Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 251 (2006) 59–65

www.elsevier.com/locate/ijms

The interpretation of mass spectra of inorganic molecules

Jan Kapała*

Department of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Received 25 August 2005; received in revised form 13 December 2005; accepted 23 December 2005
Available online 9 February 2006

Abstract

The analysis of the density of distribution function of mass spectrum coefficients and the ions intensities interdependences have been analyzed and applied for the interpretation of the ions origin. The special method of mentioned interpretation has been proposed for the mass spectra analysis improvement. The mass spectra measured over the pure CsCl, CsCl–$CeCl_3$, CsCl–$NdCl_3$ systems, and the simulated mass spectrum have been used for the presentation of the interpretation method of the qualitative determination of the ions origin. The quantitative interpretation has also been considered.

Keywords: Mass spectrum coefficient; Mass spectra of inorganic molecules; Density of distribution; Salt systems

1. Introduction

The mass spectra of gaseous inorganic molecules obtained by electron impact ionization contain usually ions that may be molecular ions (from ionization process, only) or fragment ions (from fragmentation process). The ions originated from only one gaseous molecule have been named pure ions. It is possible that stoichiometry of fragment ion is identical to molecular or fragment ion originating from other molecule. Interpretation of origin of these ions may be difficult, and sometimes impossible.

The separation of the ions according to the source and determination of the contribution to mass spectrum of molecule is very important due to thermodynamic interpretation of the Knudsen effusion-mass spectrometry results. This influence the precision of determination of the vapor pressures of gaseous species in Knudsen cell and consequently this influence the further thermodynamic calculations. This is noticeable particularly for the components, which contents in the gaseous phase is small. The mass spectrum of gaseous phase over system may contain ions originating from two gaseous molecules. The several solutions of this problem for various gaseous components and mass spectra combinations have been resolved in the previous works [1–10]. The technique of measurements of the inorganic mass spectra of similar compounds, and the associated thermodynamic equations has been also described in the work [11].

This work has been done for demonstrate the differences between measured densities of distributions of the measured mass spectrum coefficients and the normal distribution and for explain the reasons of these differences. In this work the new possibility of interpretation of the mass spectrum has been considered and the method of determine the unknown mass spectrum coefficients has been shown.

2. Experimental

The mass spectrometric investigations were carried out with substantially modified mass spectrometer MI 1201 (Sumy—Ukraine). The vapor species were ionized with electrons of energy 60 eV. The Knudsen cells made of quartz with a knife edged of effusion orifice were employed. Temperature was measured by Pt–Pt10%Rh thermocouple calibrated in situ at the melting point of silver. The temperature range of measurements was: 750–950 K for pure CsCl, 750–1025 K for CsCl–$CeCl_3$, and 730–1075 K for CsCl–$NdCl_3$. The details of the mass spectrometric measurements were described in the previous papers [9,10]. The mass spectra measured over the CsCl, CsCl–$CeCl_3$ [9], and CsCl–$NdCl_3$ [10] have been used in this work.

---

* Tel.: +48 71 320 24 98; fax: +48 71 328 43 30.
E-mail address: jan.kapala@pwr.wroc.pl.

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.12.035

3. Results and discussion

3.1. Theoretical

The mass spectrum of gaseous phase over salt system may contain ions originating from two gaseous molecules X and Y as follows:

$$I^*(\mathrm{A}^+) = I(\mathrm{A}^+, \mathrm{X}) + I(\mathrm{A}^+, \mathrm{Y}) \tag{1}$$

where $I(\mathrm{A}^+, \mathrm{X})$ is the intensity of ion A^+ from gaseous molecule X, $I(\mathrm{A}^+, \mathrm{Y})$ the intensity of ion A^+ from gaseous molecule Y, and asterisks denotes the measured ion intensity.

If the ions X^+ and Y^+ originated only from both gaseous molecules X(g) and Y(g), respectively, the quantitative assignment of the $I(\mathrm{A}^+)^*$ to both species is possible by regression method [2,6] given by equation:

$$I(\mathrm{A}^+)^* = aI(\mathrm{X}^+, \mathrm{X})^* + bI(\mathrm{Y}^+, \mathrm{Y})^* \tag{2}$$

where $I(\mathrm{X}^+, \mathrm{X})^*$ and $I(\mathrm{Y}^+, \mathrm{Y})^*$ are the measured intensities of molecular ions X^+ and Y^+ (or they may be fragment ions, but derive from respective gaseous molecules, only), and a and b are the mass spectrum coefficients defined as follows:

$$a = \frac{I(\mathrm{A}^+, \mathrm{X})}{I(\mathrm{X}^+, \mathrm{X})^*} \tag{3}$$

$$b = \frac{I(\mathrm{A}^+, \mathrm{Y})}{I(\mathrm{Y}^+, \mathrm{Y})^*} \tag{4}$$

The above method contains the assumption, that mass spectrum coefficients do not depend on temperature.

