Molecular Ions

Standard interpretation procedure for EI spectra

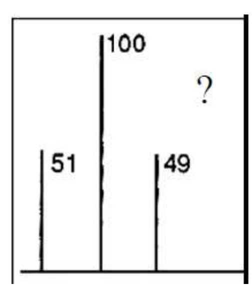
1. ***Known information*** *(other spectra, history of the sample), clear requirements for the MS measurement, control the m/z assignment (calibration)*
2. ***Elemental composition*** *– isotopic pattern (for all peaks in the spectrum)*
3. **Molecular ion** (largest mass in the spectrum, odd number of electrons, logic neutral losses). Comparison with spectra obtained with CI or other soft-ionization method
4. **Important ions**: odd number of electrons, largest abundance, high mass, largest abundance in a group of the peaks
5. **Appearance of the spectrum**: stability of molecular ion, labile bonds
6. **Possible sub-structures**
   1. Important series of ions with low masses
   2. Important neutral losses from $M^{+\cdot}$ (fragment with high masses)
   3. Characteristic ions
7. **Suggest molecular structure**

   Comparison with a reference spectrum, with spectra of similar compounds, check with fragmentation mechanisms expected for the suggested molecular ion

- Literature - Fred W. McLafferty, František Tureček: Interpretation of mass spectra

Molecular ion

- The most important information in the MS spectrum
  - Molecular mass
  - Elemental composition
  - Fragments must be consistent with the above data



- Not always detactable by EI-MS
  - Careful with interpretation
  - Use also soft ionization technique (Be aware of adducts with e.g., Na^+)
- Necessary (but not sufficient) conditions on the molecular ion
  - Must be the heaviest ion in the spectrum (with the corresponding isotopic pattern)
  - Must have an **odd** number of electrons
  - Must yield important fragments by **logic** losses

Odd vs. even numbers of electrons

- Ions with an odd number of electrons
  - EI: Molecules are ionized by a loss of an electron
    → ions with an unpaired electron – radicals
- Ions with an even number of electrons
  - All electrons paired
  - Usually more stable than radical cations
  - Often, the most abundant fragments
    $CH_4^{+\cdot} \rightarrow CH_3^+ + H^\cdot$
  - Most of the soft ionization techniques yield even-electron molecular ions (by protonation)

The nitrogen rule

- Most of the elements in organic compounds have a relation between the mass and the valence (both odd or both even)
- N is an exception
- If a compound has 0 or an even number of the nitrogen atoms, then the molecular ion will have an even mass

Element	Mass	Valence
H	1	1
C	12	4
O	16	2
F	19	1
Si	28 (30)	4
P	31	3
S	32 (34)	2
Cl	35 (37)	1
Br	79 (81)	1
I	127	1

Compound	Formula	Nominal mass
Ethane	C_2H_6	30
Octane	C_8H_{18}	114
Ethanol	C_2H_6O	46
Propanoic acid	$C_3H_6O_2$	74
Dichloromethane	CH_2Cl_2	84, 86, 88 (isotopes)
Hexafluoroethane	C_2F_6	138
Carbon disulfide	CS_2	76
Iodomethane	CH_3I	142
Ammonia	NH_3	17
Pyridine	C_5H_5N	79

Table 3.1. *Nitrogen rule.*

Mass values:	Odd	Even
$N_0, N_2, N_4, \ldots$	EE^+	$OE^{+\cdot}$
$N_1, N_3, N_5, \ldots$	$OE^{+\cdot}$	EE^+

Which ions have an odd/even number of electrons?

