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**RATIOS OF PRIMARY SEPARATIONS IN IONIC SERIES OF MASS-SPECTRA OF PERFLUOROALKANES, PERFLUOROCYCLOHEXANE, EICOSANE, CYCLOTRIACONTANE, CONTAINING REGULAR FRAGMENT GROUPS (C<sub>2</sub>H<sub>4</sub> or CF<sub>2</sub>)**

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**Abstract:** In ion series of mass spectra of alkanes, cycloalkanes, perfluoroalkanes and perfluorocycloalkanes, containing regular fragment groups (C<sub>2</sub>H<sub>4</sub> or CF<sub>2</sub>), primary separation of one or more radicals occurs by a similar mechanism. The subsequent emissions of the regular fragment groups in all ionic series of the mass spectrum of the compound, as a rule, have the same or similar total masses. That is, the relative excitation energy costs  $^+M$  of several ion series of the spectrum differ by the energies of the primary tearing and the number of radicals to be separated. Primary separation of radicals is substantially equalizing the energies of all ion series. As a result, practically identical breaks of regular fragment groups take place in all series. Ionic series of *n*-alkanes and cycloalkanes, as well as perfluoroalkanes have been presented earlier. In order to compare the primary tearing occurring in them, it is necessary to return to them again. The difference in excitation energies, molecular cation-radicals of ion series is a result of dispersion of ion source electrons energy. Ratio of maximum and minimum excitation energy of molecular cation-radicals of *n*-perfluoroalkanes, perfluorocyclohexane and eicosane equal to 3: 1 corresponds to maximum - 3 and minimum - 1 number of primary, synchronously detachable radicals. It can also be estimated by the ratio of the energies of the rupturable connections. Analysis of mass spectra of compounds containing regular fragmental groups makes it possible to conclude that triple difference of energies of primary breaks in ion series of mass spectrum does not conflict with postulate of quasi-equilibrium theory, describing uniform distribution of energy before beginning of decomposition. Synchronous primary separation of three fluorine atoms (C<sub>2</sub>, C<sub>1</sub> and C<sub>20</sub>F<sub>3</sub>) in one of series of *perfluoroicosane*, and also two hydrogen atoms and a radical  $\cdot\text{CH}_3$  (C<sub>2</sub>, C<sub>1</sub> and C<sub>20</sub>H<sub>3</sub>) in one of the eicosane series confirm the alignment of the excitation energy  $^+M$  corresponding series, even before the onset of decay.

**Keywords:** primary synchronous detachment of radicals, decay sequences, ionic series of eicosane, perfluoroicosane, cyclotriacontane, perfluorocyclohexane.

### Introduction

Compounds containing regular fragmental groups  $\text{CF}_2$  or  $\text{CH}_2$  are simple and therefore the best object for studying primary detachments occurring in their ionic series. Primary detachment of radicals and subsequent emissions of regular fragment groups with formation of corresponding ionic series in mass spectra of eicosane, 1-bromoeicosane and 1,20-dibromoeicosane was reported earlier [1].

Ionic series of perfluoroicosane, perfluorocyclohexane, cyclohexane and cyclotriacontane were presented in article [2]. The aim of the present invention is to compare and estimate the relative energies of primary detachments in ionic batches of linear and cyclic alkanes, as well as perfluoroalkanes and perfluorocyclohexane.

### The method of establishing primary detachments of ionic series

In order to determine the primary or several primary detachments occurring in one of the ionic series of the compound containing the regular fragment groups  $\text{C}_2\text{H}_4$  or  $\text{CF}_2$ , it is necessary to install the first fragment ion, the resulting at detachment of one, two or three primary radicals. In the spectra of higher homologs of *n*-alkanes and *n*-perfluoroalkanes, the peaks of molecular ions and also of the first fragment ions are either absent or have an extremely low intensity. To establish the first fragment ion of the ion series, a "reverse" sequence of fragmentation of any intense peak of the "final" ion of one of the ionic series can be used. By adding to the mass of the selected fragment ion, regular fragment groups (28)  $\text{C}_2\text{H}_4$  in alkanes or (50)  $\text{CF}_2$  in perfluoroalkanes can be produced in several variants of mass, smaller than the mass of the molecular ion by the amount of detachment of one or more primary radicals.

In the spectra of perfluoroalkanes, depending on the ionic series, the number of primary fluorine atoms to be detached varies from one to three. Primary detachments of  $\cdot\text{CH}_3$  and  $\cdot\text{C}_2\text{H}_5$  radicals occur in *n*-alkane spectra, as well as combined detachments of one or two hydrogen atoms and  $\cdot\text{CH}_3$  and  $\cdot\text{C}_2\text{H}_5$  radicals. The final stage in the decrypt of the original detachments is a comparison of total masses of primary detached radicals of all ion series and establishment of their separation sequence. To decrypt primary detachments, containing several radicals, there is desirable to analyze the fragmentation of the nearest homologues. However, the fragmentation and ionic series of the  $\text{C}_1$ - $\text{C}_5$  homologues may differ from the  $\text{C}_9$ - $\text{C}_{20}$  homologues fragmentation. Thus, only one series of consecutive separations of four fluorine atoms occurs in the mass spectrum of tetrafluoromethane.

**Primary detachments and ionic series of eicosofluoronane,  
perfluoro-2,4-dimethyl-3- ethylpentane, perfluoroicosane and perfluorocyclohexane**

Published mass spectra of higher perfluoroalkanes are few. In the NIST libraries, only the perfluoroicosane  $C_{20}F_{42}$  spectrum is presented from higher perfluoroalkanes. The mass spectrum of eicosofluorinane published in [3,4] is presented in Table 1.

