

2.5.4 Calculation of Isotope Distributions

The characteristic abundance patterns resulting from the combination of more than one polyisotopic element can be calculated from the relative abundances of the different isotopes. The following polynomial expression gives the isotope distribution of a polyisotopic molecule:

$$\{p_{i1} A^0 + p_{i2} A^{(m_{i2} - m_{i1})} + p_{i3} A^{(m_{i3} - m_{i1})} + \dots\}^{n_i} \times \\ \{p_{j1} A^0 + p_{j2} A^{(m_{j2} - m_{j1})} + p_{j3} A^{(m_{j3} - m_{j1})} + \dots\}^{n_j} \times \{ \dots$$

where p_{ix} is the relative abundance of the x th isotope of element i , the mass of the x th isotope of the element i is given by m_{ix} , and the exponent n_i stands for the number of atoms of the element i in the molecule. The expansion of this polynomial expression after inserting the p_{ix} and m_{ix} values for all the isotopes 1, 2, 3, ... of the elements i, j, \dots of a given molecule yields an expression that represents the isotope distribution:

$$w_0 A^0 + w_r A^r + w_s A^s + w_t A^t + \dots$$

where the values of $w_0, w_r, w_s, w_t, \dots$ are the relative abundances of $M^{+\cdot}, [M+r]^{+\cdot}, [M+s]^{+\cdot}, [M+t]^{+\cdot}, \dots$, respectively. The use of $A^{(m_{ix} - m_{i1})}$ allows to determine the values of r, s, t, \dots simply by expanding the general polynomial. A numerical value for A , which has no intrinsic meaning, is never needed.

For example, for CBr_2Cl_2 , the above equation gives rise to the following expression:

$$\{p_{12\text{C}} A^0 + p_{13\text{C}} A^{(m_{13\text{C}} - m_{12\text{C}})}\} \times \\ \{p_{79\text{Br}} A^0 + p_{81\text{Br}} A^{(m_{81\text{Br}} - m_{79\text{Br}})}\}^2 \times \\ \{p_{35\text{Cl}} A^0 + p_{37\text{Cl}} A^{(m_{37\text{Cl}} - m_{35\text{Cl}})}\}^2$$

For sufficient resolution, $(m_{ix} - m_{i1})$ and $(m_{jx} - m_{j1})$ differ from one another. This results in very complex isotope patterns even for very small molecules. Thus, owing to the occurrence of ^{12}C , ^{13}C , ^{79}Br , ^{81}Br , ^{35}Cl , and ^{37}Cl , there are 18 signals for CBr_2Cl_2 . However, the limited resolution of most real life experiments makes many pairs of $(m_{ix} - m_{i1})$ and $(m_{jx} - m_{j1})$ indistinguishable within experimental error, significantly reducing the number of separate peaks. For example, at unit resolution, one obtains $(m_{81\text{Br}} - m_{79\text{Br}}) = (m_{37\text{Cl}} - m_{35\text{Cl}}) = 2$. Consequently, the expression for BrCl becomes:

$$\{p_{79\text{Br}} A^0 + p_{81\text{Br}} A^2\} \times \{p_{35\text{Cl}} A^0 + p_{37\text{Cl}} A^2\} =$$

$$p_{79\text{Br}} p_{35\text{Cl}} A^0 + (p_{79\text{Br}} p_{37\text{Cl}} + p_{81\text{Br}} p_{35\text{Cl}}) A^2 + p_{37\text{Cl}} p_{81\text{Br}} A^4$$

This shows that at unit resolution, BrCl gives rise to only 3 peaks (M^{+} , $[M+2]^{+}$, $[M+4]^{+}$) rather than to 4 peaks, as they are expected for very high resolution.

Often, the contribution of isotopes of low abundance can be neglected without sacrificing much precision. For example, the effect of ^2H on isotope patterns is usually insignificant. Also, ^{13}C is often negligible when focussing on peaks of the series $[M+2n]^{+}$, which then results in patterns that are characteristic for halogens, sulfur, and silicon. In large molecules, however, isotopes of low abundance cannot be neglected. For example, in the case of buckminster fullerene (C_{60}), not only M^{+} (relative intensity, 100%) and $[M+1]^{+}$ (66.72%) but also $[M+2]^{+}$ (21.89%), $[M+3]^{+}$ (4.71%), and even $[M+4]^{+}$ (0.75%) are quite significant ions.

As shown above, typical isotope patterns can be readily calculated manually by applying the general equation and neglecting isotopes of low abundance. The outlined procedure can also be easily implemented and evaluated with generic computer software that allows simple calculations. Dedicated and user-friendly programs that already contain the necessary isotope abundances and masses are available. Incidentally, because the use of the above equation for systems with 1000 or more polyisotopic atoms results in excessive calculation times, more efficient but somewhat more complicated algorithms have been developed for implementation in dedicated programs [4]. Typical isotope patterns are given on the following pages.

2.5.5

Isotopic Abundances of Various Combinations of Chlorine, Bromine, Sulfur, and Silicon

