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Letter

Low temperature fast atom bombardment mass spectra of HCl water solution

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Abstract

Low temperature fast atom bombardment mass spectra of the frozen water solution of HCl contain a set of clusters $(H_2O)_n \cdot H^+$, which is an order of magnitude more abundant and differs in intensity distribution from a simlar cluster set usually produced from pure water ice. The cluster pattern is discussed in the light of formation of phases of crystalline hydrates in the frozen solution. (Int J Mass Spectrom 189 (1999) L1–L7) © 1999 Elsevier Science B.V.

Keywords: Low temperature fast atom bombardment; HCl; Frozen water solutions; Crystalline hydrates; Clusters

1. Introduction

Presently there is great interest in the study of ices with inclusion of inorganic compounds in connection with atmospheric research [1–4]. In the context of this problem, a number of publications are devoted to investigation of HCl uptake by water ice [5–8]. The main conclusion that follows from some recent experimental [7,8] as well as theoretical [9,10] studies is that the existence of molecular HCl species in contact with the ice surface is rather short, less than 10^{-6} s, followed immediately by dissociative adsorption and solvation of H^+ and Cl^-. Formation of HCl hydrates of different stoichiometry (dependent upon HCl concentration) in the surface layers of ice samples was suggested [7,8].

In all these works, external deposition of HCl vapours on the solid ice samples was applied. To further elucidate the nature of the species formed on the surface of thus produced samples it is of interest to make comparison with samples of frozen solutions of HCl. The low temperature fast atom bombardment (LT FAB) technique [11], recently developed in our laboratory, proved to be efficient in the study of frozen water solutions of inorganic and organic compounds [12–15]. In the present Letter LT FAB mass spectra of a frozen water solution of HCL, obtained by means of this technique, are reported.

It is known that crystalline hydrates are formed in HCl-water solutions upon cooling [16]. Low temperature conditions enables one to study such peculiar objects as crystalline hydrates as, first, many of them

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exist at the reduced temperatures only [16] and, second, decreased saturated vapor pressure at low temperatures essentially prevents dehydration under mass spectrometric vacuum conditions, thus preserving the intrinsic structure of the crystalline hydrate. In contrast to some more common objects with rather homogeneous structure, crystalline hydrates of acids, alkali, salts are characterized by the presence of both ionic and hydrogen bonds and a variety of the component arrangements in their crystalline lattices [17,18]. In this connection, information that could be of interest from the point of view of basic problems of secondary ion production (in particular, possible correlations between the structural peculiarities of the solid sample and its mass spectral pattern) can be expected to result from the crystalline hydrates investigation. Some results of our previous LT FAB studies showed that different types of cluster ions are produced from the solid samples composed of the same but differently arranged molecules or ions (e.g. assembled in crystalline hydrates, adsorbed layers or sandwich-like layered structures) [11,19]. That is, the change of mutual position of the same particles in the solid effects their inclusion into clusters during the sputtering event. The efficiency of secondary particles sputtering is dependent on the type and energy of intermolecular interactions in the solid (van der Waals, hydrogen bonds, ionic, or mixed) [11]. Change of parameters of ion sputtering during phase transitions in the solid sample, which are accompanied by the transformation of its structure, that is, change of distances between atoms or molecules and, consequently, interaction energy, was also observed [20]. Thus, to record reflection of structural peculiarities of the solids in their secondary ion spectra, comparison of samples built of the same or close compounds arranged in different structures are necessary, and water ice and crystalline hydrates seem to be suitable objects for such a comparison.

2. Experimental

The present version of the LT FAB technique [11,21] is intended for study of frozen water or organic solutions. In contrast to some other types of LT FAB or LT SIMS setups, in which samples are deposited on the cooled targets from the gas phase [22–25], the design of our secondary ion source allows direct inlet of a sample cooled and frozen under controllable atmospheric conditions.

LT FAB experiments were performed on a sector magnetic mass spectrometer MI-1201E (Electron Works, Sumy, Ukraine) equipped with a FAB ion source based on a prototype reported in [26]. The design of a cryogenic block for the LT FAB measurements was described in [21]. Temperature of the sample was controlled by a dedicated thermal stabilisation system and measured by a thermistor inserted into the bulk of the sample holder.

