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Modeling of isotopomeric cluster of the molecular ion

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Abstract The occurrence of poly-isotopic elements in a molecule or ion can result in complex isotopomeric cluster of an ion. The "isotopomer" better and correctly indicates different isotopic compositions of a molecule (compound) or ion and not a single atom. The ions of organic compounds show in accurate mass spectra single, isolated peaks or narrow sub-clusters regardless of their molecular masses. The occurrence of a PIE makes the molecular ion cluster more complex and significantly influences the location of the most abundant peak and the form of the cluster. The present study is an attempt at answering the following question: what is the mechanism of the molecular ion's isotopomeric cluster formation and is it step-by-step predictable? The accurate mass-resolved isotopomer cluster can be predicted from accurate masses and abundances of the stable isotopes. The cluster consists of several sub-patterns, each of which is composed of near signals (at the same nominal m/z). The range of the sub-cluster usually does not exceed 0.005 u. The low-resolution cluster can be predicted from the high-resolution pattern by addition of all peaks occurring over a given narrow mass range (m/z - 0.5; m/z+0.49). Surprisingly, predicting the accurate mass cluster is simpler than predicting the low-resolution one. A compliance of the model results with the experimental ones suggests a correct prediction.

Keywords Cluster modeling · Isotopomeric cluster · Mass spectrometry · Molecular ion · Molecular mass

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Introduction

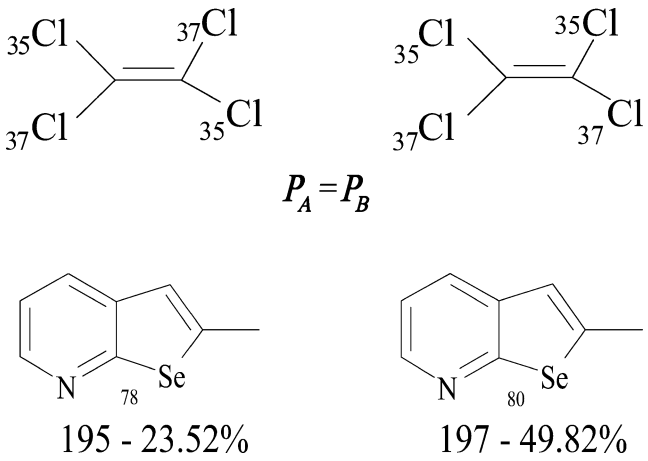
Knowledge of isotope patterns of elements, molecules or ions is useful in many ways. For example, the determination of $^{13}C/^{12}C$ ratios can be used to infer the origin of organic substances for biogeochemistry, archaeology, and adulteration detection in foods and drinks. By comparing experimental isotope patterns to the calculated ones, it is possible to determine the elemental compositions of substances. Some programs have been developed to perform such calculations [1–8].

High accuracy mass measurements by mass spectrometry are often used to determine the chemical composition of compounds. Standard practice is to select the monoisotopic peak because it is the only peak for which the accurate mass can be conveniently calculated from the chemical formula.

The isotope patterns of organometallic and coordination ions are often significantly more complex than those of the typical organic ones. About 40 chemical elements that do not occur frequently in organic compounds exist as poly-isotopic elements (PIE) [1]; for example, Dy, Gd, Hg, Mo, Nd, Ru, Sm, Sn, Te, Xe and Yb have seven or more natural isotopes.

Sometimes, there is more than one ion whose mass to charge ratios (m/z) are in the region of interest, which results in the appearance of peak clusters that are combination of their isotope patterns. This interference rarely causes serious troubles in high-resolution mass spectrometers due to the mass defect. The exact m/z values of different ions with the same nominal mass are seldom so close that a high-resolution instrument cannot distinguish them.

The present study is an attempt at answering the following question: what is the mechanism of the molecular ion's isotopomeric cluster formation and is it step-by-step predictable? The considerations concern the molecular ions patterns since they are not disturbed by other ions (fragment or multi-charged ones) overlapping.