If the ion Y^+ originated only from Y(g) is not observed in the mass spectrum Eq. (2) can be written as follows:

$$I(\mathrm{A}^+)^* = aI(\mathrm{X}^+, \mathrm{X})^* + I(\mathrm{rest}) \tag{5}$$

where $I(\mathrm{rest})$ is the unknown part of ion intensity $I(\mathrm{A}^+)^*$, which depends on other than X(g) component of gaseous phase. The possible containment of mass spectrum coefficient value determined by Eq. (3) may be also presented as follows:

$$a = \frac{\{I(\mathrm{A}^+, \mathrm{X}) + I(\mathrm{A}^+, \mathrm{Y})\}^*}{\{I(\mathrm{X}^+, \mathrm{X}) + I(\mathrm{X}^+, \mathrm{Z})\}^*} \tag{6}$$

where $I(\mathrm{X}^+, \mathrm{Z})$ is the intensity of ion X^+ from Z(g).

3.2. The simulations of the simple inorganic mass spectra

For the various possibilities of interpretation with Eq. (5) the model of the artificial mass spectrum has been build. Description of the model was following:

- the 1000 random values from 10 to 1000 have been generated—this simulates $I(\mathrm{X}^+, \mathrm{X})^*$;
- mass spectrum coefficient $a = 2$ has been assumed;
- the value of the $I(\mathrm{X}^+, \mathrm{X})^*$ has been calculated with additional random disturbance (±10%).

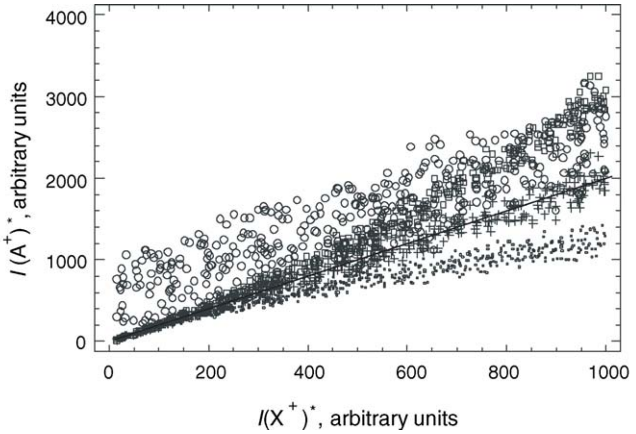

Fig. 1. The simulated dependences of $I(\mathrm{A}^+)^*$ on $I(\mathrm{X}^+)^*$ for various cases. The solid line represents the ideal value of the mass spectrum coefficient (equal to 2). The crosses are the points of the first case, the empty circles are the second case, the squares are the third case, and small points are the fourth case.

The four spectacular cases of artificial mass spectrum have been provided:

1. $I(\mathrm{rest}) = 0$. It means that $I(\mathrm{A}^+)^*$ depends on $I(\mathrm{X}^+, \mathrm{X})^*$, only. This is boundary model. It means that gaseous phase contains X(g), only. Eq. (5) is simplified and determines precisely the mass spectrum coefficient a. This is shown in Fig. 1 as crosses.
2. $I(\mathrm{rest})$ is generated randomly as a separate set from 10 to 1000. This is the reverse boundary model, but the generated values are relatively small. Note, that it contains the assumption, that second component of mass spectrum does not depend on the first one. In real system this is rather improbable. This case is shown in Fig. 1 as empty circles.
3. A^+ ion is not pure ion and the X^+ is a pure ion. It means that value of $I(\mathrm{X}^+, \mathrm{Z})$ in Eq. (6) is equal to zero. The ion intensities interdependences may be determined, for example, by the gaseous reaction of dimer dissociation. In this case the Y(g) is represented by the dimer X_2(g):

$$\mathrm{X}_2(\mathrm{g}) = 2\mathrm{X}(\mathrm{g}) \tag{7}$$

In this case the value of the $I(\mathrm{rest})$ in Eq. (5) is the $I(\mathrm{A}^+, \mathrm{X}_2)$. In Fig. 1 this case is shown as squares. The vapor pressure of gaseous component is proportional to the intensity of the ion originated from respective gaseous molecule as follows:

$$p(i) = k\sum I(i)T \tag{8}$$

where $p(i)$ is the vapor pressure of the ith gaseous species, k is the calibration constant of the apparatus, $\sum I(i)$ is the sum of ions intensities from ith gaseous species, and T is the temperature. In the presented model the intensity equilibrium constant for reaction (7) with Eq. (8) can be obtained:

$$K_I = \frac{\{I(\mathrm{A}^+, \mathrm{X})^*\}^2 T}{I(\mathrm{rest})}. \tag{9}$$