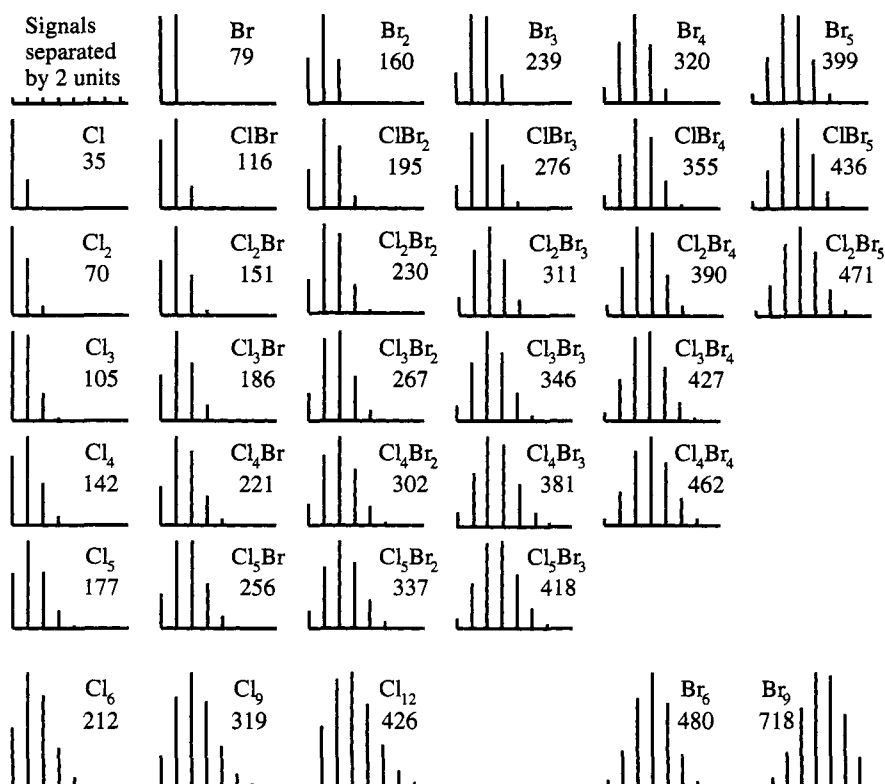
Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance
Cl ₁	35	100	Br ₁	79	100	S ₁	32	100
	37	31.98		81	97.88		33	0.79
Cl ₂	70	100	Br ₂	158	51.09	S ₂	34	4.43
	72	63.96		160	100		64	100
	74	10.23		162	48.93		65	1.58
Cl ₃	105	100	Br ₃	237	34.05	S ₃	66	8.87
	107	95.93		239	100		68	0.24
	109	30.67		241	97.89		96	100
	111	3.27		243	31.94		97	2.37
Cl ₄	140	77.96	Br ₄	316	17.40	S ₄	98	13.31
	142	100		318	68.09		99	0.21
	144	47.82		320	100		100	0.66
	146	10.19		322	65.26		128	100
	148	0.82		324	15.96		129	3.16
Cl ₅	175	62.53	Br ₅	395	10.43	S ₅	130	17.76
	177	100		397	51.09		131	0.42
	179	63.94		399	100		132	1.27
	181	20.45		401	97.94		160	100
	183	3.28		403	47.89		161	3.94
	185	0.21		405	9.38		162	22.22
Cl ₆	210	52.12	Br ₆	474	5.32	S ₆	163	0.70
	212	100		476	31.26		164	2.08
	214	79.95		478	76.62		166	0.11
	216	34.08		480	100		192	100
	218	8.21		482	73.38		193	4.73
	220	1.05		484	28.73		194	26.68
	222	0.06		486	4.68		195	1.05
Si ₁	28	100	Si ₂	56	100	Si ₃	196	3.09
	29	5.06		57	10.13		198	0.20
	30	3.36		58	6.98		84	100
				59	0.34		85	15.19
				60	0.11		86	10.85
							87	1.03
							88	0.36

Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance
Cl ₁ Br ₁	114	76.70	Cl ₁ Br ₂	193	43.83	Cl ₁ Br ₃	272	26.15
	116	100		195	100		274	85.22
	118	24.46		197	69.83		276	100
				199	13.66		278	48.90
Cl ₁ Br ₄	351	14.26	Cl ₂ Br ₁	149	61.35		Cl ₂ Br ₂	280
	353	60.41		151	100	228		38.35
	355	100		153	45.67	230		100
	357	79.93		155	6.38	232		89.63
	359	30.39			234	31.89		
	361	4.25			236	3.90		
Cl ₃ Br ₁	184	51.12	Cl ₃ Br ₂	263	31.35	Cl ₄ Br ₁	219	43.79
	186	100		265	92.01		221	100
	188	65.22		267	100		223	83.86
	190	17.73		269	50.01		225	33.42
	192	1.74		271	11.70		227	6.93
Cl ₄ Br ₂	298	24.14	Cl ₄ Br ₃	273	1.03	Cl ₄ Br ₄	229	0.48
	300	78.63		377	13.63		456	7.43
	302	100		379	57.78		458	38.40
	304	63.54		381	100		460	83.70
	306	21.54		383	91.19		462	100
	308	3.73		385	47.13	464	71.37	
	310	0.26		387	14.03	466	31.11	
Cl ₁ S ₁	67	100	Cl ₁ S ₂	389	2.22	Cl ₂ S ₁	468	8.10
	68	0.79		391	0.13		470	1.16
	69	36.41		99	100		102	100
	70	0.25		100	1.58		103	0.79
	71	1.44		101	40.85		104	68.39
Cl ₂ S ₂				102	0.57		105	0.50
				103	3.08		106	13.08
							108	0.47
	134	100	Cl ₃ S ₁	137	99.64	Cl ₃ S ₂	169	95.42
	135	1.58		138	0.79		170	1.51
	136	72.82		139	100		171	100
	137	1.08		140	0.75		172	1.51
	138	16.14		141	34.82		173	37.62
139	0.21	142		0.24	174		0.53	
140	1.06	143		4.63	175		5.94	
			145	0.15	177	0.35		

Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance
Cl_1Si_1	63	100	Cl_2Si_1	98	100	Cl_3Si_1	133	100
	64	5.06		99	5.06		134	5.06
	65	35.34		100	67.32		135	99.30
	66	1.62		101	3.24		136	4.86
	67	1.07		102	12.38		137	33.90
				103	0.52		138	1.55
				104	0.34		139	4.30

2.5.6

Isotope Patterns of Combinations of Cl and Br



The signals are separated by 2 mass units, and the combination of the lightest isotopes is given on the left side of the x axis. The mass for the most abundant signal is shown under the symbol of the element. See Chapter 2.5.5 for exact abundances of many of these combinations.

