Observation of crystallization of amorphous solid water under the conditions of secondary emission mass spectrometric experiments

M.V. Kosevich, O.A. Boryak, V.S. Shelkovsky, and V.V. Orlov

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of
Sciences of Ukraine, 47 Lenin Ave., Kharkov 61103, Ukraine
E-mail: mvkosevich@ilt.kharkov.ua

A phenomenon of termination of sputtering of protonated water clusters $(H_2O)_nH^+$ in low-temperature secondary emission mass spectrometric studies of solid water was observed in the temperature range of crystallization of amorphous solid water (ASW). In this range the mass spectra contained only H_3O^+, $H_2O^{+\bullet}$, and OH^+ ions. The following explanation of the revealed phenomenon is suggested: the heat supplied to the ASW sample by the bombarding particles is spent on initiation of an amorphous–crystalline transition within the condensed sample but not for the transfer of the sample matter to the gas phase. At the same time heat released on crystallization causes a local rise in temperature of the crystallizing sample surface, which enhances the rate of sublimation of ice. The resulting increased concentration of subliming water molecules over the sample surface is reflected in the growth of abundance of $H_2O^{+\bullet}$ molecular ion-radical, produced by gas-phase ionization mechanism. The appearance of a set of low-mass peaks in the course of crystallization observed for some types of ASW samples is explained by the release of gases trapped in the ASW film during its growth.

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1. Introduction

Investigations of solid water by means of secondary emission mass spectrometry [1−14] have used either amorphous solid water (ASW) obtained by vapor deposition on some surface cooled below the temperature of the glass transition of water T_g = 136 K [15−17] or crystalline ice. Under bombardment by energetic particles — by neutral atoms of Ar^o or Xe^o in a fast atom bombardment (FAB) mode, or ions of Cs^+ or Ar^+ in secondary ion mass spectrometry (SIMS), with the energy varied in the 5−30 keV range — sets of protonated water clusters $(H_2O)_nH^+$ with n up to 30−50 are sputtered both from ASW and crystalline ice. The distribution of clusters in the secondary emission mass spectra of the both forms of water is qualitatively very similar, with a slight quantitative difference in the abundances of some clusters. The measurements were usually conducted at some constant temperature. Secondary emission mass spectrometric experiments were not performed, however, on gradual variation of the sample temperature in the range around the temperature of crystallization of

ASW, which, according to the data of Ref.15, can start at 140−160 K and proceed in some temperature range up to 166 K.

It was revealed in our previous works on LT FAB and SIMS of a number of organic and inorganic compounds that phase transitions in the sample matter are reflected in characteristic changes in cluster patterns of the secondary emission mass spectra [13, 14, 18−20].

The aim of the present work was to obtain secondary emission mass spectra of vapor-deposited solid water in the temperature range of crystallization of ASW with the expectation of observing and investigating changes in the mass spectral pattern resulting from this type of transition.

2. Low-temperature secondary emission mass spectrometric experiments

Mass spectrometric experiments were performed using the magnetic sector mass spectrometer MI-1201E (Sumy, Ukraine) equipped with primary FAB ion source for generating a bombarding beam of argon at-

oms; the energy of the primary ion beam before neutralization was 4−5 keV. The secondary ion source contained a cryogenic unit described in detail elsewhere [12]. The cryogenic unit, cooled by liquid nitrogen, had a recess for a removable copper sample holder which could be cooled either externally or directly in the ion source. A thermistor inserted into the unit served for temperature measurements. The cryogenic unit was surrounded by a toroidal cryogenic shield cooled by liquid nitrogen, which provided efficient adsorption of residual gases inside the ion source. The pressure in the FAB secondary ion source ahead of the bombarding argon inlet was about 10^{-6} Pa.

Polycrystalline ice samples were produced by freezing of deionized water in vapors of liquid nitrogen. Layers of ASW were produced in two ways. Vapors of water were deposited onto the substrate pre-cooled to the liquid nitrogen temperature from residual gases in the evacuation chamber of the direct sample inlet system. During the deposition the temperature of the sample holder did not rise above the one recommended for the procedure 140 K [15], which was controlled by direct temperature measurement after the insertion of the sample holder to the cryogenic block. Alternatively, water vapor was deposited on the cold sample holder directly in the secondary ion source. The source of low-pressure flux of water molecules was crystalline hydrate $CuSO_4 \cdot 5H_2O$ kept in a heated ceramic ampoule near the sample holder. Substrates for ASW deposition were the bare copper sample holder, frozen crystalline H_2O and D_2O, and frozen solutions of inorganic salts.