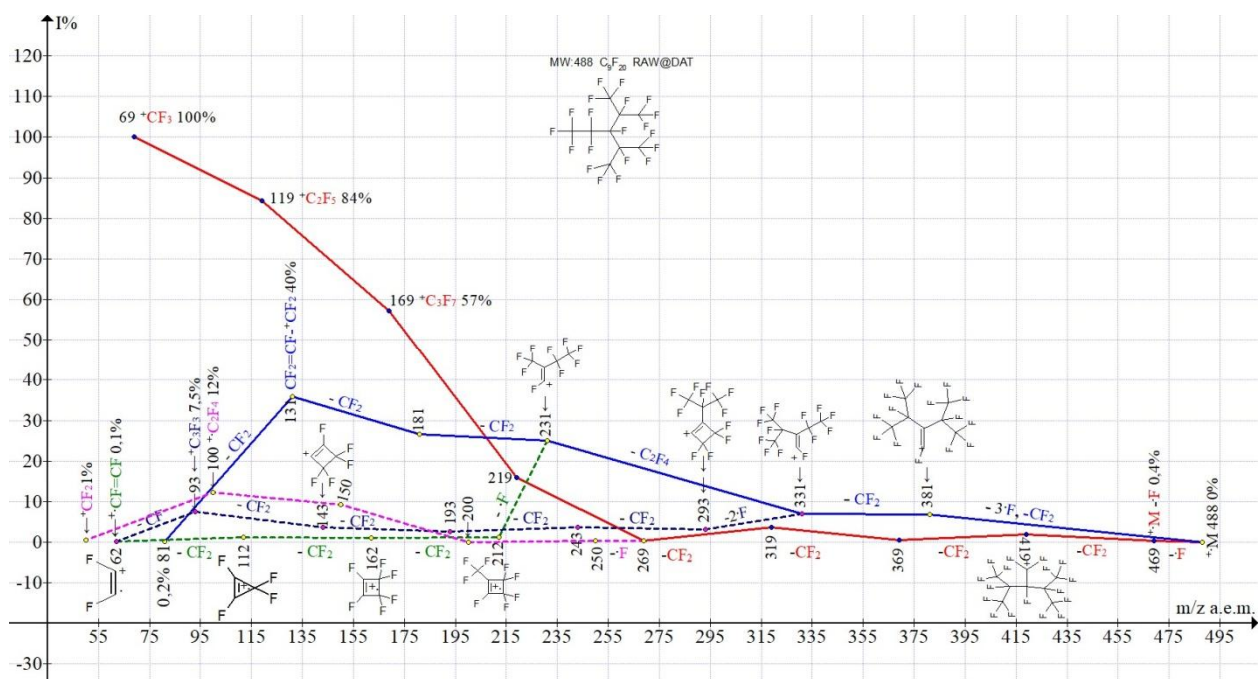
**Table 1.** The mass spectrum of eicosofluorinane  $C_{20}F_{42}$  [3,4].

Ion	Formula	m/z			
$^+M$	$C_9F_{20}$	488 0 %	488 0 %		
$^+M -F$	$C_9F_{19}$	469 0 %			
$^+M -3F$	$C_9F_{17}$		431 0,2%		
$^+M -3F -CF_2$	$C_8F_{15}$		381 0,3%		
$^+M -F -2CF_2$	$C_7F_{15}$	369 0,1%			
$^+M -3F -2CF_2$	$C_7F_{13}$		331 0,4%		
$^+M -F -3CF_2$	$C_6F_{13}$	319 0,1%			
$^+M -3F -3CF_2$	$C_6F_{11}$		281 1,6%		
$^+M -F -4CF_2$	$C_5F_{11}$	269 2,6%			
$^+M -3F -4CF_2$	$C_5F_9$		231 2,4%		
$^+M -F -5CF_2$	$C_4F_9$	219 7,1%			
$^+M -3F -5CF_2$	$C_4F_7$		181 5,6%		
$^+M -F -6CF_2$	$C_3F_7$	169 17,2%			
$^+M -F -6CF_2 -F$	$C_3F_6$			150 1,8%	
$^+M -3F -6CF_2$	$C_3F_5$		131 17,6%		
$^+M -3F -6CF_2 -2F$	$C_3F_3$				93 2,5%
$^+M -F -7CF_2$	$C_2F_5$	119 13,8%			
$^+M -F -6CF_2 -F -CF_2$	$C_2F_4$			100 7,1%	
$^+M -3F -7CF_2$	$C_2F_3$		81 0%		
$^+M -F -8CF_2$	$CF_3$	69 100%			
$^+M -F -6CF_2 -F -2CF_2$	$CF_2$			50 0,9%	
$^+M -3F -6CF_2 -2F -C_2F_2$	$CF$				31 3,6%
$^+M -3F -8CF_2$	$CF$		31 3,6%		

In linear perfluoroalkanes because of the dense "packing" of the chain with fluorine atoms, the primary detachments of the perfluoroalkyl radicals  $\cdot CF_3$  and  $\cdot C_2F_5$  are not possible. For this reason, only the detachments of fluorine atoms [5] occurs in the perfluoroalkanes. The two primary

separations from which the fragmentation of eicosofluorinane begins are the detachments of one, as well as three fluorine atoms.

As a result of these detachments, two main ion series of spectrum occur: Perfluoroalkyl (peaks are marked with red color, the last significant digit of mass 9)  ${}^+M-F-8CF_2 \rightarrow {}^+69$  and perfluoroalkenyl (peaks are marked with blue color, the last significant digit of mass 1)  ${}^+M-F(C_2)-F(C_1),-F(C_9)-6CF_2 \rightarrow {}^+131-2CF_2 \rightarrow {}^+31$ . Both ionic series are branched. When a fluorine atom is detached from the alkyl ion with  $m/z$  119, an olefin ion is formed  ${}^+C_2F_4$   $m/z$  100 (marked with a violet color and the last significant digit of mass 0), and ion  ${}^+C_3F_3$  with  $m/z$  93 is generated in case of detachment of two fluorine atoms from alkenyl ion with  $m/z$  131. Since the total number of  $CF_2$  detachments in the perfluoroalkyl and perfluoroalkenyl series is equal to eight, it can be concluded that the alkenyl series (detachment of three fluorine atoms) is three times more energy-consuming than the alkyl series which begins with the detachment of one fluorine atom. The ionic series of the non-linear structural isomer of eicosofluorinane, perfluoro-2,4-dimethyl-3-ethylpentane is given in Figure 1.



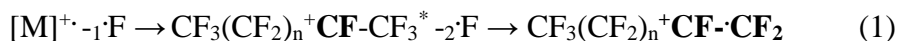
**Figure 1.** Ionic series of mass spectrum of perfluoro-2,4-dimethyl-3-ethylpentane  $C_9F_{20}$  MW:488 (ineos.ac.ru).