2.5.7

Indicators of the Presence of Heteroatoms

In low-resolution mass spectra, one often observes characteristic isotope patterns, specific masses of fragment ions, and characteristic mass differences (Δm) between the molecular ion ($M^{+\cdot}$) and fragment ions (Frag^+), or between fragment ions. High resolution mass spectra can be used to confirm the elemental composition provided that the resolution is sufficient to discriminate alternative compositions. Moreover, tandem mass spectrometry (also called MS/MS) may be used to identify heteroatom-characteristic losses from parent or fragment ions.

- Indication of O: Δm 17 from $M^{+\cdot}$, in N-free compounds
 Δm 18 from $M^{+\cdot}$
 Δm 18 from Frag^+ , particularly in aliphatic compounds
 Δm 28, 29 from $M^{+\cdot}$ for aromatic compounds
 Δm 28 from Frag^+ for aromatic compounds
 m/z 15, relatively abundant
 m/z 19
 m/z 31, 45, 59, 73, ... + $(14)_n$
 m/z 32, 46, 60, 74, ... + $(14)_n$
 m/z 33, 47, 61, 75, ... + $(14)_n$ for $2 \times \text{O}$, in absence of S
 m/z 69 for aromatic compounds meta-disubstituted by oxygen
- Indication of N: $M^{+\cdot}$ odd-numbered (indicates odd number of N in $M^{+\cdot}$)
 Large number of even-numbered fragment ions
 Δm 17 from $M^{+\cdot}$ or Frag^+ , in O-free compounds
 Δm 27 from $M^{+\cdot}$ or Frag^+ , for aromatic compounds or nitriles
 Δm 30, 46 for nitro compounds
 m/z 30, 44, 58, 72, ... + $(14)_n$ for aliphatic compounds
- Indication of S: Isotope peak $[M+2]^{+\cdot} \geq 5\% M^{+\cdot}$
 Δm 33, 34, 47, 48, 64, 65 from $M^{+\cdot}$
 Δm 34, 48, 64 from Frag^+
 m/z 33, 34, 35
 m/z 45 in O-free compounds
 m/z 47, 61, 75, 89, ... + $(14)_n$ unless compound with $2 \times \text{O}$
 m/z 48, 64 for S-oxides
- Indication of F: Δm 19, 20, 50 from $M^{+\cdot}$
 Δm 20 from Frag^+
 m/z 20
 m/z 57 without m/z 55 in aromatics
- Indication of Cl: Isotope peak $[M+2]^{+\cdot} \geq 33\% M^{+\cdot}$
 Δm 35, 36 from $M^{+\cdot}$
 Δm 36 from Frag^+
 m/z 35/37, 36/38, 49/51

Indication of Br: Isotope peak $[M+2]^+ \geq 98\% M^+$

Δm 79, 80 from M^+

Δm 80 from Frag^+

m/z 79/81, 80/82

Indication of I: Isotope peak $[M+1]^+$ of very low abundance at relatively high mass

Δm 127 from M^+

Δm 127, 128 from Frag^+

m/z 127, 128, 254

Indication of P: m/z 47 in compounds free of S or $2 \times O$

m/z 99 without isotope peak at m/z 100 in alkyl phosphates

2.5.8

Rules for Determining the Relative Molecular Weight (M_r)

The molecular ion ($M^{+\cdot}$) is defined as the ion that comprises the most abundant isotopes of the elements in the molecule. Interestingly, the lightest isotopes of most elements that frequently occur in organic compounds and their common salts (H, C, N, O, F, Si, P, S, Cl, As, Br, I, Na, Mg, Al, K, Ca, Rb, Cs) are also the most abundant ones. Notable exceptions are B, Li, Se, Sr, and Ba.

$M^{+\cdot}$ is always accompanied by isotope peaks. Their relative abundance depends on the number and kind of the elements present and their natural isotopic distribution. The abundance of $[M^{+\cdot}+1]$ indicates the maximum number of carbon atoms (C_{\max}) according to the following relationship:

$$C_{\max} = 100 [M^{+\cdot}+1] / (1.1 [M^{+\cdot}])$$

$[M^{+\cdot}+2]$ and higher masses indicate the number and kind of elements that have a relatively abundant isotope two mass units heavier (such as S, Si, Cl, Br).

$M^{+\cdot}$ is always an even number if the molecule contains only elements for which the atomic mass and valence are both even-numbered or both odd-numbered (such as H, C, O, S, Si, P, F, Cl, Br, I). In the presence of other elements, $M^{+\cdot}$ becomes an odd number unless the elements are present in an even number (this holds for N, ^{13}C , ^2H).

$M^{+\cdot}$ can only form fragment ions of masses that differ from that of the molecular ion by chemically logical values (Δm). In this context, chemically illogical differences are $\Delta m = 3$ (in the absence of $\Delta m = 1$) to $\Delta m = 14$, $\Delta m = 21$ (in the absence of $\Delta m = 1$) to $\Delta m = 24$, $\Delta m = 37$, 38 and all Δm less than the mass of an element of characteristic isotope pattern in cases where the same isotope pattern is not retained in the fragment ion.

$M^{+\cdot}$ of a compound must contain all elements (and the maximum number of each) that are shown to be present in the fragment ions.

If ionization is performed by electron impact, $M^{+\cdot}$ is the ion with the lowest appearance potential.

If a pure sample flows into the ion source through a molecular leak, $M^{+\cdot}$ exhibits the same effusion rate as can be determined from the fragment ions. The abundance of $M^{+\cdot}$ is proportional to the sample pressure in the ion source.

For polar compounds, $[M+H]^+$ is often observed in mass spectra obtained not only with fast atom bombardment and atmospheric pressure chemical ionization but also with electron impact ionization. In this latter case, the abundance of $[M+H]^+$ changes in proportion to the square of the sample pressure in the ion source.

In the absence of a signal for $M^{+\cdot}$, the molecular weight must have a value that shows a logical and reasonable mass difference, Δm , to all the observed fragment ions.

