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Production of doubly charged clusters $(H_2O)_n \cdot Ba^{2+}$ and $(H_2O)_n \cdot Ca^{2+}$ under low temperature fast atom bombardment conditions

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Abstract

Production of doubly charged ions of alkaline earth metals Ba^{2+} and Ca^{2+} and their doubly charged clusters with water molecules $(H_2O)_n \cdot Ba^{2+}$, $(H_2O)_n \cdot Ca^{2+}$ ($n = 1, 2, 3$) by means of low temperature fast atom bombardment technique is observed in the case of crystalline hydrates of $BaCl_2$ and $CaCl_2$ salts, formed during freezing of water-salt solutions. Reasons for a possibility of production of the doubly charged species in the case of the two indicated salts and their absence in the case of chlorides of some other divalent metals (Mg, Mn, Co, Cu, Zn) are discussed. As to singly charged secondary ions Me^+, $MeCl^+$, $MeOH^+$, $[(H_2O)_n \cdot MeCl]^+$, $[(H_2O)_n \cdot MeOH]^+$ (where Me is metal), high efficiency of their production from crystalline hydrates was observed and possible explanation of the phenomenon is suggested. (Int J Mass Spectrom 194 (2000) 49–52) © 2000 Elsevier Science B.V.

Keywords: Low temperature fast atom bombardment; Doubly charged metal ions; Hydrate clusters

1. Introduction

Clusters of divalent metal ions in a doubly charged state with water or organic ligands are interesting objects of cluster research. Production of such species, however, is not so easy due to the loss of one charge of metal ion in ion–molecule interactions, which are characteristic of many methods of cluster formation. Several methods of obtaining of $(ROH)_n \cdot Me^{2+}$ clusters (where Me is metal and R = H or organic radical) have been suggested [1–8]. One of them is based on preparation of clusters of Me^{2+} with water or organic ligands by a pick-up technique with electron impact ionization in the gas phase [1–4]. The others involve production of such clusters from solutions by means of electrospray [5,6] or its early analogues, which were called extraction of ions from solutions at atmospheric pressure [7] and field evaporation of ions from solutions [8].

Under fast atom bombardment (FAB) conditions production of doubly charged species is limited, in general, mainly to organic dications [9]. Divalent metals under FAB are sputtered usually in a singly charged state due to charge loss in the already mentioned ion–molecule interactions with the matrix [10]; their clusters are usually singly charged as well.

In the present article production of doubly charged

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ions of alkaline earth metals Ba^{2+} and Ca^{2+} and their doubly charged clusters with water molecules by means of a low temperature (LT) FAB technique is reported.

2. Experimental

LT FAB experiments were performed on a sector magnetic mass spectrometer MI-1201E («Electron» Works, Sumy, Ukraine). Secondary FAB ion source based on a prototype described in [11] was modified for LT experiments by installation a cryogenic block reported in [12]. The cryogenic block cooled by liquid nitrogen allows controllable change of the temperature of the sample from that of liquid nitrogen up to ambient. Volatile liquid samples can be frozen on a sample holder outside the ion source and then can be inserted into the cryogenic block through the sample inlet system. Temperature is measured by a thermistor located inside the sample holder. Cryogenic block with the sample holder is surrounded by a metal shield cooled by liquid nitrogen to reduce residual gas condensation on the sample. Argon with 4 keV energy of a primary beam is used as a bombarding gas.

10 μL droplet of 0.1 M water solution of $BaCl_2$ or $CaCl_2$ salts was frozen on a copper sample holder in the vapours of liquid nitrogen with a rate of temperature decrease of 100 °C min^{-1} and rapidly (constantly in vapours of nitrogen) inserted into the ion source.

3. Results and discussion

The pattern and temperature changes of the LT FAB mass spectra of the frozen water solutions of $BaCl_2$ or $CaCl_2$ were in good agreement with regular trends observed earlier for frozen water solutions of alkali metal salts [13]. A detailed description of these spectra will be published elsewhere [14]; here we shall outline the features directly related to production of doubly charged ions.

In accord with phase diagrams for water solutions of $BaCl_2$ and $CaCl_2$ crystalline hydrates of the salts are formed in the system upon its cooling [15]. In Fig. 1(a) one of the spectra of the frozen $BaCl_2$ water solution, taken at a temperature where intact crystalline hydrate is present in the sample, is shown. The LT FAB mass spectrum contains abundant singly charged ion of Ba^+, its cluster with counterion $BaCl^+$ and a set of hydrate clusters $(H_2O)_n \cdot Ba^+$ and $(H_2O)_n \cdot BaCl^+$. A set of OH-group containing peaks, which could be connected with the products of hydrolysis of the salt [15,16] is present as well.