Two main ionic series of asymmetric isomer  $C_9F_{20}$  (Figure 1): perfluoroalkyl (marked with a red color, the last significant number of masses 9) and perfluoroalkenyl (marked with a blue color, the last significant digit of masses 1), as well as a series of linear isomer, begin with primary detachments of one and, respectively, three fluorine atoms. At detachment of one fluorine atom there is the first ion of perfluoroalkyl series with  $m/z$  469 (0,4 %). When detachment from the

perfluoroalkyl ion with  $m/z$  269, the second in the alkyl series of the fluorine atom is branched to form an olefin series of ions with  $m/z$  250, 200, 150, 100, 50 (marked with a violet color, the last significant digit of masses is 0). The perfluoroalkenyl series is branched twice. When two fluorine atoms detachment from the ion with  $m/z$  331, there is a series of ions with  $m/z$  293, 243, 193, 143, 93 and 62. When one fluorine atom is detached from ion 231, a series of ions with  $m/z$  212, 162, 112, 62 occurs (marked with a dotted blue line). Branching of ionic series with additional fluorine atoms detachment is probably the result of energetically advantageous cyclization of ions with  $m/z$  250, 293 and 212. Fragmentation of two ion series with  $m/z$  293 and 212 is completed with ion  $^+CF\cdot CF$  with  $m/z$  62. Total number of ionic series of mass spectrum is equal to five.

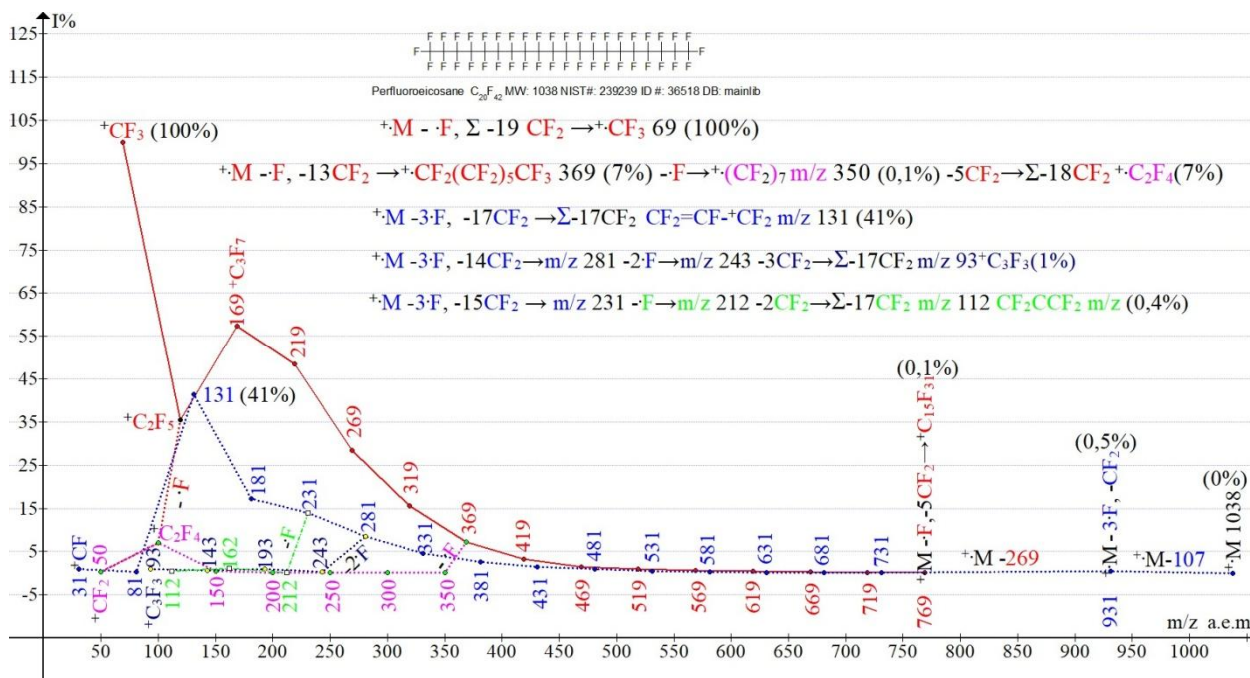
In the mass spectrum of perfluoroeicosane  $C_{20}F_{42}$  MW 1038 NIST #: 239239 ID #: 36518 DB: mainlib (Figure 2), two main ion series (perfluoroalkyl and perfluoroalkenyl) differ in the topology of electron removal ( $C_1$  and  $C_2$ ), the number of primary detachments of fluorine atoms 1 and 3 and the number of emissions of  $CF_2$  19 and 17. When the electron of the terminal group of  $CF_3$  is detached, one fluorine atom is emitted. In contrast to the mass spectrum of the asymmetric isomer  $C_9F_{20}$  (Figure 1) in which there is a peak  $^+M\cdot F$ , in the  $C_{20}F_{42}$  (Figure 2) spectrum, it is not manifested. The first peak of the perfluoroalkyl series  $C_{20}F_{42}$  is a peak with  $m/z$  769 (0.1%) corresponding to the detachment of one fluorine atom and the five  $CF_2$  groups.

Another variant of the primary detachment leading to the release of two more fluorine atoms is the detachment of one fluorine atom from the  $CF_2$  -group of the terminal perfluoroethyl group. When the electron is detached from the  $C_2F_5$  group, one fluorine atom is emitted to form a  $CF_3(CF_2)_n^+CF\cdot CF_3^*$  cation. This emission "provokes" the additional energetically advantageous detachment of the fluorine atom of the group (1).



The detachment of the third fluorine atom from the opposite terminal group  $CF_3$  results in the transfer of a positive charge and the occurrence of a double bond (2) which protects one of the flanks of the chain from fragmentation. The possibility of transferring a positive charge or a "hole" is reported in [6]. Then, the regular fragment groups of  $CF_2$  are detached.

The first detectable ion of an alkenyl series with  $m/z$  931 0.5% (M-107) (series is marked with blue, the last significant digit of masses 1) corresponds to the primary detachment of three fluorine atoms M-57 (M-3F) and the emission of  $CF_2$ .