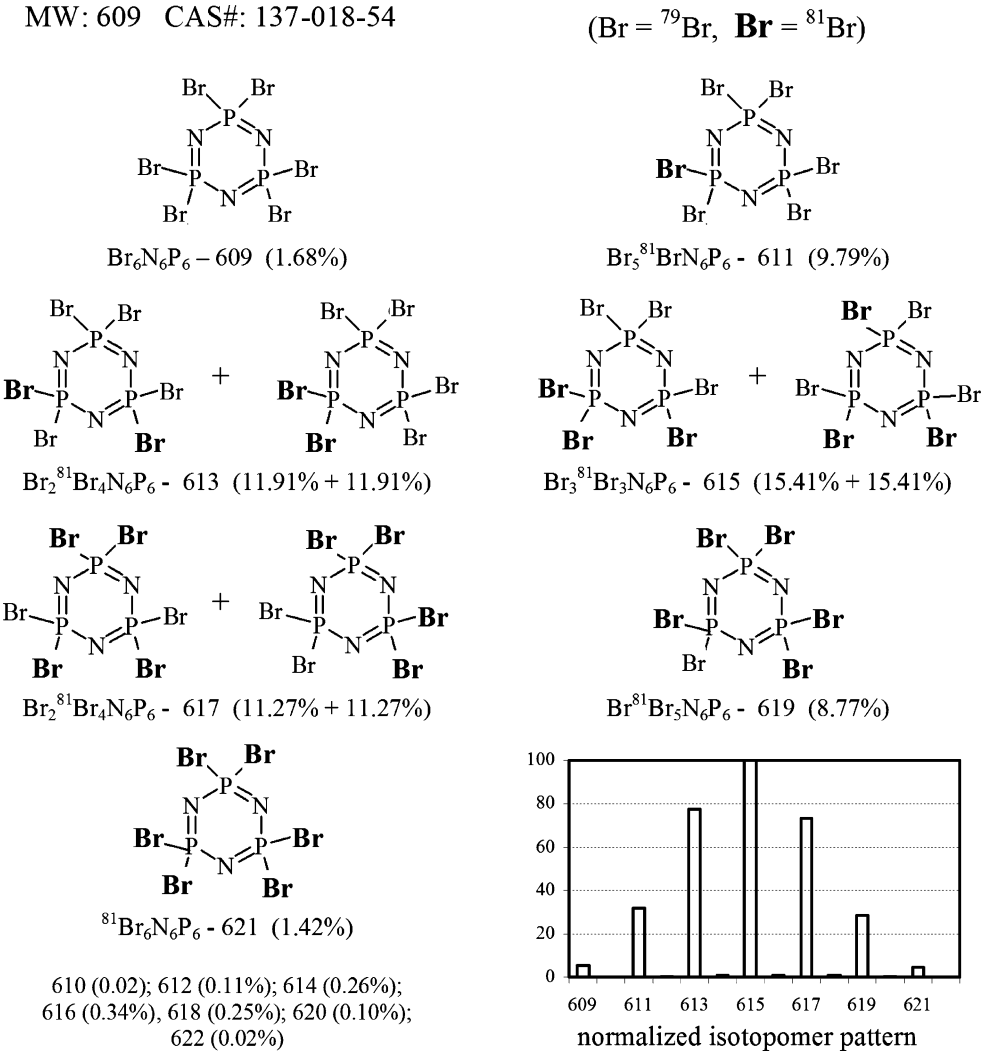
Scheme 1 Isotopomers

Isotopes and isotopomers; isotopomeric pattern

The word "isotope" refers to one atom of the specific element, but the mass spectral pattern, which is a cluster of ions comprised of many isotopes, arises owing to the occurrence of a set of ions with the same elemental content, but with different isotopic compositions and different locations of isotopes in the molecule. "Isotopomer" is a better term and indicates correctly that we are dealing with a molecule (compound) or an ion and not a single atom. The term "isotopologue = isotopic analogue" [9] denotes compounds with the same elemental composition and structure but different isotopic composition, and "isotopomers = isotopic isomers" [9] refers to compounds of the same structure and isotopic compositions, but different isotope locations. The chemical features of isotopomers are the same but some physical properties may be different, e.g., the difference of the nuclear spin generates characteristic magnetic features that can be investigated by NMR methods. Weight differences of isotopomers [10], well detected by mass spectrometry, are the result of isotopic masses dispersions of elements forming the compound.

An isotopomer pattern can give valuable information about the elemental composition of an ion and its molecular

Scheme 2 Isotopomers of hexabromocyclotriphosphazene $Br_6N_3P_3$



precursor. An understanding of the isotopomer pattern facilitates a more effective interpretation of a mass spectrum. The isotopic complexity and consequent isotopomer content can be impediments to mass spectral interpretation [10].

Additional considerations lead to yet further classification of isotopomers: position isotopomers [11] (Scheme 1): characterized by the same isotopic content but different positioning of the isotope labels in a molecule, mass isotopomers [4]: isotopic isomers that are grouped by nominal mass rather than isotopic composition.

The occurrence of poly-isotopic elements in a molecule results in more complex sub-cluster. The sub-band of the ion containing few PIE atoms can be composed of many peaks corresponding to many mass isotopomers. The isotopomeric cluster is a graphic distribution of the position isotopomers related to ions with the same isotopic contents. The explanation of the position isotopomers distribution is not possible by mass spectrometry. Mass isotopomers attributed to ions, which show little differences between masses but have different isotopic composition, are often undetectable since the detectors used do not distinguish these species (Scheme 2).

The patterns of high- and low-resolution spectrum clusters are substantially different [12].

Accurate mass isotopomeric cluster

The mass ions of organic compounds show single isolated peaks or narrow sub-clusters regardless of their molecular masses. In the isotopomeric pool, the position isotopomers, which are not separated in the spectrum, are dominant. The mass isotopomers are not rather numerous. The registration of the accurate location (m/z) of peak allows the determination of the quantity of mass isotopomers contained in the isotopometric cluster.

