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Abstract

Full Text

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Physics

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On the Formation of Protonated Ions during Thermal Ionization of Molecules of Organic Compounds

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In the mass spectra of positive ions obtained by thermal ionization of organic compounds on emitters of oxidized tungsten in weak electric fields $\varepsilon \sim 10^3$ V/cm, there were lines of so-called protonated ions with mass $(M+1)$, where M is the mass of the molecule in atomic units (^{1}). Such lines also occur in the ionization spectra of molecules in strong fields $\varepsilon \sim 10^7$–10^8 V/cm at the surface of tips (^{2}). In the present communication, results are presented from a study of the mechanism of formation of protonated ions during thermal ionization, and an attempt is made to consider the ionization process in weak and strong fields from a unified point of view.

In Table 1 are given the current densities of protonated ions during thermal ionization of certain compounds on oxidized tungsten and the percentage ratio of the current of these ions to the current of the principal line in the spectrum. The experiments were carried out in a mass-spectrometric apparatus (^{1,3}). The thermionic properties of emitters made of oxidized tungsten have been reported in (^{4}). The data in the table refer to vapor pressures of the substances $\sim 1 \cdot 10^{-7}$ torr (according to an ionization manometer) and to emitter temperatures corresponding to the maximum current densities. The temperature dependences of the currents $I^+(T)$ are presented in Fig. 1.

Fig. 1. Temperature dependence of the current of protonated ions during thermal ionization: 1—pyridine, 2—diethylamine, 3—phenol.

Below are given the results of an investigation of the ionization of phenol, in whose spectrum only $(M+1)^+$ ions are present.

Fig. 2

Figure 2: Fig. 2

In Fig. 2 are presented the volt-ampere characteristics of the current of $(M+1)^+$ ions in a retarding electric field ("retarding curves," (^{3,5})) at two emitter temperatures. It is seen that at $T = 1000°$K the contact potential difference U_k and the work function φ do not change, which indicates a small degree of coverage θ of the emitter by adsorbed molecules at this temperature. This occurs for all $T > T_{\text{max}}$ in Fig. 1. At $T > T_{\text{max}}$, admission of phenol changes φ by an amount ΔU_k (see the retarding curves at $T = 800°$K).

From a comparison of the linear portions of the retarding curves for $(M+1)^+$ and Cs^+ ions during simultaneous ionization of phenol and Cs, it follows that the $(M+1)^+$ ions have a Maxwellian distribution with respect to the initial kinetic—

···of the translational energy with the emitter temperature. This means that the accommodation coefficient of phenol molecules on oxidized tungsten is equal to unity and that particles with mass $(M+1)$ are present in the adsorbed layer and are in thermal equilibrium with the emitter.

The dependence of the protonated-ion current on pressure is quadratic (Fig. 3), whereas the ion currents in the ionization of phenol by electrons

Fig. 2. Retarding-potential curves of Cs^+ during ionization of Cs atoms (a), and retarding-potential curves of Cs ions (b) and protonated phenol ions (c) during the simultaneous ionization of Cs atoms and phenol molecules. I—$T = 800°$ K, II—1000° K, III—800° K

increase linearly with pressure up to $p \approx 10^6$ torr, and at larger p increase more slowly because of scattering of the ions on their way to the collector.

The appearance of $(M+1)^+$ ions during thermal ionization cannot be explained by ion-molecular reactions in the adsorbed layer: in none

Table 1

Substance	j, A/cm^2	%
Diethylamine	$\sim 5 \cdot 10^{-9}$	15
Phenol	$\sim 8 \cdot 10^{-11}$	100(single line)
Piperidine	$\sim 10^{-11}$	0.1
n-Amylamine	$\sim 10^{-12}$	2
Pyridine	10^{-12}–10^{-13}	100(single line)

of the compounds forming $(M+1)^+$ ions were M^+ ions found, even at $T > T_{\text{max}}$, when θ is small and the probability of reactions decreases.