**Figure 2.** Five ionic series of mass spectrum of perfluoroicosane  $C_{20}F_{42}$  MW:1038 NIST# 239239 ID: 36518 DB:mainlib.

In fragmentation and a decrease in the molecular weight of the perfluoroalkyl series ions, the probability of structural isomerization thereof increases, with a positive charge being transferred to the centre of symmetry. The structural isomerization of linear ions is also possible in a perfluoroalkenyl series (ion with  $m/z$  131). Branching of ionic series in spectra  $C_9F_{20}$  and  $C_{20}F_{40}$  occur at different masses of fragmentizing ions, except for detachment of one fluorine atom in perfluoroalkenyl series from ion with  $m/z$  231. When a fluorine atom is detached from the perfluoroalkyl series ion with  $m/z$  369 (having a mass per 100 Da that is greater than the  $C_9F_{20}$  spectrum), said fluorine atom is branched to form an olefin series of ions with  $m/z$  350, 300, 250, 200, 150, 100, 50 (marked with a violet color, the last significant digit of ionic masses is 0). When two fluorine atoms are detached from ion with  $m/z$  281 (with a mass by 50 Da less than in spectrum  $C_9F_{20}$ ), as well as one fluorine atom from ion with  $m/z$  231 of perfluoroalkenyl series two additional low-intensity series of ions occur: with  $m/z$  243, 193, 143, 93, as well as with  $m/z$  212, 162, 112, 62. Branches of a perfluoroalkenyl series with 3+2 and 3+1 fluorine atoms are likely to result from two energetically advantageous over-grouping of perfluoroalkenyl ions.

The present examples of five ionic series of  $C_9F_{20}$  isomers, as well as perfluoroicosane  $C_{20}F_{42}$ , confirm the same primary fluorine atom detachment, ionic series and the release sequences of regular fragment groups  $CF_2$ . Since the binding energy of C-F to  $n$ -perfluoroalkanes is 116 kcal/mol (5.03 eV) [5], the energy required for the primary detachment of three fluorine atoms is about 348 kcal/mol (15.09 eV). Ratio of primary detachment of fluorine atoms of two main ionic

series is 1:3, probably, is a result of two versions of electron removal, acquisition and consumption of excitation energy. However, considering the energy gain of the double bond formation, this ratio may be somewhat less. The detachment of the fluorine atom in the branching of the perfluoroalkyl series, and the three additional detachments of the fluorine atoms as a result of the two branches of the alkenyl series do not change the energies ratios of the fluorine atom detachments in the two main ionic series (alkyl and alkenyl). The ratio of the sums of the detached fluorine atoms in the two main ionic series, considering the branches thereof, is 2:6, which is also equal to 1:3. The number of CF<sub>2</sub> cuts occurring in three ionic series: in perfluoroalkyl - 19, in perfluoroalkenyl - 17, and in perfluorolevine - 18. It should be noted that synchronous detachment of three fluorine atoms from three terminal groups CF<sub>3</sub>, followed by emission of ten groups (CF<sub>2</sub>) 1-10 takes place also in one of three main fragmentation series of perfluorotert-butylamine (PFTBA) [7]. This series is terminated by formation of ion CF<sub>2</sub><sup>+</sup>N CF<sub>2</sub> with m/z 114 (0.4%).

The mass spectrum of perfluorocyclohexane C<sub>6</sub>F<sub>12</sub> MW 300 (NIST#: 34431 ID#: 115484 DB: mainlib), as well as the mass spectrum of perfluoroicosane, includes five ionic series (Table 2) [2].

**Table 2.** Five ionic series of perfluorocyclohexane C<sub>6</sub>F<sub>12</sub> MW 300.

Series	C <sub>6</sub> F <sub>12</sub>	M 300 0,7%	-CF <sub>2</sub>	-CF <sub>2</sub>	-CF <sub>2</sub>	-CF <sub>2</sub>	-CF <sub>2</sub>	∑I %= 308,8	I series current, %
1	M-F	281 3.7%	231 20.9%	181 21.4%	<b>131</b> 100.0%	81 2.1%	31 21.8%	170.6	55.2
2	M-2F	262 Tr	212 0.1%	<b>162</b> 3.9%	112 2.5%	62 1.2%		7.7	2.5
3	M-3F	243 Tr	193 2.7%	143 2.0%	<b>93</b> 15.0%	43 0.3%		20.0	6.5
4	M/2 M- C <sub>3</sub> F <sub>6</sub>	150 0.4%	<b>100</b> 29.2%	50 5.1%				34.7	11.3
5	*M- C <sub>3</sub> F <sub>5</sub>	169 Tr	119 5.5%	<b>69</b> 70.3%				75.8	24.5

Tr – the peak intensity in % at the trace level.

In the mass spectrum of perfluorocyclohexane, as in the spectra of *n*-perfluoroalkanes, primary synchronous detachments of one, two and three fluorine atoms occur, with the formation of three ionic series N1-N3 (Table 2). Formation of three ion series at detachments of one, two and three fluorine atoms of perfluorocyclohexane is difficult to explain various topologies of electron removal. In linear perfluoroalkanes, the primary separation of perfluoroalkyl radicals does not typically occur [5] because of the "packing" of the chain with fluorine atoms. In fragmentation, the non-linear perfluorocyclohexane molecule C-C of the cycle link becomes available for separation. Two ionic

series (olefinic N4 and alkyl N5) (Table 2) occur as a result of symmetric decomposition of M/2 with rupture of two C-C bonds as well as asymmetric, regrouping decomposition with detachment of perfluoroallyl radical  $^+M - \cdot C_3F_5 \rightarrow ^+CF_2CF_2CF_3$  m/z 169 Tr.

As a result of symmetric decomposition, olefin series ions  $^+C_3F_6$  m/z 150 0.4%,  $^+C_2F_4$  m/z 100 29% and  $^+CF_2$  m/z 50 5% occur.