A water solution of HCl (produced by Chemical Reagents Plant, Kiev, Ukraine, for titration purposes) of 36.5% weight concentration was used without dilution. Relatively low rates of cooling of the order of 100 °C min^{-1} were applied that provided conditions for crystalline (not amorphous) structure of the sample and the stoichiometry of the crystalline hydrates formed was governed by the initial concentration of solution. A droplet of a liquid sample ($\sim$5 μL volume) was frozen on a copper sample holder in vapours of liquid nitrogen and transferred to the direct probe inlet system constantly kept in the vapours of nitrogen. Thus, atmospheric water condensation on the sample could occur only during the first stage of vacuum pumping; its amount, however, was estimated to be rather small and methods of removing such condensed film directly in the ion source by bombardment and slight heating were developed. To reduce residual gas condensation, the cryogenic block in the ion source was surrounded by a toroidal-shaped cryogenic shield cooled by liquid nitrogen. Pressure in the secondary ion source prior to bombarding the gas inlet into the primary source was less than 10^{-6} Pa.

Argon with 4 keV primary beam energy was applied as a bombarding gas. Low density of the flux of the bombarding atoms (about 10^9–10^{10} atoms $\text{cm}^{-2}\ \text{s}^{-1}$ [26], which corresponds to static secondary ion mass spectrometric conditions), affords at least 10 min for spectra recording from the essentially undamaged surface, as some estimates give namely this

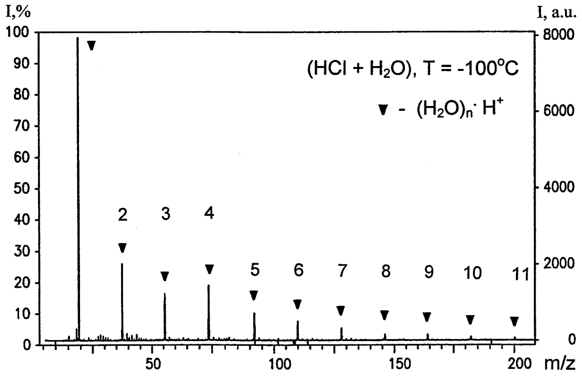


Fig. 1. Low temperature fast atom bombardment mass spectrum of frozen water solution of HCl.

mean time interval between two subsequent impacts of the bombarding particles to the same spot of the surface [27].

3. Results and discussion

LT FAB mass spectra of the frozen sample of 36.5% water solution of HCl were qualitatively the same in the −120−60 °C range. In Fig. 1 a typical spectral pattern is presented. The spectrum contains the same set of cluster ions $(H_2O)_n \cdot H^+$ ($n = 1$–12) as that usually produced from pure water ice [12,13]. There are, however, significant qualitative and quantitative differences in cluster patterns for the two types of compounds. The quantitative difference consists of about an order of magnitude higher absolute abundances of ion currents of clusters in the case of the ($HCl + H_2O$) system as compared to neat ice. The qualitative difference consists of a different abundance distribution of clusters, reflected in Fig. 2. The distribution of water clusters sputtered from neat ice was the same as that presented in Fig. 2, with good reproducibility, in all our LT FAB experiments involving water ice [12–14,19], as well as those reported from some other laboratories [28–30]. Its characteristic feature is the dominance of the H_3O^+ ion, the reduced abundance of $(H_2O)_n \cdot H^+$ clusters with $n = 2$ and 3 and local maximum of the distribution at $n = 4$. The distinctive feature of ($HCl + H_2O$) spectra is a remarkably enhanced abundance of a cluster with $n = 2$; small clusters with $n = 1$, 2 give higher yields and larger clusters with $n = 3$–10 contribute less to the total ion current as compared with pure water ice.

