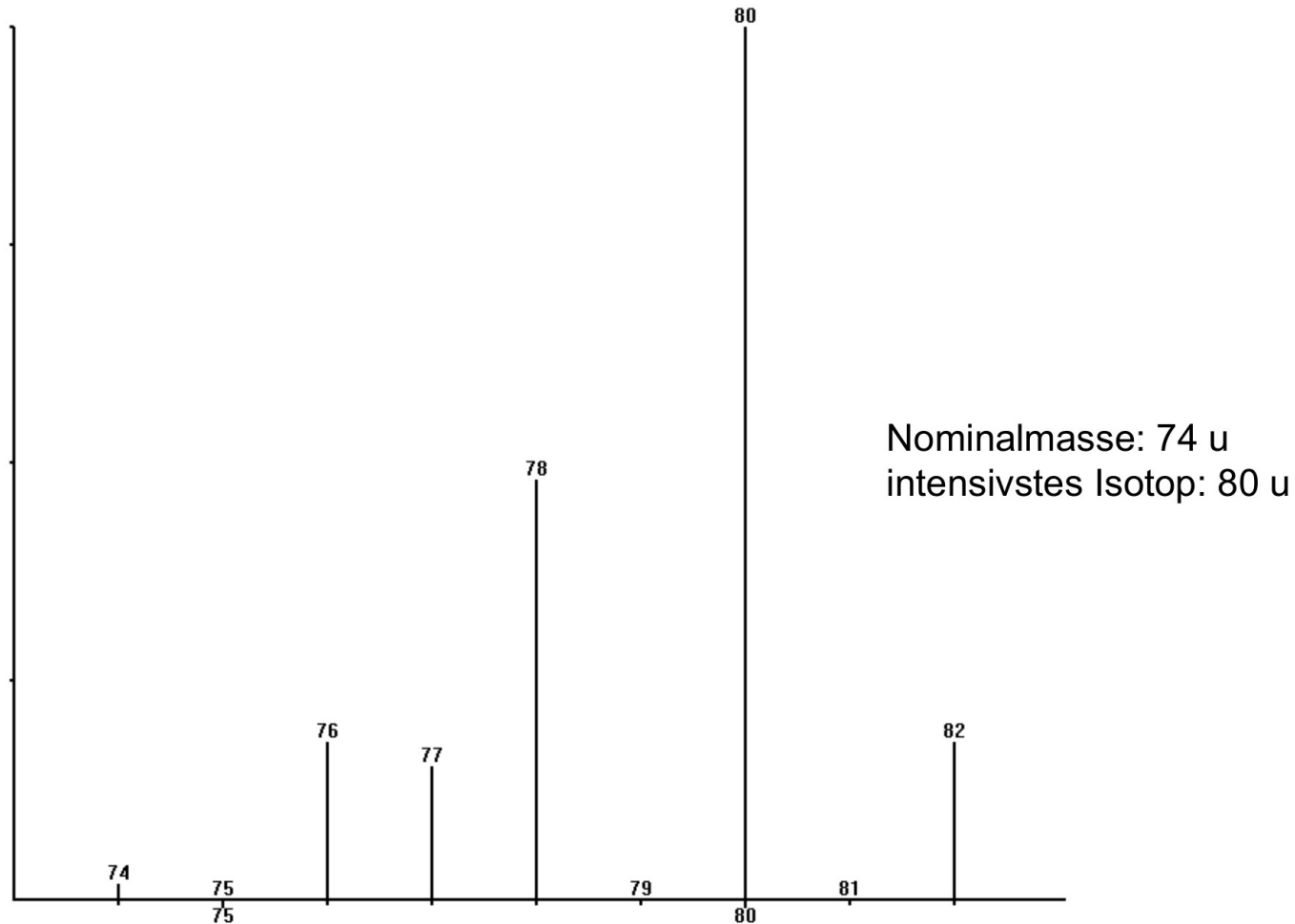


$$\text{Anzahl C} = \frac{\text{Intensität } ^{13}\text{C}\text{-Peak}}{\text{Intensität } \text{M}^{+\bullet}\text{-Peak}} \cdot \frac{1}{^{13}\text{C}\text{-Isotopenhäufigkeit } 1.1\%}$$

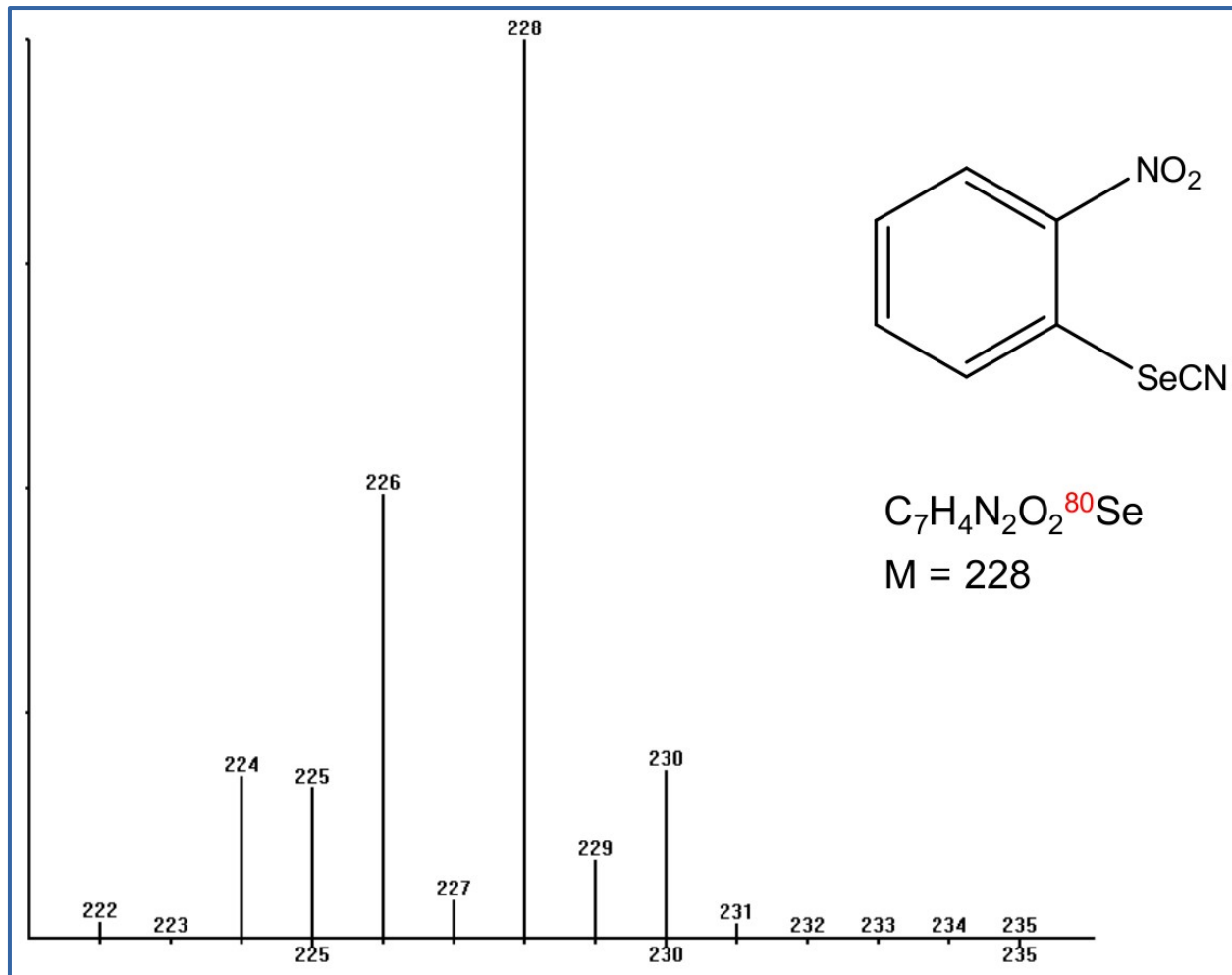
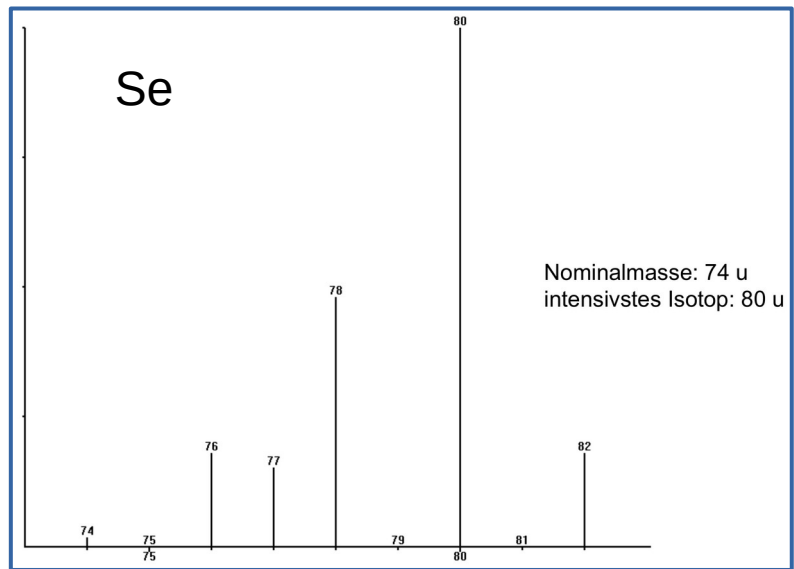
$$\text{hier:} = 8.496\% \cdot \frac{1}{1.1\%} = 7.7$$

p-Chloranisol: $\text{C}_7\text{H}_7\text{ClO}$

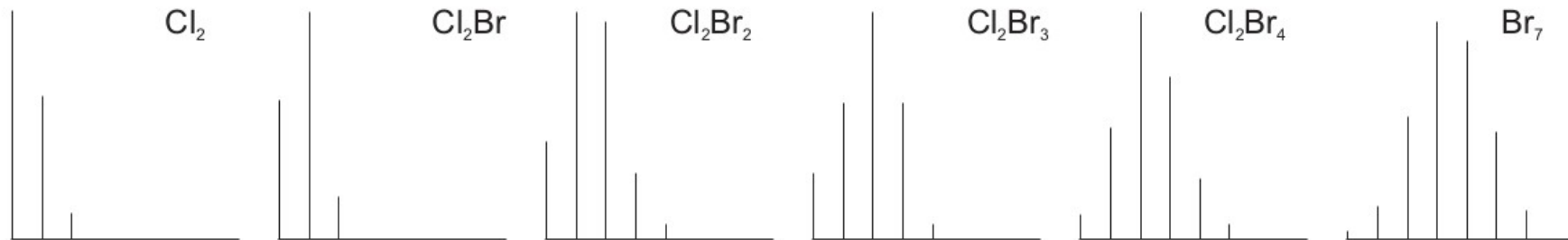
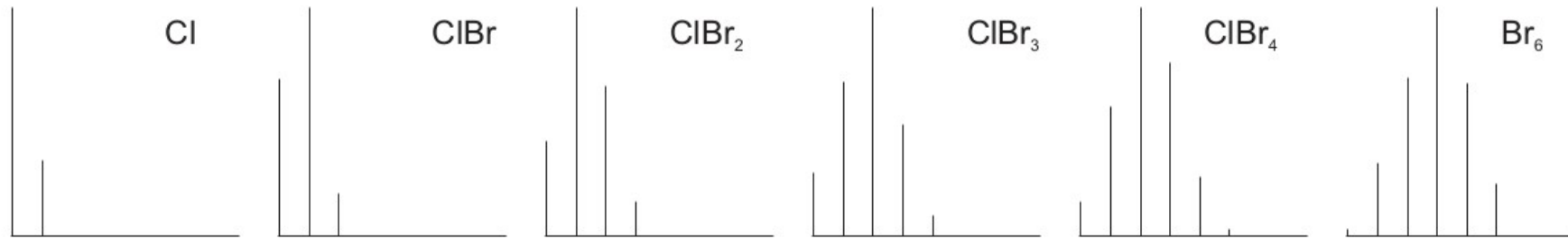
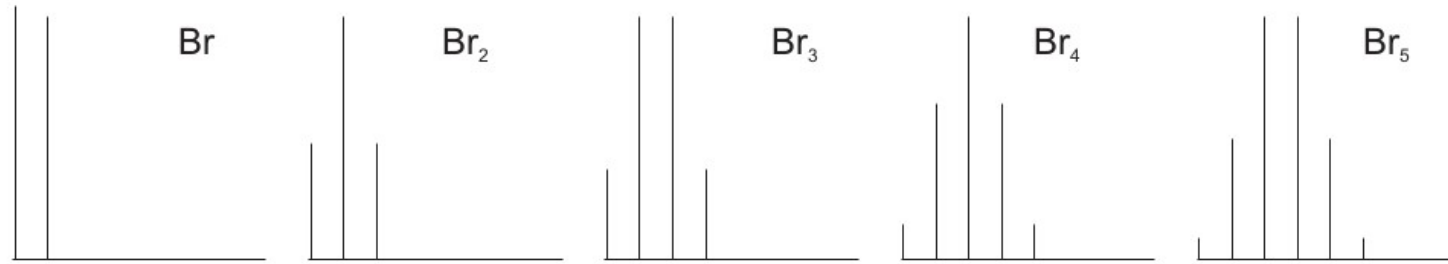
Isotopenmuster von Selen



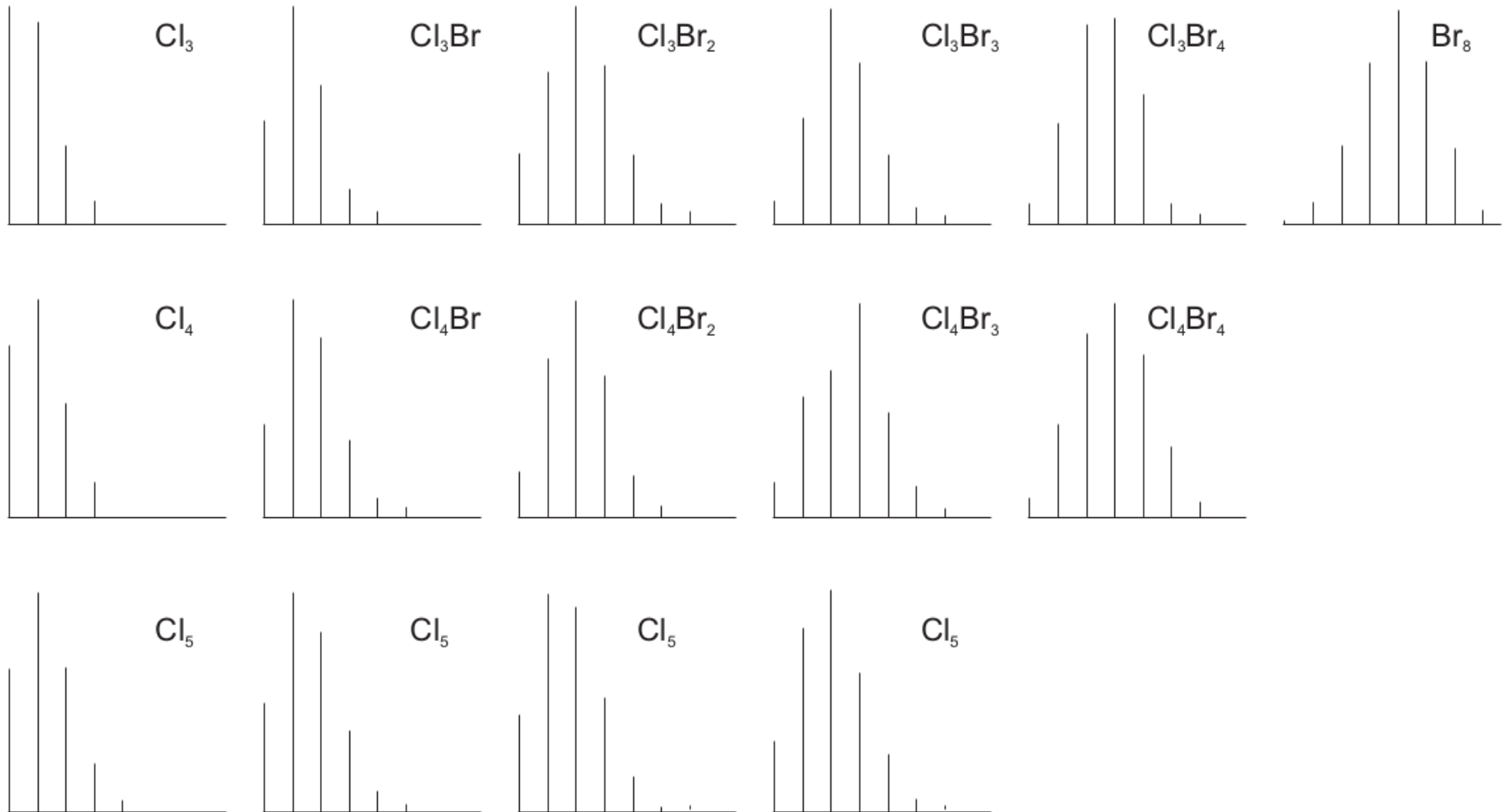
Isotopenmuster von Selen



Isotopenverteilungsmuster von Cl_nBr_m



Isotopenverteilungsmuster von Cl_nBr_m



Exakte Massen

Summenformel	Massenzahl	Exakte Masse [amu]
CO ₂	44	43,9898
C ₂ H ₄ O	44	44,0262
C ₂ H ₆ N	44	44,0500
C ₃ H ₈	44	44,0626
C ₂ ¹³ CH ₇	44	44,0581

Mehrdeutige Massendifferenzen:

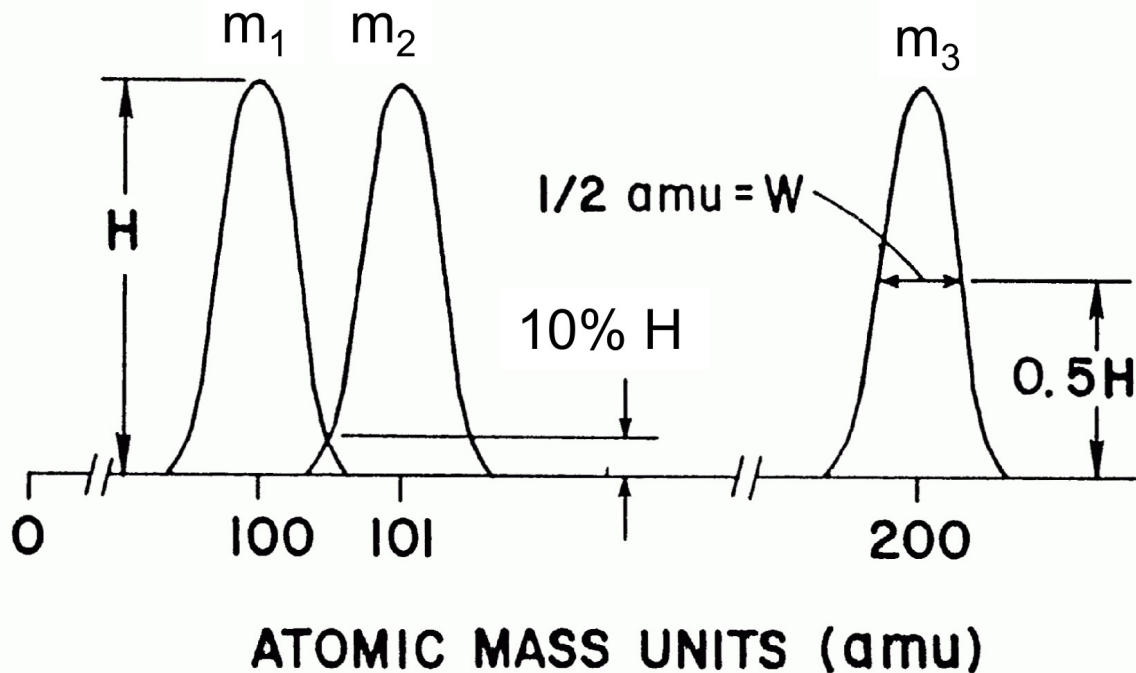
$\Delta m = 43$: C₃H₇- oder CH₃C(=O)- (43,04578 oder 43,01839)