As a result of asymmetric rearrangement decomposition  $^+C_6F_{12}$  with separation of  $\cdot C_3F_5$  there is the first ion of perfluoroalkyl series  $^+C_3F_7$  m/z 169, fragmentation with formation of ions  $^+C_2F_5$  m/z 119 5.5% and  $^+CF_3$  m/z 69 70%. Returning to the N1-N3 ionic series, it can be assumed that the first act preceding the detachments of one, two and three fluorine atoms is the break of the cycle to form **three linear cation radicals with different excitation energies**.

The difference between the alkenyl series of perfluorocyclohexane and the alkenyl series of perfluoroalkanes is that it does not require separation of three fluorine atoms for its formation, and the detachment of one fluorine atom is sufficient. The first ion of the alkenyl series with m/z 281  $CF_2=CF-(CF_2)_3-\cdot CF_2$  (3.7%) appears as a result of the break of the cycle, separation of the fluorine atom, from the second  $CF_2$  group of the broken cycle, rearrangement to form a terminal vinyl group and transfer of the positive charge to the opposite "flank". It fragments to form the series N1 (Table 2): 231, 181, 131, 81, 31.

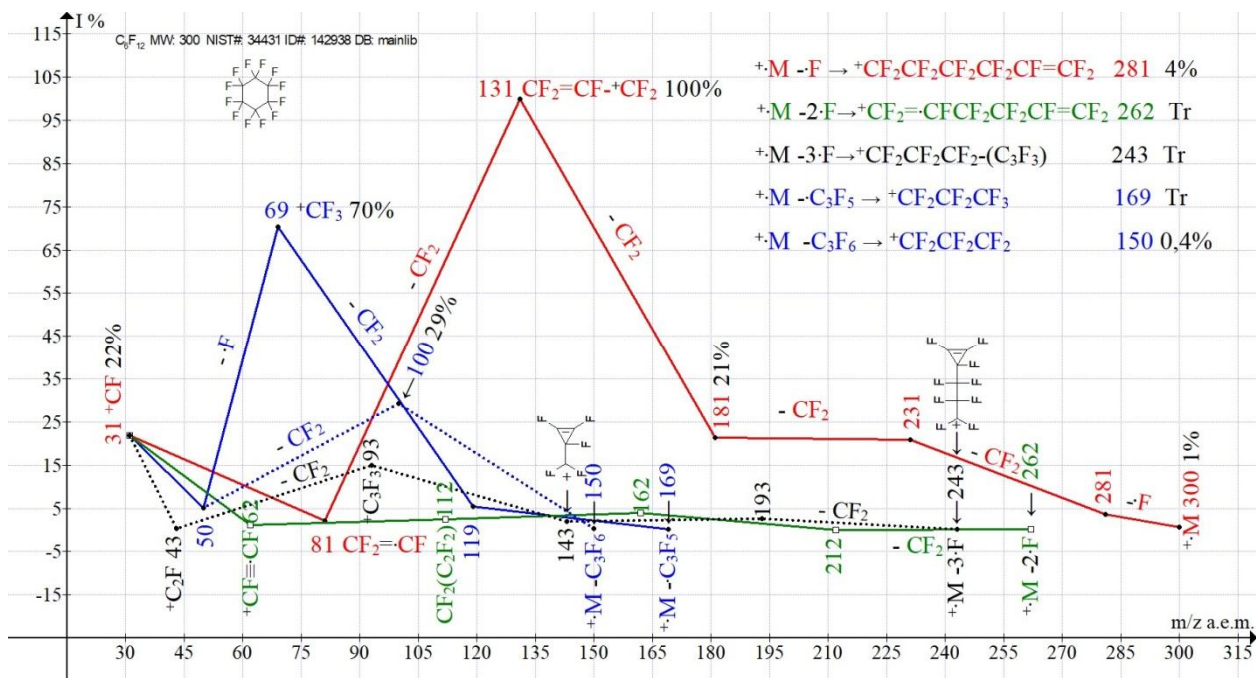
As a result of the cycle decay and two symmetrical detachments of 2-5 fluorine atoms, occurs a linear cation-radical with m/z 262 decafluorohexa-1,5-dien  $CF_2=CF-(CF_2)_2-\cdot CF=^+CF_2$ . It fragments to form the series N2 (Table 2): 212, 162, 112, 62.

At maximum excitation energy of molecular cation-radical there is a break of cycle and detachment of three fluorine atoms from terminal group  $C_3F_6$  with formation of ion with m/z 243 Tr %  $CF_2=C=CF-(CF_2)_2-\cdot CF_2$ , or the cycle  $-(C_3F_3)(CF_2)_2-\cdot CF_2$ . It fragments to form the series N3 (Table 2): 193, 143, 93, 43. Double bonds strengthening one or both flanges of the perfluoroalkyl chain occur in the ion series N1-N3 after detachment of fluorine atoms (1F,2F,3F).

When total ionic currents of series 1-5 (Table 3) are compared, maximum current intensity is 55.2% in series 1 (separation of one fluorine atom). It is followed by the series 5-24.5% и 4-11.3% (detachments  $\cdot C_3F_5$  и  $C_3F_6$ ). The most energy-consuming ionic series N3 and N2, with separation of three and two atoms, fluorine have minimum intensity of ion current 6.5 and 2.5%, respectively.

Sequences of formation and graphs of five ionic series of perfluorocyclohexane with intensities of formed ions are presented in Figure 3.