Assuming the value of K_I equal to 1000 the simulated mass spectrum has been calculated. The temperature dependence

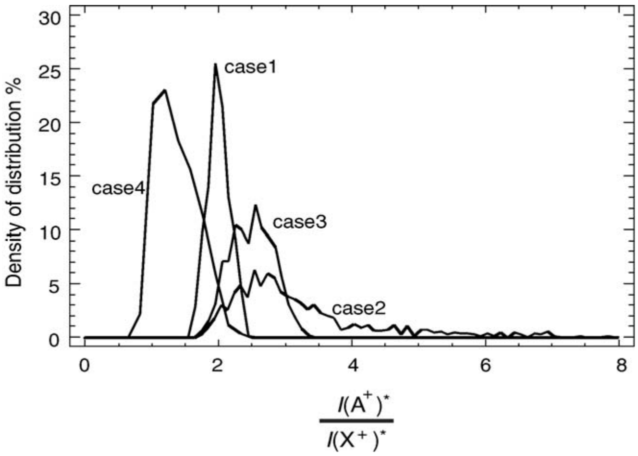

Fig. 2. The densities of distribution for the four simulated cases.

of the equilibrium constant has been neglected due to the simplification of the model.

4. The X^+ ion is not pure ion and the A^+ is a pure ion (or the A^+ ion origin from other gaseous molecule is negligible). It means that value of $I(A^+, Y)$ of Eq. (6) is equal to zero. In Fig. 1 this case is shown as small points. The Z(g) is represented now by the dimer $X_2(g)$. The calculated values of mass spectrum coefficients are significantly lower than expected ones.

The simple way of presentation above models is to plot the dependence of $I(A^+)^*$ on $I(X^+)^*$. The above cases have been shown in Fig. 1. In order to make the picture more clear, there have been shown only 400 calculated points for each case (except for the fourth case). The slope of a straight line in Fig. 1 is the ideal mass spectrum coefficient used in this cases at beginning of the calculations. The second and the third cases give the points over the straight line, and the fourth case gives the points under this line (see Fig. 1). This fact is the base for next considerations.

The other way of presentation of described models is the density distribution of the measured intensity ratio $I(A^+)^*/I(X^+)^*$. The four cases described are shown in Fig. 2. The density distribution function has been constructed using 80 classes for range from 0 to 8 for all cases. The histograms have been shown as polygons. The differences between cases are significant. The first case, is the clear mass spectrum coefficient with respective standard deviation. The density of distribution is the simple sharp peak. This is different for the other cases, which contain various disturbances of mass spectra. The density of distribution functions are characteristic for the kind of the disturbance. It is possible, that the third and the fourth cases may exist simultaneously. The respective valuation of the deflection of the density distribution on respected normal one, the standardized skewness and standardized kurtosis (see Table 1) have been assumed.

3.3. *The mass spectrum coefficient of pure CsCl*

The three separate experiments of pure CsCl have been done. The Cs^+, $CsCl^+$, and Cs_2Cl^+ ions have been observed in the equilibrium vapors. Between these measurements, both systems have been measured. The sequence of measurements has been provided for control the stability of mass spectrometer ionization conditions during the all experiments with pure CsCl and both pseudobinary systems. The measured ions intensity ratio $I(Cs^+)^*/I(CsCl^+)^*$ has been assumed to be the mass spectrum coefficient of monomer molecule, *c*. The formal description of this case is following:

$$I(Cs^+, CsCl) = I(Cs^+)^*, \tag{10}$$

$$I(CsCl^+, CsCl) = I(CsCl^+)^*, \tag{11}$$

$$c = \frac{I(Cs^+)^*}{I(CsCl^+)^*} \tag{12}$$

This assumption is confirmed by the analysis of the density of distribution of this ratio. This density of distribution is normal (standardized skewness and standardized kurtosis are close to zero). The respective histogram is shown in Fig. 3. The normal density of distribution function in this case lead to conclusion that Cs^+ and $CsCl^+$ ions are not a fragment ions from dimeric molecule, $Cs_2Cl_2(g)$. Consequently the possibility of the Cs^+ and $CsCl^+$ origin from dimer in the investigated systems may be neglected. The value of the enthalpy of sublimation of dimer is significantly higher than enthalpy of sublimation of monomer.