$\Delta m = 45$: CH₃-CH₂-O- oder -COOH? (45,03404 oder 44,99765)

$\Delta m = 28$: -CH₂-CH₂- oder >C=O? (28,03130 oder 27,99492)

Auflösungsvermögen

10%-Tal-Definition:



$$R = m_1 / (m_2 - m_1) = m / \Delta m$$

FWHM-Definition:
(full width at half maximum)

$$R = m_3 / W$$

$$R(\text{CO}_2 / \text{C}_2^{13}\text{CH}_7) = \frac{44}{44.0581 - 43.9898} = 644$$

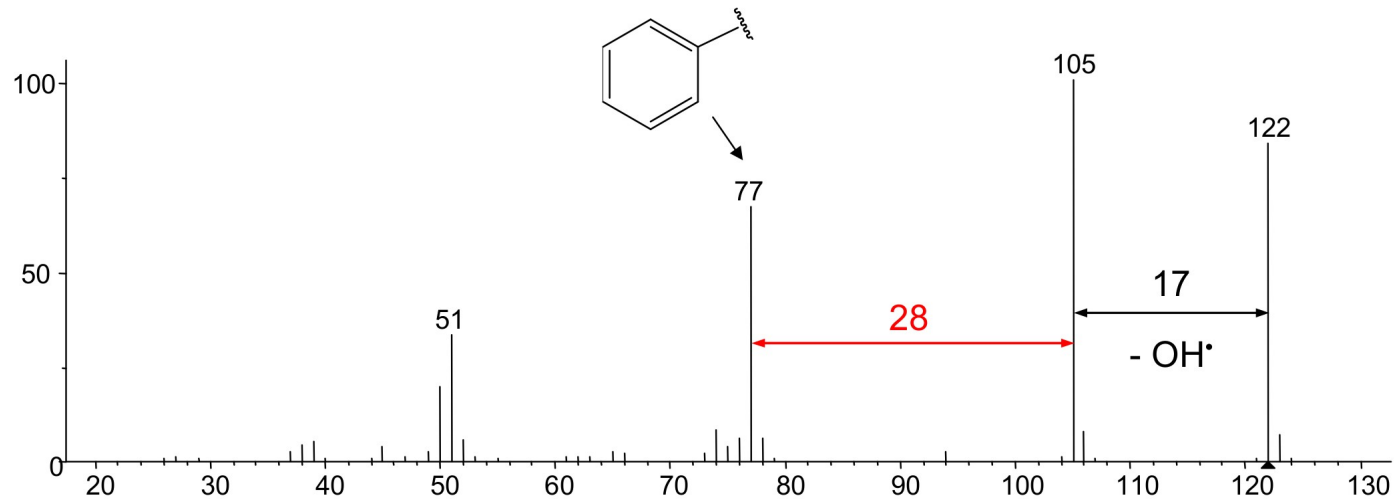
$$R(\text{C}_2^{13}\text{CH}_7 / \text{C}_2\text{H}_6\text{N}) = \frac{44}{44.0581 - 44.0500} = 5432$$

(6)	$^{12}\text{C}_7\ ^1\text{H}_6\ ^2\text{H}\ ^{35}\text{Cl}\ ^{17}\text{O}$	144	144.0290400
(7)	$^{12}\text{C}_5\ ^{13}\text{C}_2\ ^1\text{H}_7\ ^{35}\text{Cl}\ ^{16}\text{O}$	144	144.0252500

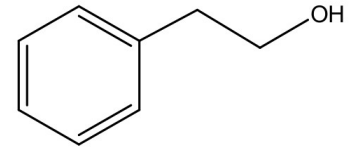
$$R_{6/7} = \frac{144}{144.0290400 - 144.0252500} = 37500$$

Präzisionsmassen der Differenzen

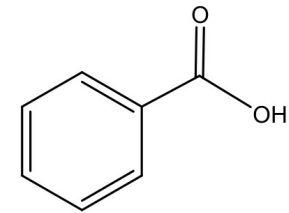
Bestimmung von Strukturelementen über die Präzisionsmasse



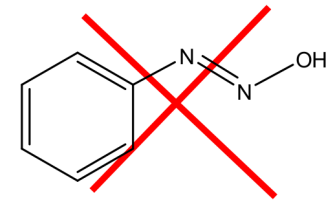
$m/z\ 105 - m/z\ 77 = 28 \Rightarrow ? (-\text{CH}_2-\text{CH}_2-, >\text{C}=\text{O}, -\text{N}=\text{N}-)$



$\text{C}_8\text{H}_{10}\text{O}$



$\text{C}_7\text{H}_6\text{O}_2$



$\text{C}_6\text{H}_6\text{N}_2\text{O}$

(z.B. N_2 ausschließen)

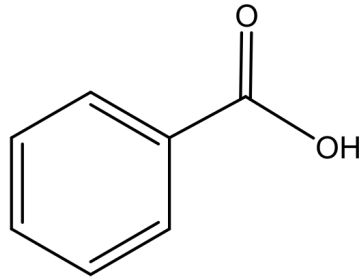
ATOMIC COMPOSITION REPORT (MANUAL)

Selected isotopes:

Symbol	Min	Max	V'cy	Name
C	0	auto	4	Carbon-12
H	0	auto	1	Hydrogen-1
N	0	auto	3	Nitrogen-14
O	0	auto	2	Oxygen-16

Allowable error = minimum of 100.0 ppm, 100.0 mmu.

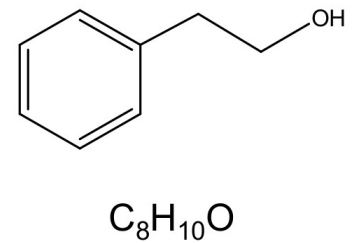
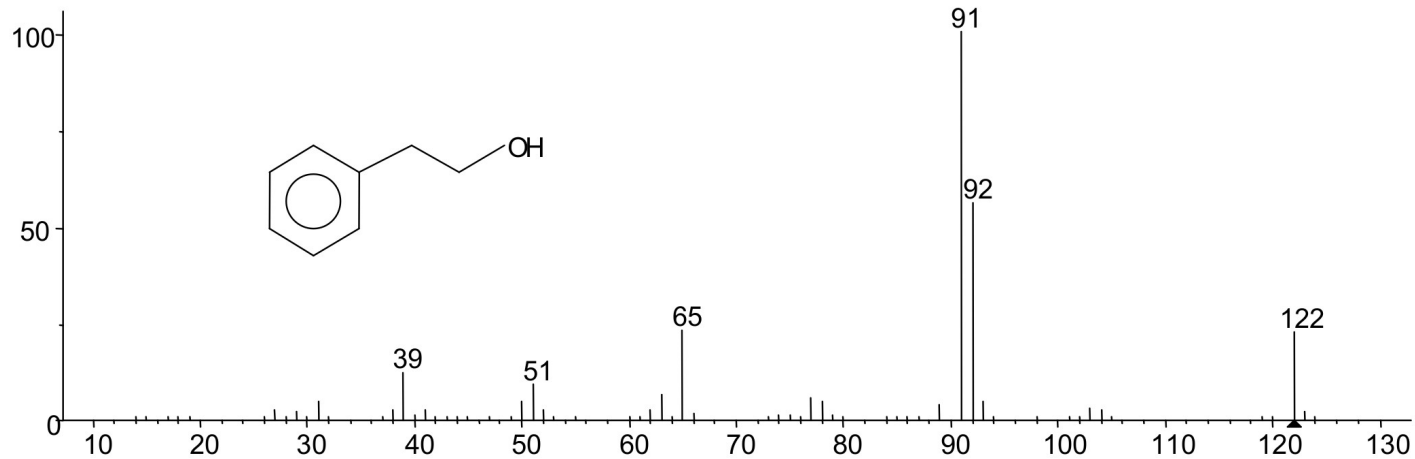
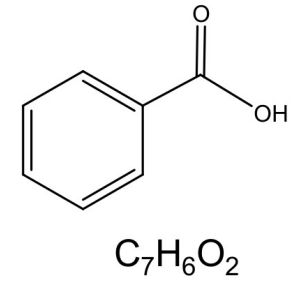
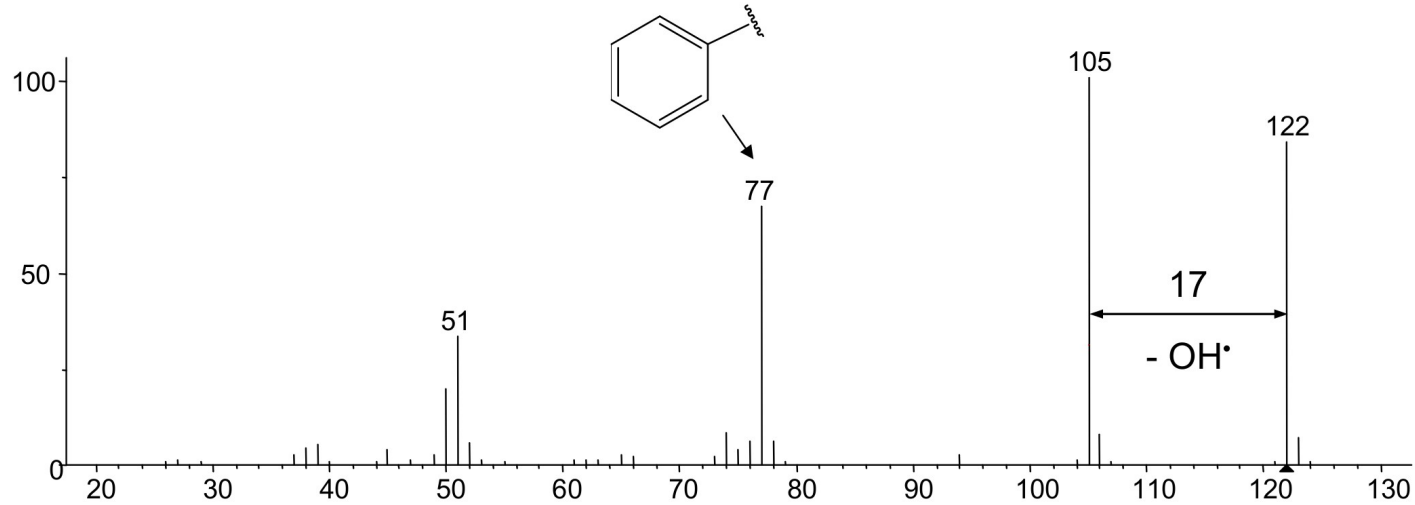
Mass	Calculated	ppm	mmu	Formula
122.03678	122.03678	-0.0	-0.0	C7.H6.O2
122.03544	122.03544	-11.0	-1.3	C5.H4.N3.O
122.03400	122.03400	-22.0	-2.7	C3.H2.N6
122.03256	122.03256	-33.0	-4.1	C.H6.N2.O4
122.03112	122.03112	-44.0	-5.5	C.N5.O3
122.02968	122.02968	-55.0	-6.9	C.O.O7
122.02824	122.02824	-66.0	-8.3	C.H6.N4.O3
122.02680	122.02680	-77.0	-9.7	C.H8.N.O4
122.02536	122.02536	-88.0	-11.1	C.H4.N5
122.02392	122.02392	-99.0	-12.5	C.H6.N2.O



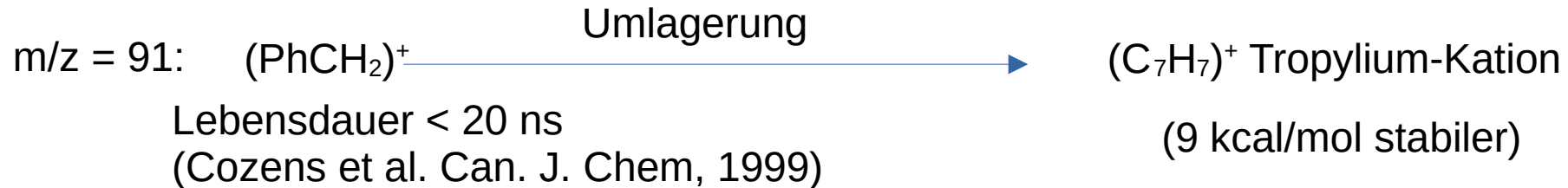
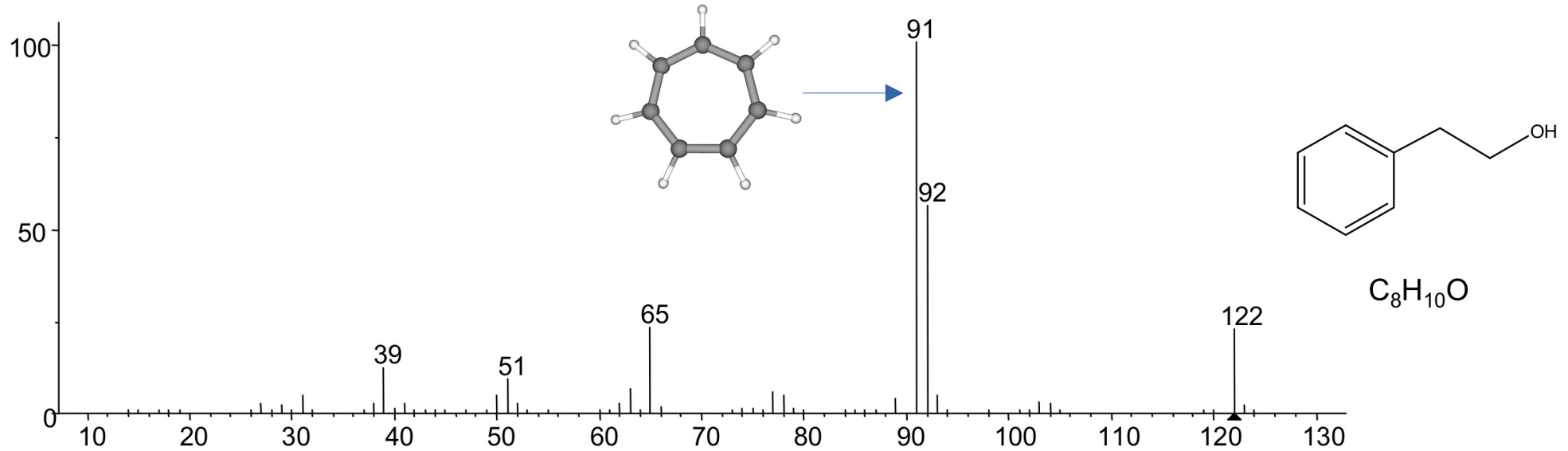
***** End of Atomic Composition Report *****

Präzisionsmasse der
Verbindung: 122,03678 Da

Fragmentierungen

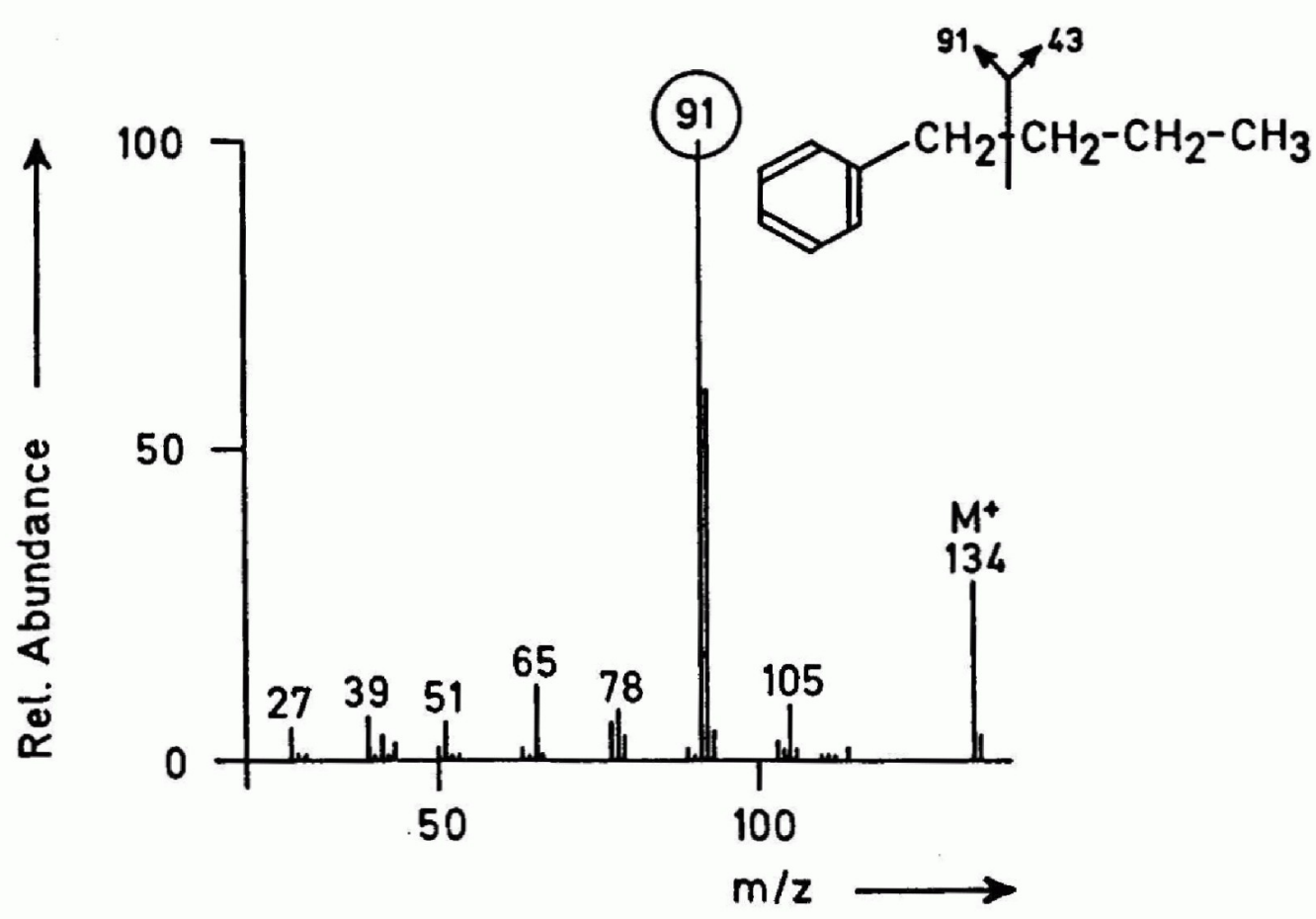


Umlagerungen



MS ist eine „langsame“ Methode ($10^{-6} - 10^{-3}$ s), nur langlebige Ionen sind „sichtbar“!

