



## CONTRIBUTIONS TO THE INTERPRETATION OF MASS SPECTRUM OF TETRAETHOXYSilANE (TEOS).

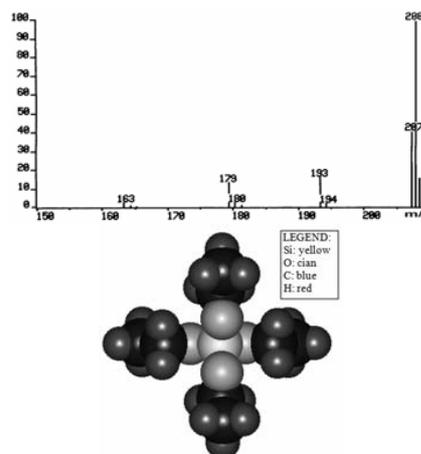
### PART I. THE MOLECULAR ION. PRIMARY EVENTS

Virgil BADESCU\*

National Research & Development Institute for Chemistry & Petrochemistry – ICECHIM, 202 Splaiul Independentei,  
060021 Bucharest, Roumania

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The aim of this article is the study of the fragmentation reactions of tetraethoxysiloxane (TEOS) as a precursor in the sol-gel process initiated by electronic impact in the ionization chamber of a mass spectrometer. Mass spectrum of an organic substance, as well as a silicon alkoxide such as TEOS is the result of a series of unimolecular consecutive and competitive chemical reactions, which constitutes a pattern of fragmentation. The molecular ion of TEOS at mass 208 is a radical cation with positive delocalized charge on the alkoxy bond Si-O-C. The primary fragmentation ions at masses 207, 193, 179 and 163 were obtained experimentally by B/E linked scan. The radical induced fragmentation reactions of the primary ions obtaining are presented and their existence is supplementary argued by measuring the ion masses at high resolution, the quantum calculations of the net atomic charges and the calculation of the double bond equivalent.



### INTRODUCTION

The first objective of the author<sup>1</sup> was the separation and identification of molecular species obtained in sol-gel process by gas chromatography coupled with mass spectrometry (GC-MS).

The basic factors that influence sol-gel process have been studied systematically by GC-MS: type of precursor alkoxide, the nature of the solvent, quantity of water used in hydrolysis, the reactant mixing order and the catalyst type. The results were published between 1994 and 2007.<sup>2-8</sup>

The second objective of the author<sup>1</sup> was the development of a procedure for the mass spectra interpretation of some silicon alkoxides and their transesters and oligomers obtained by the sol-gel process.

The relationship between the chemical structure of the molecules and their mass spectra has been highlighted by Lafferty<sup>9</sup> by applying qualitative physical-organic method; according to this theory the relative intensity of fragmentation ions is determined by (1) the stability of the reaction products and of the bond strength. A complementary theory has been developed by

\* Corresponding author: [virgil\\_badescu@yahoo.com](mailto:virgil_badescu@yahoo.com)

Djerassi<sup>10</sup> within a physical-organic method: (2) the charge and radical localization after ionization contributes to establish the initiation centers of the fragmentation reactions.

In this paper the author applies a procedure, presented below, to the TEOS mass spectrum interpretation for molecular and primary fragmentation ions and plans to publish in the next upcoming works the complete mass spectra interpretation for TEOS and other molecular species identified in the sol-gel process.

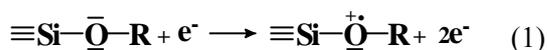
## PROCEDURE FOR THE MASS SPECTRA INTERPRETATION OF THE SILICON ALKOXIDES

### 1. Getting the structural information about silicon alkoxydes (Table 1)

In accordance with the requirements for the interpretation of mass spectra,<sup>1</sup> in Table 1 are presented selected data from literature<sup>11-23</sup> about the atoms and chemical bonds of silicon alkoxydes and oligomers, required for setting preconditions for this interpretation.

2. Singularizing for silicon alkoxydes the influence factors and favorable paths of fragmentation presented in<sup>1, 10, 23-24</sup> and whereas some of their structural data from Table 1, it appears the following general premises (P1 to P10) to be considered for the founding of a mass spectra interpretation procedure of the silicon alkoxydes:

(P1) The positive charge and radical localization occurs on the oxygen atom according to Equation (1):

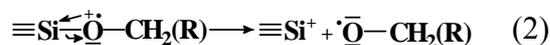


(P2) The relative stabilization of the molecular ion resulted in equation (1) by the delocalisation of the positive charge on the Si-O-C bond axis.