Table 1
The statistical analysis of the mass spectrum coefficient from Eq. (6) for the simulated cases

Case	Mean value	Standard deviation	Standardized skewness	Standardized kurtosis
1	2.00	0.16	1.52	−3.33
2	2.50	0.32	0.48	−4.24
3	4.39	5.35	82.06	324.63
4	1.39	0.30	6.60	−3.48

Table 2
The statistical analysis of the mass spectrum coefficients *c* calculated directly from the measured data

System	Mean value	Standard deviation	Standardized skewness	Standardized kurtosis
CsCl	40.59	6.30	0.13	−0.88
CsCl–$CeCl_3$	40.01	16.76	5.02	4.76
CsCl–$NdCl_3$	58.68	29.26	2.23	4.42

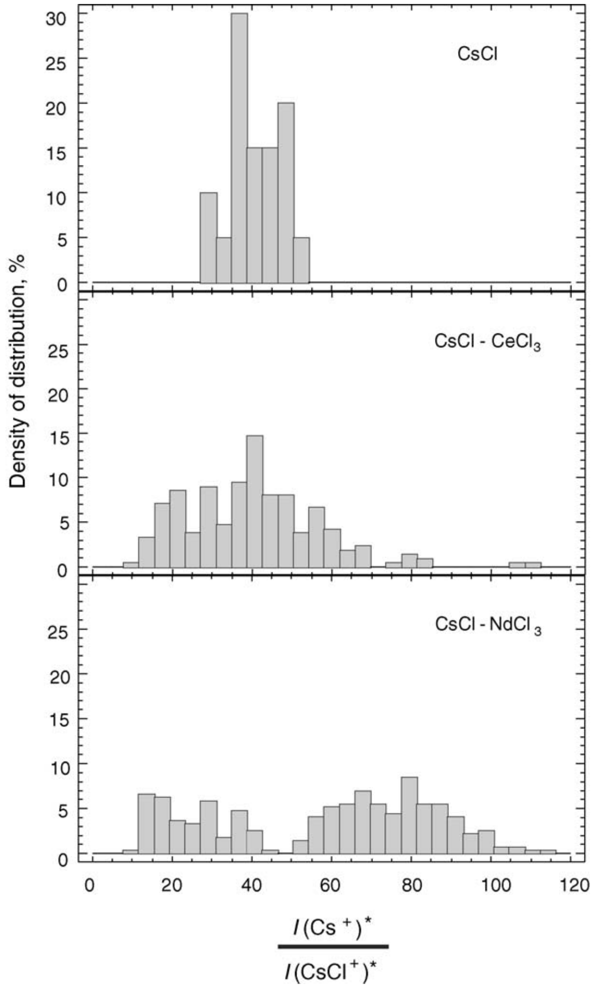

Fig. 3. The densities of distribution of the mass spectrum coefficient defined by Eq. (12) for measured intensities of the CsCl, CsCl–CeCl$_3$, and CsCl–NdCl$_3$ systems.

This means that value of slope of the dependence $\ln\{I(Cs_2Cl^+)T\}$ versus $1/T$ (straight line) is higher than slope of the similar dependence for $I(Cs^+)^*$ and $I(CsCl^+)^*$. The respective values of slopes for Cs^+ (−21,400 ± 200), for $CsCl^+$ (−23,200 ± 500), and for Cs_2Cl^+ (−24,900 ± 600) are given in parentheses. The mass spectrum coefficient c is determined directly from measured data and its distribution is close to normal (Table 2). The small difference between both slopes for Cs^+ and $CsCl^+$ ions results probable from small value of the energy of fragmentation of Cs^+. It does not disturb the normality of the density distribution function of c. This also shows that origin of Cs^+ and $CsCl^+$ ions from Cs_2Cl_2(g) is negligible.

3.4. The mass spectrum coefficients in the CsCl–CsCl$_3$ and CsCl–NdCl$_3$ systems

In the mass spectrum over the CsCl–CeCl$_3$ and CsCl–NdCl$_3$ systems the Cs^+, $CsCl^+$, Cs_2Cl^+, $CsLnCl_3{}^+$, $LnCl_2{}^+$ (Ln = Ce, Nd), and a negligible small amount of fragment ions from $LnCl_3$(g) molecule have been observed. The density of distribution of mass spectrum coefficient c calculated directly from