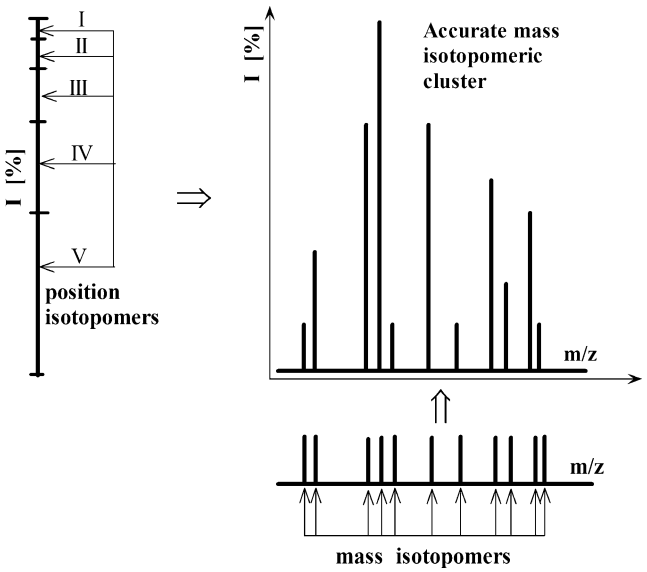
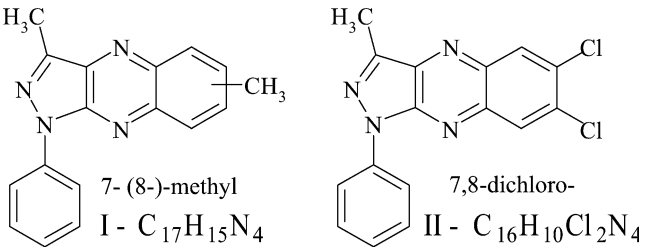


Fig. 1 Mechanism of the accurate mass sub-cluster formation in the high-resolution mass spectra



Scheme 3 Quinoxaline derivatives

The resolution of 0.0001 u is needed in this case; such precision precludes the overlapping of closely located signals of the mass isotopomers (Fig. 1).

The number of the peaks observed in the graphic representation is restricted to the dominant mass isotopomers of each sub-pattern corresponding to the specific ion. The mass isotopomers are significant for peaks locations; each mass isotopomer of respective ion has its unique position in the isotopomeric pattern. The high-resolution mass spectrum allows explaining the mass isotopomers composition, but it does not make it possible to determine the width of the isotopometric cluster (WIC) [13]. The high-resolution isotopomeric cluster can be predicted from accurate masses [14] including the mass defects and abundances of the stable isotopes [15]. The cluster consists of several sub-patterns[1] each of which is composed of signals located nearby. The range of the sub-cluster usually does not exceed 0.005 u. Let us assume that an ion may be isotopically described as $(E_1)_{n_1}(E_2)_{n_2}(E_3)_{n_3}\cdots(E_z)^+_{n_z}$. The position of each isotopomeric peak can be computed as related to the sum of the exact masses (with the mass defect) of all the isotopes contained in such isotopomer. The accurate m/z value is calculated from the following formula:

$$m_j=\sum_{i=1}^{z}(n_i\cdot m_{E_i})$$

n_i – denotes the number of the isotope atoms. and m_E – exact mass of the isotope.

The mass isotopomers differ in accurate masses and are well detectable in high-resolution mass spectrum.

Example 1. 3-methyl-1-phenyl-1H-pyrazolo[3.4-b] quinoxaline

The theoretical locations were predicted as described above and compared with the experimental accurate-mass values [16] (Scheme 3; Table 1).

[1] sub-cluster, sub-pattern or sub-band - in high resolution mass spectrum it is also a well-separated part of mass spectra containing several peaks located in the range ±0.05 u.

Table 1 Accurate masses of some fragmentation ions of the 3-methyl-1-phenyl-1H-pyrazolo[3.4-b]quinoxaline derivatives (I and II) [16]

	313 $C_{15}H_7N_4^{35}Cl_2$	287 $C_{14}H_7N_3^{35}Cl_2$	274 $C_{17}H_{14}N_4$	259 $C_{16}H_{11}N_4$	232 $C_{15}H_{10}N_3$	205 $C_{14}H_9N_2$	180 $C_{13}H_{10}N$	143 $C_9H_7N_2$
Experimental	313.0025	287.0021	274.1212	259.0972	232.0856	205.0735	180.0799	143.0604
Calculated	313.0048	287.0017	274.1216	259.0982	232.0873	205.0764	180.0811	143.0608
Δ	−0.0023	+0.0004	−0.0004	−0.0010	−0.0029	−0.0029	−0.0012	−0.0004

The experiments were performed in the Mass Spectrometry Laboratory of the A.Mickiewicz University in Poznan (Poland)

Experimental

The EI mass spectra were recorded on an AMD-402, two-sector mass spectrometer (AMD Intectra, Germany) of the B/E geometry with the acceleration voltage of 8 kV, the electron energy 70 eV and the ion source temperature 200 °C. High-resolution data were obtained using V/E high-resolution scan in relation to perfluorokerosene, with an error lower than 10 ppm for all ions discussed. The compounds were introduced by a direct insertion probe.

The modeled abundance values remain in good agreement with the experimental ones. The position isotopomers show the same $\boldsymbol{m_j}$ (m/z) values. They do not influence the peak location and so they are not separable in mass spectrum. Therefore, the abundance observed for the peaks of the same $\boldsymbol{m_j}$ is more complex. The quantities of position isotopomers (abundances) are the same, e.g.,:

$$ABBAA = ABABA = BBAAA = AABAB = \ldots\ ,$$

but in the spectrum no separate position isotopomers are distinguished; the sum of all the appropriate ones is observed only.