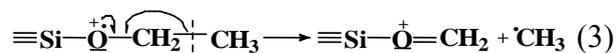
(P3) The direct fragmentation reactions occur according to the data in Table 1.b, the easiest for C-Si, C-C  $\sigma$  bonds and the hardest for H-C, O-H, O-Si  $\sigma$  bonds; O-Si bond has 46% ionic character.

(P4) According to premise (P3) the resulted fragmentation ions are in decreasing order of the stability: siliconium ions, carbocations and oxyocations.

(P5) The inductive effect electron affinity of the oxygen atom (effect -I) correlated with the electropositive character of the silicon atom relative to the other atoms of a silicon alkoxyde (O, C, H), leads to the elimination of an alkoxy radical and obtaining a stable siliconium ion, according to the Equation (2):



(P6) The radical centre is located on the oxygen atom (Equation 1); this unpaired electron with an electron of C-C  $\sigma$  bond in  $\beta$  position to the radical center forms a new bond, simultaneously with the C-C bond cleavage in  $\beta$  position, according to Equation (3):



(P7) The resonance effects lead to relative stabilization of some ions obtained by fragmentation reactions according to the premise (P3); for example the oxycation obtained in the Equation (3) is stabilized according to Equation (4):



Table 1

Information about the atoms and chemical bonds of silicon alkoxydes and oligomers<sup>11-23</sup>

a. Atoms						
Type of atom	H	C	O	Si		
Valence configuration	1s <sup>1</sup>	2s <sup>2</sup> 2p <sup>2</sup>	2s <sup>2</sup> 2p <sup>4</sup>	3s <sup>2</sup> 3p <sup>2</sup>		
The first ionization potential (eV)	13.6	11.3	13.6	8.1		
Electronegativity	2.2	2.5	3.5	1.9		
Isotopic distribution (%)	<sup>1</sup> H 99.99 <sup>2</sup> H 0.01	<sup>12</sup> C 98.90 <sup>13</sup> C 1.10	<sup>16</sup> O 99.76 <sup>17</sup> O 0.04 <sup>18</sup> O 0.20	<sup>28</sup> Si 92.23 <sup>29</sup> Si 4.67 <sup>30</sup> Si 3.10		
b. Chemical bonds						
Type of bonds	H-C	C-C	C-O	O-Si	C-Si	O-H
Bond energy (eV)	4.3	3.6	3.6	4.5	3.0	4.8
The ionic nature of bond %	2.5	0	22	47	9	35
Siloxane bond	$\equiv\text{Si}-\overset{-}{\ddot{\text{O}}}-\text{Si}\equiv \longrightarrow \equiv\text{Si}\overset{-}{\leftarrow}\overset{+}{\text{O}}\overset{+}{\rightarrow}\text{Si}\equiv$					

(P8) The elimination of small molecules, with small molecular weights, from fragmentation ions resulted according to the premises (P3) and (P4) are irreversible reactions due to the stabilities of these elimination products.

(P9) The siloxane bond Si-O-Si (Table 1.b) is very hard cleaved due to partial double bond character of this product, by the occupation of non-bonding electrons from oxygen atom of 3d free orbitals of the silicon atom. The alkoxy bond Si-O-C is easier cleaved due to the lack of free orbitals in the carbon atom for the non-bonding electrons of the oxygen atom.

(P10) The  $M + 1$ ,  $M + 2$  isotopic effects are marked for the alkoxy silanes due to the isotopic distribution of the silicon atom (Table 1.a).

3. The establishment of the molecular ion whenever is possible by comparing with the molecular mass of the analyzed species. His confirmation through the arguments mentioned in the seven step of this procedure.

4. The establishment of the reactions initiation center. According to premises (1)-(2) charge and radical localisation occurs on the oxygen atom from the alkoxy bond Si-O-C. An argument in this respect is the measurements of the net atomic charges. Thus, it is possible to confirm the molecular ion as a cation radical ion in mass spectrum.

5. The establishment of the primary events from the experimental data obtained by B/E linked scan, where B is the magnetic field and E is electric field in double focusing mass spectrometer. Thus, we obtain the daughter ions of the molecular ion. On this basis, the primary fragmentation reactions are written thus obtaining the primary fragmentation ions in a mass spectrum.

