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Orbital-Symmetry Rules for Chemisorption and Catalysis*

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A new method, based on orbital-symmetry rules, is suggested for predicting the surface sites of most importance in chemisorption and catalysis. The relationship between the orbital symmetry of reactants and products is often successfully used to predict organic reaction paths. Here we compare the symmetry of the highest occupied and lowest unoccupied absorbate molecular orbitals with the symmetry of the substrate wave functions $\phi(k_F)$ as obtained in band structure calculations. This comparison is quite distinct from previous suggestions involving the matching of charge densities or the consideration of the wave functions of isolated substrate atoms. The effect of Fermi level changes due, e.g., to doping is naturally obtained. Results for H_2, O_2, N_2, F_2, H, N, O, and F chemisorption on the graphite basal plane are presented.

I. INTRODUCTION

The success and utility of orbital-symmetry rules in understanding reaction mechanisms in organic and inorganic chemistry is now well documented.[1-7] From a set of possible reaction paths for a chemical reaction, the orbital-symmetry rules can show which paths are allowed and which are forbidden. For example, in the simple reaction

$$H_2+D_2\rightarrow 2HD,$$

the mechanism might be thought to be a broadside collision

$$\begin{array}{ccccc} \text{H-H} & & \text{H-H} & & \text{H}\ \ \text{H} \\ & & \cdot\ \ \cdot & & \\ + & \rightarrow & \cdot\ \ \ \ \cdot & \rightarrow & |+| \\ & & \cdot\ \ \cdot & & \\ \text{D-D} & & \text{D-D} & & \text{D}\ \ \text{D} \end{array}\ . \tag{1}$$

The orbital-symmetry rules, however, show that this is a forbidden reaction path. It is obvious that similar information regarding elementary reaction steps of a molecule or atom at the surface of a solid could be very valuable.

In the remainder of this section, we shall briefly outline the orbital-symmetry rules for molecules, following the presentation of Pearson,[4] and give a few examples of their use. In Sec. II we will show how a set of such rules can be deduced which are appropriate to gas-solid interactions. In Sec. III the new rules are applied to the chemisorption of simple adsorbates on graphite.

Suppose two systems A and B, which may be two molecules, are interacting and that the combined system wave function is ψ^{AB} and the separated system wave functions are ψ^A and ψ^B. At sufficiently large separation ψ^{AB} may be written as a product of ψ^A and ψ^B, i.e., $\psi^{AB}=\psi_0^{AB}=\psi_0^A\psi_0^B$. As the systems approach one another and begin to interact, the combined system wave function may be represented by second-order perturbation theory as

$$\psi^{AB}=\psi_0^{AB}+\sum_k\frac{\langle\psi_0^{AB}\,|\,\partial U/\partial Q\,|\,\psi_k^{AB}\rangle}{E_0-E_k}\,\psi_k^{AB}\,, \tag{2}$$

the summation being over all excited states. U is the nuclear-electronic and nuclear-nuclear potential energy and Q is a collection of displacement coordinates representing the "reaction coordinate." It follows from group-theoretic considerations that $\partial U/\partial Q$ must be totally symmetric and hence, for the integrals in (2) to have a nonzero value, the direct product of ψ_0^{AB} and ψ_k^{AB} must be totally symmetric (hence ψ_0^{AB} and ψ_k^{AB} must have the same symmetry). A brief consideration of the second-order-perturbation-theory expression for the energy leads one to conclude that for a reaction to occur with a reasonable activation energy there must be low-lying excited states of the combined reacting system of the same symmetry as ψ_0^{AB}, the ground state of the system.