2.5.9

Homologous Mass Series as Indications of Structural Type

Certain sequences of intensity maxima in the lower mass range and the masses of unique signals are often characteristic of a particular compound type. The intensity distribution of such ion series is in general smooth. Therefore, abrupt changes (maxima and minima) are of structural significance. The ion or ion series that is most indicative of a particular compound type is set in *italics*.

Mass values m/z	Elemental composition	Compound types
12 + 14m	C_nH_{2n-2}	alkenes, monocycloalkanes, alkynes, dienes, cycloalkenes, polycyclic alicyclics, cyclic alcohols
13 + 14m	C_nH_{2n-1}	alkanes, alkenes, <i>monocycloalkanes</i> , alkynes, dienes, cycloalkenes, polycyclic alicyclics, alcohols, alkyl ethers, cyclic alcohols, cycloalkanones, aliphatic acids, esters, lactones, thiols, sulfides, glycols, glycol ethers, alkyl chlorides
	$C_nH_{2n-3}O$	cycloalkanones
14 + 14m	C_nH_{2n}	alkanes, alkenes, monocycloalkanes, polycyclic alicyclics, alcohols, alkyl ethers, thiols, sulfides, alkyl chlorides
	$C_nH_{2n-2}O$	cycloalkanones
15 + 14m	C_nH_{2n+1}	<i>alkanes</i> , alkenes, monocycloalkanes, alkynes, dienes, cycloalkenes, polycyclic alicyclics, alkanones, alkanals, glycols, glycol ethers, alkyl chlorides, acid chlorides
	$C_nH_{2n-1}O$	alkanones, alkanals, <i>cyclic alcohols</i> , acid chlorides
16 + 14m	$C_nH_{2n}O$	<i>alkanones</i> , <i>alkanals</i>
	$C_nH_{2n+2}N$	<i>alkyl amines</i> , <i>aliphatic amides</i>
	$C_nH_{2n}NO$	aliphatic amides
17 + 14m	$C_nH_{2n+1}O$	<i>alcohols</i> , <i>alkyl ethers</i> , aliphatic acids, esters, lactones, glycols, glycol ethers
	$C_nH_{2n-1}O_2$	aliphatic acids, esters, lactones
18 + 14m	$C_nH_{2n}O_2$	<i>aliphatic acids</i> , <i>esters</i> , <i>lactones</i>

Mass values m/z	Elemental composition	Compound types
19 + 14m	$C_nH_{2n+3}O$	alcohols, alkyl ethers
	$C_nH_{2n+1}O_2$	aliphatic acids, esters, lactones
	$C_nH_{2n+1}O_2$	<i>glycols, glycol ethers</i>
	$C_nH_{2n+1}S$	<i>thiols, sulfides</i>
20 + 14m	$C_8H_8 + C_nH_{2n}$	alkylbenzenes
	$C_nH_{2n+2}O_2$	glycols, glycol ethers
	$C_nH_{2n+2}S$	thiols, sulfides
21 + 14m	$C_7H_7 + C_nH_{2n}$	alkylbenzenes
	C_7H_5O	aryl ketones
	$C_nH_{2n}Cl$	<i>alkyl chlorides</i>
	$C_nH_{2n}COCl$	acid chlorides
22 + 14m	$C_6H_6N + C_nH_{2n}$	alkylanilines
	C_nH_{2n-6}	polycyclic alicyclics
23 + 14m	C_nH_{2n-5}	polycyclic alicyclics
24 + 14m	C_nH_{2n-4}	polycyclic alicyclics
25 + 14m	C_nH_{2n-3}	<i>alkynes, dienes, cycloalkenes</i> , polycyclic alicyclics
39, 52±1, 64±1, 76±2, 91±1	$C_nH_n±1$	alkylbenzenes, aromatic hydrocarbons, phenols, aryl ethers, aryl ketones

2.5.10

Mass Correlation Table

Note: As long as it makes sense chemically, CH₂, CH₄, CH₃O, and O₂ in the formulae of the second column may be replaced by N, O, P, and S, respectively (M: molecular mass).

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
1		[M+1] ⁺ , [M-1] ⁻	particularly in FAB spectra, in which M±1 occurs even for moderately basic and acidic compounds, but intensive M ⁺ without M±1 is unusual
7	Li ⁺	[M+7] ⁺ [M-7] ⁻	in FAB spectra in the presence of Li ⁺ in FAB spectra of organic Li ⁺ salts
12	C ⁺		
13	CH ⁺		
14	CH ₂ ⁺ , N ⁺ , N ₂ ⁺⁺ , CO ⁺⁺		
15	CH ₃ ⁺	[M-15] ⁺ (CH ₃)	nonspecific; abundant: methyl, <i>N</i> -ethylamines
16	O ⁺ , NH ₂ ⁺ , O ₂ ⁺⁺	[M-16] ⁺ (CH ₄) (O) (NH ₂)	methyl (rare) nitro compounds, sulfones, epoxides, <i>N</i> -oxides primary amines
17	OH ⁺ , NH ₃ ⁺	[M-17] ⁺ (OH) (NH ₃)	acids (especially aromatic acids), hydroxylamines, <i>N</i> -oxides, nitro compounds, sulfoxides, tertiary alcohols primary amines
18	H ₂ O ⁺ , NH ₄ ⁺	[M-18] ⁺ (H ₂ O)	nonspecific; abundant: alcohols, some acids, aldehydes, ketones, lactones, cyclic ethers O indicator