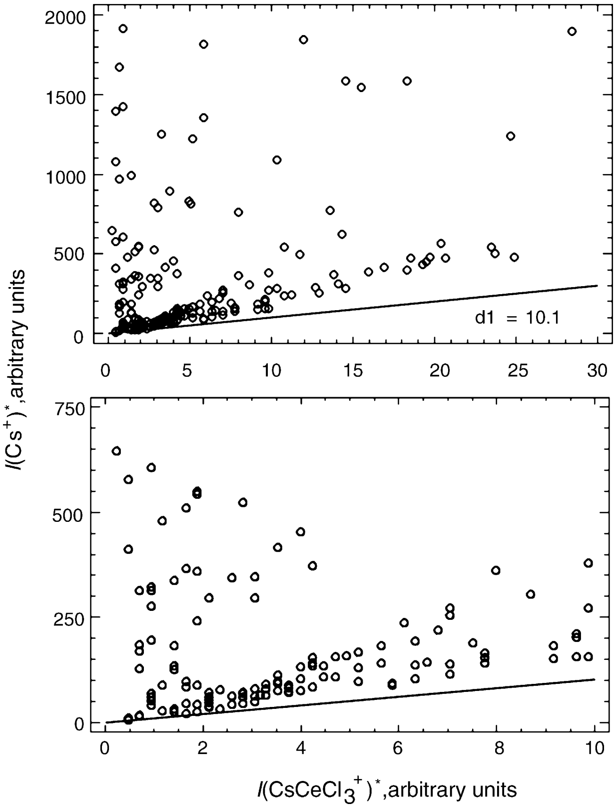

Fig. 4. The dependence of $I(Cs^+)^*$ on $I(CsCeCl_3{}^+)^*$ for the CsCl–CeCl$_3$ system. The bottom figure is the increased part of the upper one. The slope of the straight line is the value of mass spectrum coefficient (d_1) determined before [9].

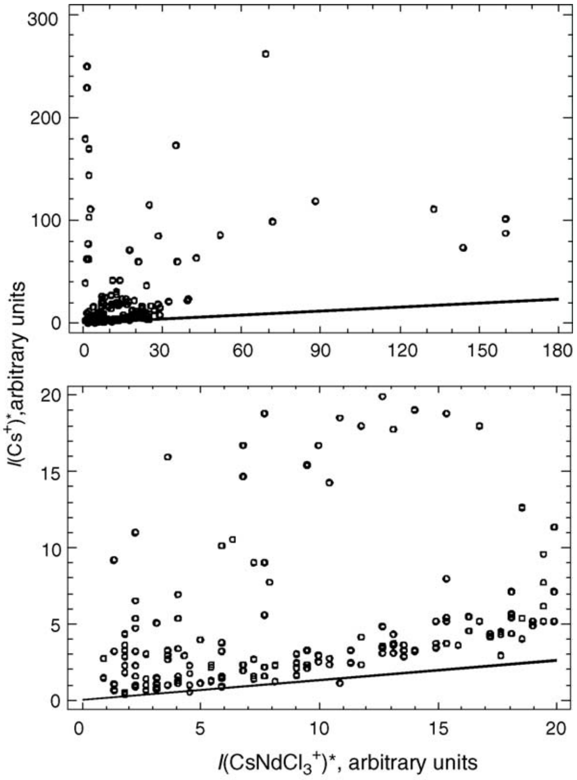

Fig. 5. The dependence of $I(Cs^+)^*$ on $I(CsNdCl_3{}^+)^*$ for the CsCl–NdCl$_3$ system. The bottom figure is the increased part of the upper one. The slope of the straight line is the value of mass spectrum coefficient $d_1 = 9.1$ determined before [10].

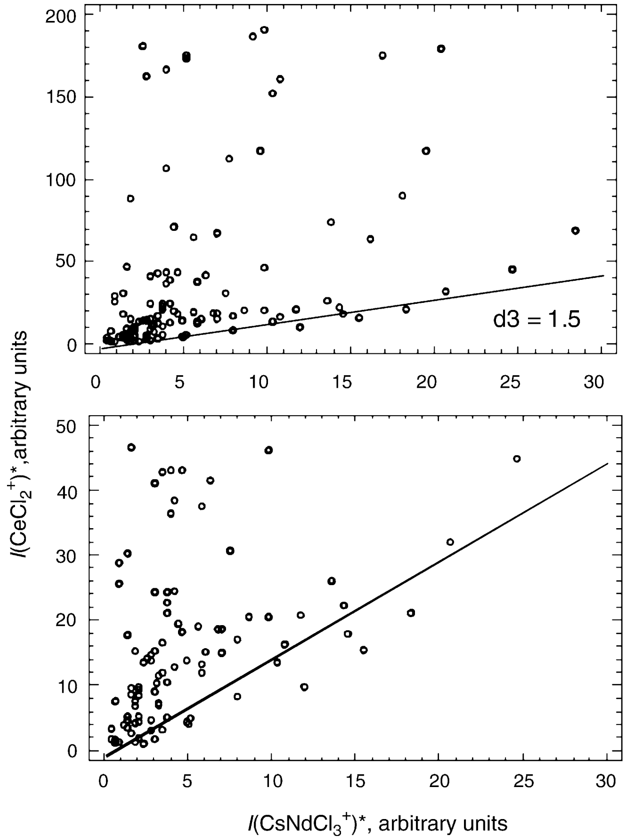

Fig. 6. The dependence of $I(\mathrm{CeCl_2}^+)^*$ on $I(\mathrm{CsCeCl_3}^+)^*$ for the CsCl–$\mathrm{CeCl_3}$ system. The bottom figure is the increased part of the upper one. The slope of the straight line is the value of mass spectrum coefficient (d_3) determined before [9].