3. Results and discussion

In the FAB mass spectra of layers of ASW deposited by various methods on various substrates, as described in the Experimental Section, a set of protonated water clusters $(H_2O)_nH^+$ (n = 1−10) was present (Fig. 1,*a*). The spectral pattern, that is the types of clusters and distribution of their abundances, did not undergo any substantial changes on temperature variation in the 77−140 K temperature range. On warming the sample up to 140−150 K a rather unexpected and pronounced effect was observed: all cluster ions of water $(H_2O)_nH^+$ except for those with n = 1 (that is H_3O^+) decreased in abundance rather rapidly (during one spectrum scan) and disappeared from the spectrum. At the same time the absolute intensity of a peak at m/z 18 which can be attributed to water radical-cation $H_2O^{+\bullet}$ increased by one to two orders of magnitude (Fig. 1,*b*). The intensity of a peak of the ion at m/z 17, which is known to be an OH^+ fragment of $H_2O^{+\bullet}$, increased similarly to that of its parent ion. Thus, the FAB mass spectrum contained only three in-
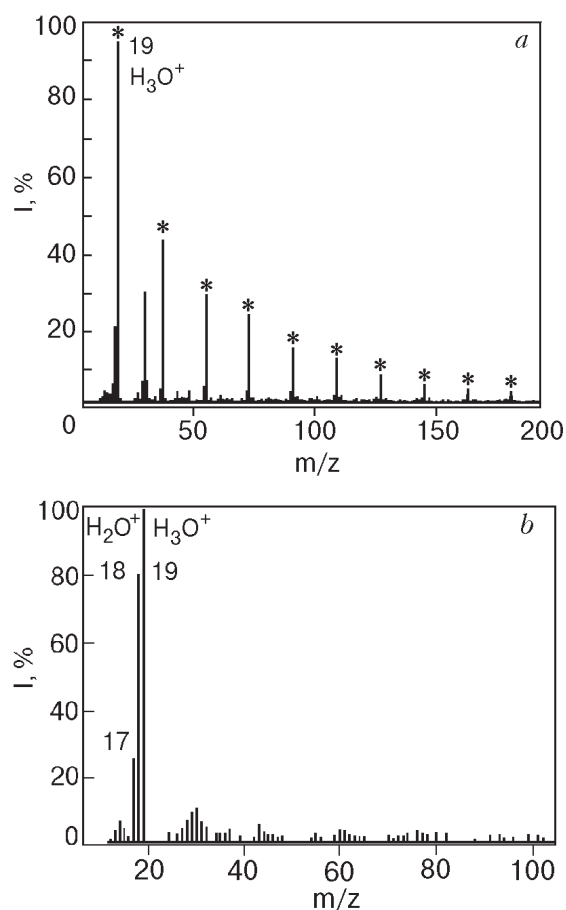

Fig. 1. FAB mass spectra of solid water: spectral pattern of ASW, characteristic in the temperature range 77−110 K (*a*); peaks corresponding to protonated water clusters in the set $(H_2O)_nH^+$ (n = 1−10) are marked by ✳; (the unmarked peak at m/z 30 corresponds to NO adsorbed from the residual gas at T < 110 K); mass spectrum recorded at ∼ 150 K (*b*).

tense peaks of H_3O^+, $H_2O^{+\bullet}$, OH^+ (Fig. 1,*b*). For some types of samples at somewhat higher temperatures of about 150−160 K a noisy spectrum with a peak at every mass started to interfere with the above three peaks in the low-mass range. It lasted for some time and then vanished, giving way to a recovered normal spectrum of ice containing a $(H_2O)_nH^+$ cluster set at temperatures of about 160−170K . The latter, in turn, after completion of rather rapid sublimation of the crystallized ice layer on further warming was replaced by the spectrum characteristic of an under-layer (substrate). Once happened on warming, the described transformations were not repeated on subsequent cyclic cooling-warming of the ice formed. The reported changes of mass spectra were qualitatively reproducible with slight quantitative variations in several tens of independent experiments.

The most remarkable feature of these changes is a temporary termination of production of all the ions except H_3O^+ and $H_2O^{+\bullet}$ when a solid water sample is still definitely present on the sample holder. Even in

the case of complete exhaustion of the water layer the spectra of the exposed under-layer should appear, but they did not.

To explain the phenomena observed, the answers to at least two questions are to be searched for: what are the reasons for termination of the production of $(H_2O)_nH^+$ clusters with $n > 1$ and continuation of the production of the H_3O^+ ion, and what is the origin of the abundant $H_2O^{+\bullet}$ ion. First of all, it is obvious that the temperature range of anomalous changes in the mass spectra is very close to the temperature range of spontaneous crystallization of ASW, which, according to the results of the relevant studies [15], can start on slow warming at 140–160 K and be completed at 166 K. The action of some external factors, including energetic particle impact, initiates the so-called explosive crystallization, which can start at 15 K lower than the spontaneous crystallization [15]. This allows us to suggest that any effect observed in this temperature range may be connected with an amorphous–crystalline transition in the sample.

