Molecule clusters adsorbed on the surface of a conductor

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The interaction of admolecules with the conduction electrons of a crystal at low degrees of surface coverage can lead to a clustering of the admolecules.

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As is known, a dipole moment, perpendicular to the surface, appears in molecules adsorbed on the surface of a crystal. If the degree of surface coverage is small, it is considered self-evident that the admolecules tend to be located as far from each other as possible because of the dipole-dipole repulsion between them. It will be shown below that in some cases of adsorption on semiconductors and metals the admolecules can attract each other and form clusters. Such clusters, in which the number of molecules can amount to a few dozen, should have a significant influence on many surface phenomena, including catalytic and emission phenomena.

We shall examine in detail the molecules that do not have a "degenerate" dipole moment, when they are chemisorbed on a nondegenerate semiconductor, without dissociating into atoms. The crystal is assumed to be ionic. Two types of chemical bond between the admolecule and crystal are possible: "neutral" and "charged".[1] In the first case the electrons of the molecule are partially attracted from it to several crystal cations nearest it, in the simplest case to the nearest cation that plays the role of an adsorption center. Because of the displacement of the molecule electrons with respect to its ionic core, a dipole moment appears in it as a result of adsorption.

An admolecule can capture an electron from the crystal or, conversely, give up its own electron to the crystal, and then its bond to the crystal becomes "charged". In this case the admolecule behaves like a surface acceptor or donor, and its charging occurs for the same reasons as for volume donors or acceptors. In addition, it may occur because of the field effect as a result of the attraction of excess charge carriers to the surface.

In the general case the number of admolecules in the charged state is small compared to that in the neutral state. Therefore, in order to prove the possibility of the formation of clusters, it is sufficient to investigate the state of the admolecule system, one of which must be in the charged state while the rest are in the neutral state. The relative arrangement of the admolecules is determined by competition between dipole-dipole repulsion and the tendency of the charge carrier, which is trapped by a admolecule (let us assume that it is a conduction electron), to attract the admolecules to each other. This attraction is caused by the fact that if the neutral admolecules are located near a charged admolecule, then the crystal electron trapped by it (superfluous compared with the rest of the admolecules) can move from one molecule to another. Because of the expansion of the electron localization region, its kinetic energy is reduced by an amount of the order of the transition integral between molecules. Let us

emphasize that we are speaking of transitions of the superfluous electron only. The electrons belonging to the molecules remain localized in them and in the corresponding adsorption centers. Rather than causing the admolecules to group together in clusters, they tend to separate them by producing dipole moments of the admolecules.

If the grouping tendency of the admolecules predominates, then they should form clusters. In a certain sense they resemble polymer molecules, since they are constructed from admolecules with saturated chemical bonds. However, the reason for formation of the adclusters is entirely different. It is essentially the same as that which causes charge-carrier autolocalization in the regions in which the phase in semiconductors has been changed (ferronic carrier states[2]).

The number n of admolecules in a cluster is determined below under the following assumptions: 1) Since the total number of admolecules on the crystal surface is small, it can be assumed that the admolecules that do not form a cluster are located at such large distances from the cluster and from each other that their dipole-dipole interaction with other molecules can be ignored. 2) The cluster radius R is large compared with the lattice constant a. Inside a circle of this radius the admolecules occupy all the adsorption centers (cations) that form a simple square lattice, so that $n = \pi/(R/a)^2$.

The dipole-dipole interaction energy of the admolecules in a cluster increases with its size in accordance with the formula $E_d \approx 2p^2/\epsilon_s a^3$, where $\epsilon_s = (\epsilon + 1)/2$ is the surface dielectric constant of the cyrstal — the dipole moment of a neutral admolecule. The electrostatic interaction energy of the superfluous electron with the dipoles can be ignored, since it is of a higher order in $1/n$ compared with E_d. We point out that the moment p of an admolecule in a cluster is reduced compared with the moment p_0 of an isolated neutral admolecule in order to decrease E_d, although this increases the binding energy of the cluster molecules with the crystal by an amount $E_e = R(p - p_0)^2 n/2$, where $R = \alpha E_A/p_0^2$, $\alpha \sim 1$, E_A is the binding energy of an isolated admolecule with the crystal. In the simplest adsorption model, when E_A is small compared with the dissociation energy of the molecule, and the chemical bond between the molecule and the crystal occurs because of the attraction of two paired electrons of the molecule to the crystal cation nearest to it, $\alpha \approx 0.25$.

The energy gain of the electron, which is trapped by the cluster, as compared with its energy at the isolated admolecule, increases with cluster size:

$$E_B = -|B|\left[4 - \left(\frac{2.3a}{R}\right)^2\right]. \tag{1}$$

The p dependence of the transition integral B of the superfluous electron from molecule to molecule is ignored. The capture energy of the crystal electron by the admolecule is not taken into account in Eq. (1), since it is the same regardless of whether or not a cluster forms.

Minimizing the total energy $E = E_d + E_l + E_B$ with respect to R and p, we obtain with allowance of Eq. (1), the optimum values of E and R:

$$E = 4.6\sqrt{\pi E_p | B |} - 4 | B |, \qquad E_p = \frac{2p_0^2}{\epsilon_s a^3} \left(1 + \frac{4}{\epsilon_s a^3 R} \right)^{-1},$$

$$R = [(2.3)^2 | B | / \pi E_p]^{1/4} \tag{2}$$

For the parameters $|B| = 1$ eV, $a = 3$Å, $p_0 = 0.25ea$, $\epsilon_s = 5$, $E_A = 1$ eV, and $\alpha = 0.25$ in Eq. (2), we find that 15 molecules are contained in the cluster, and because of its formation the energy gain is equal to 2 eV.

Since the energy of the superfluous electron in the cluster is lower than that in an individual admolecule, clusters can appear even in those cases when the individual admolecule cannot capture an electron from the crystal: even if the "charged" bond of admolecule to crystal is impossible, such a bond is possible for clusters of admolecules. The energy advantage of the clusters can be increased if several electrons from the crystal are localized in it, and its size increases correspondingly (an analog of the multielectron ferrons in Ref. 2).

A periodic adcluster structure should form for the same reasons that give rise to the appearance of a periodic admolecule structure on the crystal surface. In the latter case the picture is complicated by the fact that clusters of different sizes and admolecules, which are not contained in the clusters, can coexist. Since the cluster characteristics depend on the carrier density at the surface, by altering it by means of the field effect, we can alter the dimensions and spatial periodicity of the clusters.

Admolecule clusters can also be produced as a result of adsorption on metals and degenerate semiconductors. In them the admolecules produce resonance levels below the Fermi surface. The grouping of admolecules into clusters lowers these levels for the same reason as in nondegenerate semiconductors. As a result, the energy of electron gas decreases, which in turn decreases its Fermi level. This also gives rise to a tendency for adclusters to form.

[1]F. F. Vol'kenshtein, Fiziko-khimiya poverkhnosti poluprovodnikov (Surface Physical Chemistry of Semiconductors), Nauka, Moscow, 1973.
[2]E. L. Nagaev, Fizika magnitnykh poluprovodnikov (Physics of Magnetic Semiconductors), Nauka, Moscow, 1979.