6. The experimental determination of the small molecules, which are eliminated from the primary fragmentation ions by B/E  $(1-E)^{1/2}$  linked scan, in order to obtain the fragmentation ions for all reaction pathways.

7. The confirmation of the molecular ion and the fragmentation ions obtained in the 3, 5 and 6 steps through experimental mass-spectrometry determinations of their accurate mass, by measuring the  $M + 1$ ,  $M + 2$  isotopic effects, the calculation of the double bond equivalent and the quantum calculations of net atomic charges.

8. Getting the complete model of the silicon alkoxide fragmentation on the basis of the results obtained in the 1-7 steps.

## EXPERIMENTAL

Experimental data for this paper were obtained on a GC-MS tandem produced by VG-Analytical, England. Speed scans for GC-MS applications have been performed on a 70-SE double-focusing mass spectrometer.

Hewlett Packard 5890 Gas Chromatograph with a fused silica capillary column was effective for the separations of complex mixtures such as those obtained in the sol-gel process. GC-MS interface was direct one and it was done inert by glass plating. Complete control of all scan functions of the instrument was provided by a VG Digital Scan Controller interface.

### Working conditions

For the HP 5890 gas chromatograph: A fused silica high performance capillary column of 25 m x 0, 25 mm, with 70,000 theoretical plates; stationary phase: silicone oil OV-1, with a thickness of 0.1 $\mu$ m; the temperature inside the oven: 40°C, for 3 minutes; temperature programming up to 220 °C with a temperature gradient of 15 °C/min; injector temperature: 250 °C; carrier gas (helium) flow-rate: 1 mL/min; splitting injection 1: 70; the volume of injected sample: 0.1-0.3 $\mu$ L.

For 70-SE, VG Analytical double focusing mass spectrometer: Excitation source with electronic impact at 70 eV; response time: 0.03 ms; accelerating voltage: 8 kV; temperature in the ion source: 180 °C; electronic amplifier: 250.

For the interpretation of mass spectrum TEOS, the linked scans were used to study the metastable ions obtained in the first region without field (FFR1):

The B/E linked scan: This method of scanning allows obtaining daughter ions  $m_2^+$  from a preset precursor ion  $m_1^+$ . The condition for obtaining the daughter ion is B/E = constant, where B is the magnetic field, and E is the electric field applied in the magnetic and electric sectors of the mass spectrometer.

The (B/E)(1-E)<sup>1/2</sup> linked scan: It is used to obtain the ions which lose small molecules with a preset mass (e.g. ethylene, acetaldehyde, etc.).

## RESULTS AND DISCUSSION

### Contributions to the interpretation of mass spectrum of tetraethoxysilane (TEOS)

Mass spectrum of TEOS in NBS spectra library as described in<sup>1</sup> contains the molecular ion at m/e 208 together with  $M + 1$  and  $M + 2$  isotopic effects at m/e 209 and 210 and 46 fragmentation ions.

For this work has been achieved a library of the mass spectra obtained for TEOS in the different sol-gel reaction mixtures<sup>1</sup>, analyzed by GC-MS at a resolution of R=1000 and presented in Fig. 1 shows the TEOS mass spectrum obtained by averaging the 12 TEOS mass spectra and contains the molecular ion at m/e 208 with adjacent isotopic

ions at  $m/e$  209 and 210 together with 84 fragmentation ions. Increased numbers of TEOS fragmentation ions at high resolution ( $R=5000$  and  $R=6600$ ) will be presented in the upcoming works.

Code name (TEOS), molecular formula, structural formula and molecular weight are shown in the text box on a white background. Net distribution of charges in the TEOS molecule was calculated by the MOPAC 7 (PM3) program and is presented in Fig. 2.

### The molecular ion of TEOS

Data about the molecular ion  $M^+$  at mass 208 and intensity  $I = 15.2\%$  in the mass spectrum are specified in the text box on a white background. This ion is obtained according to the

Equation (5) with the underlined structural formula.

The net atomic charges for the molecular ion are given in Fig. 3. Comparing Fig. 2 and 3 with net atomic charges of the TEOS molecule and the molecular ion obtained by the reaction (6) shows the following:

(i) The charge center is located on the oxygen atom; decrease in net negative charge varies from  $-0.442$  to  $-0.283$ .