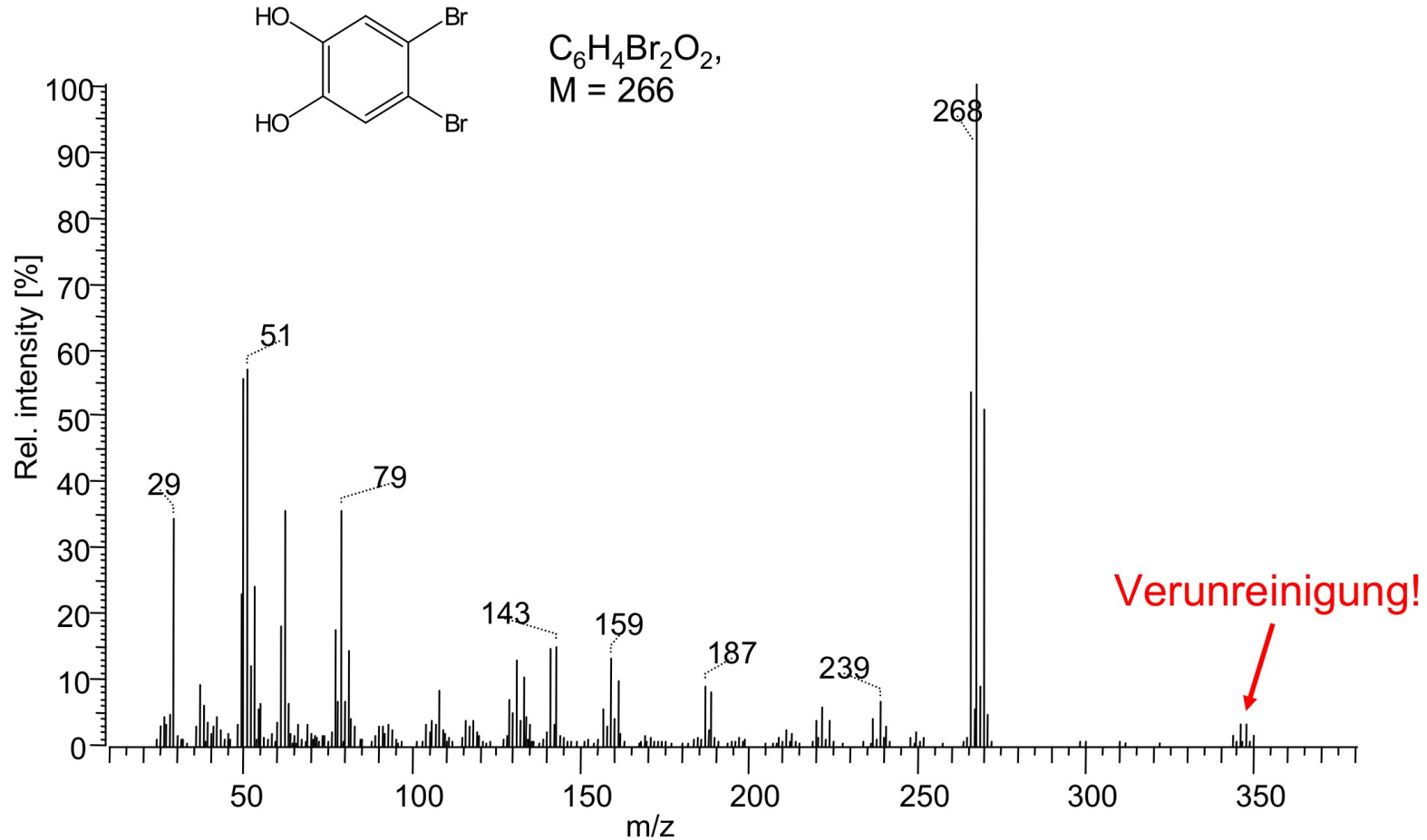
Spaltung der benzylicischen Bindung



Eigenschaften des Moleküliions

- M^{+} ist das Ion mit der höchsten Masse, das eine Verbindung liefern kann.
- M^{+} ist geradzahlig, wenn kein N oder eine gerade Zahl von N-Atomen vorhanden ist, und ungeradzahlig bei einer ungeraden Zahl von N-Atomen („Stickstoff-Regel“).
- Alle Fragmente müssen von M^{+} aus chemisch sinnvolle Massendifferenzen haben.
- M^{+} muss alle Elemente enthalten, die in den Fragmenten festzustellen sind.

Eigenschaften des Moleküliions



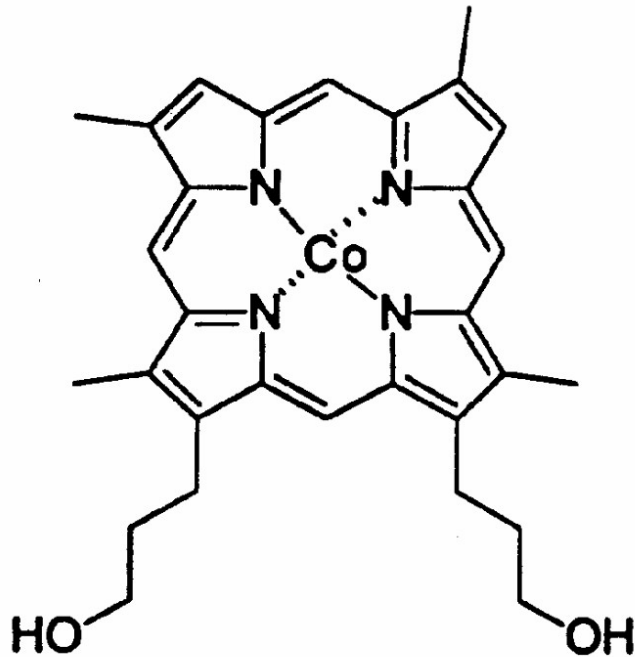
Stickstoff-Regel

Ist die Masse des Molekül-Ions geradzahlig, spricht dies für eine gerade Zahl N-Atome (0, 2, 4, ...), ist sie jedoch ungeradzahlig, kann man auf eine ungerade Zahl (1, 3, 5, ...) schließen.

Atom	Massenzahl	Wertigkeit
^{12}C	12	4
^1H	1	1
^{16}O	16	2
^{35}Cl	35	1
^{14}N	14	3

Stickstoff-Regel

Co^{2+} , Cu^{2+} : analoge Gültigkeit der Stickstoffregel, z.B:



Co^{2+} : Massenzahl 59
Wertigkeit 2

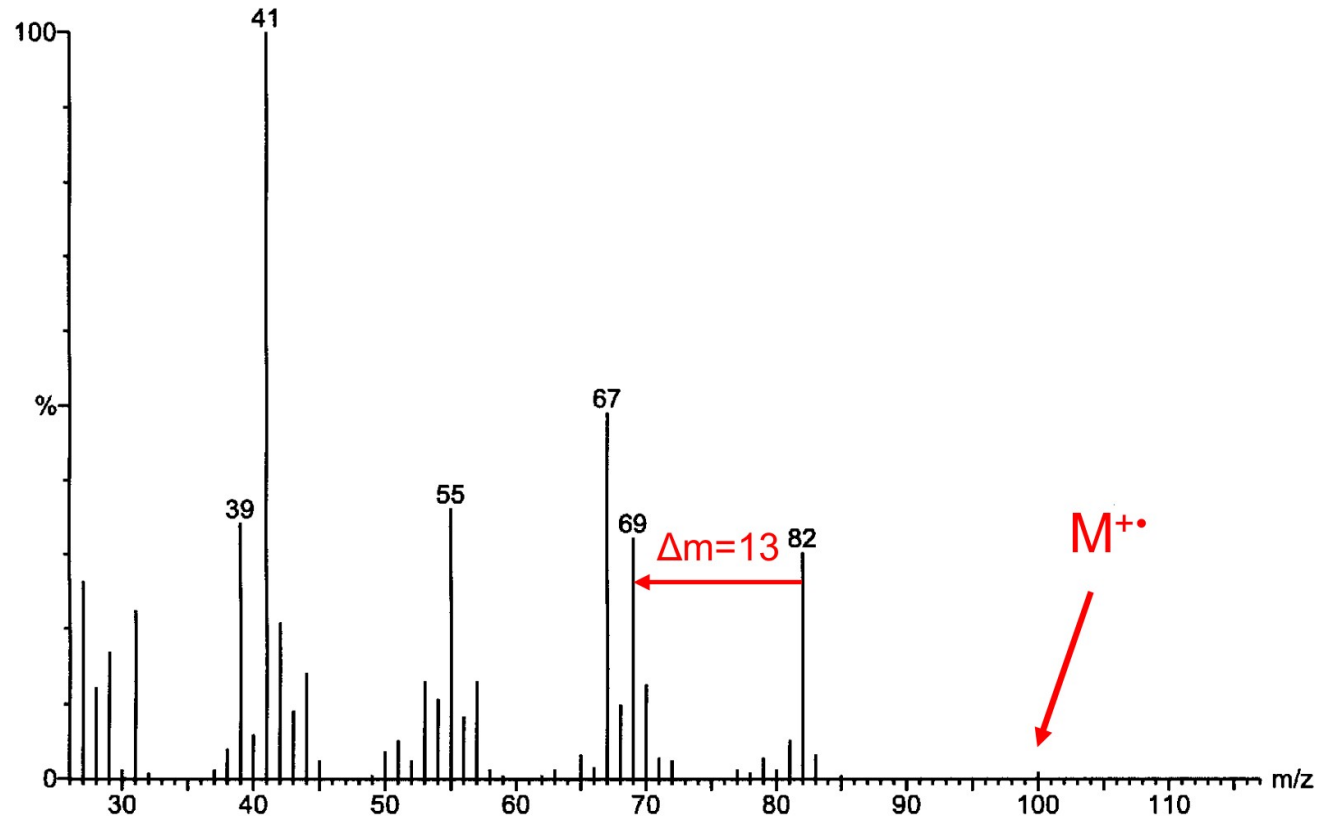
$\text{C}_{30}\text{H}_{32}\text{CoN}_4\text{O}_2$

MW = 539

Massendifferenzen

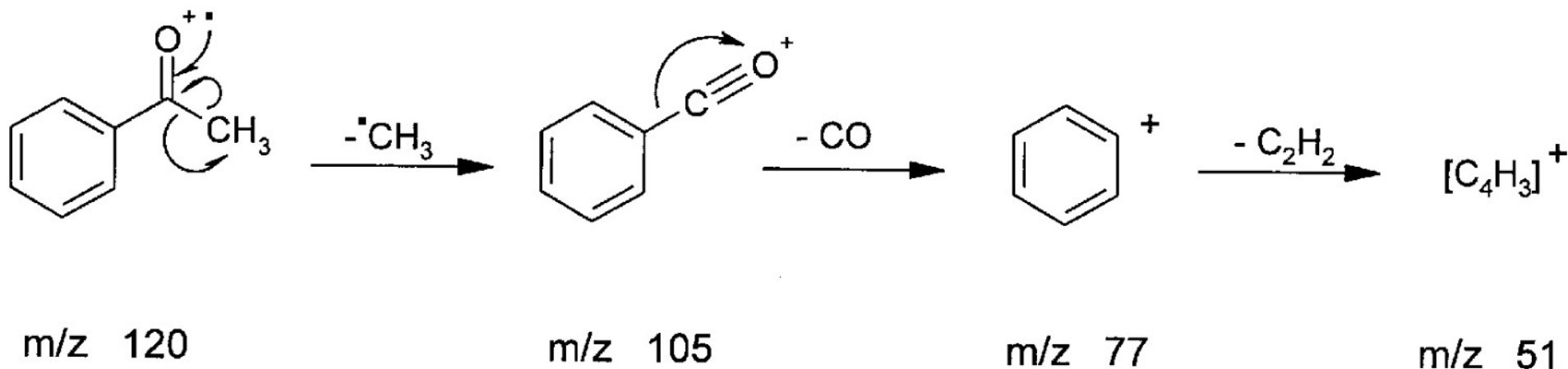
Alle Fragmente müssen von M^+ aus chemisch sinnvolle Massendifferenzen haben.

Ist die m/z 82 ein Molekölion?
→ Nein!



„Even-electron rule“

Geradelektronische Ionen zerfallen bevorzugt unter Bildung eines geradelektronischen Ions und eines geradelektronischen Neutralteilchens.



m/z 120

m/z 105

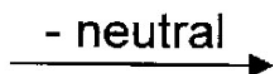
m/z 77

m/z 51

odd $\uparrow^{+\cdot}$



even \uparrow^+



even \uparrow^+



even \uparrow^+

Zerfallsreaktionen

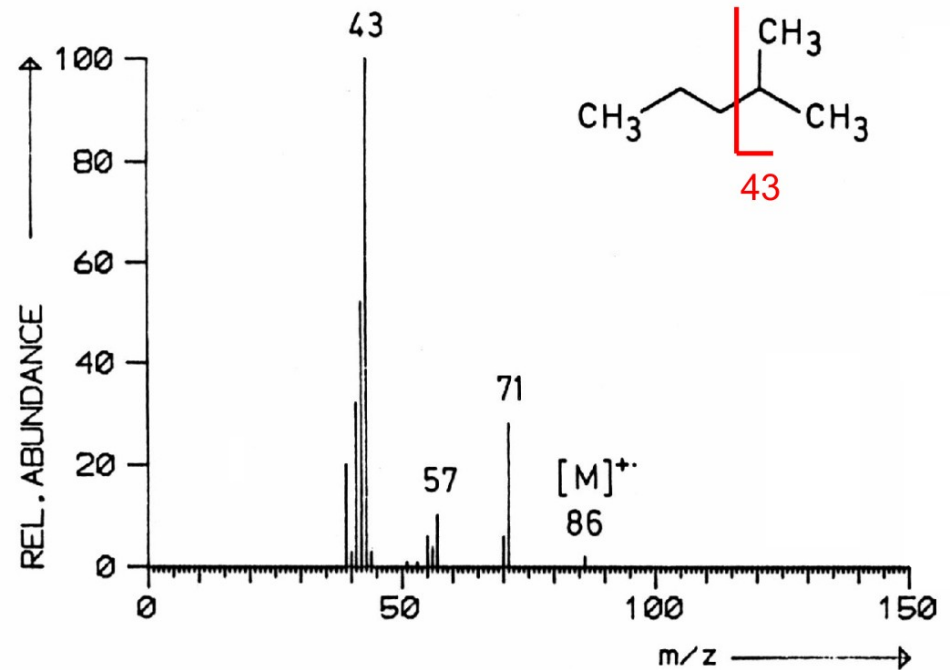
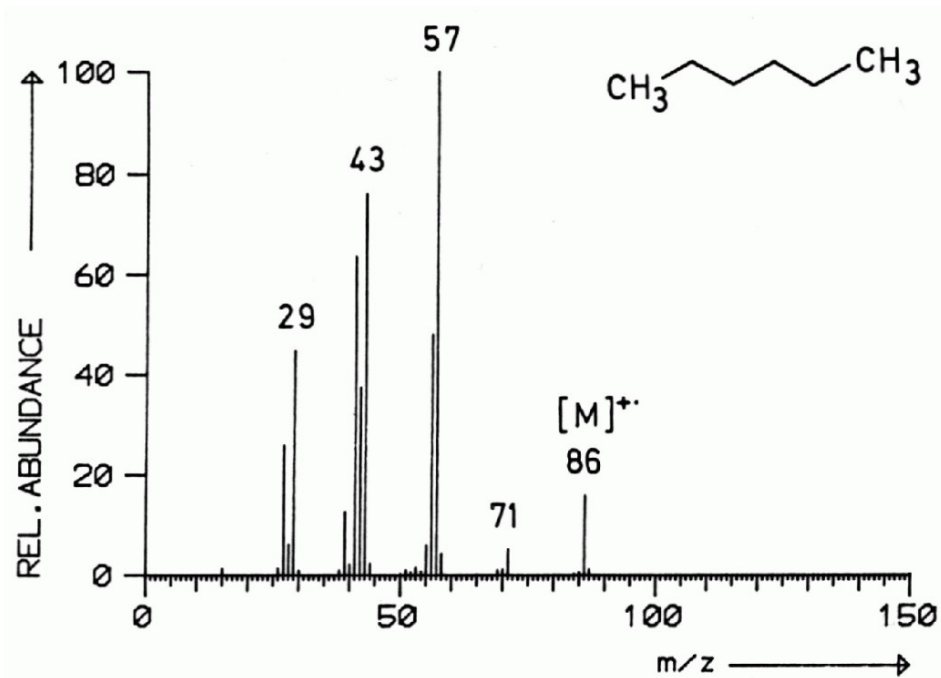
- C-C-Bindungen an Verzweigungsstellen werden bevorzugt gespalten.
- Doppelbindungen oder Doppelbindungssysteme fördern die Spaltung der allylischen oder benzyllischen Bindung. Sonderfall: Retro-Diels-Alder-Reaktion (RDA).
- Heteroatome fördern als Elektronendonatoren die Fragmentierung der Bindung zum heteroatomtragenden Kohlenstoffatom.
 - Wenn die Bindung zum Heteroatom gespalten wird, verbleibt die Ladung bevorzugt auf der Seite des Kohlenstoffatoms.
- Doppelbindungen und Heteroatome fördern als Wasserstoffakzeptoren die Umlagerung eines Wasserstoffs in einem sechsgliedrigen (weniger oft vier- oder x-gliedrig), cyclischen Übergangszustand (McLafferty-Umlagerung).

Fragmentierung

Bestimmende Faktoren der Fragmentierung:

1. Größe der Anregungsenergie.
2. Bindungsenergie der Spaltstelle.
3. Stabilität der Bruchstücke, geladen und ungeladen.
4. Räumliche Anordnung.

