

FORMATION OF CLUSTERS IN ION BOMBARDMENT OF FILMS OF FROZEN POLAR SUBSTANCES

G.D. Tantsyrev and E.N. Nikolaev

Institute of Chemical Physics, USSR Academy of Sciences

Submitted 16 March 1971

ZhETF Pis. Red. 13, No. 9, 473 - 477 (5 May 1971)

Investigation of ion-ion emission has made it possible to obtain a large amount of information on the structure and composition of metal surfaces [1], on the composition of oxide films on them, and on chemical transformations of layers adsorbed on their surface [2].

This method can be used to investigate substances that are in gaseous or liquid state under normal conditions, by freezing them solid. Particular interest would attach in this case to an investigation of charged particles consisting of several molecules, since this would uncover a possibility of investigating intermolecular and ion-molecular interactions in the investigated substances. Such particles, namely ions of type $\text{Li}^+(\text{H}_2)_n$ with n up to 6, were recently observed [3] when a hydrogen film frozen on a metal substrate at 3°K was bombarded with Li^+ ions.

We have investigated the secondary ions produced by bombarding films of water, ammonia, and methyl and ethyl alcohol, frozen on a nickel substrate, with different ions having energies 1 - 2 keV. A diagram of the instrument used for the measurements is shown in Fig. 1. The beam of bombarding ions was produced with the mass analyzer 1 of the MI-1305 instrument; the installed slits gave a resolving power of ~ 100 . Measurement of the intensity of the primary ion beam was made with the aid of a movable collector 2 and an electrometric amplifier. Directly behind the collector, at an angle 30° to the bombarding beam, there was located a nickel target 3, which was fastened through an insulator to a reservoir with liquid nitrogen. On the rear side of the target were fastened a tungsten-wire heater and a thermocouple. Such a target construction makes it possible to vary its temperature from 200 to -196°C . The film of the investigated substance was produced by condensing vapor admitted into the instrument with the aid of a measuring valve. The film thickness was varied by varying the temperature of the nickel substrate and by varying the vapor pressure. The produced secondary ions in a direction 90° to the primary beam were drawn out by electrode 4, accelerated to 1 keV, and guided through the aperture slit 5, to another, smaller magnetic analyzer 6, with a working-trajectory radius 100 mm and a beam inclination angle 60° .

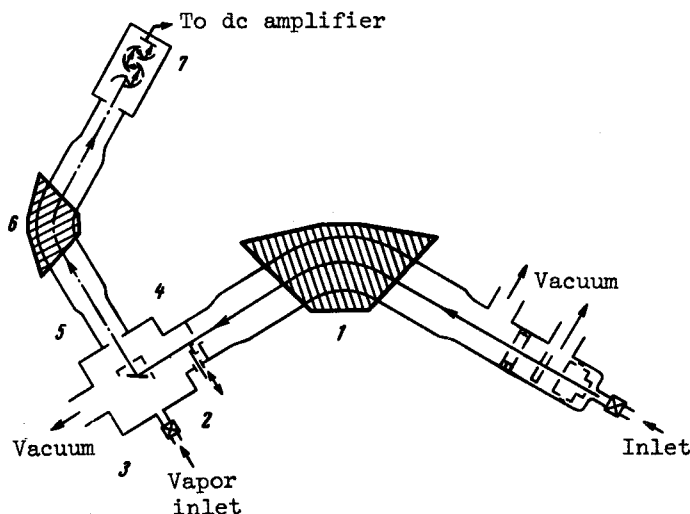


Fig. 1. Diagram of instrument: 1 - mass analyzer of instrument, MI-1305, 2 - movable collector and electrometric amplifier, 3 - nickel slit, 4 - electrode, 5 - aperture slit, 6 - magnetic analyzer, 7 - electron multiplier

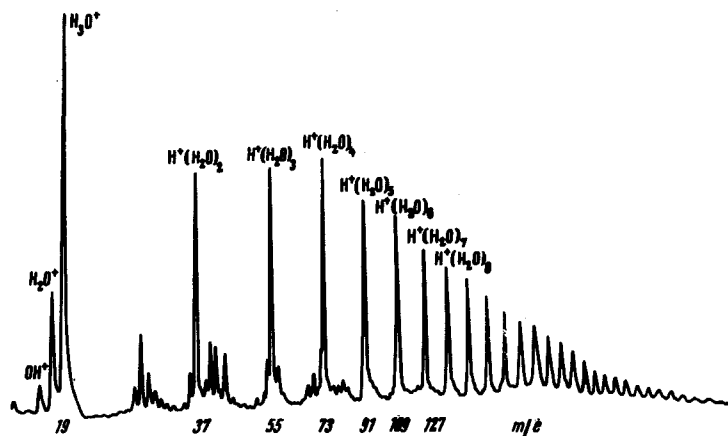


Fig. 2

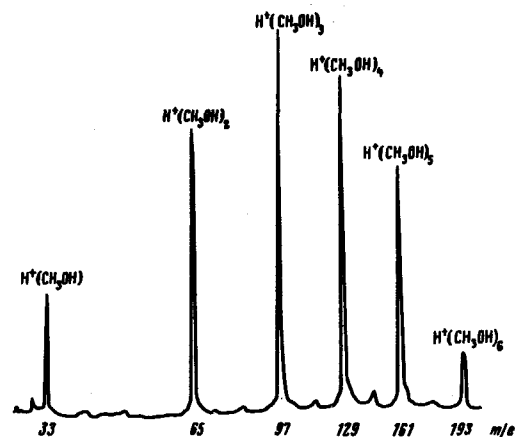


Fig. 3

Fig. 2. Mass spectrum of water clusters.