(ii) Along the alkoxy bond Si-O-C a delocalization of positive charge occurs by increasing the net positive charge for the silicon from  $+1.185$  to  $+1.335$ , and for the carbon atom from  $+0.127$  to  $+0.160$ ; this delocalization of the positive charge stabilizes the molecular ion and explains its appearance in the mass spectrum.

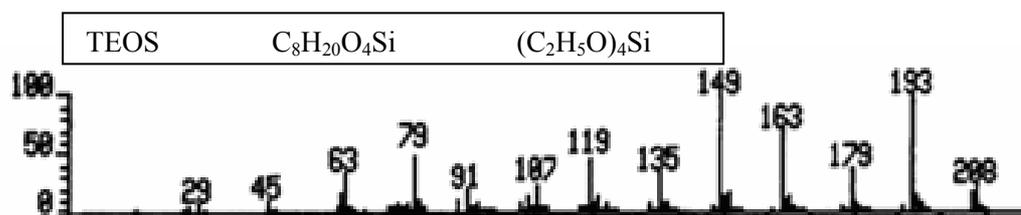


Fig. 1 – Mass spectrum of tetraethoxysilane (TEOS) as an average of 12 mass spectra at resolution 1000.

$M^+$      $m/e$  208     $I=15.2\%$

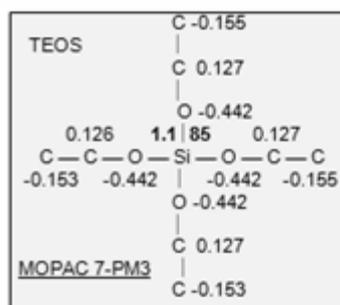


Fig. 2 – TEOS: The net atomic charges.

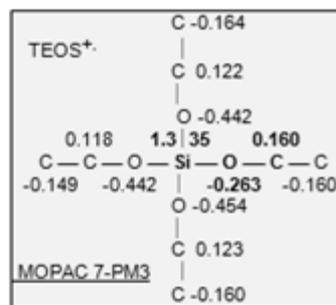
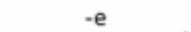
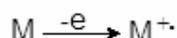
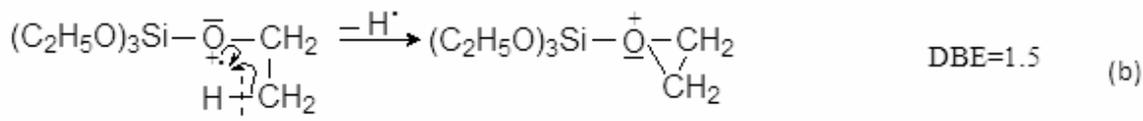
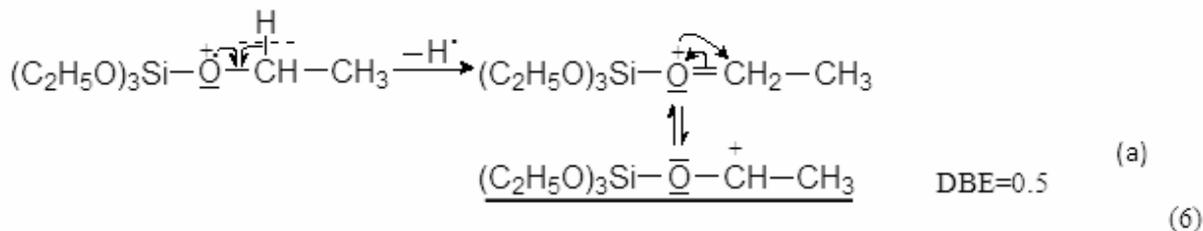


Fig. 3 – The molecular ion of TEOS: The net atomic charges.