The fractional abundance of this isotopomer, having $\boldsymbol{z}$ atoms, is: $a_f = \prod_{f=1}^{z} A_f^{n_f}$ and can be described as the effect of natural abundances of all the isotopomers, which occur in the molecule. The value concerns the mass isotopomers only. General abundance $\boldsymbol{A}_{\mathrm{HR}}$ of the mass isotopomer (and the peak intensity, proportionally) can be therefore also predicted with a glance position isotopomers using the following formula:

$$A_{HR} = p_i \cdot \prod_{i=1}^{z_e} a_i \text{ for one PIE element,}$$

$$A_{HR} = \sum_{e=1}^{f} \prod_{i=1}^{z_e} a_i \text{ for } f \text{ PIE elements,}$$

in which $\mathrm{p}_{\boldsymbol{i}}$ - is the number of possible position isotopomers with the isotopic contents, $\boldsymbol{a}_{\mathrm{i}}$ - stands for the natural abundance of each atom from the elements forming the formula, and $\boldsymbol{z}_{\mathrm{e}}$ - denotes the number of PIE element isotopes.

The abundances of individual isotopes (for elements) or mass isotopomers (for molecules) account for a fraction of the total abundance represented by that particular isotope or mass isotopomer. The theoretical modeling seems to be simple, each step is logical and easy enough for any spreadsheet program to perform calculations.

The graphic representation of accurate-mass isotopomeric clusters of organometallic or coordination compounds creates new problems. The image looks simplified because not all the mass isotopomers are represented. The picture of high-resolution molecular cluster contains local dominant peaks selected by the following formula:

$$I_{LR} = \underset{i=(m/z-0.5)}{\overset{(m/z+0.49)}{MAX}} \left(I_p\right) \text{ (see Fig. 2a).}$$

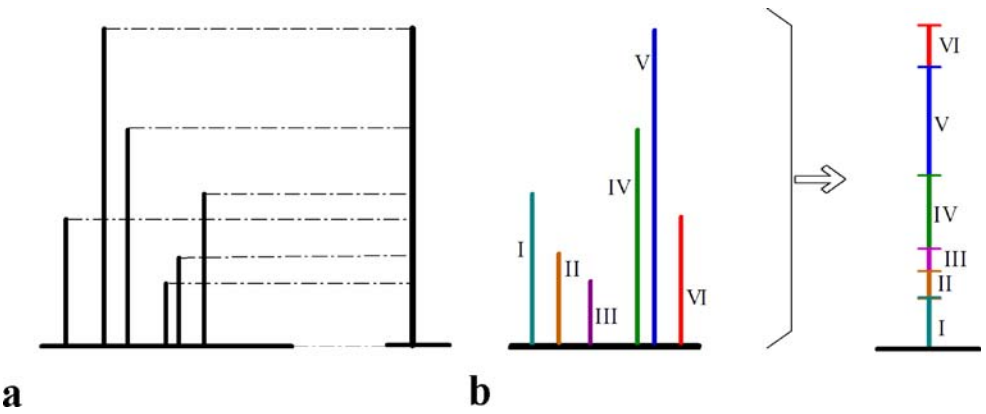


Fig. 2 Graphic representation of the isotopomeric model of the molecular ion cluster: **a** - shadow-form of the accurate-mass model, **b** - normalized sum of the low-resolution pattern

Table 2 Accurate mass isotopomers model and low-resolution model of the diphenyl-zinc molecular clusters