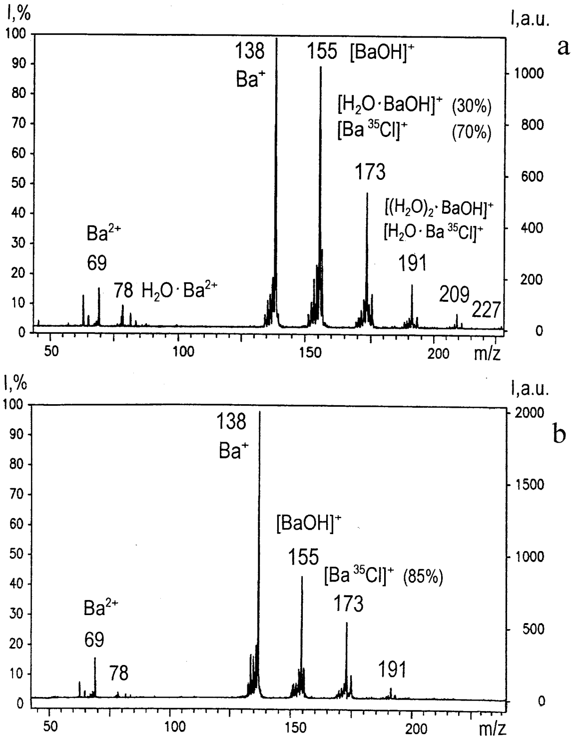

Fig. 1. Low temperature fast atom bombardment mass spectrum of a 0.1 M frozen aqueous solution of $BaCl_2$; T = (a) −85 and (b) −35 °C.

In the lower mass range a doubly charged ion Ba^{2+} and $(H_2O)_n \cdot Ba^{2+}$ (n = 1, 2; n = 3 small) ions are observed [Fig. 2(a)]. Similar types of ions Ca^{2+} and $(H_2O)_n \cdot Ca^{2+}$ (n = 1, 2) were recorded for $(CaCl_2 + H_2O)$ system.

Efficiency of production of doubly charged species appeared to be dependent on the temperature which affects composition and structure of the sample due to phase transitions. The highest abundances of Me^{2+} and $(H_2O)_n \cdot Me^{2+}$ clusters [Fig. 2(a)] were obtained in the temperature range in which crystalline hydrates

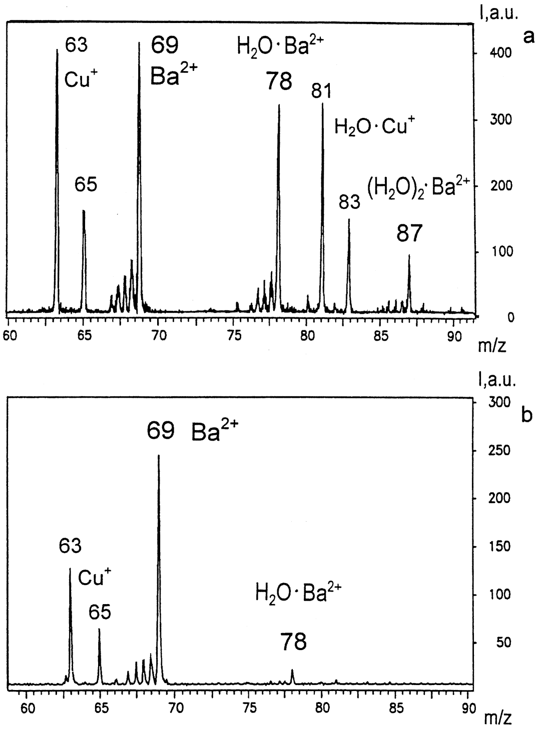

Fig. 2. Fragments of LT FAB mass spectra of a 0.1 *M* aqueous solution of $BaCl_2$, which contain doubly charged ions; $T = $ (a) -100 and (b) -30 °C. Singly charged copper ions, sputtered from small regions of a sample holder, exposed, obviously, in some micro cracks of the crystalline sample, provide a pictorial reference for doubly charged Ba ions (in the case of continuous crystalline samples copper ions were absent in the spectra).

exist (starting from the liquid nitrogen up to about 0 °C under our experimental conditions for a given salt). Temperature rise during warming of the sample facilitates dehydration of the crystalline hydrate [13,15]. This process is reflected in the spectra as a gradual decrease of abundance of singly charged hydrate clusters $(H_2O)_n \cdot Me^+$ [Fig. 1(b)]; abundance of $(H_2O)_n \cdot Me^{2+}$ decreases in relation to M^{2+} as well [Fig. 2(b)]. At the temperature when all hydrate clusters finally disappear from the spectra which could, obviously, mean that the conversion to anhydrous salt occurs, the doubly charged ion M^{2+} decreases dramatically.