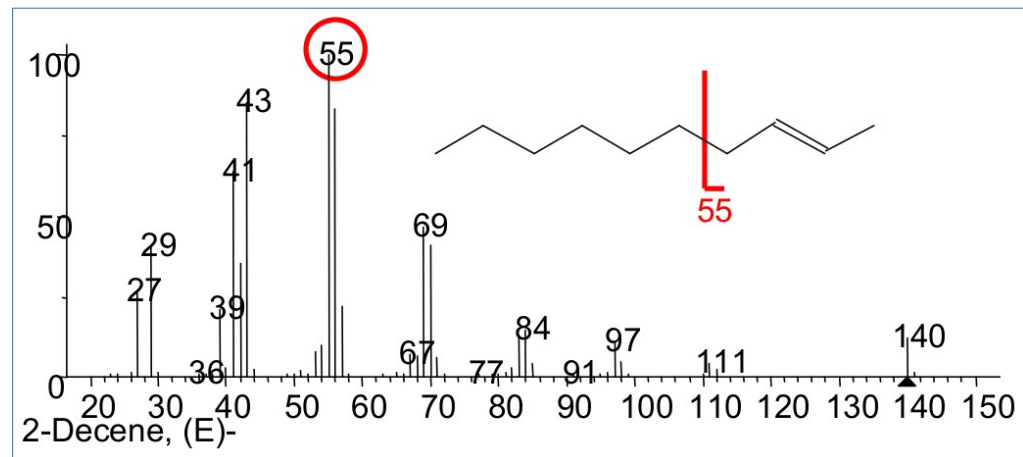
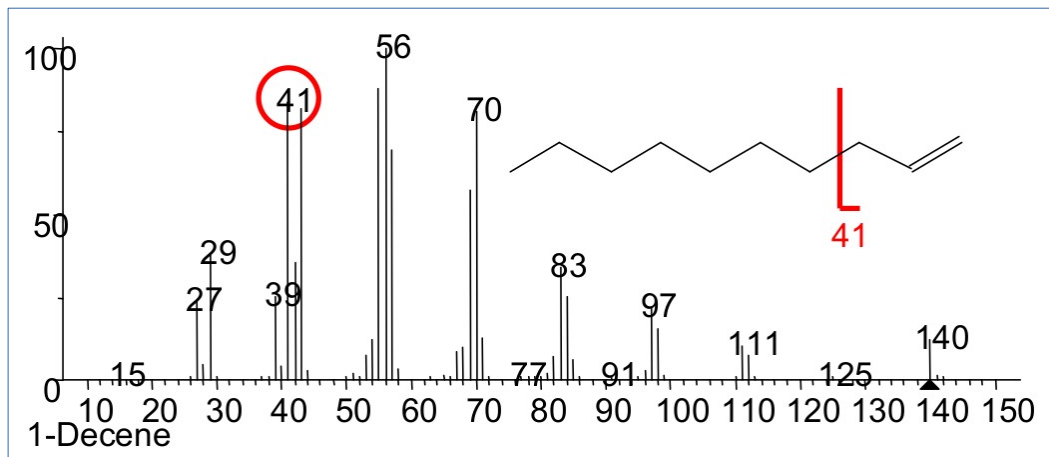
Verzweigungsstellen



Stabilität von Carbeniumionen: primär < sekundär < tertiär

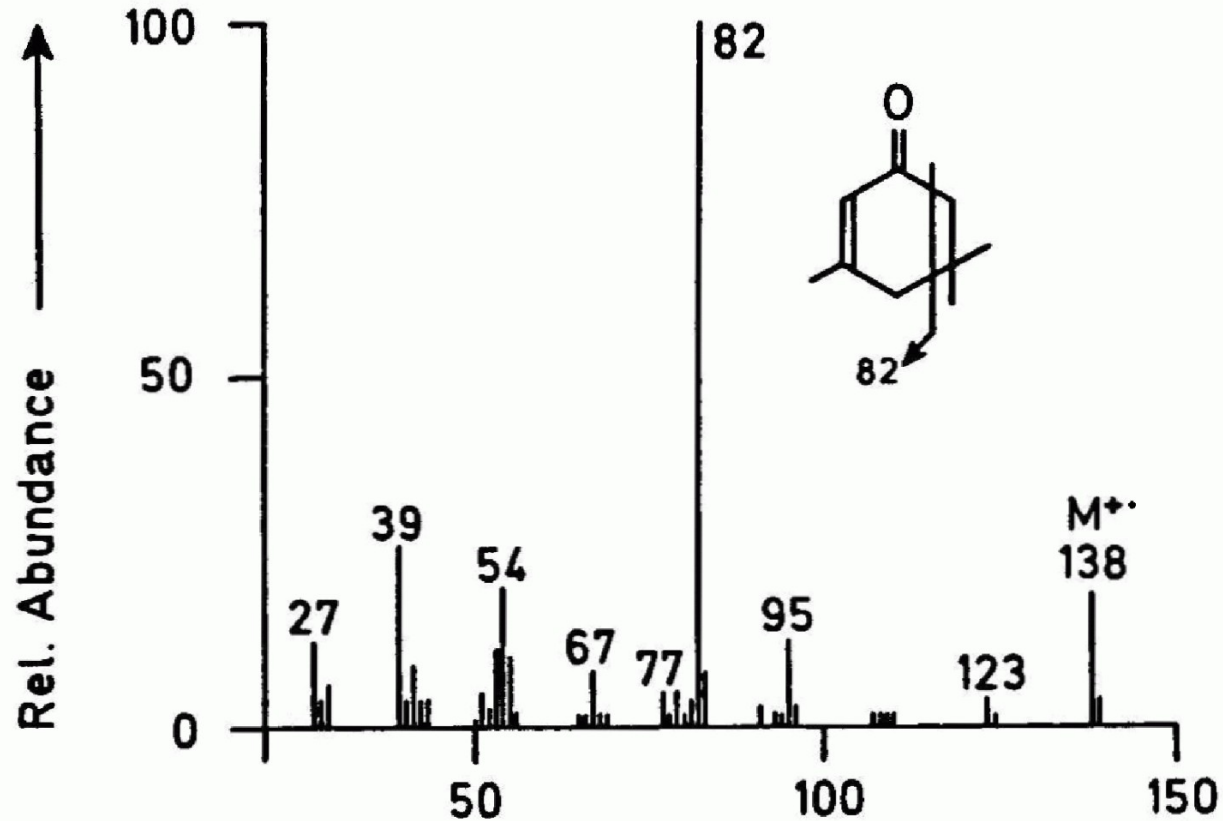
Doppelbindungen

Doppelbindungen oder Doppelbindungssysteme fördern die Spaltung der allylischen oder benzyllischen Bindung.



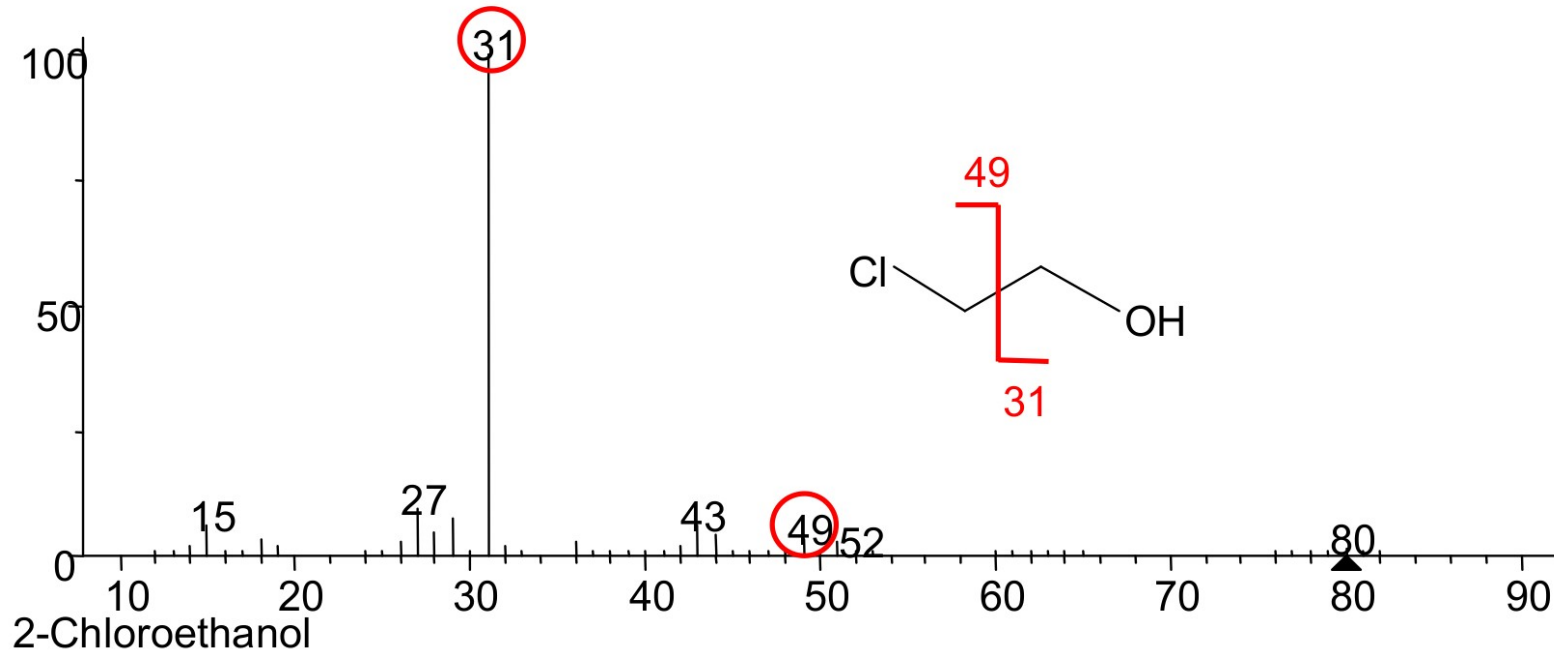
Retro-Diels-Alder-Reaktion (RDA)

Massenspektrum von Isophoron



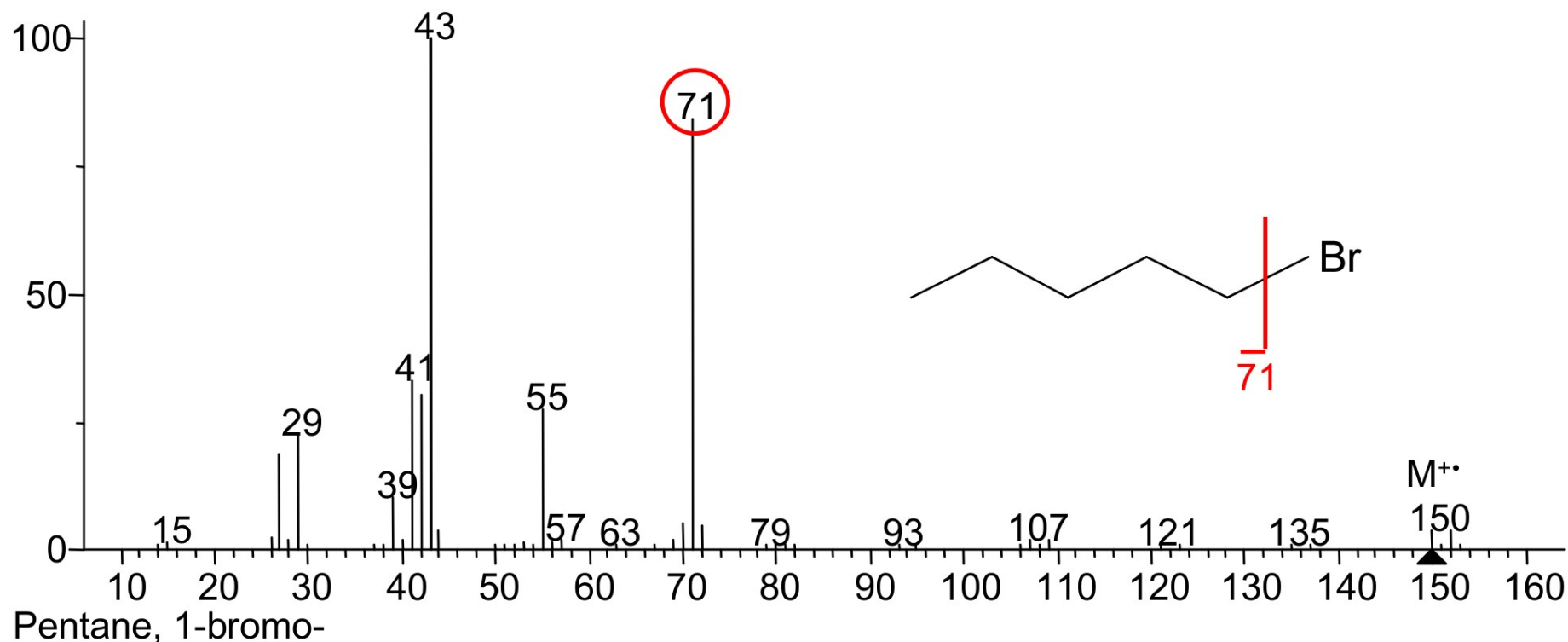
Heteroatome

Heteroatome fördern als Elektronendonatoren die Fragmentierung der Bindungen am heteroatom-tragenden C-Atom.



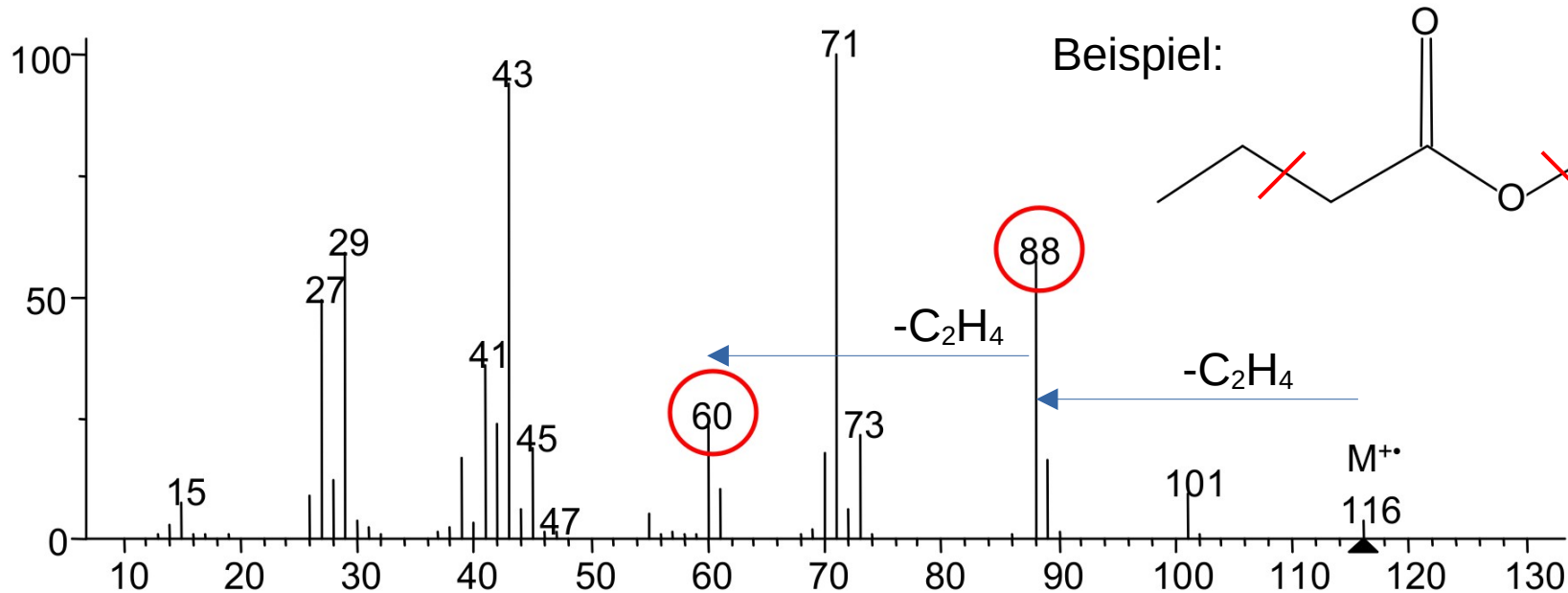
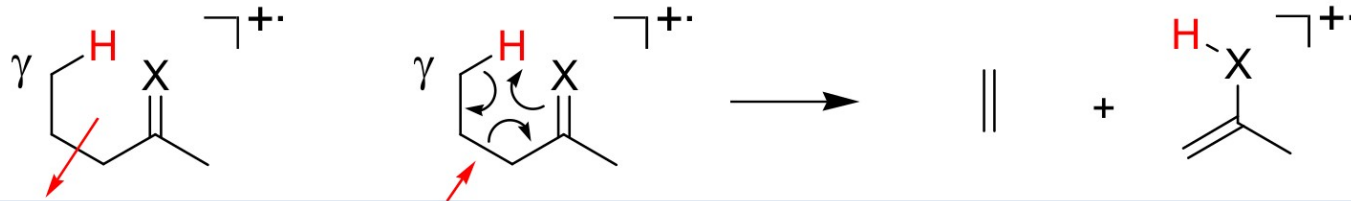
Heteroatome

Wenn die Bindung zum Heteroatom gespalten wird, bleibt die Ladung bevorzugt auf der Seite des C-Atoms.

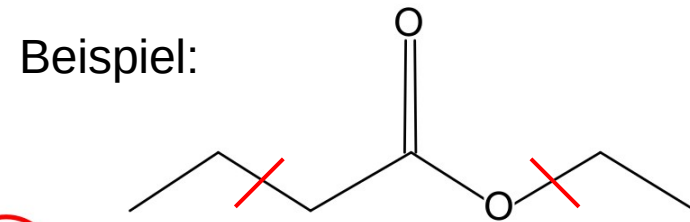


McLafferty-Umlagerung

Doppelbindungen und Heteroatome fördern als Wasserstoffakzeptoren die Umlagerung eines H-Atoms in einem sechsgliedrigen (weniger oft vier- oder x-gliedrigen) Übergangszustand.

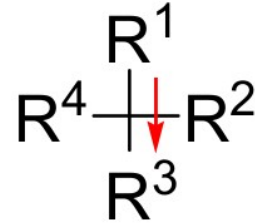


Butanoic acid, ethyl ester

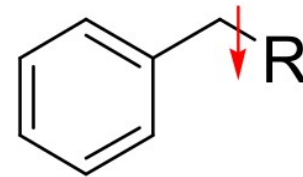
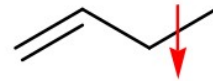


Zf. der Fragmentierungsregeln

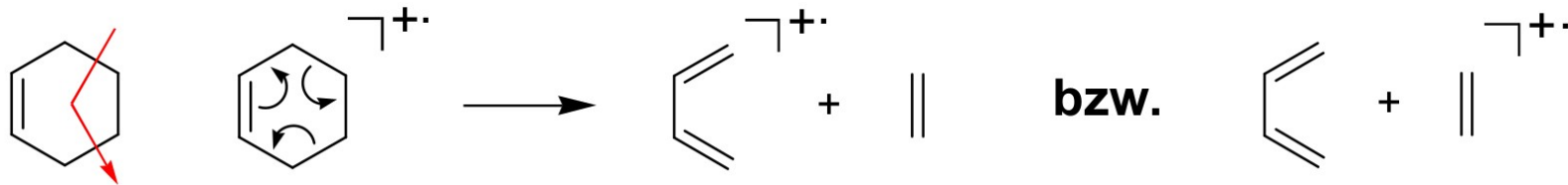
Regel 1 (Spaltung an Verzweigungsstellen)



Regel 2 (Allyl- /Benzylspaltung)

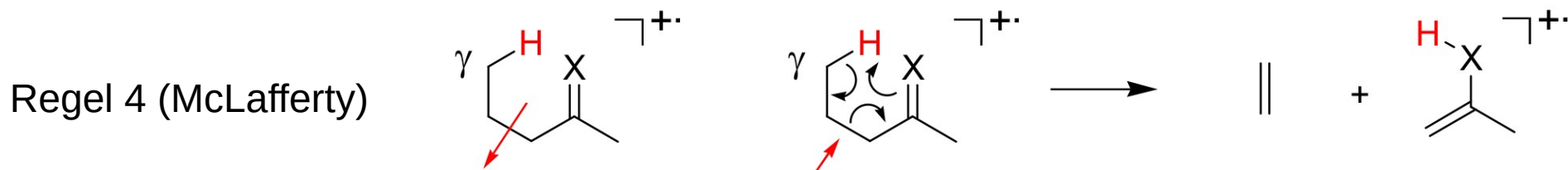
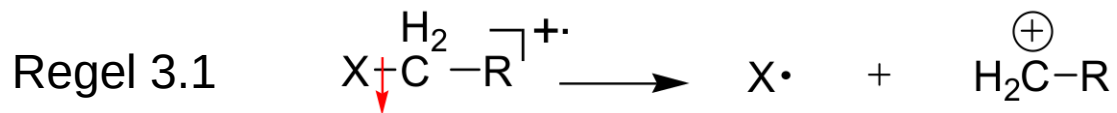