In order to proceed, one must make some simplifying assumptions. The first simplification is to replace the exact functions ψ_0^{AB} and ψ_k^{AB} by their approximate linear-combination-of-atomic-orbitals–molecular-orbitals (LCAO–MO)-theory counterparts. Provided we are only interested in the symmetry properties of the wave function, this simplification presents no problems because the MO theory correctly shows the symmetries of the excited electronic states. However, we will further assume that the LCAO–MO approximation is sufficient to provide reasonable estimates of the second term in Eq. (2). Then if one is interested only in the order of magnitude of this term, one may consider only the low-lying excited states.[8]

In Fig. 1(a) a schematic representation of an MO approximation to the ground state of ψ^{AB} is presented. ϕ_o^{AB} and ϕ_u^{AB} designate the highest occupied MO and lowest unoccupied MO, respectively. Fig-

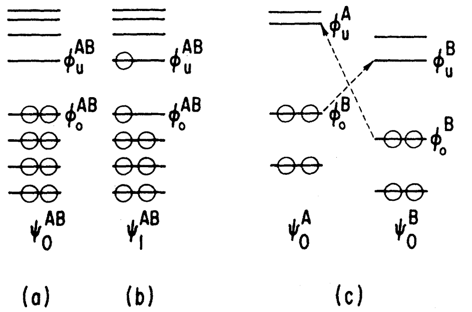


FIG. 1. Schematic representation of an MO approximation to the (a) ground state of Ψ^{AB}, (b) first-excited state of Ψ^{AB}, and (c) ground states of ψ^A and ψ^B.

ure 1(b) shows a schematic representation of the first excited state; thus the symmetry of the product $\psi_0^{AB}\psi_1^{AB}$ is given by $\phi_o^{AB}\phi_u^{AB}$. This may be further simplified by recalling that $\psi_0^{AB}=\psi_0^A\psi_0^B$. In Fig. 1(c), ψ_0^{AB} is represented by an MO approximation in terms of ψ_0^A and ψ_0^B; two possible transitions which would lead to low-lying excited states with charge transfer A and B are suggested by the dotted arrows.

We thus represent the highest occupied and lowest unoccupied molecular orbitals (ϕ_o and ϕ_u) of two molecules A and B as ϕ_o^A, ϕ_u^A and ϕ_o^B, ϕ_u^B, respectively. In order to conclude whether an elementary process is allowed or forbidden, one assumes that the major effects are due to the initial interaction between ϕ_o^A and ϕ_u^B or ϕ_u^A and ϕ_o^B. These are the critical orbitals and as the molecules approach, electrons will flow from ϕ_o to ϕ_u. *Then for a reaction path to be allowed,* ϕ_o^A *and* ϕ_u^B *or* ϕ_u^A *and* ϕ_o^B *must have the same symmetry properties*, i.e., *they must have a net positive overlap.*

The energy differences between ϕ_o and ϕ_u can be used to define a "degree of forbiddenness"—the larger the difference, the higher the potential barrier which must be overcome for the reaction to take place and the more forbidden it is said to be.

It should be emphasized that one must know that the over-all reaction $A+B\rightarrow C+D$ occurs; the symmetry rules only tell us how it can take place. The more general question of whether the reaction takes place is one of thermodynamics and kinetics.

Let us consider a few examples. In the case of the reaction $H_2+D_2\rightarrow 2HD$ mentioned above, ϕ_o is a $\sigma(s)$ bonding orbital and ϕ_u is a $\sigma^*(s)$ antibonding orbital [Fig. 2(a)]. It is clear that in the reaction of Eq. (1), $\phi_o^{D_2}$ and $\phi_u^{H_2}$ do not have a net positive overlap and hence the reaction is forbidden.