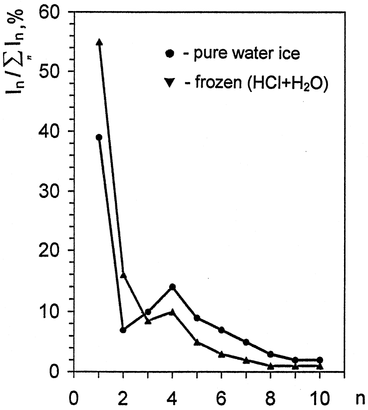


Fig. 2. Comparison of contribution of absolute abundances I_n of individual cluster ions $(H_2O)_n \cdot H^+$ to the total ion current $\Sigma_n I_n$ of the cluster set in the LT FAB mass spectra of pure water ice (●) (based on data from [12,13]) and frozen water solution of HCL (▲) (averaged over several runs).

These experimental facts can be explained in the framework of a model for interpretation of the LT FAB mass spectra, developed in a series of our works [11–14,31]. The basic point of this model consists in the account of the composition and morphology of the samples of the frozen solutions, which are predetermined by their phase diagrams. Such a reference diagram for the ($HCl + H_2O$) system in question [16] is presented in Fig. 3. The diagram shows that new compounds that are crystalline hydrates of HCl are formed in the system upon its cooling, and their stoichiometry depends on the initial concentration of solution. Upon cooling of a solution of 36.5% concentration, used in the present study, the appearance of the first crystals of the crystalline hydrate $HCl \cdot 3H_2O$ must occur at a point marked as A in Fig. 3. On further cooling, the composition of the system changes along the line A–B. Complete solidification of the sample occurs at point B with formation of a eutectic phase, which must consist of the crystallites of two hydrates $HCl \cdot 3H_2O$ and $HCl \cdot 6H_2O$ (the latter in minority). There are no pure water ice

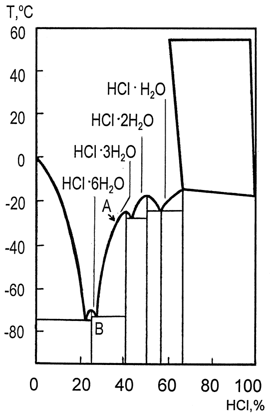


Fig. 3. Phase diagram of (HCl + H_2O) system, adapted from [16]. Point A marks initial concentration of solution under study; point B corresponds to complete solidification of the sample.

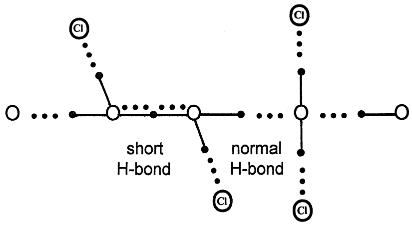
crystals in such a system, and the only source of any ions to be produced form the sample is crystalline hydrates.

Thus, $(H_2O)_n \cdot H^+$ clusters in Fig. 1 must originate from the crystalline hydrate $HCl \cdot 3H_2O$ and, to a much lesser extent, from $HCl \cdot 6H_2O$. The mechanism of cluster formation is the same as was observed earlier for crystalline hydrates of salts, for example, $NaCl \cdot 2H_2O$, which gives cationized hydrate clusters $(H_2O)_n \cdot Na^+$, $n = 1$–3 [12]. Similarly, H^+ in the $(H_2O)_n \cdot H^+$ clusters must represent a cation of the acid.

The origin of the $(H_2O)_n \cdot H^+$ cluster set from an individual compound different from water ice predetermines specific features of its pattern. One order higher abundance of $(H_2O)_n \cdot H^+$ clusters produced from $HCl \cdot n(H_2O)$ crystalline hydrates as compared with those sputtered from neat ice cannot be explained simply by higher acidity (higher concentration of protons) of the HCl-containing sample, as the Cl^- counterion would compete with crystallization water molecules for proton binding during cluster formation. The observed increase in $(H_2O)_n \cdot H^+$ production is in agreement with an earlier conclusion about the dependence of the cluster pattern, not only on chemical composition of the sample, but on the type of intermolecular interactions in the crystalline lattice as well [11,19]. In particular, it was noticed that the absolute abundance of the same types of ions, that is, the efficiency of ion production, in the case of crystalline hydrates of salts with both ionic and H bonds is much higher than that in the cases of purely hydrogen-bonded solids, including neat water ice and frozen organic, and solids with purely ionic lattice, such as anhydrous salts. It can be suggested that, in comparison with anhydrous salts, filling of the crystalline lattice with dielectric water molecules in the crystalline hydrate provides spatial separation of charged particles and reduces coulomb interactions [32] in the media with smaller dielectric penetrability, which facilitates easier dispersion of the ionic species during sputtering. Preformed cations, at the same time, provide larger amounts of charge carriers than the number of protons released due to cleavage of covalent bonds in H-bonded solids. Similar effects can be responsible for the total increase of abundances of the whole set of $(H_2O)_n \cdot H^+$ ions, produced from $HCl \cdot n(H_2O)$ crystalline hydrates.