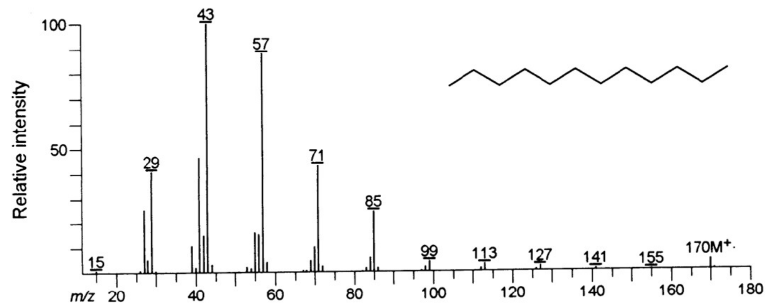
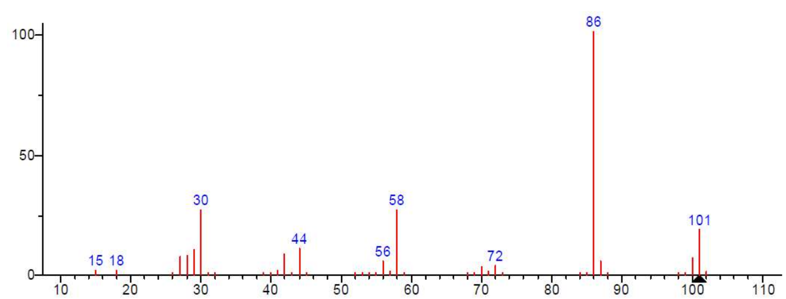


Figure 3.2. Mass spectrum of dodecane.

Which ions have an odd/even number of electrons?



- $OE^{+\bullet}$ are important for fragmentation mechanism (mark them)
- Importance increases with
  - Intensity, m/z, mass in the group of the peaks
- Important $OE^{+\bullet}$ ions are not probable for low m/z fragments ions

Logic neutral losses

- Only a limited number of common small fragments
- Loss of masses 4 – 14 and 21 – 25 are not probable
  (if such fragments appear, then the largest *m/z* does not correspond to the molecular ion)

Table A.5. *Common neutral fragments.*

Δ[a]	Mass	Formula	Example[b,c]
−4	79	Br	R⌇Br
	121	$C_7H_5O_2$	Benzoates
	51 65	C_3HN, C_4H_3N	Some nitrogen heterocyclic compounds
−3	38	H_6O_2	Some polycarboxylic acids
−2	39 53 67	C_nH_{2n-3}	Allyl esters and some cyclic carbonates—specific rearrangement loss of (C_nH_{2n-1} − 2H); some propargyl and allenic derivatives
−1	26 40 54	C_nH_{2n-2}	Aromatics; alkenyl aryl ethers
	54 68 82	C_nH_{2n-2}	4-Y-cycloalkenyls; $M^{+\cdot}$ − 69 − $(68)_n$ in polyisoprenes[c]
	54	C_3H_2O	Cyclic—CO—CH=CH—
	26 40	$C_nH_{2n}CN$	R⌇CN, R⌇CH_2CN (stable R^+ only)
0	27 41 55 69, etc.	C_nH_{2n-1}	RCOOR′-specific rearrangement loss of (R − 2H) or (R′ − 2H) + (R − H), also from carbonates, amides, larger ketones, etc.; loss of activated C_nH_{2n-1} groups
	27	HCN	Nitrogen heterocyclic compounds, cyanides, aryl-NH_2, enamines, imines
+1	(±14: Homologous impurity)		
	28 42 56	C_nH_{2n}	RCH_2COCH_2R-specific rearrangement loss of (R − H) or $(R - H)_2$, also from many unsaturated functional groups; retro-Diels-Alder[c]
	14	N	Aryl—NO
	28	N_2	Aryl—N=N—Aryl, >C=N_2, cyclic—N=N—
	28	CO	Aromatic oxygen compounds (carbonyls, phenols), cyclic ketones, R⌇C=O^{+c}
	42 56 70	$C_nH_{2n}CO$	Unsaturated acetamides, alkanoates; di-, cyclic, and complex ketones; specific H rearrangement loss of —CR_2—CO—
+2	29	CH_3N	Some unsaturated-, aryl—$N(CH_3)_2$
	43 57 71	HNCO, $C_nH_{2n-1}NO$	Loss of—NR—CO—from carbamates, cyclic amides, uracils
	1	H	Labile H; aryl—CH_2—H, RC≡CH, alkyl cyanides, lower fluorides and aldehydes (stable RCO^+), cyclopropyl compounds
	15 29 43 57 71, etc.	C_nH_{2n+1}	Alkyl loss: α-cleavage or branched site favored (loss of largest R); elimination from cycloalkyl group with H rearrangement[b]
	29 43 57	$C_nH_{2n+1}CO$	$C_nH_{2n+1}CO$⌇R (stable R^+ only)