Thus, sputtering of doubly charged ions of Ba^{2+} and Ca^{2+} and their hydrate clusters was recorded only for the crystalline hydrate state of the sample. It should be noted also that Ba and Ca were the only metal ions among a row of chloride salts of Mg, Zn, Cu, Mn, Co, tested in preliminary studies, for which doubly charged species were observed. Both notions are in agreement with earlier observed fact that the efficiency and mechanisms of ion production under LT FAB depend not only on the chemical composition, but on the structure and type of intermolecular interactions in the condensed sample [13,17,18]. It was noticed that absolute abundance of the ions of the same type is much higher for the samples with mixed ionic and hydrogen bonds in the lattice (which is the case of the crystalline hydrates), than in the samples with purely ionic or hydrogen-bonded lattice [18]. It is assumed that in the crystalline hydrates water molecules assist in stabilisation of the crystals of ionic compounds due to separation of ionic species [19,20]. Under secondary ion mass spectrometric conditions water molecules in the crystalline lattice may facilitate sputtering process due to reduction of coulombic attraction of the ions in the solid. On the other hand, preformed cations in the lattice provide more easy formation of the charged clusters.

Although facilitation of ion production due to peculiar structure of the crystalline lattice relates to all crystalline hydrates, observation of doubly charged ions for Ca and Ba only must be connected with some electronic parameters of these particular metals. In Table 1 ionization energies (V_I, eV, numerically

Table 1
Ionization energies V_I (eV) of the first and second stages of ionization for a number of divalent metals and water [15]

Stage of ionization	Ionization energy V_I (eV) of metal atoms							
	Mg	Ca	Mn	Co	Cu	Zn	Ba	H_2O
I	7.6	6.1	7.4	7.9	7.7	9.4	5.2	12.7
II	15.0	11.9	15.6	17.1	20.1	18.0	10.0	

equal to ionization potential) for a set of divalent metal atoms are presented. It can be seen that among this row Ca and Ba have the lowest second ionization energy. It is remarkable, that the ionization energy of water molecule, 12.7 eV [15], is higher than the second ionization energy of Ca and Ba, but lower than that for other metals. Such a balance, virtually, reduces a probability of electron transfer from the neighbouring water molecules to Ca^{2+} and Ba^{2+} in the sample spot excited by impact of a bombarding particle, while for other metal ions this event is more probable. Occupation of some sites around metal ions by water molecules in the crystalline hydrate lattice decreases the number of Cl^- anions in the surrounding of the dication, which reduces the chances of electron transfer from Cl^- (which recombination energy is 3.61–3.81 eV [15]) as well. Phase transition from the crystalline hydrate to anhydrous salt is accompanied by structural transition of the crystalline lattice to a new state. The increase of the number of chlorine atoms around metal ions is, virtually, a reason for the termination of doubly charged ion production from the anhydrous salts.

In the course of the process of dehydration desorbed water molecules leave empty vacancies in the crystalline hydrate lattice. This process is reflected in the LT FAB mass spectra in an absolute increase of production of «bare» metal ions and a relative decrease of abundances of all cluster ions [Fig. 1(b)]. On the basis of the above as well as of some other observations [17] it can be tentatively suggested that the cluster formation process during sputtering is sensitive to the structure of the solid sample on the level of several neighbouring molecules.

4. Conclusions

Production of the doubly charged ions of Ca^{2+} and Ba^{2+} and their clusters with water from the crystalline hydrates by means of LT FAB was recorded, as to our best knowledge, for the first time. High efficiency of ion production from the crystalline hydrates of $CaCl_2$ and $BaCl_2$ was explained, similar to the cases of other crystalline hydrates, by peculiarities of their crystalline lattice. Possibility of retention of two positive charges on Ca and Ba, in contrast to some other divalent metals, was connected with the relatively lower value of their second ionization potential (energy).

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