In favor of the first path reaction in which is obtained underlined carbocation at mass 207 are the following arguments:

(i) The positive charge is localized on the carbon atom (Fig. 5);

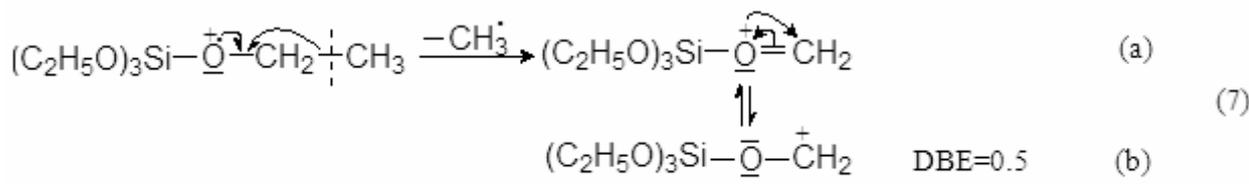
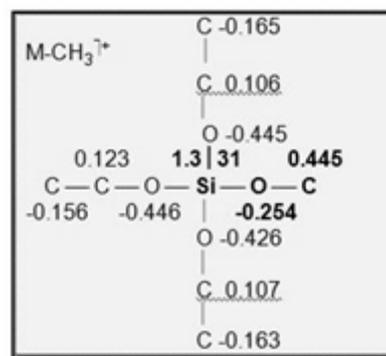
(ii) The formation heat has the value  $H_f = -163.9$  kcal/mol for the linear cation, and the value  $H_f = -119.8$  kcal/mol for cyclic cation (MOPAC 7 quantum calculations). In addition, MOPAC 7 quantum calculations reveals that the cyclic ion

obtained according to Equation (6.b) passes in the carbocation obtained according to Equation (6.a), by breaking the O-C bond at an activation energy of only 23 kcal/mol.

A.2. The second primary event for removing a methyl radical ( $M-\text{CH}_3^{\cdot}$ ) may occur on the path of the Equation (7.a) by the cleavage of a methyl group and the stabilization of the oxycation ion to obtain a carbocation.

<b>A.2. <math>M - \text{CH}_3^{\cdot}</math> m/e 193 I=100 %</b>
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Fig. 6 – The ion of mass 193:  
The net atomic charges →.



The stabilization of oxycation (7.a) occurs through resonance to yield the carbocation (7.b); this stabilization is confirmed by the positive charge on the carbon atom (+ 0.446) as shown in Fig. 6. The underlined carbocation (7.b) is the base peak in the mass spectrum of the tetraethoxysilane (Fig. 1).

A.3. The third primary event for removing an ethyl radical ( $M-C_2H_5\dot{\uparrow}$ ) may occur on the path of

the Equation (8.a) by the cleavage of an ethyl group and the stabilization of the oxycation ion to obtain a carbocation.

Oxycation (10.a) with the formation heat  $H_f = -72.02$  kcal/mol (Fig. 7) is stabilized as carbocation (8.b) with the formation heat  $H_f = -116.04$  kcal/mol by hydrogen transposition in a five atoms center.

**A.3.  $M-C_2H_5\dot{\uparrow}$  m/e 179 I= 22.9 %**

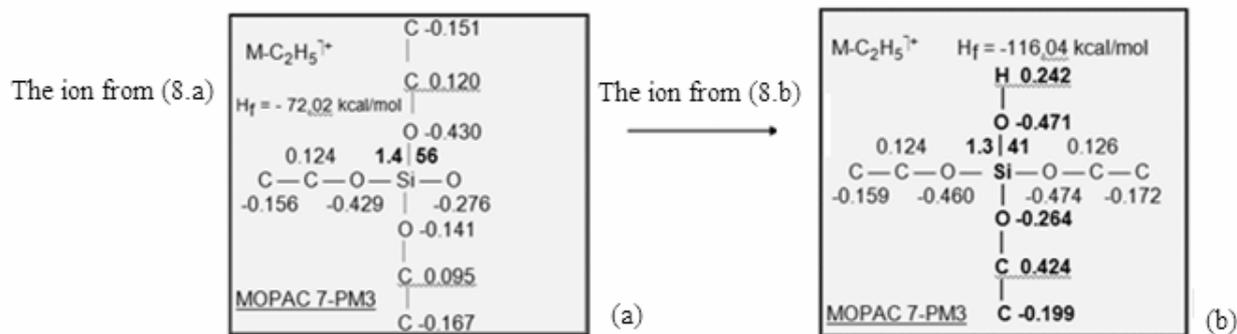
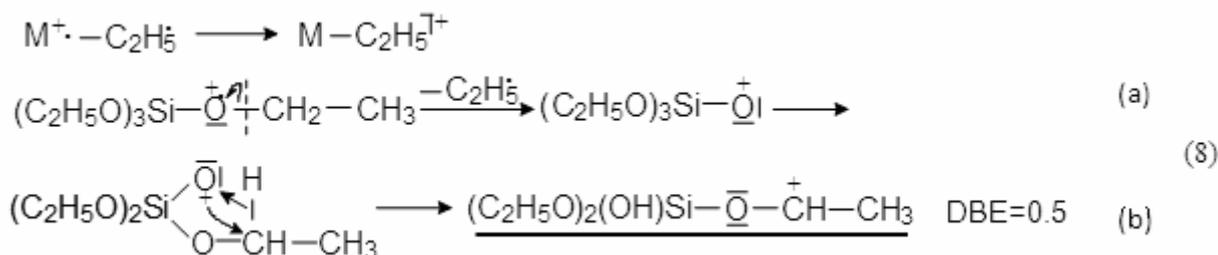