Intensity of molecular peak

- Intensity of molecular peak depends on:
  - The stability of the molecular ions
  - Ionization energy (the smaller *IE*, the larger intensity of $M^{+\cdot}$)
- Generally, chemical stability of $M^{+\cdot}$ correlates with the stability of the molecule M
  - Intensity of $M^{+\cdot}$ provides a link to the structure of the molecule
  - Intensity of $M^{+\cdot}$ increases with unsaturation and with the number of rings
  - Intensity of $M^{+\cdot}$ decreases with chain branching

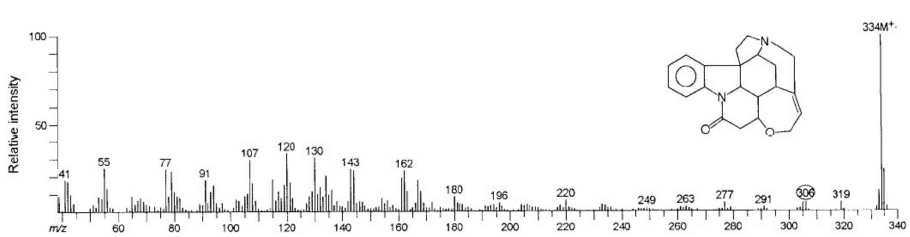


Figure 3.28. Mass spectrum of strychnine.

Which ions have an odd/even number of electrons?

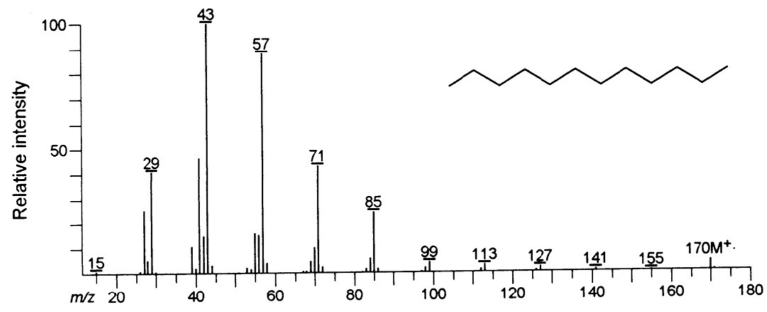
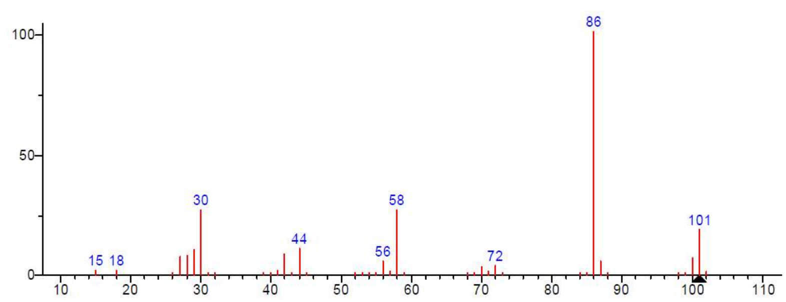


Figure 3.2. Mass spectrum of dodecane.

Which ions have an odd/even number of electrons?



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m/z	Int.	m/z	Int.	m/z	Int.
38	0.4	75	1.7	127	0.4
39	1.1	76	4.3	151	1.1
50	6.2	77	62.	152	3.4
51	19.	78	4.2	153	1.8
52	1.4	104	0.4	154	1.4
53	0.3	105	100.	181	7.4
63	1.3	106	7.8	182	55.
64	0.6	107	0.5	183	8.3
74	2.0	126	0.6	184	0.6