Mass	Ion	Product ion and composition of the neutral particle lost		Substructure or compound type	
19	H_3O^+ , F^+	$[\text{M}-19]^+$	(F)	fluorides	F indicator
20	HF^+ , Ar^{++} , $\text{CH}_2\text{CN}^{++}$	$[\text{M}-20]^+$	(HF)	fluorides	F indicator
21	$\text{C}_2\text{H}_2\text{O}^{++}$				
22	CO_2^{++}				
23	Na^+	$[\text{M}+23]^+$		in FAB spectra in the presence of Na^+ ; sometimes strong even if Na^+ is only an impurity in FAB spectra of organic Na^+ salts	
		$[\text{M}-23]^-$			
24	C_2^+				
25	C_2H^+	$[\text{M}-25]^+$	(C_2H)	terminal acetylenyl	
26	C_2H_2^+ , CN^+	$[\text{M}-26]^+$	(C_2H_2) (CN)	aromatics nitriles	
27	C_2H_3^+ , HCN^+	$[\text{M}-27]^+$	(C_2H_3) (HCN)	terminal vinyl, some ethyl esters and <i>N</i> -ethylamides, ethyl phosphates aromatic N, nitriles	
28	C_2H_4^+ , CO^+ , N_2^+ , HCNH^+	$[\text{M}-28]^+$	(C_2H_4) (CO) (N_2)	nonspecific; abundant: cyclohexenes, ethyl esters, propyl ketones, propyl-substituted aromatics aromatic O, quinones, lactones, lactams, unsaturated cyclic ketones, allyl aldehydes diazocompounds; air (intensity 3.7 times larger than for O_2^+ , m/z 32)	
29	C_2H_5^+ , CHO^+	$[\text{M}-29]^+$	(C_2H_5) (CHO)	nonspecific; abundant: ethyl phenols, furans, aldehydes	

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
30	CH ₂ O ⁺ , CH ₂ NH ₂ ⁺ , NO ⁺ , C ₂ H ₆ ⁺ , BF ⁺ , N ₂ H ₂ ⁺ N indicator	[M-30] ⁺ (C ₂ H ₆) (CH ₂ O) (NO)	ethylalkanes, polymethyl compounds cyclic ethers, lactones, primary alcohols nitro and nitroso compounds
31	CH ₃ O ⁺ , CH ₃ NH ₂ ⁺ , CF ⁺ , N ₂ H ₃ ⁺ O indicator	[M-31] ⁺ (CH ₃ O) (CH ₃ NH ₂) (N ₂ H ₃)	methyl esters, methyl ethers, primary alcohols N-methylamines hydrazides
32	O ₂ ⁺ , CH ₃ OH ⁺ , N ₂ H ₄ ⁺ , S ⁺ O indicator	[M-32] ⁺ (O ₂) (CH ₃ OH) (S)	cyclic peroxides; air (intensity 3.7 times smaller than for N ₂ ⁺ , m/z 28) methyl esters, methyl ethers sulfides (together with isotope signal for ³⁴ S)
33	CH ₃ OH ₂ ⁺ , SH ⁺ , CH ₂ F ⁺	[M-33] ⁺ (SH) (CH ₃ + H ₂ O) (CH ₂ F)	nonspecific (together with isotope signal for ³⁴ S) S indicator nonspecific; O indicator fluoromethyl
34	SH ₂ ⁺	[M-34] ⁺ (SH ₂) (OH + OH)	nonspecific (together with isotope signal for ³⁴ S) S indicator nitro compounds
35	SH ₃ ⁺ , Cl ⁺	[M-35] ⁺ (Cl) (OH + H ₂ O)	chloro compounds (together with isotope signal for ³⁷ Cl) nitro compounds 2 × O indicator
36	HCl ⁺ , C ₃ ⁺	[M-36] ⁺ (HCl) (H ₂ O + H ₂ O)	chloro compounds 2 × O indicator
37	C ₃ H ⁺ ³⁷ Cl ⁺		chloro compounds (together with isotope signal for ³⁵ Cl)

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
38	$C_3H_2^{+}$		
39	$C_3H_3^+$ K^+	$[M-39]^{+}$ (C_3H_3) $[M+39]^+$ $[M-39]^-$	aromatics in FAB spectra in the presence of K^+ ; sometimes strong even if K^+ is only an impurity in FAB spectra of organic K^+ salts
40	$C_3H_4^{+}$, CH_2CN^+ , Ar^+	$[M-40]^{+}$ (CH_2CN)	cyanomethyl
41	$C_3H_5^+$, CH_3CN^+	$[M-41]^{+}$ (C_3H_5) (CH_3CN)	alicyclics (especially polyalicyclics), alkenes 2-methyl-N-aromatics, N-methylanilines
42	$C_3H_6^{+}$, $C_2H_2O^{+}$, CON^+ , $C_2H_4N^+$	$[M-42]^{+}$ (C_3H_6) (C_2H_2O)	nonspecific; abundant: propyl esters, butyl ketones, butylaromatics, methylcyclohexenes acetates (especially enol acetates), acetamides, cyclohexenones, α,β -unsaturated ketones
43	$C_3H_7^+$, $C_2H_3O^+$, $CONH^+$	$[M-43]^{+}$ (C_3H_7) (CH_3CO)	nonspecific; abundant: propyl, alicyclics, cycloalkanones, cycloalkylamines, cycloalkanols, butylaromatics methyl ketones, acetates, aromatic methyl ethers
44	CO_2^{+} , $C_2H_6N^+$, $C_2H_4O^{+}$, CS^+ , $C_3H_8^{+}$, CH_4Si^+	$[M-44]^{+}$ (C_3H_8) (C_2H_6N) (C_2H_4O) (contd.)	propylalkanes N,N-dimethylamines, N-ethylamines cycloalkanols, cyclic ethers, ethylene ketals, aliphatic aldehydes (McLafferty rearrangement)