Mass isotopomer formula	High-resolution model				Low-resolution model		Experimental pattern [18]
	Calculated cluster		Picture		Calculated cluster		
	M/z [u]	I_{norm} [%]	m/z [u]	I_{norm} [%]	m/z [u]	$\Sigma I = I_{norm}$ [%]	I_{norm} [%]
1	2	3	4	5	6	7	9
$C_{12}H_{10}{}^{64}Zn$	218.0071	100.000	218.0071	100.000	218	100.00	100
$C_{12}{}^{13}CH_{10}{}^{64}Zn$	219.0105	13.500	219.0105	13.500	219	13.50	14.31
$C_{12}H_{10}{}^{66}Zn$	220.0040	57.407	220.0040	57.407	220	58.25	58.22
$C_{10}{}^{13}C_2H_{10}{}^{64}Zn$	220.0139	0.840	220.0139				
$C_{10}H_{10}{}^{67}Zn$	221.0051	8.436	221.0051	8.436	221	16.22	16.44
$C_{10}{}^{13}CH_{10}{}^{66}Zn$	221.0074	7.750	221.0074				
$C_9{}^{13}C_3H_{10}{}^{64}Zn$	221.0173	0.030	221.0173				
$C_{12}H_{10}{}^{68}Zn$	222.0028	38.683	222.0028	38.683	222	40.30	39.46
$C_{11}{}^{13}CH_{10}{}^{67}Zn$	222.0085	1.139	222.0085				
$C_{10}{}^{13}C_2H_{10}{}^{66}Zn$	222.0108	0.482	222.0108				
$C_8{}^{13}C_4H_{10}{}^{64}Zn$	222.0207	>0.001	222.0207				
$C_{11}{}^{13}CH_{10}{}^{68}Zn$	223.0062	5.222	223.0062	5.222	223	5.31	5.03
$C_{10}{}^{13}C_2H_{10}{}^{67}Zn$	223.0119	0.078	223.0119				
$C_9{}^{13}C_3H_{10}{}^{66}Zn$	223.0142	0.017	223.0142				
$C_{12}H_{10}{}^{70}Zn$	224.0033	1.235	224.0033	1.235	224	1.56	1.55
$C_{10}{}^{13}C_2H_{10}{}^{68}Zn$	224.0096	0.325	224.0096				
$C_9{}^{13}C_3H_{10}{}^{67}Zn$	224.0153	0.003	224.0153				
$C_8{}^{13}C_4H_{10}{}^{66}Zn$	224.0176	>0.001	224.0176				
$C_{11}{}^{13}CH_{10}{}^{70}Zn$	225.0067	0.167	225.0067	0.167	225	0.18	0.19
$C_9{}^{13}C_3H_{10}{}^{68}Zn$	225.0130	0.012	225.0130				
$C_8{}^{13}C_4H_{10}{}^{67}Zn$	225.0187	>0.001	225.0187				
$C_{10}{}^{13}C_2H_{10}{}^{70}Zn$	226.0101	0.010	226.0101	0.010	226	0.01	–
$C_8{}^{13}C_4H_{10}{}^{68}Zn$	226.0164	>0.001	226.0164				
$C_9{}^{13}C_3H_{10}{}^{70}Zn$	227.0135	0.001	227.0135	0.001			
$C_8{}^{13}C_4H_{10}{}^{70}Zn$	228.0169	>0.001	228.0169	0			

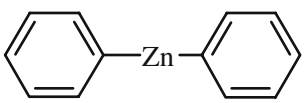
Theoretical abundances values of isotopomers were limited to dominant isotopes and these proper values have been found successively by mass spectral experiment.

Transformation of accurate mass pattern in low-resolution isotopomeric cluster

The high-resolution mass spectral cluster corresponds to the real mass isotopomeric cluster. In the case of low-resolution pattern, this opinion is correct for organic compounds only. The occurrence of PIE atoms in the structures of coordination or organometallic compounds results in a complex structure of the mass spectral clusters and correlation of the peak with the isotopomer can be very difficult to explain. The abundances of individual isotopes (for elements) or mass isotopomers (for molecules) account for a fraction of the total abundance represented by that particular isotope or mass isotopomer. However, commonly the relative abundance is used in which the most abundant peak stands for 100% and all the others are calculated respectively. A cluster in low-resolution mass spectra contains closely located peaks, usually distanced by 1 u. The peaks represent all position isotopomers of the same value m/z. The peak intensity $\boldsymbol{I}_p$ is a relative function of the sum of such isotopomers abundances $\boldsymbol{A}_{pi}$ $I_p = f\left(\sum_{i=1}^{n} A_{pi}\right)_{m/z=\text{const}}$.

Example 2. Diphenyl-zinc

[17].



The simple organometallic compound is a connection $Zn + C_{12}H_{10} = C_{12}H_{10}Zn$ (polyisotopic zinc and simple