It is generally recognized that excitation caused by a bombarding particle in a condensed sample is ultimately converted to thermal energy [21]. It is known also that all heat deposited in a system in the phase transition state is consumed on carrying out the transition to its completion. In this light, it may be suggested that in the present experiments practically all the energy supplied by a bombarding particle to an ASW sample at 140–166 K is spent on performing the amorphous–crystalline transition. In the zone heated by a bombarding particle water molecules in the amorphous layer acquire some degrees of freedom which allows them to rearrange in a regular crystalline structure. Thus, heat is spent on initiation and support of the crystallization process within the condensed sample but not for evaporation (sublimation) of molecules to the gas phase. This can explain the absence of «sputtering» of sample matter to the gas phase (the latter usually being revealed by registering charged water clusters). The effects described are valid both for spontaneous and particle-initiated scenarios of crystallization. The low flux of bombarding particles used in FAB experiments provides incidence of particles to the surface areas undamaged by preceding impacts for at least 5 minutes, which means that the probability of a new particle impact to the zone crystallized after a previous particle impact (from which cluster sputtering becomes possible) is rather low in the time frame of the experiment.

Concerning the origin of H_3O^+ ions under the above described conditions, it is known that the very first event on contact of a bombarding particle with the condensed sample surface can consist in direct mechanical knock-out by direct momentum transfer or by recoil atoms of one or a few surface atoms or molecules, either in the neutral or charged forms [22–24]. The H_3O^+ ion can be produced by this surface mechanism, which is independent of further events caused by the bombarding particle in the bulk sample [25]. The difference in the origin of the H_3O^+ ion and $(H_2O)_nH^+$ clusters with $n > 1$ is supported by the results of early experiments on the determination of the kinetic energy of the sputtered species, which appeared to be higher for H_3O^+ in comparison with larger water cluster ions [2].

This mechanism, however, could not be responsible for the appearance of the abundant molecular radical ion $H_2O^{+\bullet}$, since its abundance in ordinary secondary ion emission mass spectra of both ASW and crystalline ice is relatively small. The appearance of $H_2O^{+\bullet}$ is usually conditioned by the increase of water concentration in the gas phase over the sample surface [7], since it was proved that $H_2O^{+\bullet}$ ion is formed by the so-called gas-phase FAB mechanism [7,26]. The increase of absolute and relative intensity of the peak corresponding to $H_2O^{+\bullet}$ in the FAB mass spectra of ice was observed earlier [13,14,25] under conditions of high-rate sublimation of ice samples at a temperature of about 200–220 K [27] preceding complete rapid exhaustion of the sample. This suggests that in the experiments under discussion (Fig. 1,*b*) the concentration of water molecules in the gas phase becomes relatively high apparently for the same reason, that is, due to active sublimation. Although the temperature of the sample holder and bulk sample is kept rather low (140–160 K), the temperature of the sample surface can become noticeably higher due to the known thermal effect characteristic of ASW crystallization. It was found earlier that the heat released on rapid crystallization can cause a rise in the temperature of the sample surface in the crystallizing region of about 60–80 K [15]. Assuming that the starting temperature of the sample is above 140 K, its increase by 60–80 K will raise the local temperature to a value of 200–220 K, at which the rate of sublimation is high and sufficient for recording abundant $H_2O^{+\bullet}$ ions.

As to the temporary appearance of a noisy spectrum, this effect can be explained by ionization of gaseous species trapped within ASW on its deposition and released on its structural rearrangement during crystallization [17,28]. Some data on ASW deposition show that the amount of gases trapped by ASW can exceed by a factor of three the weight of the ASW sample [29]. The intense release of gases at a certain stage of ASW crystallization has been named the «molecular volcano» effect [30].

Thus, the chain of events leading to the changes in the spectra presented in Fig. 1 can be summarized as follows. In the temperature range of ASW crystallization the energy deposited by a bombarding particle contributes to carrying out the crystallization. This alternative channel of heat dissipation prevents transfer of the sample matter to the gas phase on the interaction of the bombarding particle with the sample. Only relatively simple H_3O^+ species are released by direct sputtering from the surface. Upon both spontaneous and initiated crystallization the latent heat of crystallization is released and the temperature of the sample surface rises to values at which the sublimation rate is rather high and provides a concentration of water vapor over the sample surface sufficient for abundant production of $H_2O^{+\bullet}$ by gas-phase FAB ionization.

The effects described should be taken into account in the models of the interaction of accelerated particles with amorphous ices in outer space [11].

3. Conclusions

In FAB mass spectrometric studies of solid water in the temperature range of ASW crystallization a phenomenon of the termination of sputtering of clusters $(H_2O)_nH^+$, which are always the main constituents of mass spectra of both amorphous solid and crystalline water, was revealed. The spectra contained only H_3O^+, $H_2O^{+\bullet}$ and OH^+ ions. An explanation of the observed phenomenon is suggested: the heat supplied to the sample by the bombarding particles is spent on carrying out the amorphous–crystalline transition but not for the transfer of the sample matter to the gas phase. At the same time heat released on crystallization causes a rise of the sample surface temperature, which enhances ice sublimation. The increased concentration of subliming water over the sample surface is reflected in the increase of the abundance of the $H_2O^{+\bullet}$ molecular ion-radical, produced by gas-phase ionization.

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