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## Abstract

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# THE EFFECT OF PRESSURE, TEMPERATURE, AND AN ELECTRIC FIELD ON THE BEHAVIOR OF MOLECULAR PATTERNS

The behavior of molecular patterns (m.p.), i.e., emission images observed on the screen of an electron projector during the adsorption of various vapors and gases on a tip, has been described in a number of works. However, many points essential for understanding the nature of these patterns remain unclear. In particular, little is known about the nature of the bond with the surface of the molecules responsible for the m.p., and about the influence of an electric field on them. The role of filling the surface with adsorbate is also unclear. In some cases (phthalocyanine, flavanthrene) m.p. are already observed on the clean surface of the emitter (⌒1); in others (gases, vapors of low-boiling liquids) m.p. do not appear immediately even at a pressure of $1 \cdot 10^{-6}$ mm (2,3). In this work an attempt has been made to obtain an answer to some of the questions posed by studying the effect of an electric field, pressure, and temperature on the behavior of m.p.

## Experimental results and their discussion

**Effect of pressure.** Pressure has a dual effect on the behavior of m.p. First of all, pressure, other conditions being equal, determines the number of ions bombarding the emitter. In the case of gases and vapors of low-boiling liquids, pressure also affects the filling of the surface with adsorbate. This can easily be traced if adsorption of the gas under study, say $CO_2$, $H_2$, or $C_3F_6$, is begun from a pressure of $5 \cdot 10^{-9}$ mm (and not $10^{-6}$ mm). At first, up to a pressure of $\sim 1 \cdot 10^{-7}$ mm Hg, adsorption is accompanied by a noticeable decrease in the emission of strongly emitting faces. During an exposure of the order of several minutes, discrete bright points cover all strongly emitting directions; however, brighter mobile spots are not observed at this pressure. These spots (molecular patterns), initially only round, appear for the first time at a pressure of $1 \div 2 \cdot 10^{-7}$ mm, and their number and brightness increase with pressure. For observing m.p. of complex form, either additional exposure or an increase in pressure is required. For example, "double-leaf" patterns for $CO_2$ first appear

Fig. 1

Figure 1: Fig. 1

at a pressure close to $10^{-5}$ mm. By the moment the m.p. appear, regions of enhanced emission already look multilayered. Even within a single face, m.p. differ greatly from one another in brightness (and size). This is easily observed with a gradual decrease in the voltage. A decrease in pressure leads to a decrease in the number of mobile patterns, which indicates the reversible character of the adsorption of the molecules responsible for the m.p. At the same time, the lifetime of the m.p. increases.

It is interesting to note that, irrespective of the nature of the molecules, the appearance of a large number of m.p. is always accompanied by an increase in the emission current. This effect depends strongly both on pressure and on the anode voltage. Figure 1 presents curves characterizing the change in emission current with the pressure of $H_2$ in the projector. The solid curves show the increase in current with increasing pressure at constant anode voltage; moreover, because of the danger of blunting the tip, each time the current reached $5\,\mu$A, a lower voltage was set. The dashed curve was obtained upon decreasing $p_{H_2}$ from $1 \cdot 10^{-7}$ to $1 \cdot 10^{-6}$ mm at $U = 4.0$ kV. Similar results were obtained for $O_2$ and $N_2$. The regularities described are basically also valid for more complex molecules, but in the case of un-

stable compounds, the usual picture is complicated by the formation of parasitic microprotrusions.

**Effect of the electric field.** The time required to reach the degree of filling at which molecular patterns begin to appear depends substantially on the magnitude of the field applied during adsorption. This can be explained by two reasons. First of all, a nonuniform field will draw polarized molecules out of the volume adjacent to the tip. As a result, the actual number of impacts of molecules on the surface will exceed, by several times, the gas-kinetic number of impacts in the absence of a field (4). Secondly, the sticking coefficient, which for neutral molecules undergoes a sharp drop in the transition from the first to the second layer, may remain fairly high in the case of polarized particles. This leads to a more rapid decrease in the emission current, since all the substances investigated (with the exception of inert gases) increase the work function.

**Fig. 1.** Change of the emission current with the pressure of $H_2$ (mm Hg) at constant values of the anode potential.
1 –$U = 4.0$ kV; 2 –$U = 4.2$ kV; 3 –$U = 4.4$ kV; 4 –4.6 kV. The dashed curve was obtained while the pressure was decreasing.

However, there is always a critical value of the anode voltage, beginning with which the emission current no longer falls during exposure at constant voltage and pressure. Above this voltage the current increases with time, reaching saturation. This is accompanied by an increase in the number of bright molecular patterns. What has been said above is illustrated by Fig. 2, where the curves for $N_2$ are presented. The regularities described are manifested even more sharply during adsorption on tips restructured in the field, since the formation of protrusions during such restructuring leads to the creation of especially strong local fields near their surface.

It is also necessary to mention the influence of the field on the shapes of molecular patterns. As the voltage is increased at a given pressure, the ratio of the number of complex molecular patterns ( “double leaves,” “rings,” “rosettes” ) to the number of simple circles increases. In the case of toluene and benzene, “rosettes” on protrusions, where the field is higher, were observed often, whereas on regions that appeared flat they were rare*.