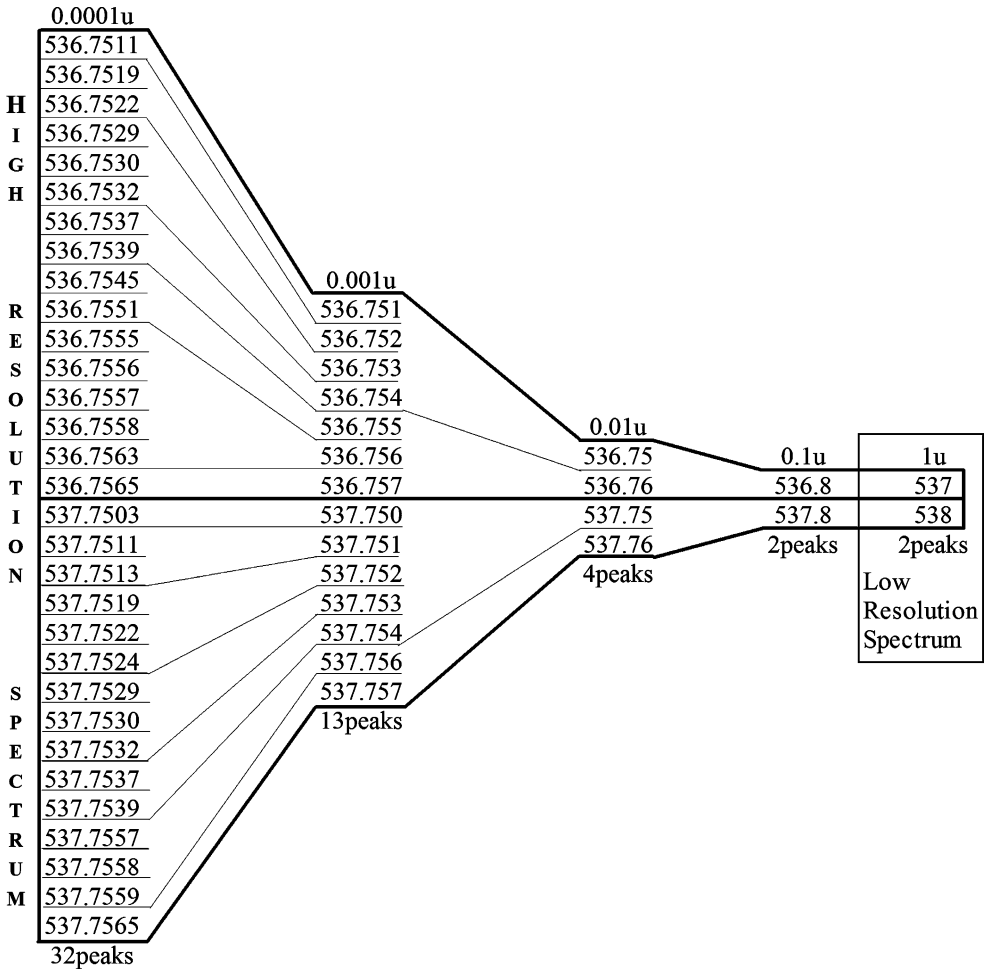


Fig. 3 Number of the mass spectral peaks versus the resolution of the peaks location (the transformation of the high-resolution model to the low-resolution one)

organic part). The molecular ion (high-resolution form) can be related to 24 mass isotopomers, associated with 11 groups. The graphic representation as well as the low-resolution cluster shown 8 peaks only, but their intensities are different each other.

The signal groups of the accurate mass form are represented by one dominant peak, the other ones are not visible. Similarly, the low-resolution cluster consists of one representative signal formed by the integration of all the peaks located in the group range. The details are shown in Table 2.

The model fits the experimental data very well, which suggests that modeling of the low-resolution mass pattern by transformation of the accurate mass model may be appropriate. The model is tested using the compound of more complex isotopomeric composition.

Table 3 High-resolution pattern transformation into the low-resolution one in the molecular ion cluster of tris(benzo[b]selenopheno)[2.3:2′.3′:2″.3″]benzene

	Peak location accuracy				
	0.0001 u	0.001 u	0.01 u	0.1 u	1 u
peaks number	218	113	38	27	27
in the range 536÷538 u	31	14	4	2	2
with I > 1%	13	9	2	2	2
$\Sigma I_{1\%}$ [%]	199.2	199.6	147.1	147.6	147.6
part of $\Sigma I_{1\%}$ in ΣI [%]	99.4	99.6	73.4	73.6	73.6
normalization	–	–	+	+	–
normalization factor η	(100%)	(100%)	1.35720	1.00143	(100%)
integration limits*	from m/z	*m/z,abc*−0.0005	*m/z,abc*−0.005	*m/z,abc*−0.05	*m/z,abc*−0.5
	to m/z	*m/z,abc*+0.00049	*m/z,abc*+0.0049	*m/z,abc*+0.049	*m/z,abc*+0.49

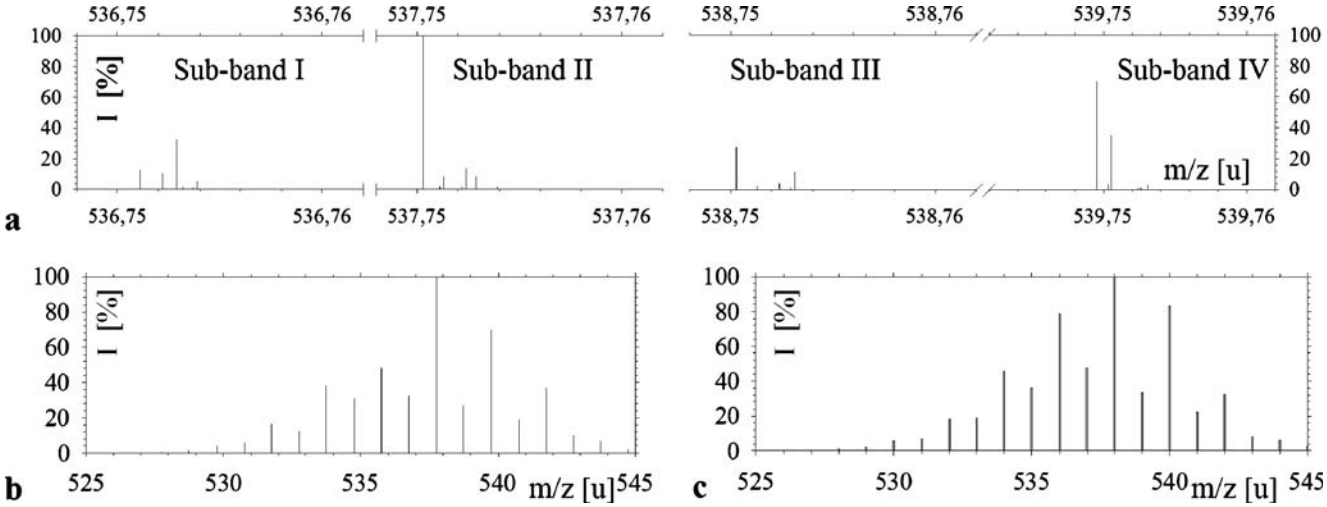
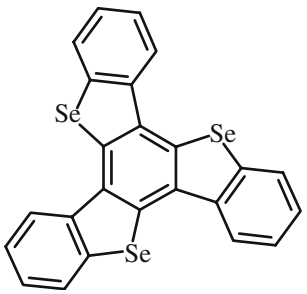