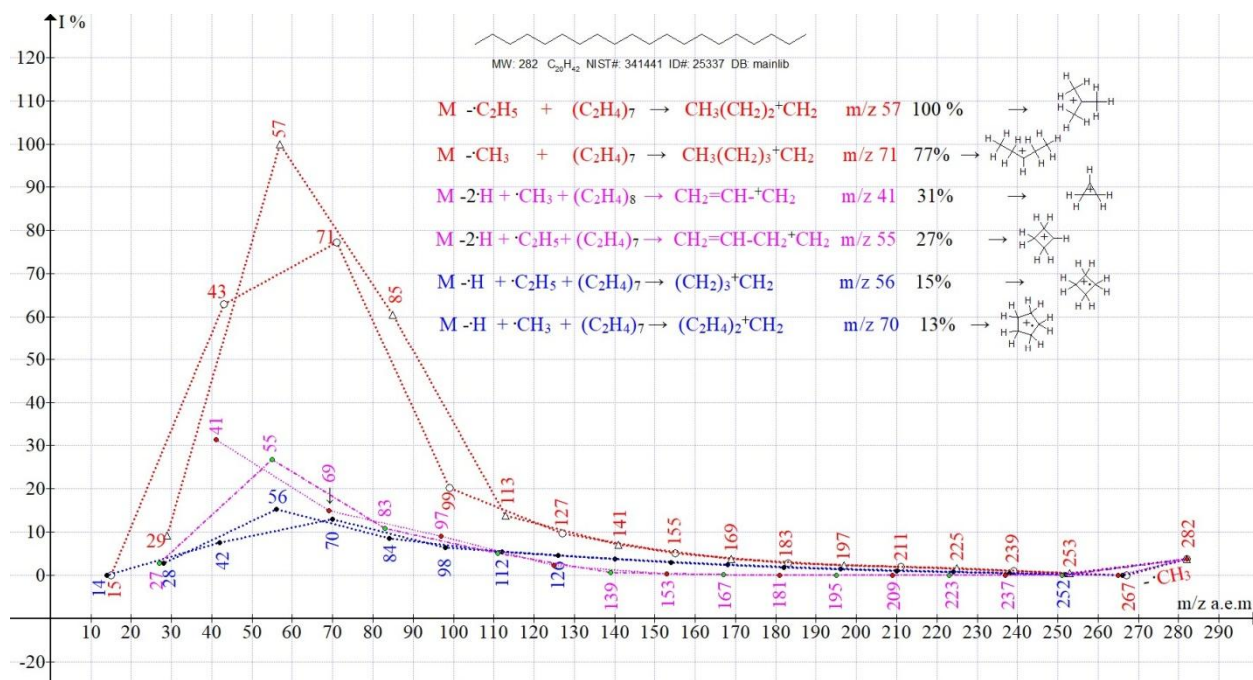
**Figure 3.** Five ionic series of mass spectrum of perfluorocyclohexane  
 $C_6F_{12}$  MW:300 NIST#: 34431 ID#: 142938 DB: mainlib

In the ionization of perfluorocyclohexane, five variants  $+M_{1-5}$  with different excitation energies are produced, while only two  $+M_{1-2}$  are used for ionizing the perfluorocyclohexane. It is possible that this result is that the ratio of their molecular weights is  $300:1038 = 1:3.4$ . An increase in the molecular weight of the compound helps to reduce the specific energy of the chain links when equalizing the excitation energy. If there are no branches in five series of perfluorocyclohexane, the third branches of two main series (1+2) occur in the series of perfluoroeicosane. So, if the excitation energy after decay of cycle in the spectrum of perfluorocyclohexane is sufficient for occurrence of the five "independent" ionic series, then in the spectrum of perfluoroeicosane due to the possible energy deficit the additional separation of fluorine atoms takes place as a result of energetically favorable isomerization and cyclization of emerging ions.

### Primary detachments and ionic series of eicosane and cyclotriacontane

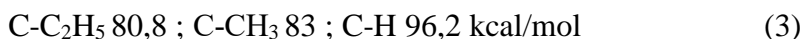
In the mass spectra of eicosane, its halogen-derivatives [1], as well as cyclotriaftane [2], decay sequences-their ionic series were established. Including six ionic series of eicosane  $C_{20}H_{42}$ , eight series of 1-bromoeicosane  $C_{20}H_{41}Br$  and 1,20-dibromoeicosane  $C_{20}H_{40}Br_2$  [1] and six series of cyclotriacontane [2].

The eicosane spectrum,  $C_{20}H_{42}$  MW 282 NIST#: 341441 ID#: 25337 DB: mainlib, includes six series of ions. The sequences of separations in six ionic series are presented in Figure 4.



**Figure 4.** Six ion series of mass spectrum of eicosane  
C<sub>20</sub>H<sub>42</sub> NIST#: 341441 ID#: 25337 DB: mainlib

Two alkyl series of ions are marked with red lines, two alkenyl series with violet lines, two olefinic series with blue lines. According to the calculated reference data on the bond energies of n-alkanes [8] energy of separation of alkyl radicals and hydrogen atom increase in the row:



Using data [5], the C-H bond energy in n-alkanes is 99.5 kcal/mol (4.3 eV), which is 16.5 kcal/mol less than the C-F bond energy in n-perfluoroalkanes (116 kcal/mol (5.03 eV)).

In comparison with ease of detachment of CF<sub>2</sub> in mass-spectra of perfluoroalkanes, separation of CH<sub>2</sub> in spectra of n-alkanes does not occur [9], and release of molecules C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> takes place.

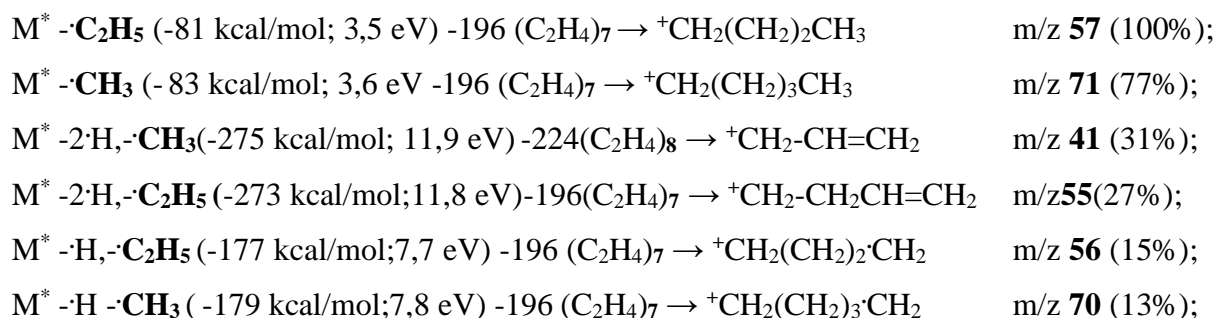
In contrast to primary detachments of perfluoroalkanes, in which only fluorine atoms participate, in the spectrum of alkanes there are primary detachments -C<sub>2</sub>H<sub>5</sub> and ·CH<sub>3</sub>, as well as synchronous combined separation of two and three radicals. In particular, the separation of ·H + ·CH<sub>3</sub> and ·H + ·C<sub>2</sub>H<sub>5</sub> atoms, as well as 2·H + ·CH<sub>3</sub> and 2·H + ·C<sub>2</sub>H<sub>5</sub>.