Retro-Diels-Alder

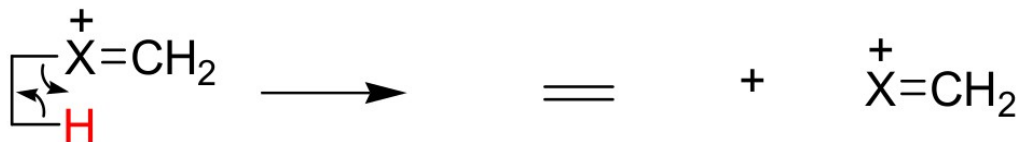


Zf. der Fragmentierungsregeln

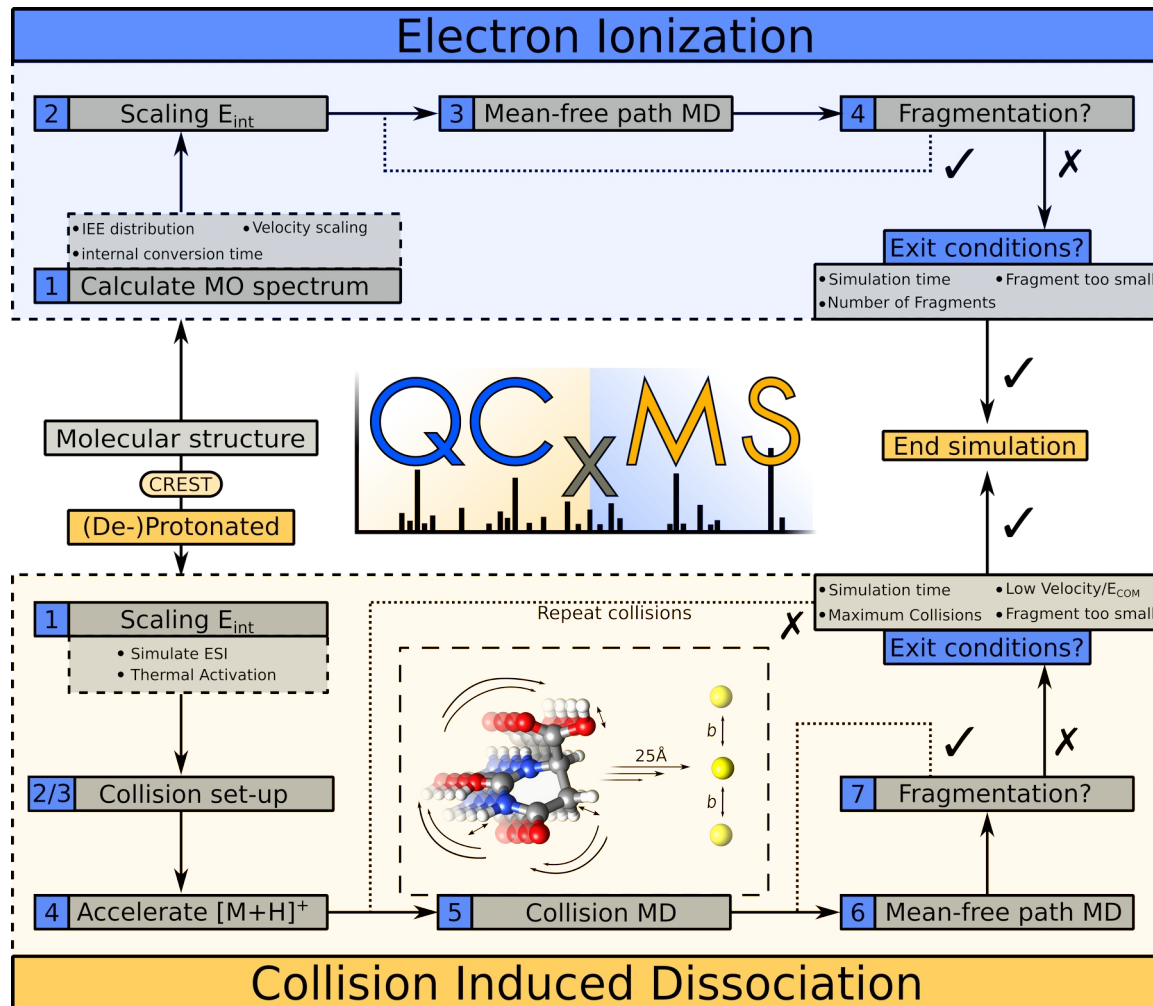
Regel 3 (heteroatom-induzierte Spaltung, α - Spaltung)



Onium-Reaktion (Sekundärfragmentierung)



Quanten-chemische Rechnungen



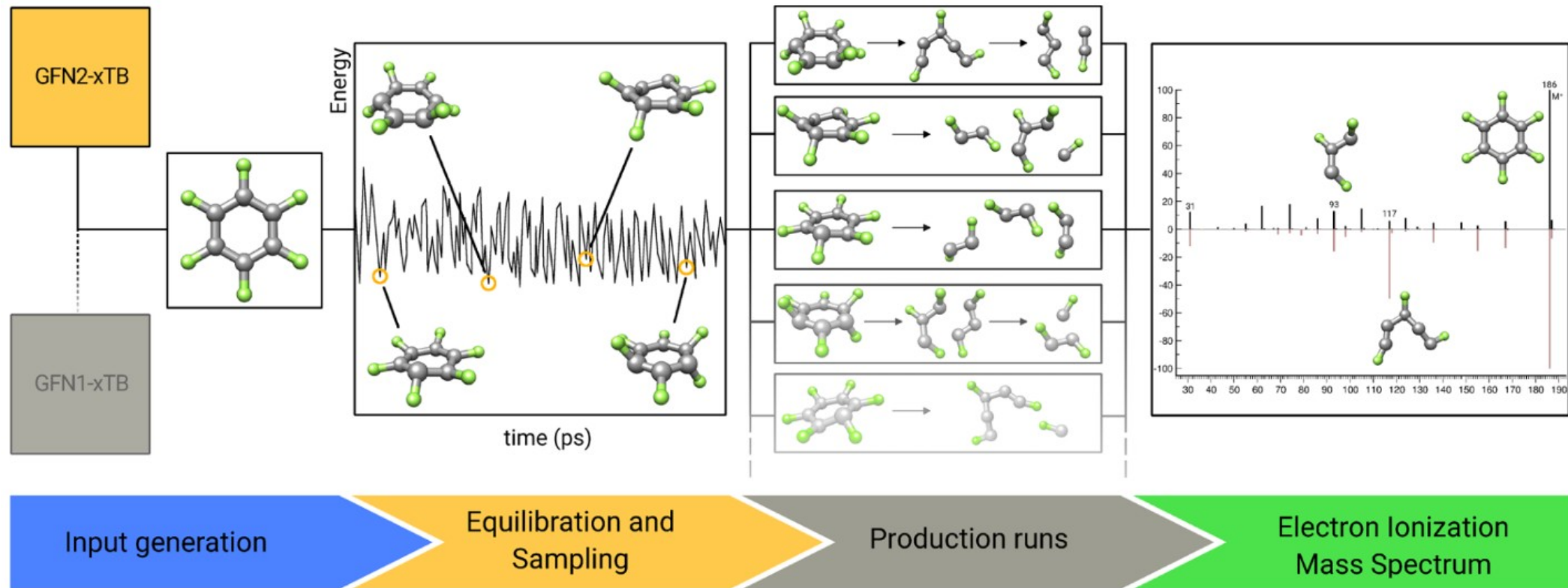
QCxMS Programm:

J. Koopman, S. Grimme, *ACS Omega*, 4 (2019) 15120–15133.

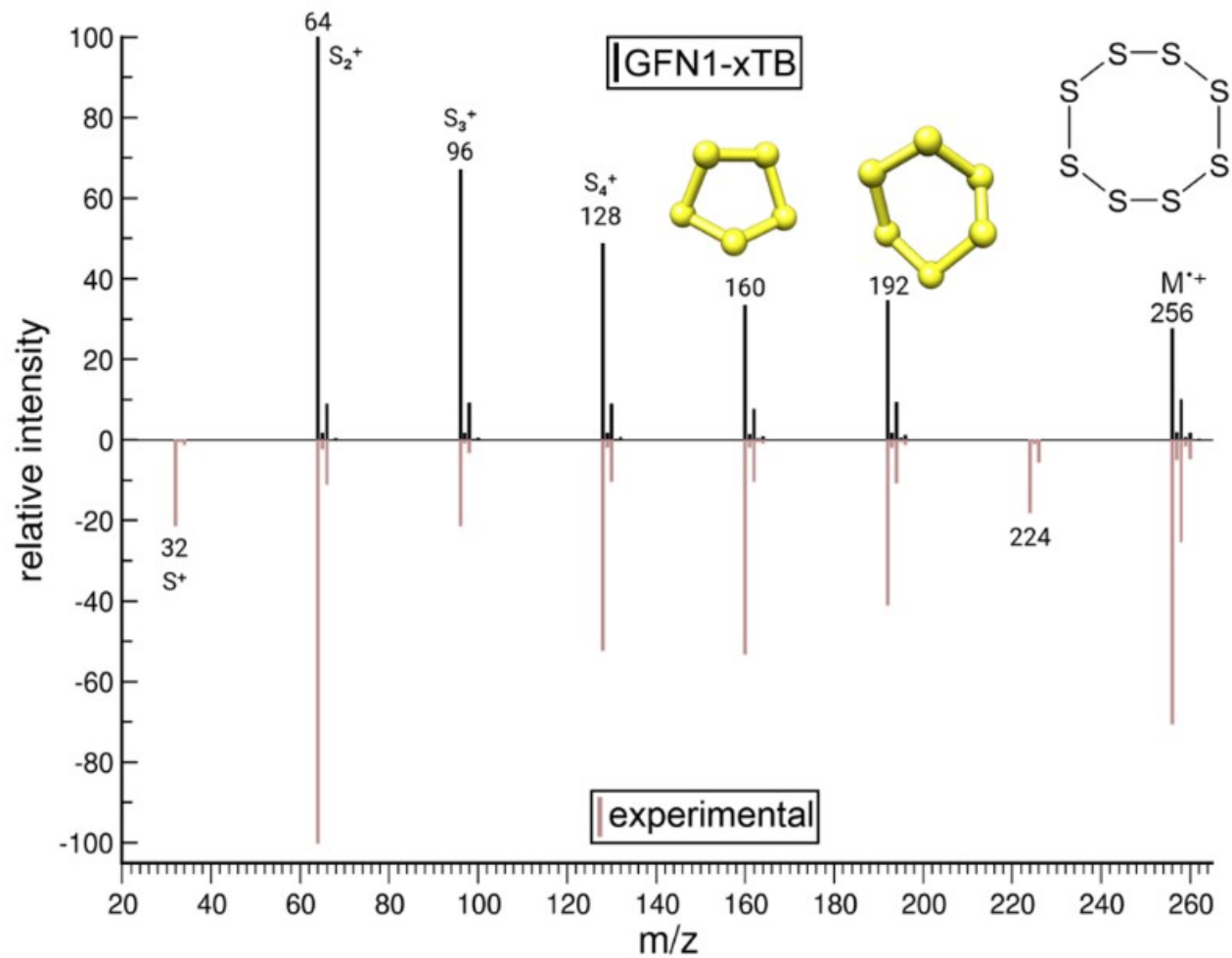
C. A. Bauer, S. Grimme, *J. Phys. Chem. A*, 120 (2016) 3755–3766.

S. Grimme, *Angew. Chem. Int. Ed.* 52 (2013) 6306–6312.

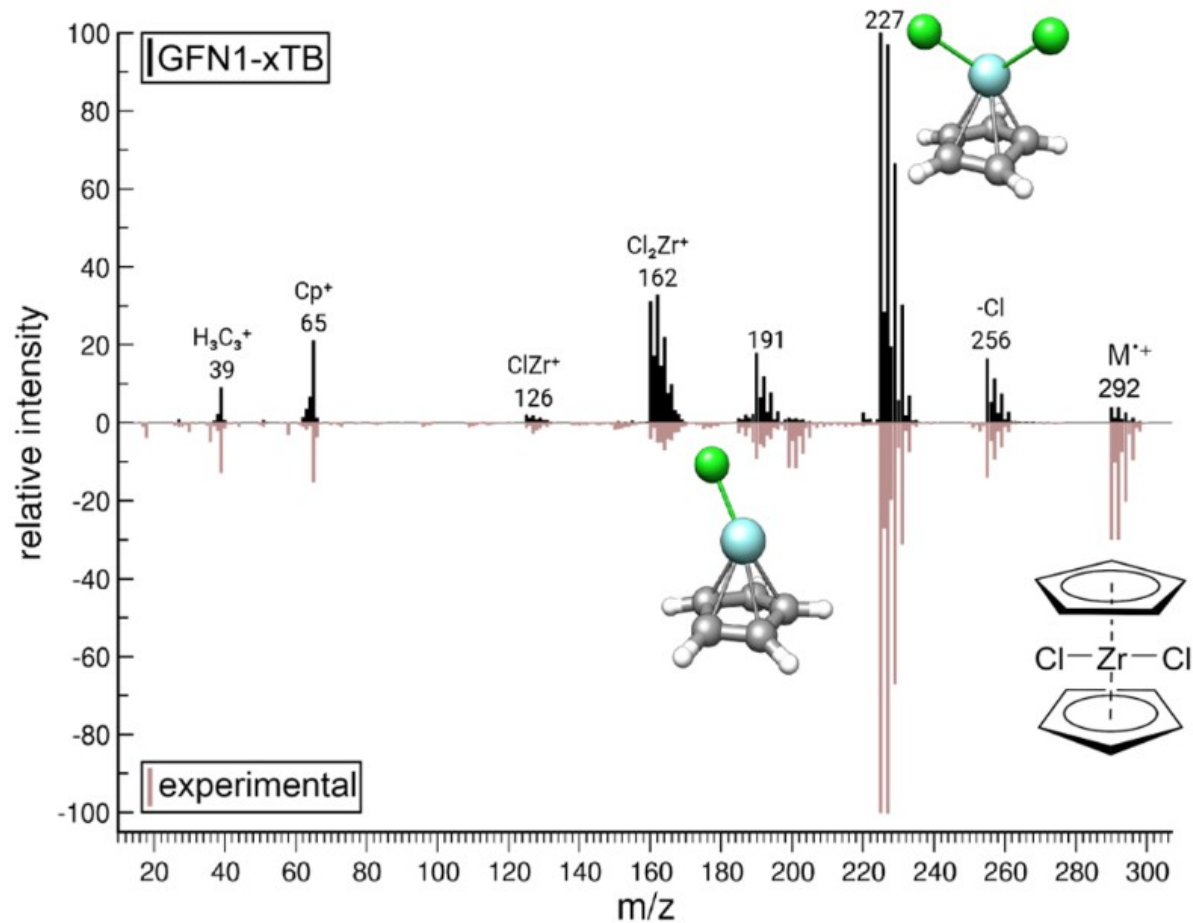
QCxMS



QCxMS: S₈

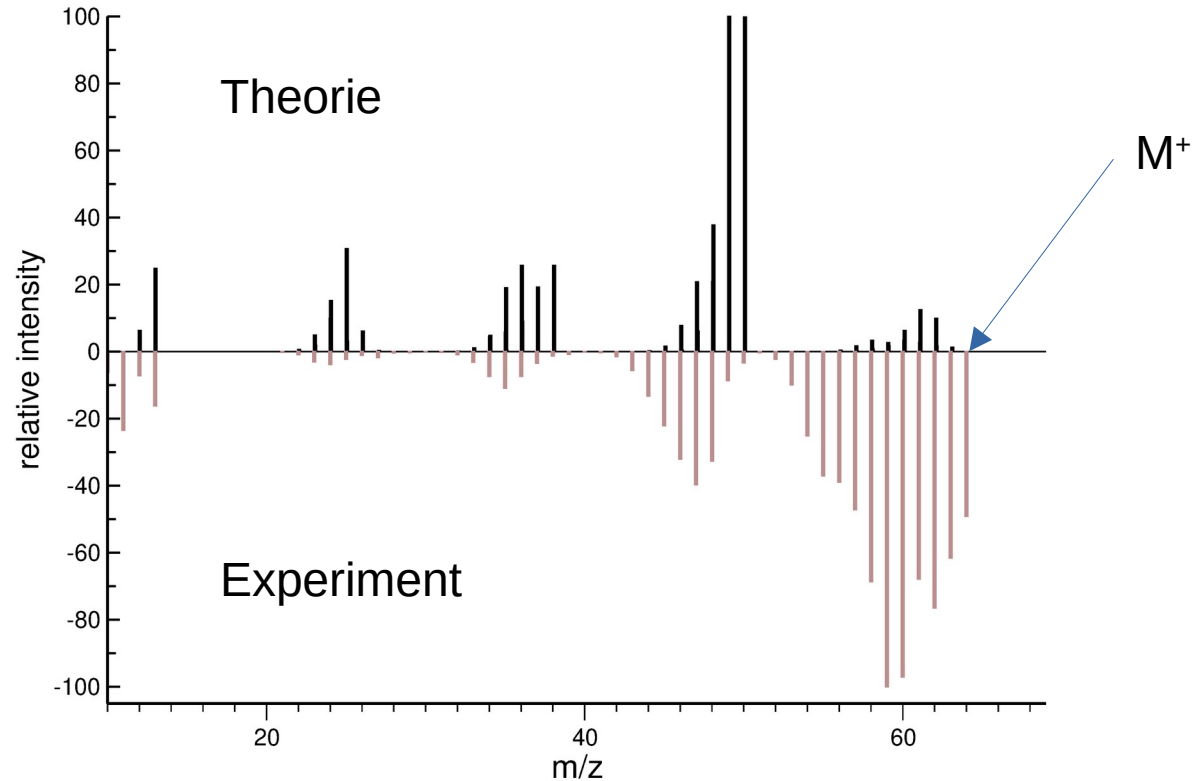
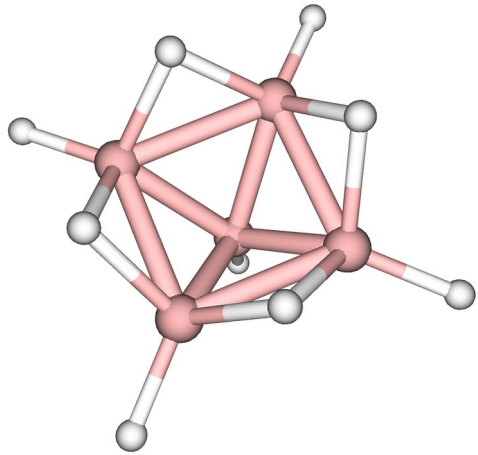


QCxMS: Zirconocendichlorid



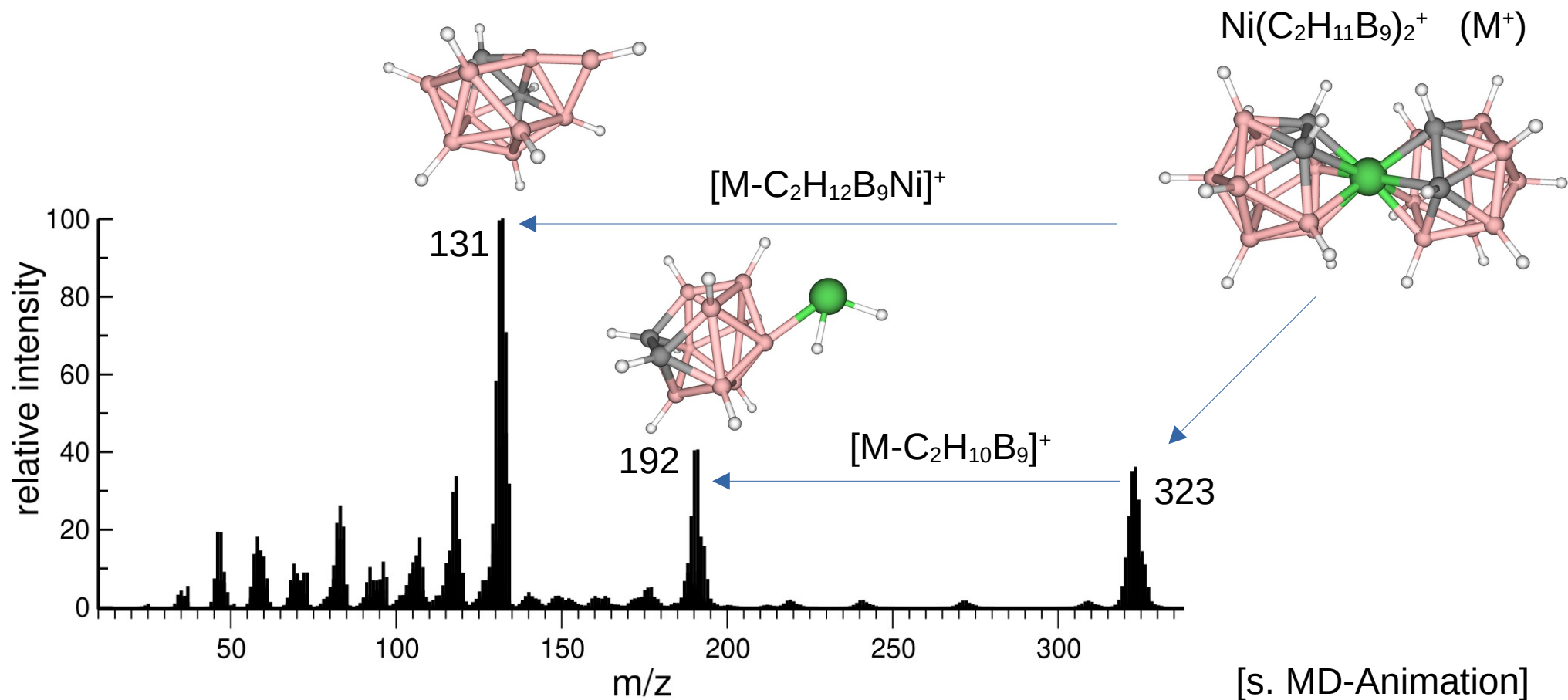
Ein komplizierterer Fall: B₅H₉

QCxMS (GFN1-xTB)



Sehr kompliziert: NiSAN

QCxMS (GFN2-xTB), nur theoretische Vorhersage!