Significant relative increase of a particular $(H_2O)_2 \cdot H^+$ cluster is of special interest. A number of observations, obtained in our LT FAB studies [12], show that the cluster distribution correlates with the structure and stoichiometry of the frozen solid and, in general, does not coincide with the pattern of the clusters, formed from the same species in the gas-phase experiments [14]. In particular, in hydrate clusters that originate from crystalline hydrates of salts, the number of water molecules attached to a cation roughly correlates with the number of water molecules available on the basis of the crystalline hydrate stoichiometry (composition) [12] and do not coincide with that of hydration shells produced in the gas-phase experiments (or obtained in theoretical calculations).

In this connection, examination of data on the structure of $HCl \cdot nH_2O$ crystalline hydrates was undertaken to determine the reasons for the enhanced production of the $(H_2O)_2 \cdot H^+$ cluster. Indeed, a surprisingly good reason was found in crystallographic x-ray data on $HCl \cdot 3H_2O$ crystalline hydrates [18,33]. These data show that peculiar $H_5O_2^+$ elements are present in the structure of $HCl \cdot 3H_2O$ (Scheme 1). The shift of one H^+ from one HCl entity to a water



Scheme 1. A scheme of arrangement of H bonds in the crystalline structure of the hydrochloric acid trihydrate (on the basis of x-ray data [18,33]).

molecule causes rearrangement of the H bonds in the ($2H_2O + H^+$) structural element: the central H bond between water molecules becomes shorter (~0.24 nm) as compared with normal H bonds (0.256 nm for O–H . . . O and 0.3–0.31 nm for O–H . . . Cl), and a proton-bound dimer $H_2O \ldots H^+ \ldots H_2O$ is formed in the crystalline lattice. In the case of HCl dihydrate, that is the only form of water coordination, and a formulation of $H_5O_2^+Cl^-$ was suggested for this compound [34]. In the case of the trihydrate, the third water molecule is bound by a normal H bond (Scheme 1), and the formulation of the compound is $H_5O_2^+ \ Cl^- \cdot H_2O$ [18]. Thus, preformed ionic $(H_2O)_2 \cdot H^+$ species exist in the crystalline lattice of the trihydrate, although they cannot be regarded as separated preformed clusters, as they are bound with their surrounding by H bonds in the continuous lattice network.

In the assumption that, along with monoatomic dispersion of the sample material in the site of the energetic particle impact, some share of material can be sputtered as pieces of solid from more distant regions of the exited zone, enhanced abundance of the $(H_2O)_2 \cdot H^+$ cluster may reflect the presence in the lattice of two water molecules more strongly bound with the central proton than with other surroundings. We rather would not engage here the long-standing discussion of the mechanisms of cluster ion formation under atom/ion bombardment; however, an assumption that the mechanisms are the same for the solids of similar nature gives a basis for comparison of clusters produced from HCl crystalline hydrates, water ice, and some other crystalline hydrates. Experimental facts are that water molecules are differently arranged in these structures and water cluster patterns differ as well. It is of interest also that water molecules form extended H-bound chains in $HCl \cdot 3H_2O$ crystals (Scheme 1), which provides condition for sputtering of water clusters with relatively large n, while the latter were not observed in the case of crystalline hydrates of salts with spatially separated water molecules [12]. The relative abundances of water clusters with larger n decrease more rapidly for $HCl \cdot 3H_2O$ than for water ice (Fig. 2), as only relatively small water chains exist in the crystalline hydrate, in contrast to a continuous network in ice and limits dimensions of the sputtered clusters. While in the case of salts of alkali metal (Me) clusters with inclusion of Cl^- anion $(MeCl)_m \cdot Me^+$, $(MeCl)_m \cdot (H_2O)_n \cdot Me^+$ are formed, no chlorine-containing clusters are produced by desorption techniques from HCl-containing samples [7].