Fig. 4 Isotopomeric composition of molecular ion cluster of the tris(benzo[b]selenopheno) [2.3:2′.3′:2″.3″] benzene, $C_{24}H_{12}Se_3$: **a** - fragment of accurate mass model, **b** - high-resolution pattern, **c** - low-resolution model

Example 3. tris(benzo[b]selenopheno)[2.3:2′.3′:2″.3″] benzene

[19].



The compound may be presented as the sum of isotopically complex elemental aggregate (24 mass isotopomers between 222 and 246 u) and a relatively simple organic part (5 mass isotopomers in range 300–304 u):

$$Se_3 + C_{24}H_{12} = C_{24}H_{12}Se_3.$$

The combination of both parts results in a highly complex structure of the isotopomeric molecular cluster located at 522–550 m/z.

The high-resolution form of the cluster can contain up to 3500 isotopomers. Fortunately, after the elimination of low intensity signals (normalized intensity I<0.001%) and the consideration of position isotopomers, only 218 peaks remain. The high-resolution model was step-by-step trans-

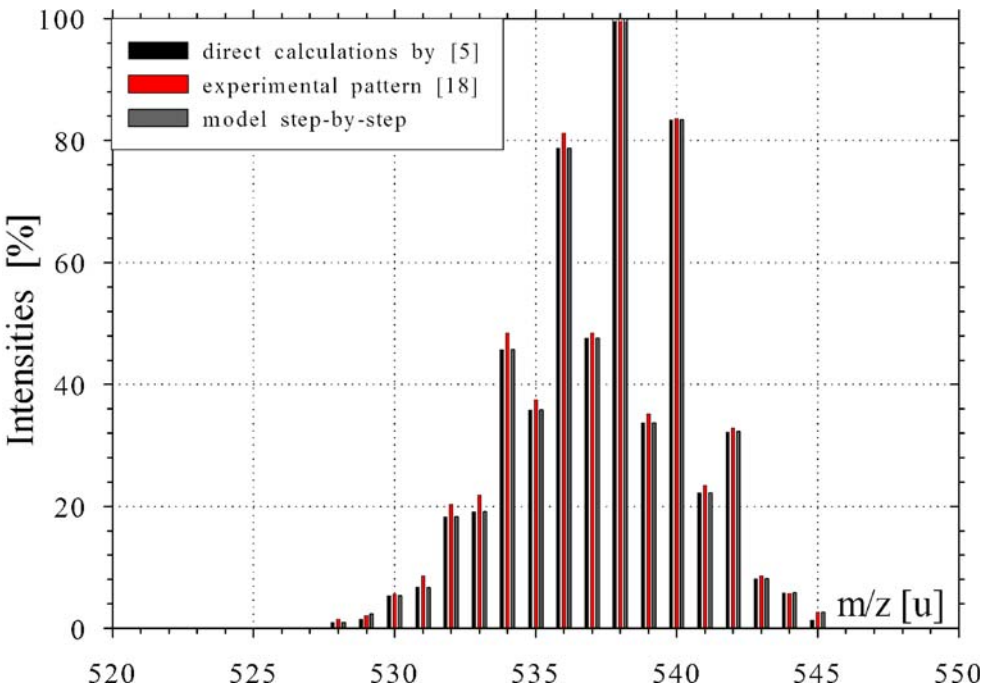


Fig. 5 Low-resolution molecular ion cluster of tris(benzo[b] selenopheno) [2.3:2′.3′:2″.3″] benzene $C_{24}H_{12}Se_3$