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
44		(CO ₂)	anhydrides, lactones, carboxylic acids
45	C ₂ H ₅ O ⁺ , C ₂ H ₇ N ⁺ , CHS ⁺ (together with isotope signal for ³⁴ S) O indicator S indicator	[M-45] ⁺ (C ₂ H ₅ O) (CHO ₂) (C ₂ H ₇ N)	ethyl esters, ethyl ethers, lactones, ethyl sulfonates, ethyl sulfones carboxylic acids <i>N,N</i> -dimethylamines, <i>N</i> -ethylamines
46	C ₂ H ₅ OH ⁺ , NO ₂ ⁺	[M-46] ⁺ (C ₂ H ₆ O) (H ₂ O + C ₂ H ₄) (H ₂ O + CO) (NO ₂)	ethyl esters, ethyl ethers, ethyl sulfonates primary alcohols carboxylic acids nitro compounds
47	CH ₃ S ⁺ , CCl ⁺ , C ₂ H ₅ OH ₂ ⁺ , CH(OH) ₂ ⁺ , PO ⁺ 2 × O indicator S indicator P indicator	[M-47] ⁺ (CH ₃ S)	methyl sulfides (together with isotope signal for ³⁴ S)
48	CH ₃ SH ⁺ , CHCl ⁺ , SO ⁺	[M-48] ⁺ (CH ₄ S) (SO)	methyl sulfides sulfoxides, sulfones, sulfonates (together with isotope signal for ³⁴ S)
49	CH ₂ Cl ⁺ , CH ₃ SH ₂ ⁺	[M-49] ⁺ (CH ₂ Cl)	chloromethyl (with corresponding signal for ³⁷ Cl)
50	C ₄ H ₂ ⁺ , CH ₃ Cl ⁺ , CF ₂ ⁺	[M-50] ⁺ (CF ₂)	trifluoromethylaromatics, perfluoroalicyclics
51	C ₄ H ₃ ⁺ , CHF ₂ ⁺		
52	C ₄ H ₄ ⁺		
53	C ₄ H ₅ ⁺		

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
54	$C_4H_6^+$, $C_2H_4CN^+$	$[M-54]^+$ (C_4H_6) (C_2H_4CN)	cyclohexenes cyanoethyl
55	$C_4H_7^+$, $C_3H_3O^+$	$[M-55]^+$ (C_4H_7)	nonspecific; abundant: alicyclics, butyl esters, <i>N</i> -butylamides
56	$C_4H_8^+$, $C_3H_4O^+$	$[M-56]^+$ (C_4H_8) (C_3H_4O)	butyl esters, <i>N</i> -butylamides, pentyl ketones, cyclohexenes, tetralins, pentylaromatics methylcyclohexenones, β -tetralones
57	$C_4H_9^+$, $C_3H_5O^+$, $C_3H_2F^+$	$[M-57]^+$ (C_4H_9) (C_3H_5O)	nonspecific ethyl ketones
58	$C_3H_8N^+$, $C_3H_6O^+$ N indicator O indicator	$[M-58]^+$ (C_4H_{10}) (C_3H_6O)	alkanes α -methylalkanals, methyl ketones, isopropylidene glycols
59	$C_3H_7O^+$, $C_2H_5NO^+$ O indicator	$[M-59]^+$ (C_3H_7O) ($C_2H_3O_2$) (C_3H_9N)	propyl esters, propyl ethers methyl esters amines, amides
60	$C_2H_4O_2^+$, $CH_2NO_2^+$, $C_2H_6NO^+$ O indicator	$[M-60]^+$ (C_3H_8O) ($C_2H_4O_2$) ($CH_3OH + CO$)	propyl esters, propyl ethers acetates methyl esters
61	$C_2H_5O_2^+$, $C_2H_5S^+$ 2 \times O indicator S indicator	$[M-61]^+$ ($C_2H_5O_2$) (C_2H_5S)	glycols, ethylene ketals ethyl sulfides (together with isotope signal for ^{34}S)
62	$C_2H_6O_2^+$, $C_2H_3Cl^+$	$[M-62]^+$ ($C_2H_6O_2$) (C_2H_6S)	methoxymethyl ethers, ethylene glycols, ethylene ketals ethyl sulfides (together with isotope signal for ^{34}S)

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
63	$C_5H_3^+$, $C_2H_4Cl^+$, $COCl^+$	$[M-63]^{+•}$ (C_2H_4Cl) ($CO + Cl$)	chloroethyl acid chlorides
64	$C_5H_4^{+•}$, $SO_2^{+•}$, $S_2^{+•}$	$[M-64]^{+•}$ (SO_2) (S_2)	sulfones, sulfonates disulfides (together with isotope signal for ^{34}S)
65	$C_5H_5^+$, $H_2PO_2^+$	$[M-65]^{+•}$ (S_2H) (SO_2H)	disulfides (together with isotope signal for ^{34}S)
66	$C_5H_6^{+•}$ S_2H_2	$[M-66]^{+•}$ (C_5H_6)	cyclopentenes disulfides (together with isotope signal for ^{34}S)
67	$C_5H_7^+$, $C_4H_3O^+$	$[M-67]^{+•}$ (C_4H_3O)	furyl ketones
68	$C_5H_8^{+•}$, $C_4H_4O^{+•}$, $C_3H_6CN^+$	$[M-68]^{+•}$ (C_5H_8) (C_4H_4O)	cyclohexenes, tetralins cyclohexenones, β -tetralones
69	$C_5H_9^+$, $C_4H_5O^+$, $C_3HO_2^+$, CF_3^+	$[M-69]^{+•}$ (C_5H_9) (CF_3)	alicyclics, alkenes trifluoromethyl
70	$C_5H_{10}^{+•}$, $C_4H_6O^{+•}$, $C_4H_8N^+$		alkanes, alkenes, alicyclics cycloalkanones pyrrolidines

Mass	Ion	Compound type	
71	$C_5H_{11}^+$ $C_4H_7O^+$	alkanes, larger alkyl groups alkanones, alkanals, tetrahydrofurans	
72	$C_4H_8O^{+•}$, $C_4H_{10}N^{+•}$, C_6^+	alkanones, alkanals aliphatic amines perhalogenated benzenes	O indicator N indicator
73	$C_4H_9O^+$, $C_3H_5O_2^+$, $C_3H_9Si^+$	alcohols, ethers, esters acids, esters, lactones trimethylsilyl compounds	O indicator