Six ionic series of eicosane C<sub>20</sub>H<sub>42</sub> involve:

- two series of alkyl ions terminating in intense, probably regrouping peaks with m/z 57 <sup>+</sup>C(CH<sub>3</sub>)<sub>3</sub> (100%) and m/z 71 <sup>+</sup>CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (77%);
- two series of alkenyl ions terminating in intense peaks with m/z 41 <sup>+</sup>C<sub>3</sub>H<sub>5</sub> (31%) and m/z 55 <sup>+</sup>C<sub>4</sub>H<sub>7</sub> (27%), probably with cyclopropylium and cyclobutylium structures;

- two series of olefin ions terminating in peaks with m/z 56 cyclobutane  $^+\cdot(\text{CH}_2)_4$  (15%) and m/z 70 cyclopentane  $^+\cdot(\text{CH}_2)_5$  (13%);

The energies of six variants of radicals primary separation (in kcal/mol and eV)  $^+\cdot\text{M}_{1-6}$  eicosane vary (from 81 to 275 kcal/mol) or (from 3.5 eV to 11.9 eV). So, the ratio of the minimum and maximum energies of the primary separations in the n-alkane spectra, as in the n-perfluoroalkane spectra, is equal to 1: 3.

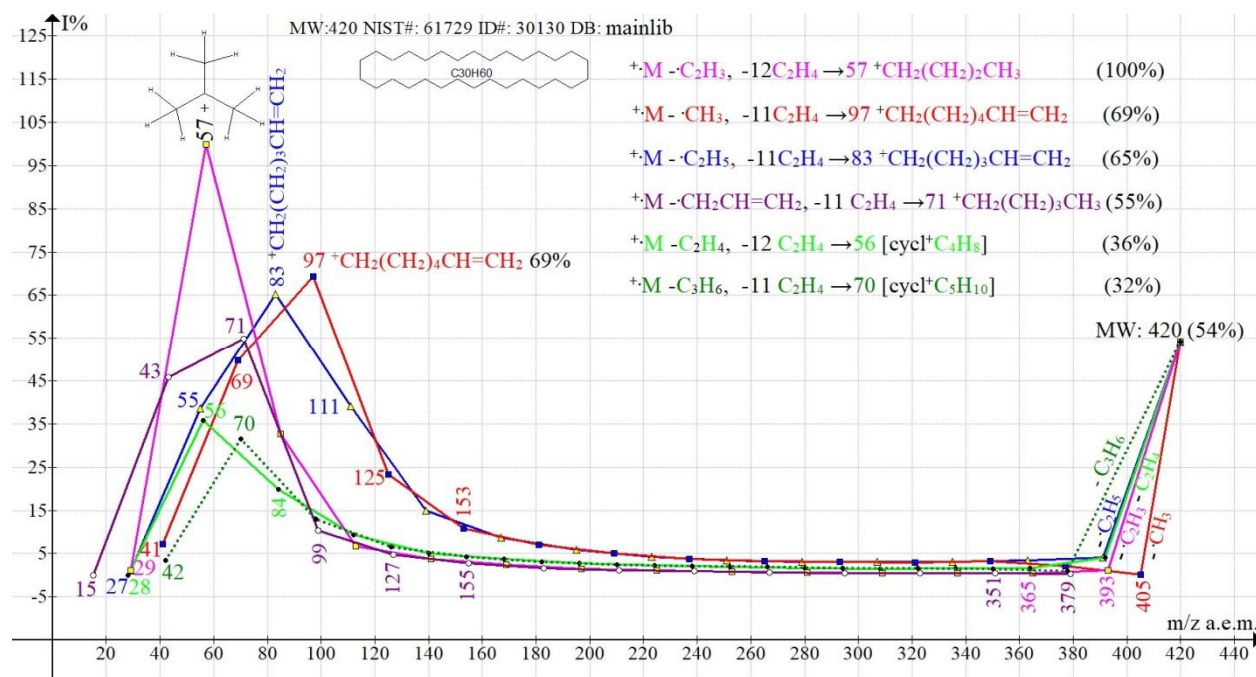


As a result of the primary detachments  $-2\cdot\text{H}$ , ions with a terminal vinyl group occur. The subsequent separation of the methyl or ethyl radical is completed by forming two series of alkenyl ions.

Two olefin series of ions are formed as a result of primary  $-(\cdot\text{H} + \cdot\text{CH}_3)$  and  $-(\cdot\text{H} + \cdot\text{C}_2\text{H}_5)$ .

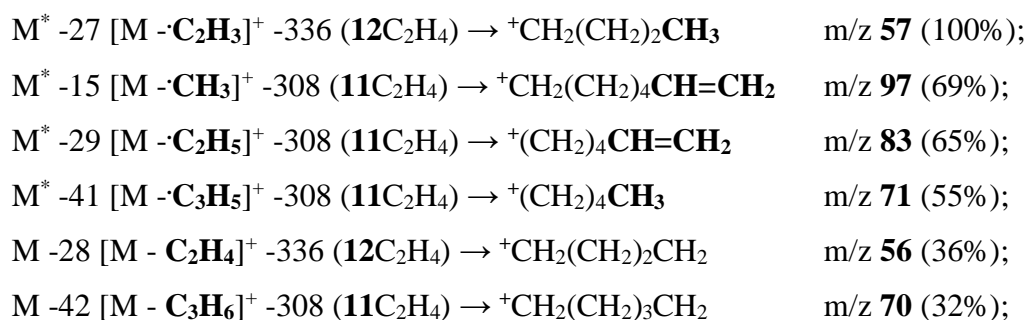
After primary separation of radicals, in five series, the same total weight of ethylene  $(\text{C}_2\text{H}_4)_7=196$  Da is released. In the sixth ion series, after separation of two hydrogen atoms and  $\text{CH}_3$  radical, eight ethylene molecules  $(\text{C}_2\text{H}_4)_8=224$  Da are released. The detachment of eight ethylene molecules, in one of the six series of eicosane, compared to the detachment of seven ethylene molecules in five other series, makes it possible to conclude that the total energy of the regular fragment groups detachment in all six series is practically the same.

