ANNALES
UNIVERSITATIS MARIAE CURIE-SKLODOWSKA
LUBLIN — POLONIA
VOL. XLVI/XLVII SECTIO AAA 1991/1992

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Electronic States of Two-Atomic Molecules Adsorbed on an Ionic-Dielectric Surface

To describe the quantum properties of an oxygen molecule adsorbed on the surface of an ionic dielectric, we use the following model. The surface is square lattice of attractive and repulsive sites. The surface potential barrier with height U_0 equal to the electron affinity in the dielectric allows for the presence of the crystal in the half-space $z > 0$. In the coordinate representation, the Hamiltonian of the system comprising the adsorbed molecule and the crystal surface writes as

$$\hat{H} = \hat{H}_{\text{mol}} + U_e + V_n + V_e, \tag{1}$$

where $\hat{H}_{\text{mol}}$ is the Hamiltonian of a free oxygen molecule,

$$U_e = \begin{cases} 0, & z < 0 \\ -U_0, & z \geq 0 \end{cases} \tag{2}$$

is the surface potential for the molecule valence electrons, V_n and V_e are the model potentials of the interaction between the surface sites and the molecule nuclei and valence electrons, respectively. An electron-electron interaction between the molecule and the crystal surface is ignored in (1) assuming that it is taken into account partially in both the surface potential U_e and the model potential V_e.

A salient feature of a surface is an appreciable weakening of the bonds between the surface lattice atoms due to the break of symmetry, the corresponding dehybridization of the bonds, the depression of valency directivity [1]. The studying of the Hamiltonian (1) displays that the adsorption of the molecule not only weakens the lattice bonds, which is verified by experiment [2], but also changes the shapes of the valence-electron clouds substantially, which weakens the molecule bond. As

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is shown in [3,4], the similar effect arises for the hydrogen molecule near the structureless surface (neglecting the model potentials V_n and V_e).

The weakening of the molecule bond depends on the molecule orientation relative to the surface. The energy of the molecule near the surface has been approximated by [3,4]

$$E_{\mathrm{mol}}(R_{12}, z_1, z_2) = \tag{3}$$

$$E_{\mathrm{mol}}(R'_{12})\Delta E_{\mathrm{at}}(z_1) + \Delta E_{\mathrm{at}}(z_2) + \frac{d_{\mathrm{at}}(z_1)d_{\mathrm{at}}(z_2)}{R_{12}^3}(1 - 3\sin\vartheta_{12}^2), \tag{4}$$

where R_{12} is the separation between the nuclei of the molecule, z_1 and z_2 are the distances from the nuclei 1 and 2 to the surface, $\sin\vartheta_{12} = (z_1 - z_2)/R_{12}$, ϑ_{12} is the angle between the molecule axis and the surface, $\Delta E_{\mathrm{at}}(z_0) = E_{\mathrm{at}}(z_0) - E_{\mathrm{at}}(z_\infty)$, $E_{\mathrm{at}}(z_0)$ and $d_{\mathrm{at}}(z_0)$ are the energy and dipole moment of the hydrogen atom at the distance z_0 from the structureless surface [5], $E_{\mathrm{mol}}(R'_{12})$ is the energy of a free molecule at the effective interatomic separation

$$R'_{12} = [R_{12}^2 + 2(z_2 - z_1)(d_{\mathrm{at}}(z_2) - d_{\mathrm{at}}(z_2)) + (d_{\mathrm{at}}(z_1) - d_{\mathrm{at}}(z_1))^2]^{1/2}$$

equal to the distance between the centers of mass of the electron clouds.

For an adsorbed oxygen molecule, the bond weaking was obtained by the classical method [6].

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