Fig. 3. Mass spectrum of methyl-alcohol clusters.

This analyzer was used at a resolution ~ 50 , and permitted ions with mass up to ~ 600 at.un. to be deflected to the collector. The secondary ions were registered with an electron multiplier 7 connected in series with an electro-metric amplifier. The instrument was evacuated with three N10-R mercury diffusion pumps equipped with liquid-nitrogen traps. The vacuum limit of the instrument was 5×10^{-7} Torr.

To prevent the target from acquiring a surface charge, which would become manifest in the appearance of a number of singularities in the mass spectra (these are of special interest and will be described in a separate communication), we worked either with sufficiently thin film or else neutralized the charge by a weak beam of 8 - 10 eV electrons.

Figure 2 shows a typical mass spectrum of the secondary ions produced when a film of water frozen on a nickel substrate is bombarded, at a water vapor pressure 10^{-6} Torr and at a substrate temperature -196°C . The bombardment was with 1.5-keV Ar^+ ions, and the current to the target had a density 10^{-7} A/cm². We see that the main ions produced under these conditions are not H_2O^+ or their fragments, but clusters of the type $\text{H}^+(\text{H}_2\text{O})_n$. We observed in our experiments clusters with $n = 30$.

Mass spectra were obtained also for ammonia under the same conditions. The main ions in this spectrum were clusters of the type $\text{H}^+(\text{NH}_3)_n$. Just as in the case of water, the intensity of the clusters decreased with increase in their mass. Clusters with $n = 30$ were observed.

Figure 3 shows the mass spectrum of the secondary ions produced by bombardment of a film of methyl alcohol frozen on a nickel substrate at an alcohol vapor pressure 5×10^{-6} Torr and a substrate temperature -170°C . The remaining conditions were the same as in the case of water.

The mass spectrum obtained by us consists of $\text{H}^+(\text{CH}_3\text{OH})_n$ clusters. Unlike water, for which the most intense current was produced by H_3O^+ ions, the main ion in methyl alcohol was the cluster $\text{H}^+(\text{CH}_3\text{OH})_3$. We observed clusters with n up to 6. For ethyl alcohol, clusters of the type $\text{H}^+(\text{C}_2\text{H}_5\text{OH})_n$ with n up to 4 were observed. It should be noted that the maximum values of n for all the investigated types of clusters were limited in our measurements by the capabilities of the secondary magnetic analyzer, and heavier clusters were

apparently also produced.

For light water clusters with n up to 10, the measured dependence of their current on the bombarding-ion current turned out to be linear. A qualitative investigation was made of the influence of the mass and of the structure of the bombarding ions on the mass spectrum of the secondary water ions. We used for the bombardment the ions H_2^+ , He^+ , N^+ , N_2^+ , Ar^+ , and $C_3H_7^+$ with energy 1.5 keV. When the light ions H_2^+ and He^+ were used, no cluster formation was observed. All the other ions gave cluster mass spectra of the same type, with roughly the same yield, which can be estimated at one secondary H_3O^+ ion per 10^6 primary ions.

The obtained data lead to certain conclusions concerning the mechanism whereby the light clusters are produced, predominantly water, which was investigated in greatest detail. When an ion strikes a target on which the water is apparently in the form of a small-crystallite film, the individual water molecules are ionized and the film becomes locally heated. At the first instant of time after the impact, the density of the water molecules in this region is very large, and this is precisely the instant when the clusters are produced and their internal excitation is deactivated. That the produced clusters have no noticeable internal excitation is evidenced by the fact that none of the spectra revealed ions that are metastable with respect to dissociation, even for clusters with large n . The clusters observed in this manner are then evaporated from the heated section of the substrate. Favoring this mechanism is possibly also the absence of clusters in the case of bombardment with light ions, which have a large mean free path in the substance and consequently produce less local heating.

The described method makes it possible to investigate clusters of different substances, including also nonpolar compounds, as was demonstrated in [3]. Unlike the method developed by Kaberle for obtaining clusters in the gaseous phase [4], which is limited to a relatively narrow range of working pressures, our method makes it possible to obtain much heavier clusters.

The described observation of secondary emission of predominantly ionic clusters in the "cold" state from the surface of molecular crystals of polar substances uncovers, in accordance with the statement made at the beginning, new possibilities for investigating the thermodynamics of solvation and for determining the coordination numbers in solvates.

In comparison with studies of the "clusterization" in the gas phase, ion-ion emission has obvious advantages, at least because in gases it is impossible to obtain such heavy clusters as obtained in our work.

The authors are grateful to V.L. Tal'roze for valuable remarks made during a discussion of the results.

- [1] Castany, Slodzian, in: *Advances in Mass Spectrometry* 3, 91, London, 1966.
- [2] V. F. Rybalko, V. Ya. Kolot, and Ya. M. Fogel', *Zh. Tekh. Fiz.* 39, 1717 (1969) [*Sov. Phys.-Tech. Phys.* 14, 1290 (1970)].
- [3] R. Clappitt and D. K. Jeffries, *Nature* 226, 141 (1970).
- [4] P. Kaberle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arschadi, *J. Am. Chem. Soc.* 89, 6393 (1967).