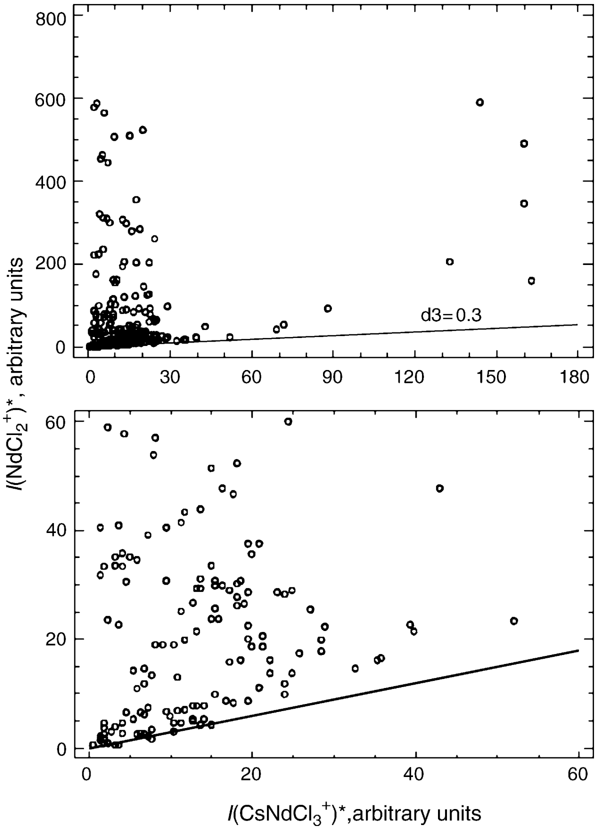

Fig. 7. The dependence of $I(\mathrm{NdCl_2}^+)^*$ on $I(\mathrm{CsNdCl_3}^+)^*$ for the CsCl–$\mathrm{NdCl_3}$ system. The bottom figure is the increased part of the upper one. The slope of the straight line is the value of mass spectrum coefficient (d_3) determined before [10].

measured intensities of Cs^+ and CsCl^+ ions are shown in Fig. 3. The values of standardized skewness and standardized kurtosis (Table 2) show significant deflection from normality. The calculated average values of coefficient c are close to those in pure CsCl [9,10], but wide range of the density distribution function shows that both ions may be not pure ions. The excess values of $I(\mathrm{Cs}^+)^*$ generate the deflection of coefficient c close to higher values and the excess values of $I(\mathrm{CsCl}^+)^*$ trends the values of c to be lower than in pure CsCl. Finally, average value of coefficient c for the CsCl–$\mathrm{CeCl_3}$ system is incidentally similar to this one obtained for pure CsCl. This is described by the simulated third and fourth cases, simultaneously. The histogram for pure CsCl (Fig. 3) has been treated as the model of density distribution function for undisturbed coefficient c. However, in works [9,10] the assumption that CsCl^+ originated only from CsCl(g) have been made.

The additional parent of the Cs^+, and CsCl^+ ions could be gaseous molecule of $\mathrm{CsLnCl_4}$ (Ln = Ce, Nd), only:

$$I(\mathrm{Cs}^+)^* = I(\mathrm{Cs}^+, \mathrm{CsCl}) + I(\mathrm{Cs}^+, \mathrm{CsLnCl_4}), \tag{13}$$

$$I(\mathrm{CsCl}^+)^* = I(\mathrm{CsCl}^+, \mathrm{CsCl}) + I(\mathrm{CsCl}^+, \mathrm{CsLnCl_4}). \tag{14}$$

In the previous works [9,10] the intensities of Cs^+ ions were resolved by regression method, described by Eq. (2). The mass spectrum coefficients:

$$d_1 = \frac{I(\mathrm{Cs}^+, \mathrm{CsLnCl}^4)}{I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^*} \tag{15}$$

have been calculated. The obtained values are (10.1 ± 1.2) for the CsCl–$\mathrm{CeCl_3}$ and (9.1 ± 0.8) for the CsCl–$\mathrm{NdCl_3}$ systems. The mass spectrum coefficients:

$$d_2 = \frac{I(\mathrm{CsCl}^+, \mathrm{CsLnCl_4})}{I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^*} \tag{16}$$

have not been calculated earlier because of the luck of respective method of interpretation.