Moleküle des Tages

J. Phys. Chem. **1986**, *90*, 2075–2080

Mass Spectrometric Investigations of Alkylolithium Compounds in the Gas Phase

D. Plavšić, D. Srzić,

“Rudjer Bošković” Institute, Zagreb, Croatia, Yugoslavia

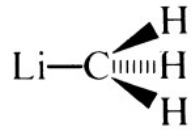
and L. Klasinc*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

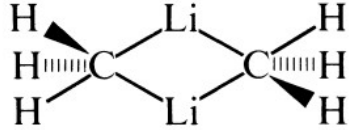
$(\text{LiR})_n$ R = Me, *i*-Pr, *n*-Pr, *n*-Bu, *s*-Bu, *i*-Bu, *t*-Bu

n = ?

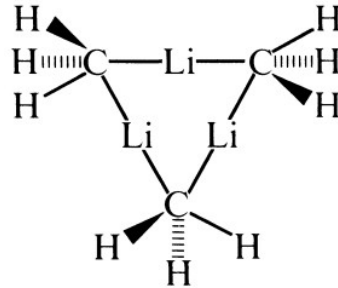
(MeLi)_n: Theoretische Varianten



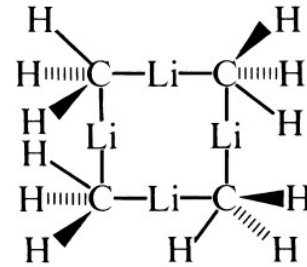
$n = 1$



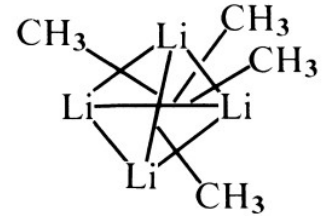
$n = 2$



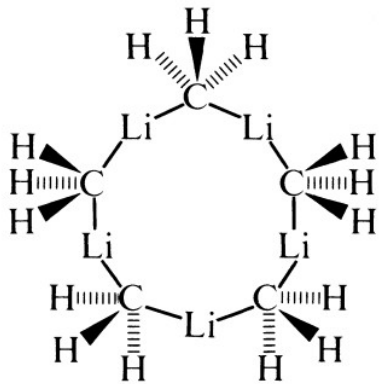
$n = 3$



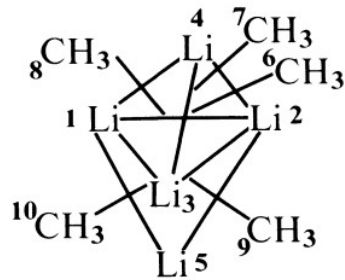
$n = 4$



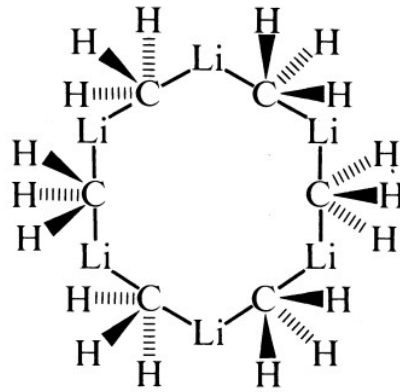
$n = 4$



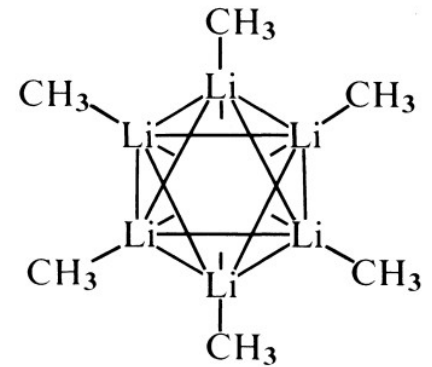
$n = 5$



$n = 5$



$n = 6$



$n = 6$

(MeLi)_n: EI-MS

TABLE I: Mass Spectrum of Methyllithium (70 eV)

assignments ^a	<i>m/z</i>	contribution to total ionic current, %
CLi ₂ ⁺	26	10
CHLi ₂ ⁺	27	9
CH ₂ Li ₂ ⁺	28	28
RLi ₂ ⁺	29	34
R ₂ Li ₃ ⁺	51	8
R ₃ Li ₄ ⁺	73	11

^aR = CH₃.

n = 3, 2 ?

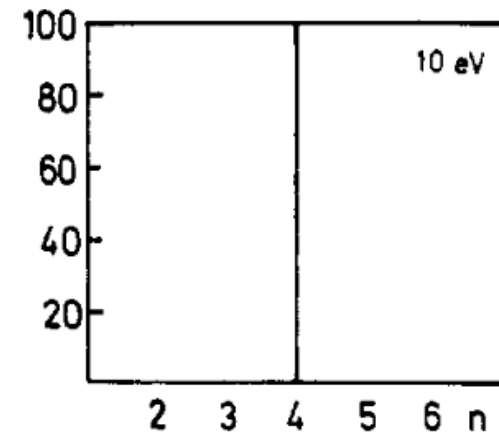
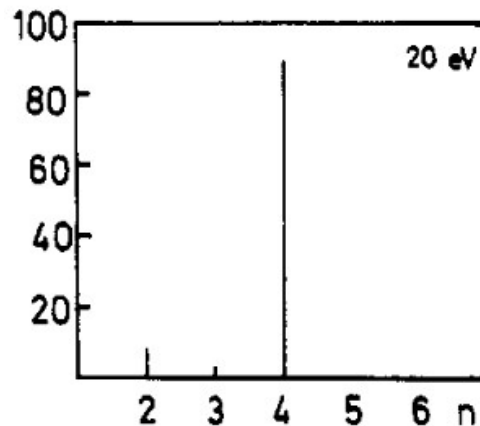
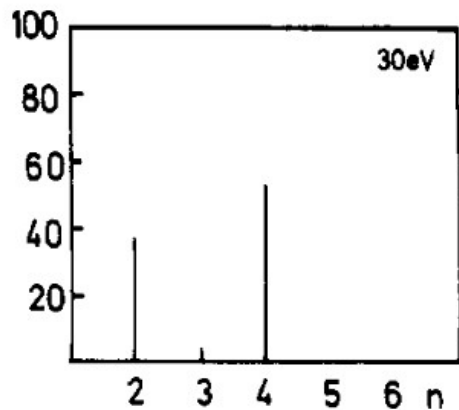
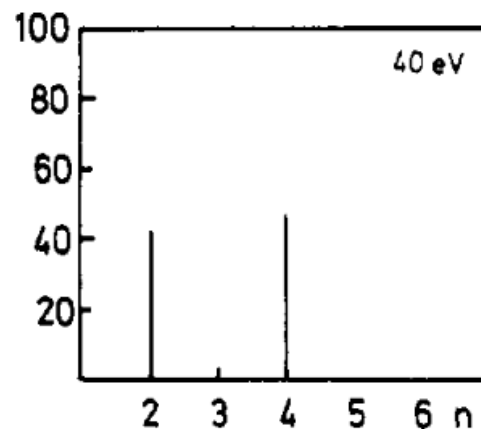
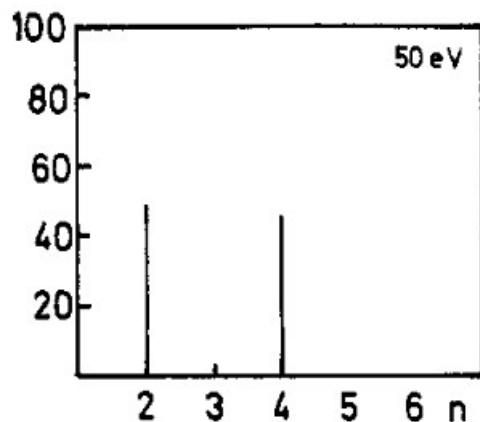
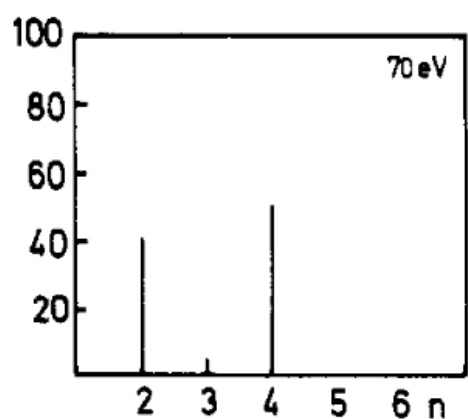
$(i\text{-PrLi})_n$: EI-MS

Mass Spectrum of Isopropylolithium (70 eV)

assignments ^a	m/z	contribution to total ionic current, %	m/z^*	metastable transitions	
				process	neutral fragment lost
RLi_2^+	57	39	20.7	$\text{R}_3\text{Li}_4^+ \rightarrow \text{RLi}_2^+$	R_2Li_2
HRLi_3^+	65	4	28.3	$\text{HR}_2\text{Li}_4^+ \rightarrow \text{RLi}_2$	HRLi_2
R_2Li_3^+	107	5	39.5	$\text{R}_2\text{Li}_3^+ \rightarrow \text{HRLi}_3^+$	$\text{H}_3\text{CCH}=\text{CH}_2$
HR_2Li_4^+	115	3	84.2	$\text{R}_3\text{Li}_4^+ \rightarrow \text{HR}_2\text{Li}_4^+$	$\text{H}_3\text{CCH}=\text{CH}_2$
R_3Li_4^+	157	49			

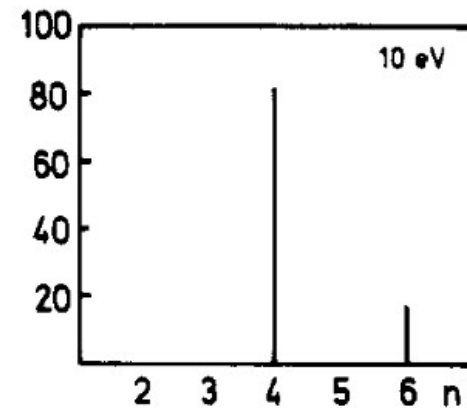
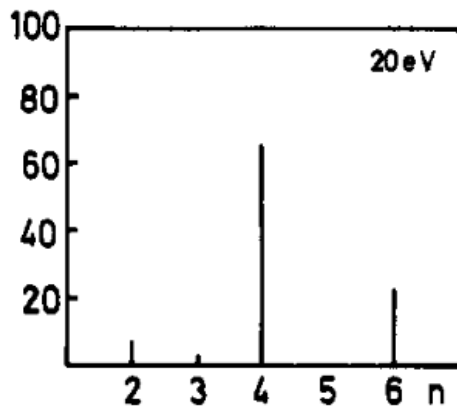
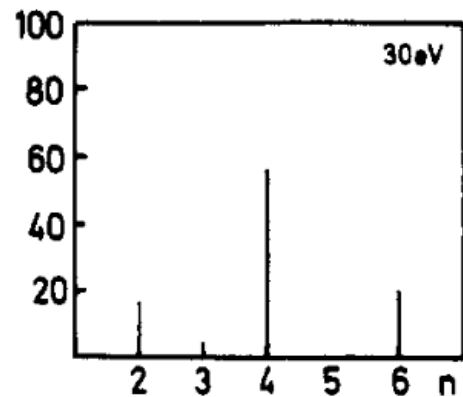
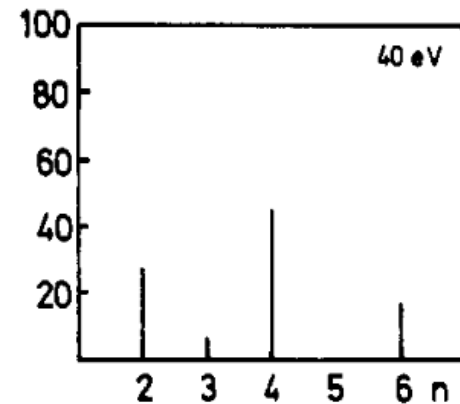
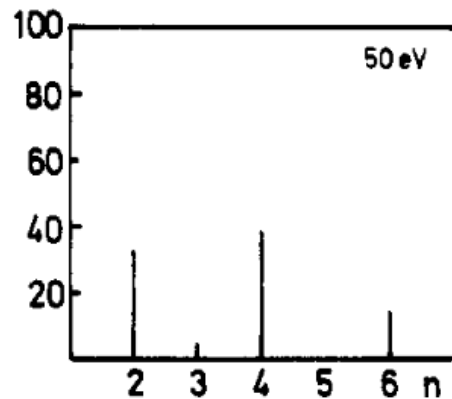
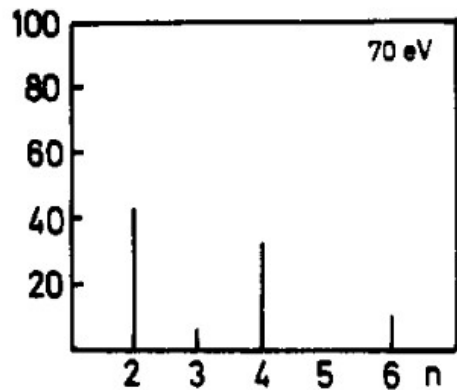
$n = 2 ?$

$(i\text{-PrLi})_n$: EI-MS 70 – 10 eV



$n = 4!$

$(n\text{-PrLi})_n$: EI-MS 70 – 10 eV



$n = 4$ und 6

$(\text{RLi})_n$: EI-MS Ergebnisse

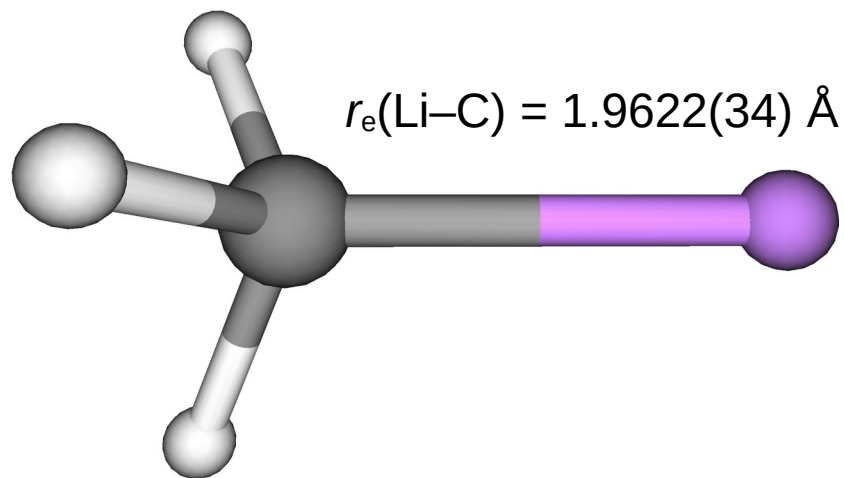
In der Gas Phase:

MeLi, *i*-PrLi, *s*-BuLi, *t*-BuLi sind Tetramere

n-PrLi, *n*-BuLi, *i*-BuLi sind Tetramere und Hexamere

Aber: MeLi Monomer (MW Untersuchung)

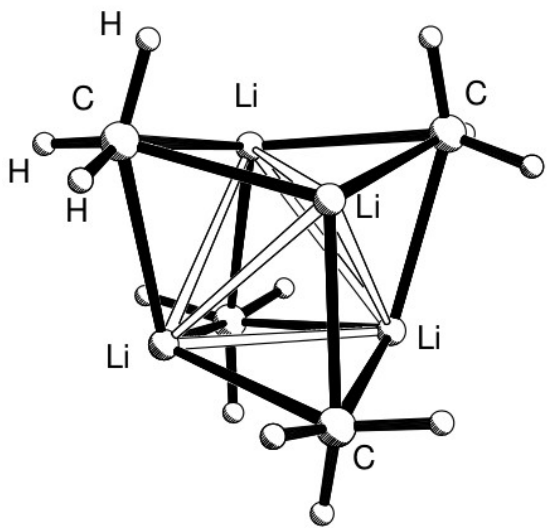
Mikrowellenspektroskopie + Quantenchemie:



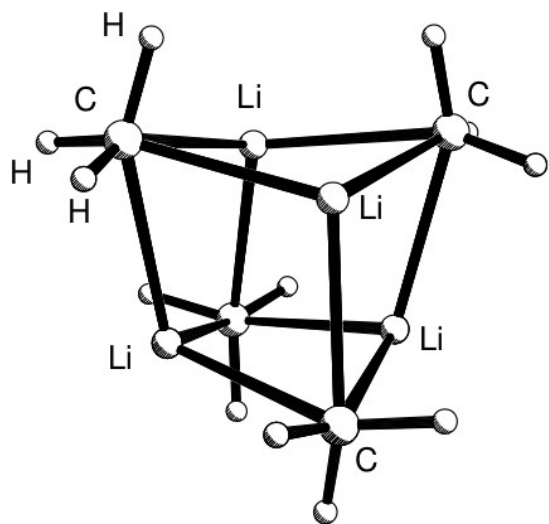
Theorie [ae-CCSD(T)/cc-pCVQZ]: $r_e(\text{Li-C}) = 1.9666 \text{ \AA}$

MeLi: XRD

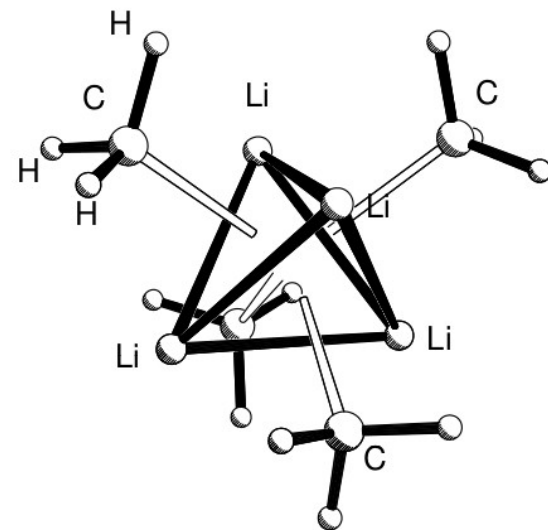
Tetramer im Kristall:



$$r(\text{Li}\dots\text{Li}) = 2.588 \text{ \AA}$$



$$r(\text{Li}\dots\text{C}) = 2.256 \text{ \AA}$$

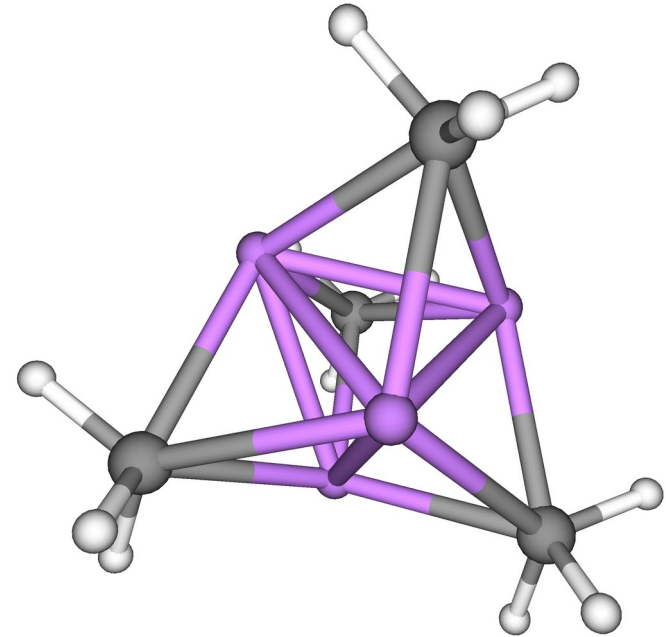
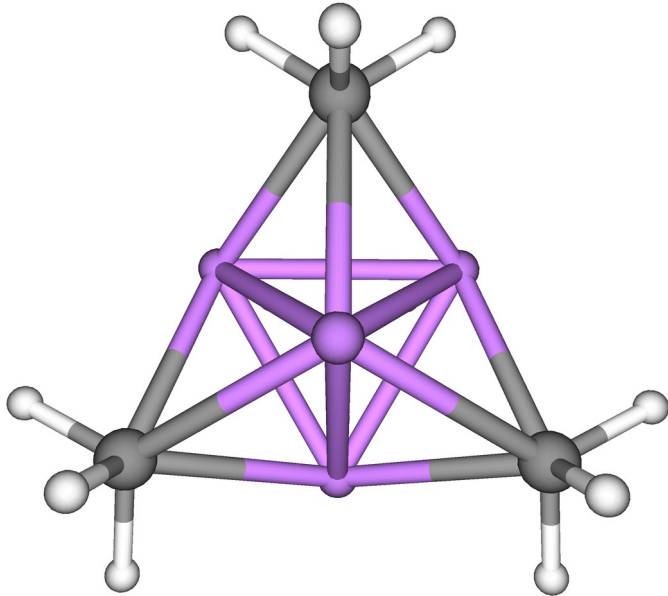


Wo sind die Bindungen?