Mass	Ion	Compound type
74	$C_4H_{10}O^{+}$ $C_3H_6O_2^{+}$	ethers methyl esters of carboxylic acids, α -methyl carboxylic acids
75	$C_3H_7O_2^{+}$ $C_3H_7S^{+}$ $C_2H_7SiO^{+}$	methyl acetals, glycols 2 × O indicator sulfides, thiols (together with isotope signal for ^{34}S) S indicator trimethylsilyloxyl compounds
76	$C_6H_4^{+}$	aromatics
77	$C_6H_5^{+}$ $C_3H_6Cl^{+}$	aromatics chloro compounds
78	$C_6H_6^{+}$ $C_5H_4N^{+}$ $C_3H_7Cl^{+}$	aromatics pyridines chloro compounds
79	$C_6H_7^{+}$ $C_5H_5N^{+}$ Br^{+}	aromatics with H-containing substituents pyridines, pyrroles bromo compounds (together with isotope signal for ^{81}Br)
80	$C_6H_8^{+}$ $C_5H_4O^{+}$ HBr^{+} $C_5H_6N^{+}$	cyclohexenes, polycyclic alicyclics cyclopentenones bromo compounds pyrroles, pyridines
81	$C_6H_9^{+}$ $C_5H_5O^{+}$ $^{81}Br^{+}$	cyclohexanes, cyclohexenyls, dienes furans, pyrans bromo compounds (together with isotope signal for ^{79}Br)
82	$C_6H_{10}^{+}$ $C_5H_6O^{+}$ $C_5H_8N^{+}$ $C_4H_6N_2^{+}$ CCl_2^{+}	cyclohexanes cyclopentenones, dihydropyrans tetrahydropyridines pyrazoles, imidazoles chloro compounds (together with isotope signals at m/z 84 and 86)
83	$C_6H_{11}^{+}$ $C_5H_7O^{+}$	alkenes, alicyclics, monosubstituted alkanes cycloalkanones
84	$C_5H_{10}N^{+}$	piperidines, <i>N</i> -methylpyrrolidines

Mass	Ion	Compound type
85	$C_6H_{13}^+$	alkanes
	$C_5H_9O^+$	alkanones, alkanals, tetrahydropyrans, fatty acid derivatives
	$CClF_2^+$	chlorofluoroalkanes (with isotope signal at m/z 87)
86	$C_5H_{10}O^+$	alkanones, alkanals
	$C_5H_{12}N^+$	aliphatic amines N indicator
87	$C_5H_{11}O^+$	alcohols, ethers, esters O indicator
	$C_4H_7O_2^+$	esters, acids
88	$C_4H_8O_2^+$	ethyl esters of carboxylic acids, α -methyl-methyl esters, α -C ₂ -carboxylic acids
89	$C_4H_9O_2^+$	diols, glycol ethers 2 × O indicator
	$C_4H_9S^+$	sulfides (together with isotope signal for ³⁴ S)
90	$C_7H_6^+$	disubstituted aromatics
91	$C_7H_7^+$	aromatics
	$C_4H_8Cl^+$	alkyl chlorides
92	$C_7H_8^+$	alkylbenzenes
	$C_6H_6N^+$	alkylpyridines
93	$C_6H_5O^+$	phenols, phenol derivatives
	$C_6H_7N^+$	anilines
	CH_2Br^+	bromo compounds
94	$C_6H_6O^+$	phenol esters, phenol ethers
	$C_5H_4NO^+$	pyrrol ketones, pyridone derivatives
95	$C_5H_3O_2^+$	furyl ketones
96	$C_7H_{12}^+$	alicyclics
97	$C_7H_{13}^+$	alicyclics, alkenes
	$C_6H_9O^+$	cycloalkanones
	$C_5H_5S^+$	alkylthiophenes (together with isotope signal for ³⁴ S)
98	$C_6H_{12}N^+$	N-alkylpiperidines

Mass	Ion	Compound type
99	$C_7H_{15}^+$ $C_6H_{11}O^+$ $C_5H_7O_2^+$ $H_4PO_4^+$	alkanes alkanones ethylene ketals alkyl phosphates
104	$C_8H_8^+$ $C_7H_4O^+$	tetralin derivatives, phenylethyl derivatives disubstituted α -ketobenzenes
105	$C_8H_9^+$ $C_7H_5O^+$ $C_6H_5N_2^+$	alkylaromatics benzoyl derivatives diazophenyl derivatives
106	$C_7H_8N^+$	alkylanilines
111	$C_5H_3OS^+$	thiophenoyl derivatives (together with isotope signal for ^{34}S)
115	$C_9H_7^+$ $C_6H_{11}O_2^+$ $C_5H_7O_3^+$	aromatics esters diesters
119	$C_9H_{11}^+$ $C_8H_7O^+$ $C_2F_5^+$ $C_7H_5NO^+$	alkylaromatics tolyl ketones perfluoroethyl derivatives phenyl carbamates
120	$C_7H_4O_2^+$ $C_8H_{10}N^+$	γ -benzopyrones, salicylic acid derivatives pyridines, anilines
121	$C_8H_9O^+$ and $C_7H_5O_2^+$	hydroxybenzene derivatives
127	$C_{10}H_7^+$ $C_6H_7O_3^+$ $C_6H_6NCl^+$ I^+	naphthalenes unsaturated diesters chlorinated <i>N</i> -aromatics iodo compounds
128	$C_{10}H_8^+$ $C_6H_5OCl^+$ HI^+	naphthalenes chlorinated hydroxybenzene derivatives iodo compounds
130	$C_9H_8N^+$ $C_9H_6O^+$	quinolines, indoles naphthoquinones

Mass	Ion	Compound type
131	$C_{10}H_{11}^+$ $C_5H_7S_2^+$ $C_3F_5^+$	tetralins thioethylene ketals (together with isotope signal for ^{34}S) perfluoroalkyl derivatives
135	$C_4H_8Br^+$	alkyl bromides
141	$C_{11}H_9^+$	naphthalenes
142	$C_{10}H_8N^+$	quinolines
149	$C_8H_5O_3^+$	phthalates
152	$C_{12}H_8^{+ \cdot}$	diphenyl aromatics
165	$C_{13}H_9^+$	diphenylmethane derivatives (fluorenyl cation)
167	$C_8H_7O_4^+$	phthalates
205	$C_{12}H_{13}O_3^+$	phthalates
223	$C_{12}H_{15}O_4^+$	phthalates