The $\mathrm{LnCl_2}^+$ ion also derive from two parents [9,10]:

$$I(\mathrm{LnCl_2}^+)^* = I(\mathrm{LnCl_2}^+, \mathrm{LnCl_3}) + I(\mathrm{LnCl_2}^+, \mathrm{CsLnCl_4})$$
$$(\mathrm{Ln} = \mathrm{Ce, Nd}) \tag{17}$$

and the respective defined mass spectrum coefficient is:

$$d_3 = \frac{I(\mathrm{LnCl_2}^+, \mathrm{CsLnCl_4})}{I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^*} \tag{18}$$

In this work, another way of interpretation has been proposed. The new interpretation is usable, if the mass spectrum does not contains enough amount of pure ions for numerical interpretation by the regression method. This problem is described by Eqs. (5) and (6). The examples considered, contained additional

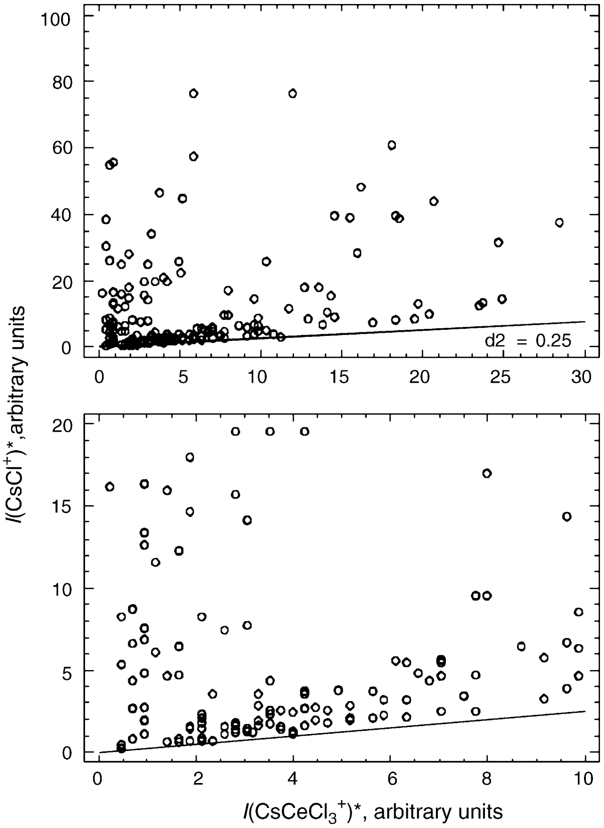

Fig. 8. The dependence of $I(\mathrm{CsCl}^+)^*$ on $I(\mathrm{CsCeCl_3}^+)^*$ for the CsCl–CeCl$_3$ system. The bottom figure is the increased part of the upper one. The slope of the straight line is the estimated value of mass spectrum coefficient (d_2) [this work].

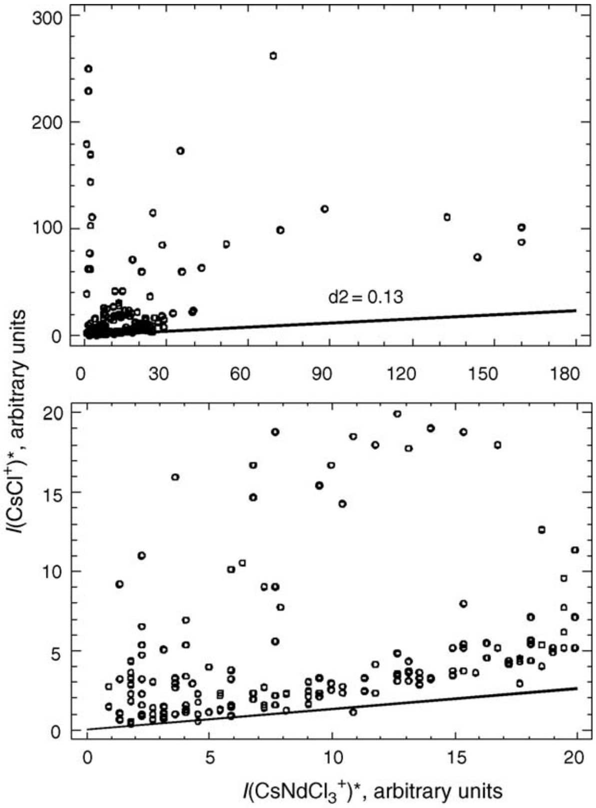

Fig. 9. The dependence of $I(\mathrm{CsCl}^+)^*$ on $I(\mathrm{CsNdCl_3}^+)^*$ for the CsCl–NdCl$_3$ system. The bottom figure is the increased part of the upper one. The slope of the straight line is the estimated value of mass spectrum coefficient (d_2) [this work].