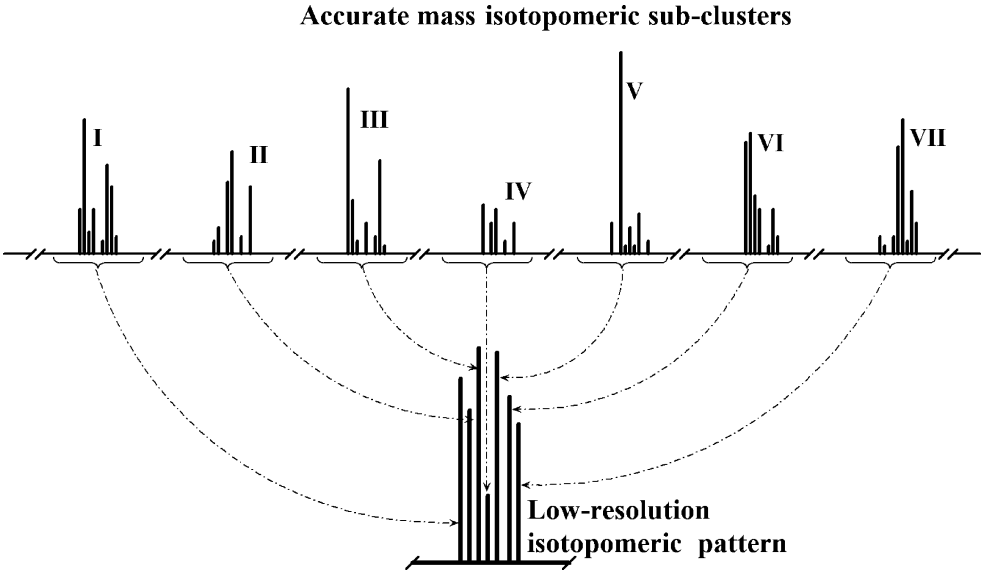


Fig. 6 Model of the accurate mass high-resolution clusters transformation into low-resolution isotopic cluster

formed to the low-resolution one by the method presented in Fig. 2 for m/z range between 536 and 538 u. The reduction of the location accuracy needs adding all the peaks, which occur in the region. Figure 3 shows some details of transformation process.

The method of the transformation from the accurate mass cluster to the low-resolution one as the final effect is summarized in Table 3. The normalization, which must be made at 0.01 u accuracy significantly, disturbs the intensities of the cluster components due to a decrease in all the values.

The complexity of the calculated isotopomeric cluster is noticeable in a very detailed scale pictures only (Fig. 4a). The general picture of the high-resolution isotopomeric cluster (Fig. 4b) differs significantly from the low-resolution model (Fig. 4c, 5, and 6).

The variance defined by Biemann [20] as: $s^2 = \frac{1}{n}\sum_{i=1}^{n}\left(I_{i(\exp.)} - I_{i(calc.)}\right)^2$ is 2.08 for 18 experimental points, denoting a good fit of the model to experimental data.

Examples 2 and 3 allow us to propose a mechanism of transformation of high resolution mass data in the low-resolution ones.

Conclusions

The isotopomeric clusters of organic ions usually contain a few peaks only and the m/z values of mass isotopomers are considerably different and so their isotopomeric pattern is easily interpretable. The occurrence of PIE increases the number of mass isotopomers as well as changed the cluster picture. The presence of a few PIE atoms results in a complex isotopomeric structure of the ion. The investigations of the ion formula happen to be quite difficult and the help of a specialized program is often needed. Normalization of the mass spectrum significantly disturbs information about the isotopomers composition of the ion investigated. This problem can be avoided by considering the total ion current mass spectra but the points are not precise.

Mass spectra collected in spectral bases were registered integrally, i.e., signals located in the range defined by the resolution have been added. No details about the number of mass and position isotopomers and their intensities can be obtained from the experimental low-resolution ionic cluster, which is due to a dense packing of the peaks in the $\left(m/z \pm 0.5\right)$ range.

The modeling of isotopomeric ion cluster is realizable and consists of two stages.

Each peak for specific m/z represents the sum of all the isotopomers in the range $\left(m/z - 0,5;\ m/z + 0,49\right)$ and its intensity corresponds to the sum of fractional abundances of all isotopomers[2]: $I_{LR} = k \cdot \sum_{i=(m/z-0.5)}^{(m/z+0.49)} I_p$.

The first one is the prediction of accurate mass pattern from natural isotopes abundances and from isotopic mass defects. All possible isotopomers, the position ones as well as the mass isotopomers, are considered and are part of the final numerical cluster. In the graphic representation the m/z scale of the accurate mass pattern must be compressed (graphically shortened) and an observable molecular pattern involves several peaks only and such cluster differs from the experimental one which occurs in the mass spectrum. The source of these discrepancies is the formation mechanism of isotopomeric cluster of the molecular ion. The graphic form of the accurate-mass pattern is perhaps formed as a shadow of all the peaks located nearby (Fig. 3a). The biggest one represents the peak group and the other peaks are unnoticeable. Therefore accurate mass spectra for

[2] k - denotes the normalization factor

organometallics and complexes are usually not suitable (too low sensitivity) for the interpretation even if they concern the molecular ion cluster.

The second step of modeling is the transformation of the high-resolution cluster to the low-resolution pattern by the integration of peaks (Fig. 3b) located nearby (in the area m/z±0.5 u). The low-resolution ionic cluster can be predicted from the accurate mass model. The location of respective peaks is the integer value of m/z (see Fig. 4). The isotopomeric cluster provides information about the dominant sub-patterns only and details of the isotopomers located in the m/z range are not easily accessible. The determination of mass isotopomers by low-resolution mass spectrometry is not effective because the number of peaks in ionic cluster does not correspond to the number of main mass isotopomers related to the ion investigated.

The low-resolution pattern can be a source of mass isotopomers compositions for simple organic compounds only. Low-resolution mass spectra are performed in integral m/s values and the spectrometer works like other integrators used as detectors in instrumental chemical techniques.

Surprisingly, predicting the high-resolution mass cluster is simpler than the calculation of the low-resolution one. The mechanism of low-resolution pattern generation proceeds, perhaps, through the high-resolution intermediate form. A compliance of the model results with the experimental ones suggests a correct prediction.

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