Pilot experiments were made for samples with higher and lower HCl initial concentrations, though guaranteed production of other types of crystalline hydrates $HCl \cdot nH_2O$ is connected with substantial experimental difficulties. The cluster patterns of the LT FAB mass spectra for such samples were qualitatively the same as for trihydrate, but quantitative differences were hard to follow. Enhanced abundance of the $(H_2O)_2 \cdot H^+$ cluster was recorded both for higher and lower HCl concentrations. In the first case, some share of $HCl \cdot 2H_2O$, which also has the $H_5O_2^+$ element in the lattice [34], is formed. In the second case, $HCl \cdot 6H_2O$ is present in the system and, although x-ray data are not available, there are no obvious obstacles for existence of the proton-bound elements in the lattice. It should be noted that in the systems with HCl concentration smaller than 23% (Fig. 3), water ice crystals are formed (and hexahydrate is in eutectic), but, because the absolute abundance of $(H_2O)_n \cdot H^+$ originating from ice is about an order lower, their contribution to the intensity of the corresponding peaks does not affect significantly the distribution of abundances of clusters originating from $HCl \cdot n(H_2O)$. While the relative yield of the same types of clusters sputtered from different phases is impossible to separate directly for the HCl-water system, it was demonstrated earlier in the example of dilute water-salt solution: the abundance of $(H_2O)_n \cdot H^+$ clusters corresponding to ice in these cases is five to tenfold lower than the abundance of $(H_2O)_n \cdot Me^+$ clusters corresponding to crystalline hydrates [12]. A more detailed quantitative study of concentration dependencies for the HCl-water system will be a subject of further investigations.

It is noticeable that the cluster pattern obtained in the present work for the $(HCl + H_2O)$ system (Fig. 1) practically coincides with that of the SIMS spectrum reported in [7] for a water ice sample with HCl deposited from the gas phase. In particular, the $(H_2O)_2 \cdot H^+$ cluster was also relatively high in the latter spectrum. The similarity of the spectra allows one to suggest that they correspond to similar objects. It can be assumed that dissociative adsorption and solvation observed in [7] may be considered as the first stage of formation of the crystalline hydrates of HCl in the upper layers of the sample. In accordance with the structure of the phase diagram in Fig. 3, no solid solutions of HCl and water can be formed in the system, and thus, a phase of a crystalline hydrate is the most probable choice.

In some theoretical [9,10] and experimental [35] studies of HCl adsorption on the ice surface it was conceived that H_3O^+ species are formed in ice due to ionic adsorption of HCl. Comparison of the present and the above cited [7] results suggests that more extensive rearrangement of H bonds occurs, which leads to formation of $H_5O_2^+$ structures. H_3O^+ species are formed in the lattice of a monohydrate $HCl \cdot H_2O$ [18], which exists at high concentrations of hydrochloric acid (Scheme 1).

4. Conclusions

It may be concluded that the $(H_2O)_n \cdot H^+$ cluster set in the LT FAB mass spectrum of the frozen hydrochloric acid water solutions depicted in Fig. 1 originates from $HCl \cdot n(H_2O)$ crystalline hydrates. The high efficiency of cluster ion production from the crystalline hydrates is connected with the mixed type of ionic and hydrogen bonds and existence of preformed charged species in the crystalline lattice. A suggestion about correlation between the presence of $H_5O_2^+$ species in the lattice of hydrochloric acid trihydrate and noticeable increase of $(H_2O)_2 \cdot H^+$ cluster in its LT FAB mass spectra (in comparison with pure water ice spectra) was made. Similarity of the FAB spectra produced from the frozen solutions and SIMS spectra produced from the ice with HCl deposited from the gas phase [7] allowed us to suggest that crystalline hydrates are formed in the ice surface layers upon HCl dissociative adsorption and that the latter process leads to formation of $H_2O_5^+$ rather than H_3O^+ species.

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