contribution of the ions from respective CsLnCl$_4$(g) molecule. Taking into account that Cs$^+$, and CsCl$^+$ ions are not pure ions, there is no possibility for resolving of the mass spectra with Eq. (2). The origin of the ion CsLnCl$_3{}^+$ from one molecule only (pure ion) has been assumed due to fact that the traces of other molecules have not been observed in the measured mass spectrum. Eq. (5) used to interpretation of Eqs. (13)–(16) have form:

$$I(\mathrm{Cs}^+)^* = d_1 I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^* + I(\mathrm{Cs}^+, \mathrm{CsCl}) \quad (19)$$

$$I(\mathrm{CsCl}^+)^* = d_2 I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^* + I(\mathrm{CsCl}^+, \mathrm{CsCl}) \quad (20)$$

And similarly for $I(\mathrm{LnCl_2}^+)^*$ ion:

$$I(\mathrm{LnCl_2}^+)^* = d_3 I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^* + I(\mathrm{LnCl_2}^+, \mathrm{LnCl_3}) \quad (21)$$

The part of ions intensities from CsCl(g) and LnCl$_3$(g) in Eqs. (19)–(21) have been treated as the I(rest) in Eq. (5). The values of respective I(rest) is shown in Figs. 4–9 by the points over the line. Figs. 4–6 show good agreement between the known mass spectrum coefficients [9,10] and the measured intensities. The expected solution is the slope of the straight line at bottom boundary of measured points area. If the bottom boundary determines the inclined line from zero then the slope of this line estimates the upper possible value of the mass spectrum coefficients.

In fact, the bottom boundary of measured points of dependence of $I(\mathrm{Cs}^+)^*$ on $I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^*$ is not a straight line for whole range of the data of the analyzed examples. The straight line with the slopes measured before [9,10] agree to the bottom of the points area of equations for small values of $I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_3}^+)^*$. These interpretations are shown in Figs. 4 and 5. The dependences of $I(\mathrm{NdCl_2}^+)^*$ on $I(\mathrm{CsLnCl_3}^+, \mathrm{CsLnCl_4})^*$ show the same property in Figs. 6 and 7. The slopes of the bottom boundary line in Figs. 8 and 9 are the unknown mass spectrum coefficient d_2 for both analyzed systems. This is the estimation only, because these slopes of the line show the maximal possible values of respective coefficients, only.

The values of equilibrium constant K_p of reaction:

$$\mathrm{CsCl(g)} + \mathrm{LnCl_3(g)} = \mathrm{CsLnCl_4(g)} \quad (22)$$

calculated in previous works [9,10] been recalculated. The estimated differences between the K_p values calculated before and from mass spectra after correction are about 5% and may be lower, due to fact, that the presented method only maximal value of mass spectrum coefficients d_2 estimates.

4. Conclusions

In this work the new possibilities of interpretation of the mass spectra of inorganic molecules has been considered and the method of estimation of the unknown mass spectrum coefficients has been shown.

The way of interpretation described in this work enriches the information about the nature of systems investigated by the high temperature mass spectrometry. By the simple method of analysis of density of distribution of selected mass spectrum coefficients is possible to determine the presence of the containment of more than one parent in respective intensity of ion.

The proposed way of analysis of the ion intensities interdependences is in good agreement with the known mass spectrum coefficients and leads to estimation of the mass spectrum coefficients, which values are inaccessible by other methods.

Acknowledgement

The author is grateful to Dr. Iwona Rutkowska from Department of Chemistry at Wroclaw University of Technology for helpful discussion and help in preparation of this manuscript.

References

[1] L.N. Sidorov, V.B. Sholts, Int. J. Mass Spectrom. Ion Phys. 8 (1972) 437.
[2] K. Skudlarski, J. Kapała, Pol. J. Chem. 52 (1978) 701.
[3] K. Wagner, H. Schäfer, Z. Anorg. Allg. Chem. 451 (1979) 107.
[4] J. Kapała, K. Skudlarski, Int. J. Mass Spectrom. Ion Phys. 47 (1983) 257.
[5] J. Kapała, K. Skudlarski, Int. J. Mass Spectrom. Ion Process. 55 (1983/1984) 133.
[6] M. Miller, Int. J. Mass Spectrom. Ion Process. 61 (1984) 293.
[7] J. Kapała, Int. J. Mass Spectrom. Ion Process. 105 (1991) 31.
[8] M. Miller, J. Kapała, Annales Universitatis Mariae Curie-Sklodowska Lublin—Polonia 28 (1991/1992) 283.
[9] I. Lisek, J. Kapała, M. Miller, J. Alloys Compd. 280 (1998) 77.
[10] I. Lisek, J. Kapała, M. Miller, J. Alloys Compd. 278 (1998) 113.
[11] K. Hilpert, Fresenius J. Anal. Chem. 370 (2001) 471.