(MeLi)₄ in der Gas-Phase (theoretisch)

PBE0-D3BJ/def2-QZVPP

Symmetrie: T_d



$$r_e(\text{Li-Li}) = 2.375 \text{ \AA}$$

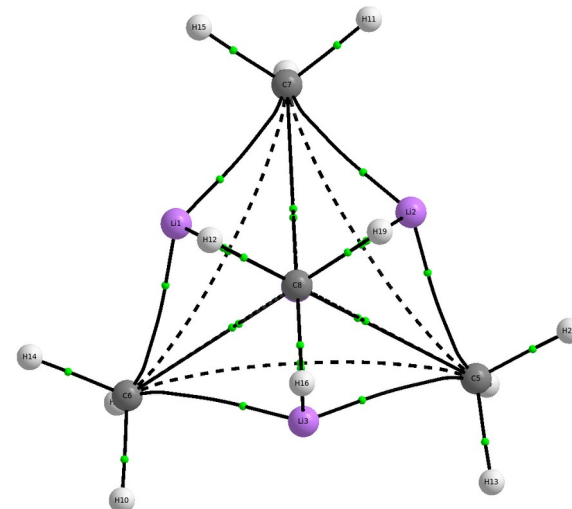
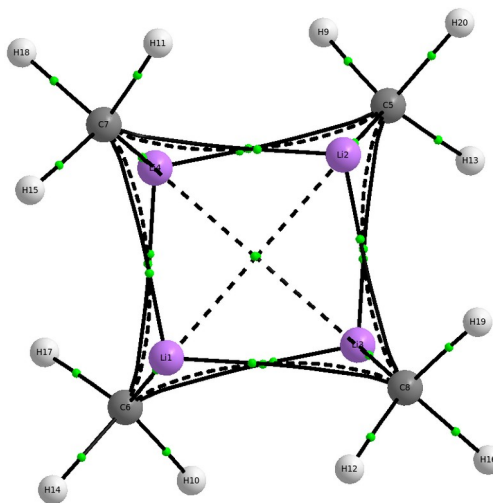
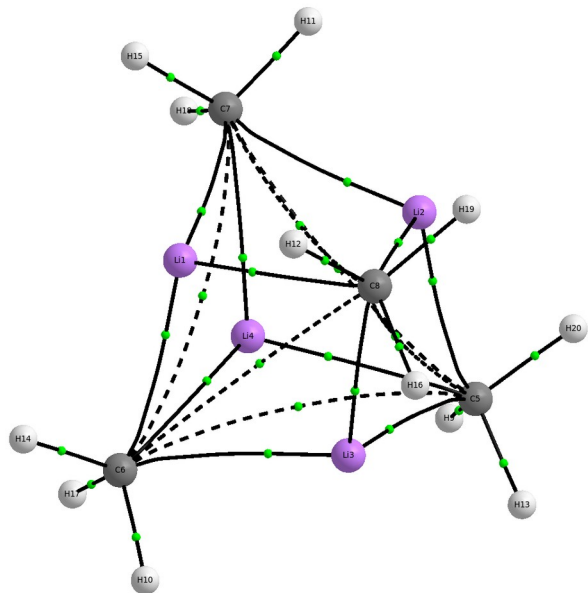
$$r_e(\text{Li-C}) = 2.166 \text{ \AA}$$

[Vgl. XRD: 2.588 \AA]

2.256 \AA]

(MeLi)₄: QTAIM

QTAIM: Quantum Theory of Atoms In Molecules



QTAIM Ladungen:

$$q(\text{Li}) = +0.87 e$$

$$q(\text{C}) = -0.62 e$$

Bond Critical Points (BCP):

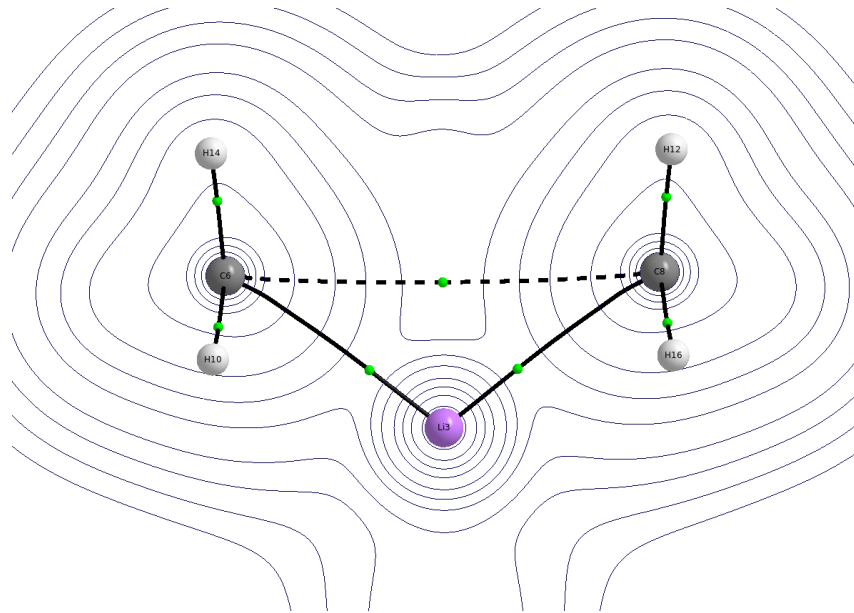
$$\text{BCP: Li-C: } \rho = 0.027 e/\text{bohr}^3 \quad \Delta\rho = 0.12 e/\text{bohr}^5 \quad \text{Ellipticity} = 0.15$$

$$\text{BCP: C...C: } \rho = 0.015 e/\text{bohr}^3 \quad \Delta\rho = 0.21 e/\text{bohr}^5 \quad \text{Ellipticity} = 1.24$$

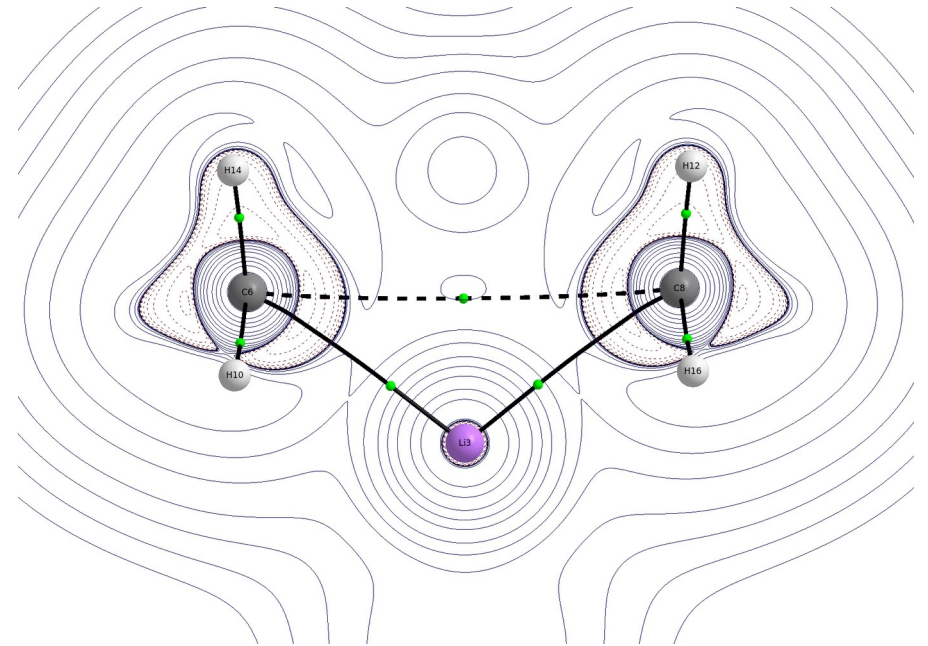
[Vgl. NBO: $\text{WBI}(\text{Li...Li}) = 0.007$, $\text{WBI}(\text{Li...C}) = 0.09$]

Li-C ist eine ionische Bindung!

(MeLi)₄: QTAIM



Elektronendichte

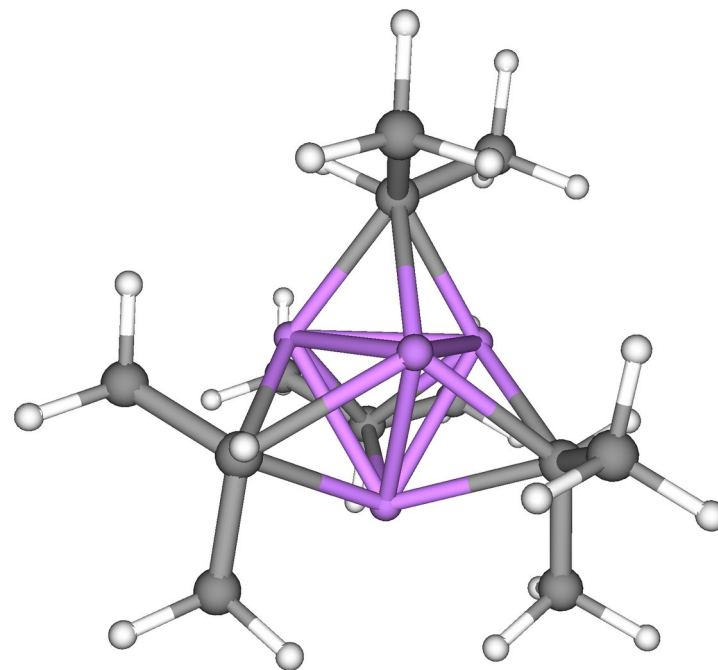
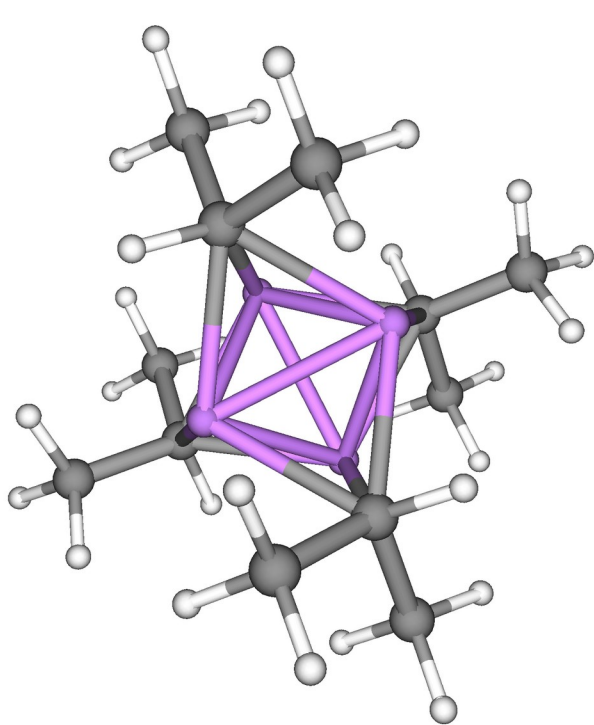


E-Dichte-Laplacian

$(i\text{-PrLi})_4$

PBE0-D3BJ/def2-QZVPP

Symmetrie: S_4



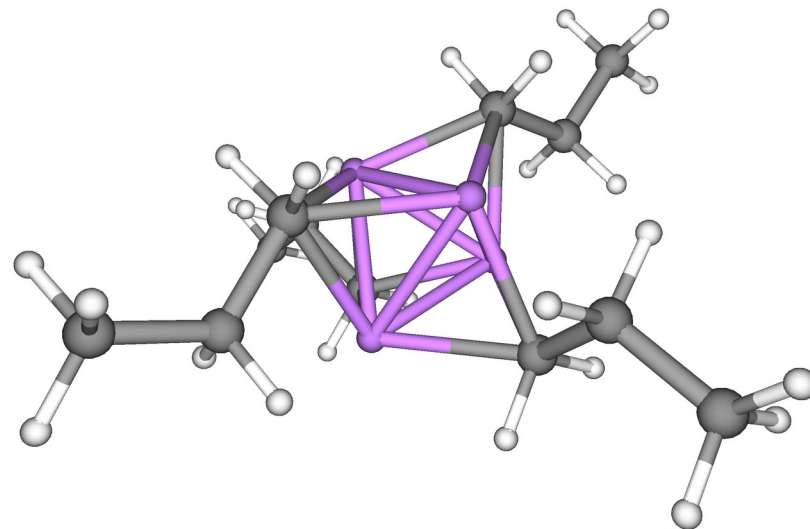
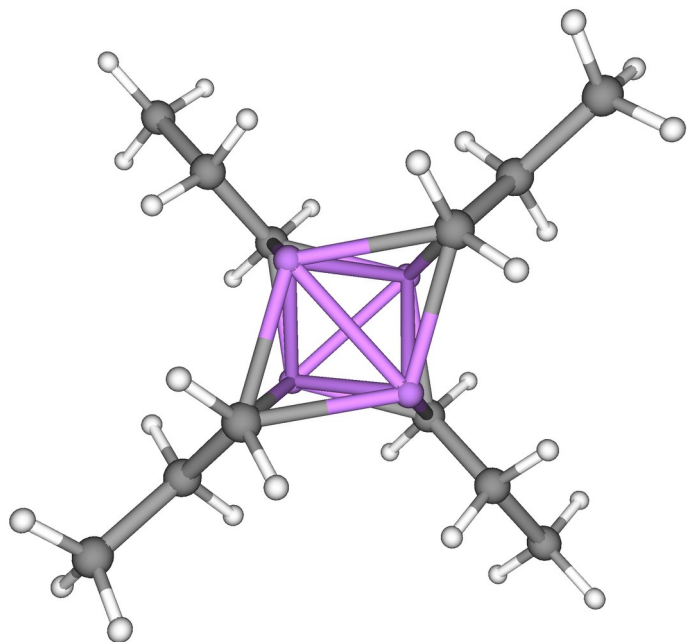
$$r_e(\text{Li-Li}) = 2.379 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.183 - 2.199 \text{ \AA}$$

$(n\text{-PrLi})_4$

PBE0-D3BJ/def2-QZVPP

Symmetrie: D_{2d}



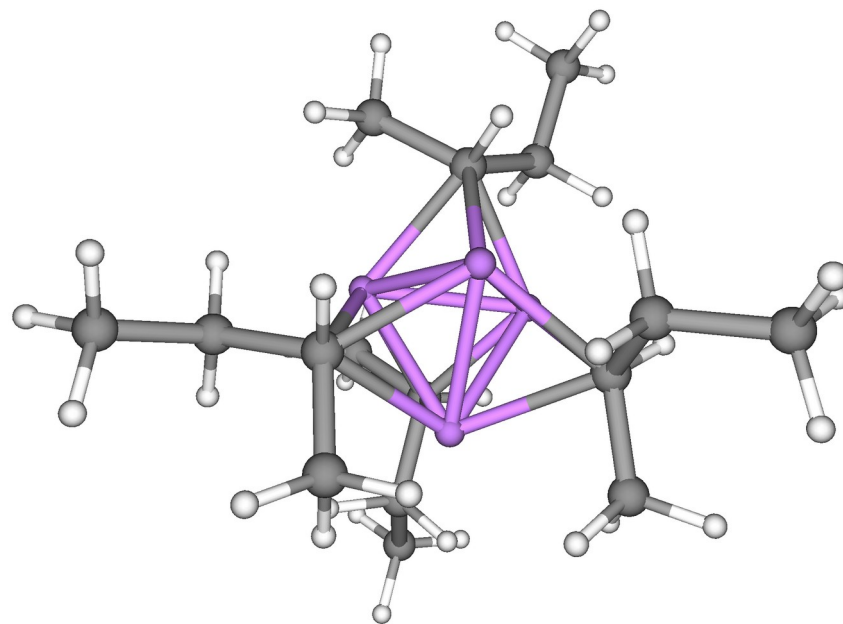
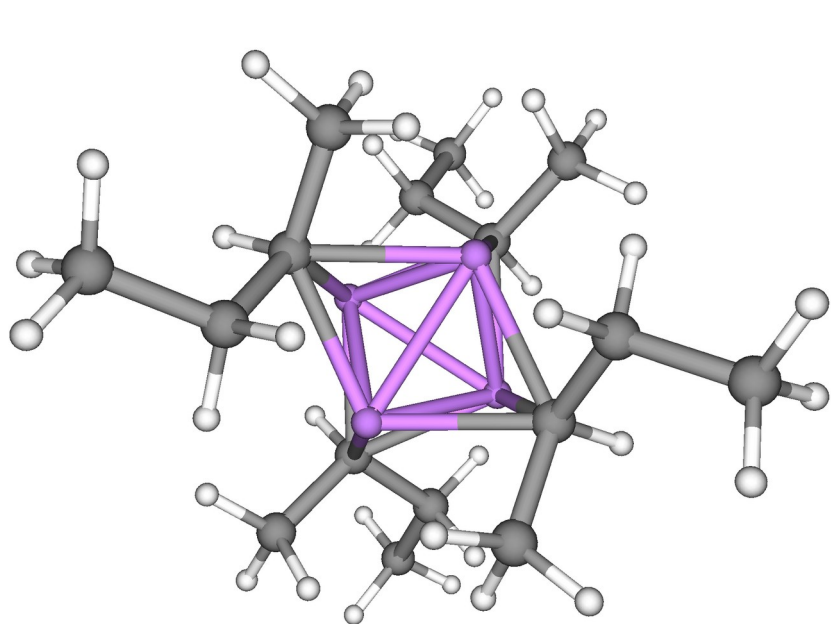
$$r_e(\text{Li-Li}) = 2.336 - 2.384 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.172 - 2.180 \text{ \AA}$$