The cyclotriacontane spectrum  $\text{C}_{30}\text{H}_{60}$  MW#:420 also includes six ionic series [2] as the eicosane spectrum. The sequences of excerpts occurring in the ionic series  $\text{C}_{30}\text{H}_{60}$  are shown in Figure 5.



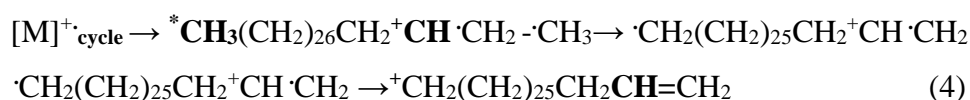
**Figure 5.** Six ion series of mass spectrum of cyclotriacontane  
 $C_{30}H_{60}$  MW#: 420 NIST#: 61729 ID#: 26169 DB: mainlib

Four ionic series of cyclotriacontane occur at break of cycle and primary detachments of four regrouping radicals: vinyl, methyl, ethyl and allyl. Two more olefin series occur in the event of a break in the cycle and in the primary detachments of two olefin fragments of the chain: ethylene and propylene. Unlike perfluorocyclohexane, decomposition  ${}^+M/2 \rightarrow m/z$  210 of cyclotriacontane to form olefin series terminating in peaks 98, 70, 42 does not occur. In four ionic batches of six, terminating with peaks with  $m/z$  97, 83, 71 and 70, the detachment of eleven ethylene molecules occurs. Separation of twelve ethylene molecules takes place in two other ionic series terminating in formation of base peak with  $m/z$  57 and intensive peak with  $m/z$  56. When the cycle is broken and the alkenyl radicals  $C_2H_3$  or  $C_3H_5$  are detached, one of the  $CH_2$  groups of the broken chain acquires "unused by the broken radical" hydrogen atom, turning into the terminal group  $CH_3$ .



When the cycle is broken and the alkyl radicals  $\cdot\text{CH}_3$  or  $\cdot\text{C}_2\text{H}_5$  are separated, one of the  $\text{CH}_2\text{CH}_2$  groups of the broken chain loses an additional hydrogen atom, "necessary" for detached  $\text{CH}_2$  или  $\text{C}_2\text{H}_4$  groups, turning into the terminal group  $\text{CH}=\text{CH}_2$ .

Detachment of radicals:  $-\text{CH}_3$  and  $-\text{C}_2\text{H}_5$  can be explained also as a rearrangement of the excited molecular cation-radical with formation of linear rearrangement ions, in which one of terminal  $\text{CH}_2\text{CH}_2$  groups of the broken cycle at the moment of rupture loses a hydrogen atom, turning into a vinyl group, and the other acquires a hydrogen atom, turning into the detachable terminal group  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ .



When separating the methyl or ethyl radical from the linear rearrangement cation-radical, a fragmenting with  $\text{C}_2\text{H}_4$  detachments alkenyl cation is formed.

The radicals:  $-\text{C}_2\text{H}_3$  and  $-\text{C}_3\text{H}_5$  confirm the rearrangement of the molecular cation of the cyclotriacontane radical to form linear rearrangement ions, in which, when the cycle is broken, one of the terminal groups of  $\text{CH}_2\text{CH}_2$  or  $\text{CH}_2\text{CH}_2\text{CH}_2$  of the broken cycle loses a hydrogen atom, turning into a vinyl or propenyl radical, and the other acquires a hydrogen atom, turning into a methyl or ethyl group.

In case of cycle breaks, a primary separation of the rearrangement radicals of the chain takes place in four of the six series of cyclotriacontane, and only two olefin ionic series begin with the separation of ethylene and propylene.

### Conclusion

Upon ionization with electrons, molecular cation-radicals acquire excess internal energy of from 0 to 20 eV. The branching of the ionic series  $^+\text{M}$  can be the cause of the energy-close isomerization variants  $^+\text{M}$ . An example of a molecular ion isomerization is six ion series of benzene spectrum, five of which occur as a result of restructuring its carbon backbone, according to five variants of  $\pi$ -conjugations [10]. In the spectra of considered compounds, containing regular fragmental groups  $\text{C}_2\text{H}_4$  or  $\text{CF}_2$ , isomerization  $^+\text{M}$  does not occur. Analysis of primary separations in ionic series of mass-spectrum makes it possible, according to the number of radicals to be detached, fluorine atoms or hydrogen atoms and alkyl radicals, to evaluate the energy consumption of its ionic series. The detachments of one, two or three radicals depend on the value of the acquired energy of the molecular ion. In some cases, radical separation may be associated with a specific electron removal topology and a radical detachments sequence. The number of occurring ionic series

corresponds to variants of acquiring different excitation energies. The spread of the excitation energies  ${}^+M_{1-3}$  *n*-perfluoroalkanes, perfluorocyclohexane and eicosane, which is estimated at 1:3, the result of the energies dispersion of ion source ionizing electrons, as well as possibly unequal costs of electron removal energies.

The analysis of the spectra containing regular fragmental groups makes it possible to conclude that the triple difference in the excitation energies of ionic series molecular ions and that of primary separations does not conflict with the quasi-equilibrium theory postulate (QET) [11,12]. According to this theory,  $10^{-12}$  sec excess energy is evenly distributed among all bonds of the molecular ion. So, the quasi-equilibrium is achieved before the decomposition begins.

Synchronous primary separation of three atoms  $\cdot F$  ( $C_2, C_1$  and  $C_{20}F_3$ ) in one of series of perfluoro-eicosane, as well as two atoms  $\cdot H$  and radical  $\cdot CH_3$  ( $C_2, C_1$  and  $C_{20}H_3$ ) in one of eicosane series, complete **alignment** of excitation energy  $C_2-C_{20}$   ${}^+M$  is confirmed even before decomposition.

The difference in the energies of the primary detachments of one, two and three radicals in the compounds containing the regular fragment groups, and an almost equal number of emissions from the regular fragment groups makes it possible to conclude that the excitation energy  ${}^+M_{1-6}$  of the ionic series differs mainly by the energies of the primary separations, after which the energy of the ionic series is averaged.

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