**Effect of temperature.** Lowering the temperature to 80°K leads to a considerable increase in the sharpness of the molecular patterns and in their lifetime. This time, which depends on the pressure of the residual gases and on the vapor pressure of the substance under study, at 80°K may reach several seconds. Raising the temperature above room temperature produces the opposite effect. As was already noted above, molecular patterns of $H_2$ or $CO_2$ disappear already at room temperature if the pressure in the projector is again lowered to $1 \cdot 10^{-8}$ mm. But in the case of more complex molecules, disappearance of the molecular patterns occurs at higher temperatures. These temperatures, depending on the nature of the molecules, range from 400 to 800°C. The fact deserves attention that the brightness of molecular patterns does not depend substantially on temperature. The data we obtained on the temperatures at which molecular patterns disappear agree with the data of other authors (1—3).

**Discussion of the results.** In discussing the present work, we shall try, using oxygen as an example, to draw a picture of the adsorption of molecules in a field. Apart from differences in the forms of the molecular images that appear at the last stage of adsorption, this picture is common to all the gases and low-boiling liquids we have studied.

Adsorption of the first portions of active gases on a clean surface leads to the formation of a chemisorbed layer and is accompanied by an increase in the work function. For oxygen, two sublayers have been found with binding energies of 5.0 eV and 2.5 eV, respectively (5), which indicates the formation of valence bonds with the surface. In addition, the adsorbed molecules are still under the action of two antiparallel electric fields: the field of the anode ($2 \div 7 \cdot 10^7$ V/cm), which tends to increase the negative dipole of the molecule, and the surface field $7 \div 8 \cdot 10^7$ V/cm (meaning local fields created by individual surface atoms)*, acting in the opposite direction. The resulting negative sign of the charge shows that in this case the polarity of the valence bond is decisive.

The influence of the external field is manifested in a noticeable graininess of the

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* Müller and Mamedov (1), in a study of phthalocyanine, were able to observe the transition of “double leaves” into “rosettes” simply by increasing the anode potential.

Fig. 2. Change of emission current with time at pressure $N_2 \sim 5 \cdot 10^{-6}$ mm: 1 $-U = 10.5$ kV; 2–$U = 11.0$ kV; 3–$U = 11.5$ kV; 4–$U = 12.0$ kV; 5–$U = 12.5$ kV; 6–$U = 13.0$ kV; 7–$U = 13.5$ kV

Figure 2: Fig. 2. Change of emission current with time at pressure $N_2 \sim 5 \cdot 10^{-6}$ mm: 1–$U = 10.5$ kV; 2–$U = 11.0$ kV; 3–$U = 11.5$ kV; 4–$U = 12.0$ kV; 5–$U = 12.5$ kV; 6–$U = 13.0$ kV; 7–$U = 13.5$ kV

image. This indicates that the external field is already sensitive to inhomogeneity on the scale of molecular dimensions (for $O_2$, 3.6 Å). Molecules adsorbed on the surface of these layers and giving rise to the molecular patterns can no longer form ordinary valence bonds with W atoms. This is confirmed both by the low temperature at which the molecular patterns disappear and by the strong dependence of their number on pressure. The filling of the third layer is much lower than that of the first two layers and in any case must be less than 0.01. This assertion is based on a simple calculation of the number of observed molecular patterns. Taking the concentration of an $O_2$ monolayer to be $4 \cdot 10^{14}$ mol/cm$^2$ ($^7$), for a tip with $R = 3000$ Å one would expect a number of molecular patterns equal to $2 \cdot 10^5$. This value is much greater than the observed one. The influence of the surface on the molecules of this layer becomes insignificant and, on the contrary, the influence of the anode field sharply increases. This influence is due to the interaction of the field with polarized molecules and should affect the placement of molecules and increase their binding energy. In a field of $\sim 7 \cdot 10^7$ V/cm, $O_2$ molecules, with their low polarizability ($2.6 \cdot 10^{-24}$ cm$^{-3}$), form induced dipoles $\mu = 0.42 \cdot 10^{-18}$. A consequence of the dipolar character of the molecules will be their migration in an inhomogeneous electric field to places of maximum field strength, where the binding energy of the polarized molecules with the surface is higher. At the same time, bombardment will increase the number of submicroprotrusions formed when neutralized ions are embedded into the surface. Owing to the anisotropy of polarizability characteristic of most molecules, the position of a molecule adsorbed in the field on such a submicroprotrusion will be quite definite: the axis of greatest polarizability will be oriented along the field. The height of such a built-up microprotrusion should largely be determined by the shape and size of the adsorbed molecule. The local field at the summit of a microprotrusion may substantially exceed the macroscopic one. This circumstance is important for understanding the high brightness of the molecular patterns, which in first approximation does not depend on the nature of the molecule. In this connection, one should also take into account possible autoionization of molecules adsorbed in the upper layer. Table 1 gives the ionization times of molecules in real fields (taking into account the local po-

**Fig. 2.** Change of the emission current with time at a pressure of $N_2 \sim 5 \cdot 10^{-6}$ mm:
1–$U = 10.5$ kV; 2–$U = 11.0$ kV; 3–$U = 11.5$ kV; 4–$U = 12.0$ kV; 5–$U = 12.5$ kV; 6–$U = 13.0$ kV; 7–$U = 13.5$ kV

* Experimental proof of the existence of fields of this magnitude was obtained from experiments on the adsorption of inert gases on a clean W surface (see in particular (6)).