Fig. 7.a,b – The ions with m/e 179: The net atomic charges.



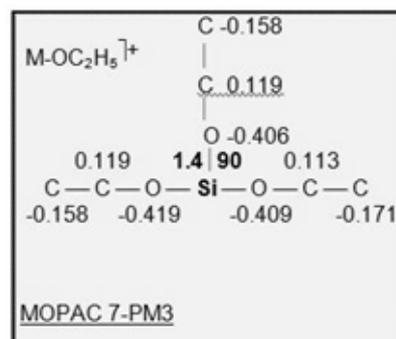
The distributions of net charges calculated with the MOPAC 7 software program confirm the existence of carbocation (8.b) by locating positive charge on a carbon atom at the value of + 0.424; the relative stabilization of the ion with m/e 179 is produced by the positive charge delocalization of

bond axis C-C-O-Si-O-H highlighted with bold characters in Fig. 7.

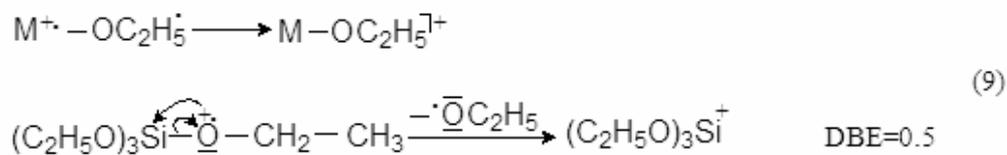
A.4. The fourth primary event for removing an ethoxy radical ( $M-C_2H_5O\dot{\uparrow}$ )

**A.4.  $M-O-C_2H_5\dot{\uparrow}$  m/e 163 I= 55.9 %**

Fig. 8 – The ion of mass 163: The net atomic charges →.



Siliconiu ion is obtained by the reaction (9) due to the electron-withdrawing inductive effect of the oxygen atom and it is an intense ion in mass



## CONCLUSIONS

The procedure for the interpretation of mass spectra for alcoxysilanes previously presented was applied for tetraethoxysilane (TEOS). TEOS is the precursor alkoxide in sol-gel process studied in GC-MS literature and was considered the reference system. The average mass spectrum obtained from 12 reaction mixtures has been used for the interpretation. The molecular ion of TEOS at mass 208 was established by comparison with a mass spectrum of a standard and by comparison with NBS mass spectra library. The initiation reaction center of TEOS was established on the oxygen atom from an ethoxy group by measuring of net atomic charges. Delocalization of positive charge on the Si-O-C bond axis stabilizes the molecular ion and explains its appearance in the mass spectrum. Based on the experimental data obtained with B/E linked scan for the molecular ion at mass 208, the primary fragmentation reactions were written in which are obtained the ions at masses 207, 193, 179 and 163 that correspond to the mass differences of 1 amu, 15 amu, 29 amu and 45 amu respectively, which in this case corresponds at the radical eliminations:  $H^{\cdot}$ ,  $CH_3^{\cdot}$ ,  $C_2H_5^{\cdot}$  and  $OC_2H_5^{\cdot}$ .

The existence of the molecular ion at mass 208 and of the primary ions at masses 207, 193, 179 and 163 are supplementary argued by measuring the ion masses at high resolution, the quantum calculations of the net atomic charges and the calculation of the double bond equivalent.

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spectrum of tetraethoxysilane, ( $I = 34.7\%$ ) (Fig. 1) due to the stability of siliconiu ion.

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