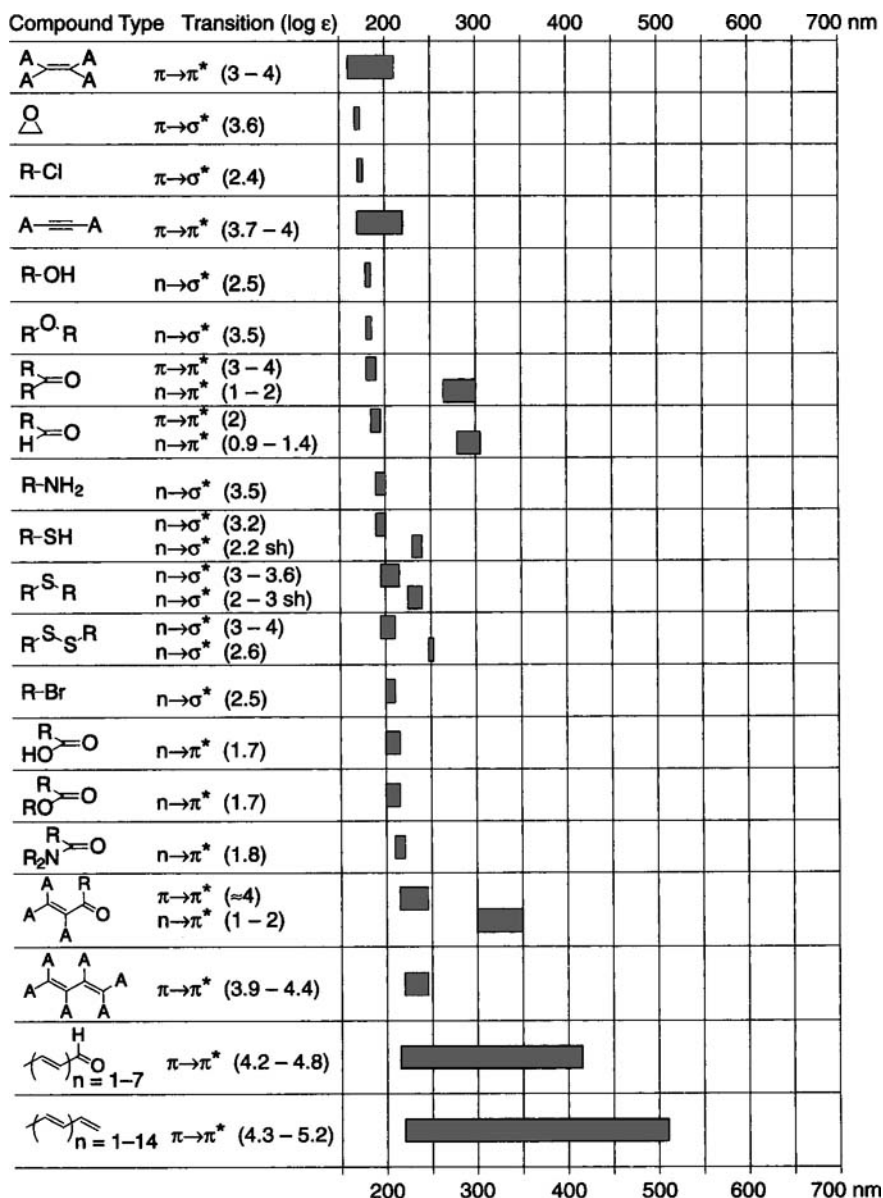
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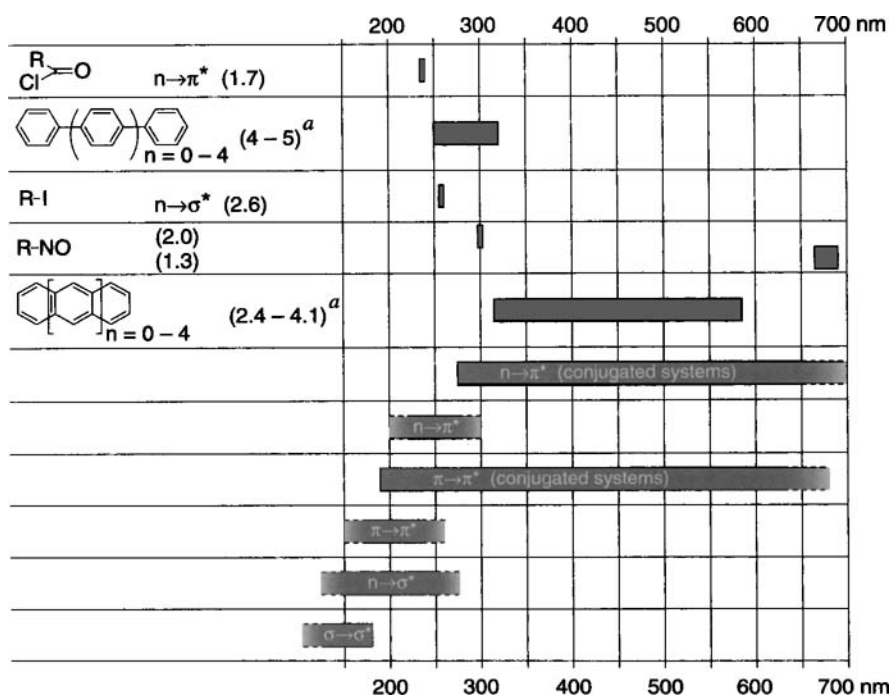
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2.6 UV/Vis Spectroscopy

UV/Vis Absorption Bands of Various Compound Types (A: alkyl or H; R: alkyl; sh: shoulder)





^a longest wavelength absorption maximum