Fig. 3

Figure 3: Fig. 3

Since the particles $(M+1)$ in the adsorbed layer are in thermal equilibrium with the emitter, upon thermal desorption they can

ionized by surface ionization [6]. The production of measurable ion currents by surface ionization is possible when the ionization potentials V of the particles are comparable with φ. Noticeable currents of phenol M^+ ions cannot be formed, since $V = 8.5$ V [7] and considerably exceeds φ. The particles $(M+1)$ in phenol have a substantially smaller V: according to our estimates $V_{M+1} < 7.6$ V.

It is necessary to explain by what route the complexes $(M+1)$ are formed in the adsorbed layer. Since the process is bimolecular $(I^+ \sim p^2)$, the particles $(M+1)$ are formed either as a result of reactions between two phenol molecules, or between a phenol molecule and its fragment formed upon dissociation of molecules on the emitter (for example, with hydrogen). However, an additional admission into the instrument of H_2, H_2O vapors, as well as D_2 and D_2O, did not affect the formation of $(M+1)^+$ ions. Apparently, on the emitter surface phenol molecules can be linked by a hydrogen bond and exist similarly to NH_4 complexes [8]. Table 1 shows that $(M+1)^+$ ions are observed upon ionization of compounds with heteroatoms of nitrogen and oxygen, possessing strongly pronounced proton-acceptor and proton-donor properties. The position of the heteroatom in the molecule must also play an essential role, since the distribution of electron density depends on it. Thus, upon ionization of aniline, $(M+1)^+$ ions were not detected, which can be explained by the inclusion of the free electron pair of nitrogen in the conjugation system with the π-electrons of the benzene ring.

Fig. 3. Dependence of the current of protonated phenol ions on pressure during thermal ionization. $T = 1100^\circ$K

In surface ionization in the absence of reactions, I^+ either increases with increasing T, or changes only very weakly [6]. In the case of phenol, the dependence $I^+(T)$ is bell-shaped, since with increasing T at $p = \text{const}$ the concentration of $(M+1)$ particles in the adsorbed layer decreases substantially because of a decrease in θ, and also because of an increase in the probability of decomposition of weakly bound particles (hydrogen bond).

Thus, all the regularities observed for phenol $(M+1)^+$ ions can be explained by surface ionization of complex compounds arising in the layer adsorbed on the emitter. In the same way, in our opinion, one may also explain the appearance of $(M+1)^+$ lines in desorption spectra in strong electric fields. In these spectra there are also M^+ lines and $(M+1)^+$ lines, and with increasing ε the current of $(M+1)^+$ ions decreases, while that of M^+ ions increases [9]. Therefore in [9] and in subsequent works it is assumed that $(M+1)^+$ ions arise in ion-molecular reactions between M^+ ions formed at the tips and molecules of the adsorbed layer of high concentration, which is associated with polarization attraction of particles to the tip in an inhomogeneous field.

Field desorption of ions can be regarded as a special case of surface ionization, in which the field substantially lowers the heat of evaporation of ions, so that ion desorption becomes possible at low temperatures. In [10], quantitative relations were obtained for describing, within the framework of the theory of surface ionization, the process of field desorption of atomic ions. If chemical reactions occur in the adsorbed layer on the tip, then in analyzing the dependences $I^+(\varepsilon)$ it is necessary to take into account the dependence of the yield of these reactions on ε. With increasing ε, the yield of reactions should at first increase because of an increase in the concentration of particles in the adsorbed layer owing to the attraction effect, and then decrease because of [[unclear: continuation on next page]]

ionization of particles on the way to the tip. In this case the ion current of $(M+1)^+$ will decrease, beginning at certain values of ε, while the ion current of M^+ will increase, which is in fact observed. The lines of the $(M+1)^+$ ions will be narrow at all ε, whereas the M^+ lines broaden with the onset of autoionization. As in thermal ionization, the $(M+1)^+$ ions in the spectra of field desorption are formed in compounds with heteroatoms of nitrogen and oxygen ([2], [11], [12]).

Substantial information on the mechanism of formation of protonated ions in strong fields could be provided by studies of the energy distribution of these ions.

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Note: Figure translations are in progress. See original paper for figures.