(s-BuLi)₄

PBE0-D3BJ/def2-QZVPP

Symmetrie: C₂



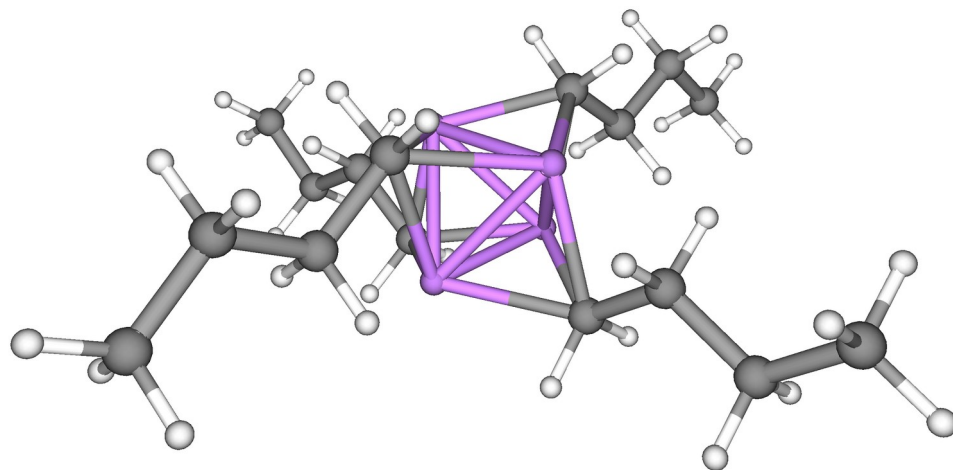
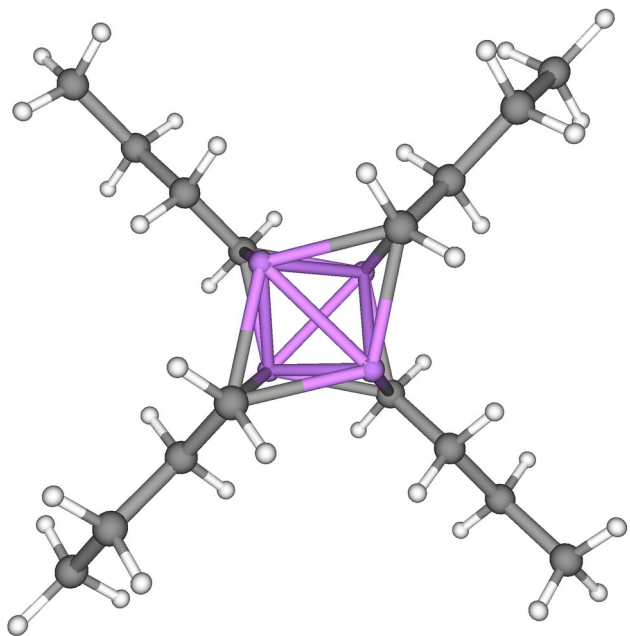
$$r_e(\text{Li-Li}) = 2.346 - 2.369 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.176 - 2.178 \text{ \AA}$$

$(n\text{-BuLi})_4$

PBE0-D3BJ/def2-QZVPP

Symmetrie: D_{2d}



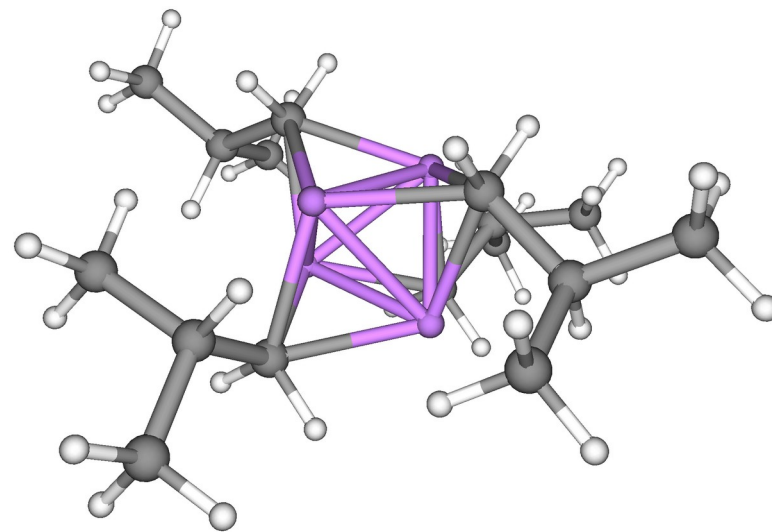
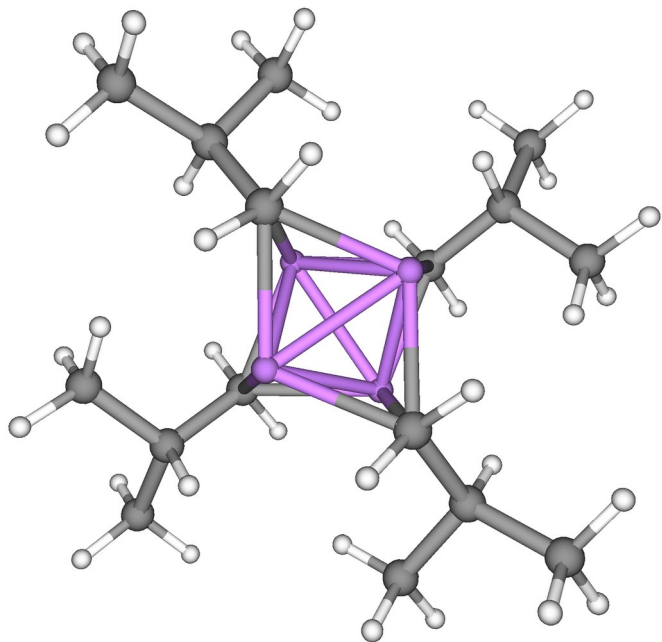
$$r_e(\text{Li-Li}) = 2.335 - 2.385 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.174 - 2.179 \text{ \AA}$$

$(i\text{-BuLi})_4$

PBE0-D3BJ/def2-QZVPP

Symmetrie: S_4



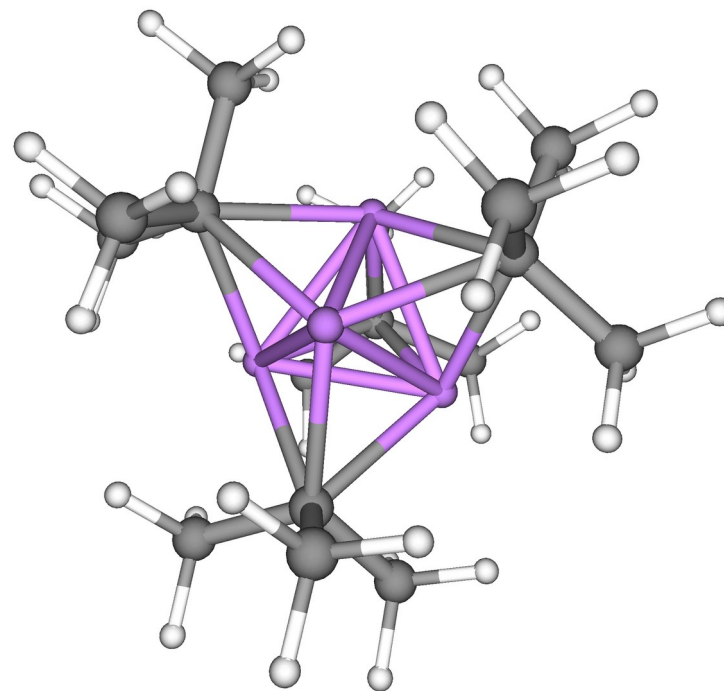
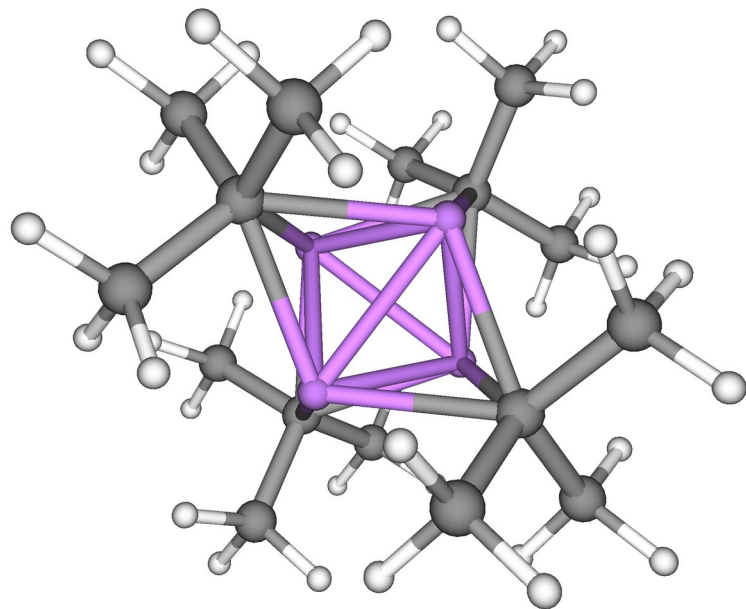
$$r_e(\text{Li-Li}) = 2.360 - 2.392 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.165 - 2.200 \text{ \AA}$$

$(t\text{-BuLi})_4$

PBE0-D3BJ/def2-QZVPP

Symmetrie: T

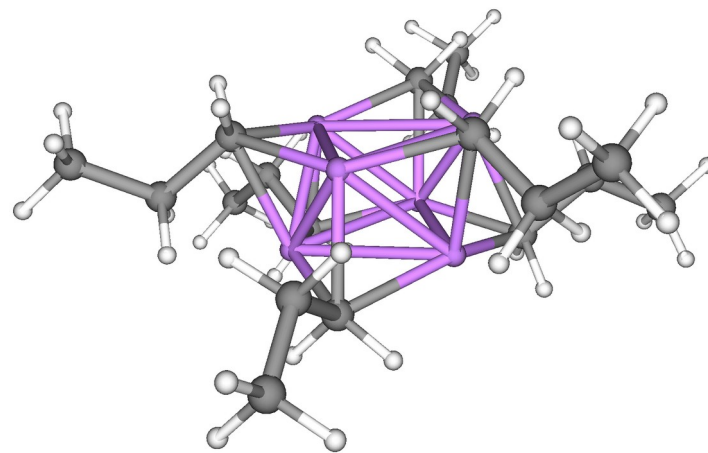
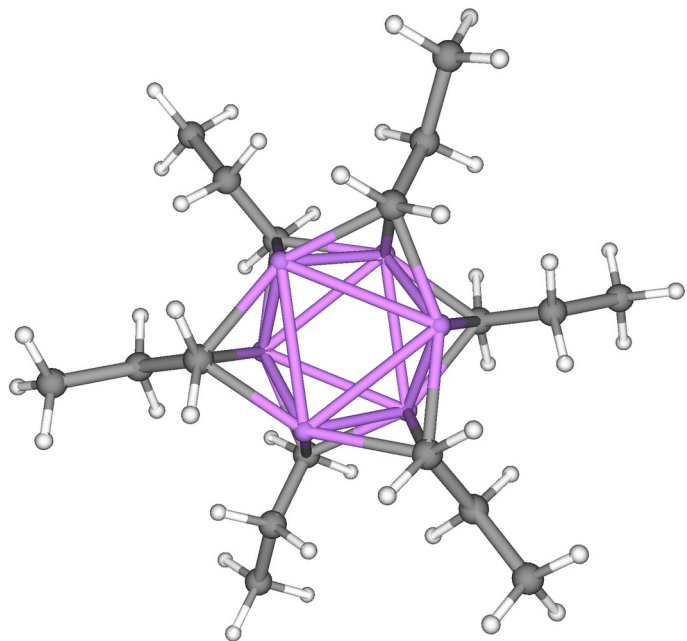


$$r_e(\text{Li-Li}) = 2.375 \text{ \AA} \quad r_e(\text{Li-C}) = 2.225 \text{ \AA}$$

$(n\text{-PrLi})_6$

PBE0-D3BJ/def2-QZVPP

Symmetrie: C_i



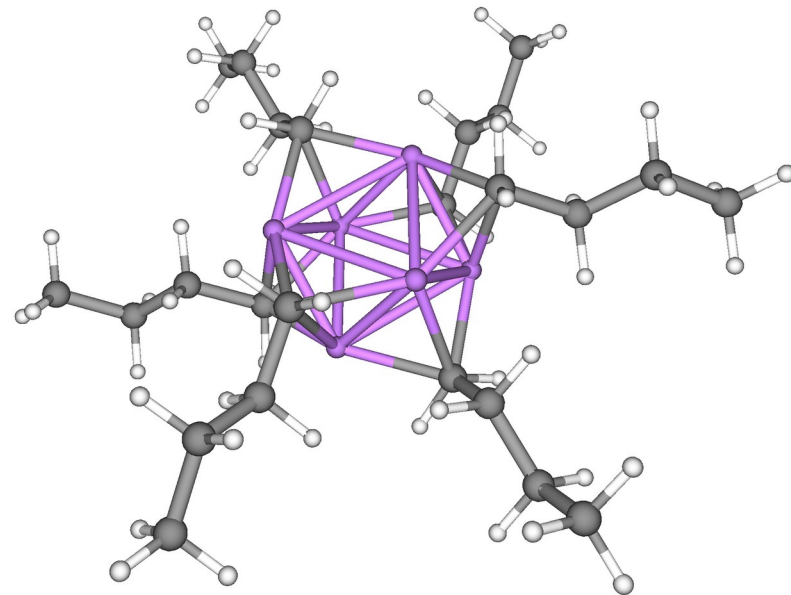
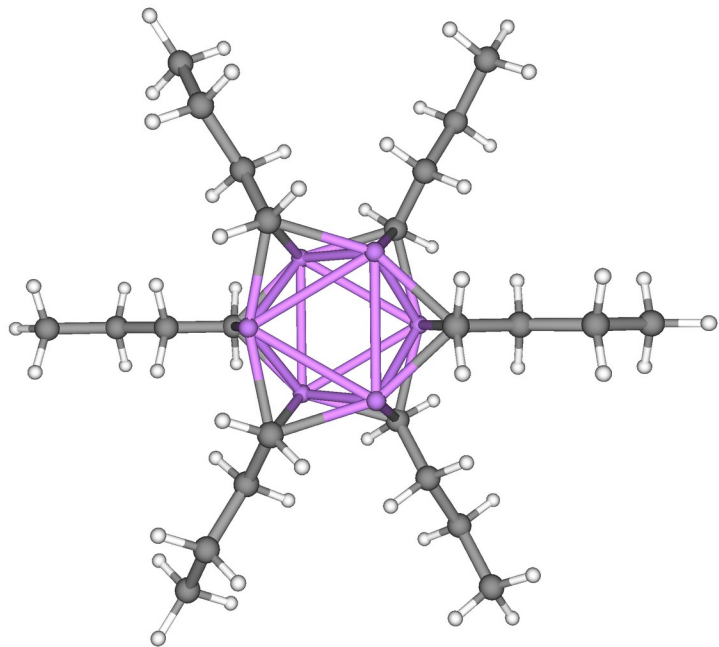
$$r_e(\text{Li-Li}) = 2.378 - 2.885 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.145 - 2.221 \text{ \AA}$$

$(n\text{-BuLi})_6$

PBE0-D3BJ/def2-QZVPP

Symmetrie: S_6



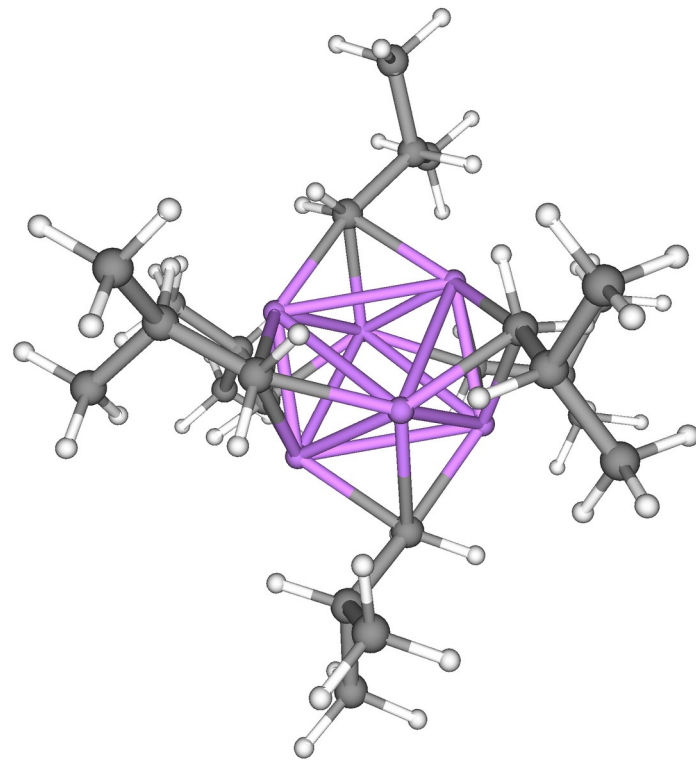
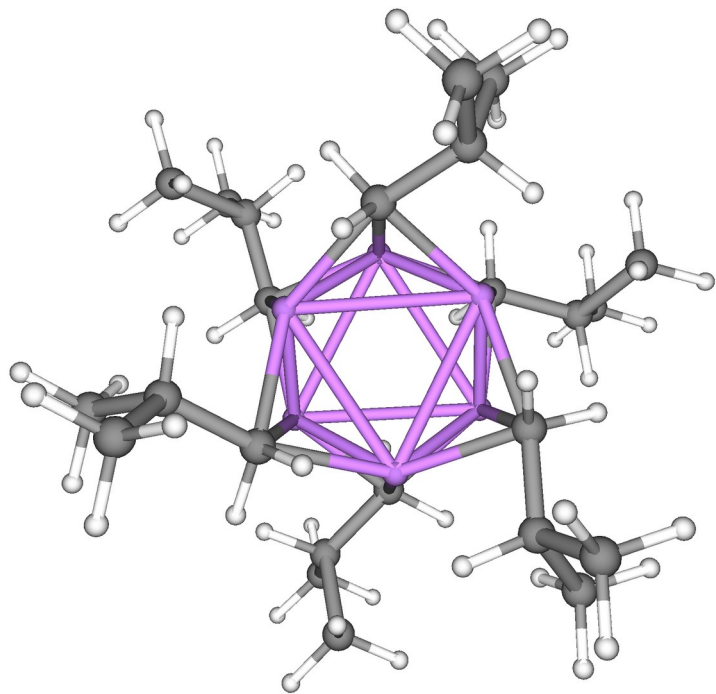
$$r_e(\text{Li-Li}) = 2.377 - 2.884 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.145 - 2.220 \text{ \AA}$$

$(i\text{-BuLi})_6$

PBE0-D3BJ/def2-QZVPP

Symmetrie: C_3



$$r_e(\text{Li-Li}) = 2.303 - 3.001 \text{ \AA}$$

$$r_e(\text{Li-C}) = 2.080 - 2.298 \text{ \AA}$$

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