Table 1

Ionization times (in sec.) for molecules with ionization potentials from 6 to 25 eV, calculated from the equation $\tau = 10^{-16}\exp(0.68V_i^{3/2}/F)$

| Ionization poten-tial, eV | Field strength, V/Å | Field strength, V/Å | Field strength, V/Å | Ionization poten-tial, eV | Field strength, V/Å | Field strength, V/Å | Field strength, V/Å |
|---|---|---|---|---|---|---|---|
| | 0.5 | 1.0 | 2.0 | | 0.5 | 1.0 | 2.0 |
| 6 | $5\cdot10^{-8}$ | $2\cdot10^{-12}$ | $4\cdot10^{-14}$ | 13 | $6\cdot10^{11}$ | $8\cdot10^{-3}$ | $1\cdot10^{-9}$ |
| 7 | $8\cdot10^{-6}$ | $3\cdot10^{-11}$ | $6\cdot10^{-14}$ | 14 | $1\cdot10^{15}$ | $3\cdot10^{-1}$ | $6\cdot10^{-9}$ |
| 8 | $7\cdot10^{-3}$ | $3\cdot10^{-10}$ | $2\cdot10^{-13}$ | 15 | $6\cdot10^{18}$ | $2\cdot10^{1}$ | $5\cdot10^{-8}$ |
| 9 | $8\cdot10^{-1}$ | $9\cdot10^{-9}$ | $9\cdot10^{-13}$ | 16 | $6\cdot10^{21}$ | $8\cdot10^{2}$ | $1\cdot10^{-7}$ |
| 10 | $8\cdot10^{2}$ | $3\cdot10^{-7}$ | $5\cdot10^{-12}$ | 20 | $5\cdot10^{36}$ | $2\cdot10^{10}$ | $2\cdot10^{-3}$ |
| 11 | $6\cdot10^{4}$ | $5\cdot10^{-6}$ | $2\cdot10^{-11}$ | 25 | $2\cdot10^{44}$ | $1\cdot10^{18}$ | $2\cdot10^{1}$ |
| 12 | $2\cdot10^{8}$ | $2\cdot10^{-4}$ | $1\cdot10^{-10}$ | | | | |

···of elevation) 0.5 V/Å, 1 V/Å, and 2 V/Å, calculated by Müller' s formula* (4). If one assumes that the lifetime of an m.p., reaching several seconds, reflects the residence time of the molecule in the given energy state, then these times should be recognized as sufficient for autoionization. From Table 1 it is seen that molecules whose ionization potentials lie from 7 to 15 eV should already be ionized in fields $< 2\cdot10^8$ V/cm.

The above considerations can apparently explain the fact that in the case of He and Ne it was not possible to observe m.p. at all. Their weak polarizability hinders the formation of microprotrusions, while their high ionization potentials require fields up to $2\cdot10^8$ V/cm.

It is more difficult to understand the nature of the bond with the surface of the molecules giving rise to m.p. The temperatures of complete disappearance of m.p., reaching 800° K, correspond to bond energies up to 1.5–2.0 eV (chemisorption). On the other hand, the dependence of the concentration of m.p. on pressure in the case of a number of substances indicates the physical character of the adsorption. This contradiction is probably explained by the fact that the bond energies (2 eV) correspond not to the molecules giving rise to m.p., but to molecules of the underlying adsorbed layer, since according to the ideas developed above, the nonuniform relief of this layer creates the conditions necessary for observing m.p.; the latter should be observed up to the complete desorption of this layer. An estimate of the bond energies of molecules from their lifetimes can be made by the formula $\tau \leqslant 10^{-11}\exp Q/RT$. For $\tau = 1$ sec, $Q$ at 80 and 300° K proves to be, respectively, 4.0 kcal and 13.9 kcal. The observed $\tau$ for Ar,

$N_2$, $O_2$, Xe at 80° K lie within the range 0.1 sec–1 sec. Taking into account that the heats of evaporation, together with the additional binding energies due to polarization in a field $1 \cdot 10^8$ V/cm ($Q_F = \frac{1}{2}\alpha F^2$), range from 3.8 to 5.0 kcal, the agreement with $Q = 4$ kcal is good. The second value, 13.9 kcal, agrees in order of magnitude with the heats of evaporation of iodine, naphthalene, and larger molecules. This does not exclude the possibility of weak chemisorption, say, with participation of the free *d*-orbitals of W and unshared electron pairs of molecules (8), or (if radicals are formed) of unpaired electrons.

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* As the author himself notes, the formula gives overestimated results, since it does not take into account the lowering of the ionization potential of the molecule.

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