Does the reaction $N_2+O_2\rightarrow 2NO$ take place by a four-center process similar to Eq. (1)? In this case, we have two alternatives: $\phi_u^{O_2}$ interacting with $\phi_o^{N_2}$, or $\phi_o^{O_2}$ interacting with $\phi_u^{N_2}$. $\phi_o^{N_2}$ is a σ (bonding) orbital [Fig. 2(b)] and $\phi_u^{N_2}$, $\phi_u^{O_2}$, and $\phi_o^{O_2}$ are π^* (antibonding) orbitals [Figs. 2(b) and 2(c)]. From a consideration of the orbitals in Fig. 2, it is clear that the combination of $\phi_u^{O_2}$ and $\phi_o^{N_2}$ does not have a net positive overlap and hence this path is forbidden. For the case of the combination $\phi_o^{O_2}$ and $\phi_u^{N_2}$, there is a net positive overlap; however, the flow of electrons from $\phi_o^{O_2}$ to $\phi_u^{N_2}$ is inconsistent with energy condiderations and electronegativity arguments. Thus, although the path is symmetry allowed, it is physically forbidden. This latter case shows that a combination of the symmetry rules and simple physical arguments is more powerful than either alone.

An example of a simple symmetry-allowed reaction is $H+D_2\rightarrow HD+D$. ϕ_o^H is a hydrogen 1s orbital [Fig. 2(e)] and $\phi_u^{D_2}$ is a $\sigma^*(s)$ orbital [Fig. 2(a)]. In a collinear encounter, a net positive overlap is obtained. Hence the over-all reaction $H_2+D_2\rightarrow 2HD$ is a result of two simple steps: $H_2\rightarrow 2H$ and $2H+D_2\rightarrow 2HD$ as well as these two steps with the hydrogen and deuterium species interchanged. It should be pointed out that in each of the simple cases considered above and in many other more complex cases which have been considered,[1-7] the symmetry rules are always found to be consistent with experiment.

II. SYMMETRY RULES FOR SUBSTRATE-ADSORBATE INTERACTIONS

In analogy to the molecular case considered above, we will here assume that the major effects responsible for a reaction at the surface of a solid are due to the initial interaction of the highest occupied and lowest unoccupied crystal orbitals, $\{\phi_o\}$ and $\{\phi_u\}$, and the highest occupied and lowest unoccupied molecular (or atomic) orbitals, ϕ_o and ϕ_u. For the case of the crystal, $\{\phi_o\}$ is the set of occupied states at energies in a small energy region below E_F which occur at the surface of the crystal; E_F is the Fermi energy. Likewise, the set of orbitals

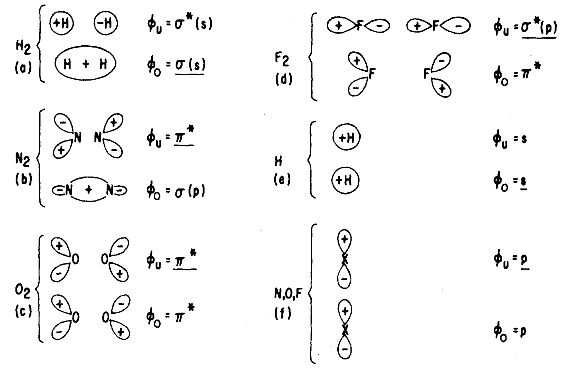


FIG. 2. Schematic representation of the relevant molecular orbitals for the homonuclear diatomics [(a)–(d)] and atomic orbitals [(e)–(f)]. The underlined orbitals are involved in chemisorption on graphite.

$\{\phi_u\}$ is of those which occur in a small energy region above the Fermi level.

In the bulk of the crystal, the orbitals $\{\phi_o\}$ and $\{\phi_u\}$ are determined by a band-structure calculation. However, for the surface, no viable computation procedure of sufficient accuracy has been advanced as yet for the calculation of the wave functions. Hence, in what follows, we will have to assume that the wave functions at the surface of a crystal can be reasonably approximated by the bulk states. In some cases, this is not a bad approximation (e.g., in graphite and other laminar materials), but in other cases, it is quite inappropriate (e.g., silicon, where localized surface states and reconstruction occur). It should be emphasized, however, that if one can determine the appropriate states at the surface near the Fermi energy for a general material, then in principle the symmetry rules outlined below should apply and give reliable predictions. In his catalysis studies, Mango[7] has previously considered the substrate atoms to be isolated and thus did not treat band effects.

We can now state the procedure for determining whether an elementary reaction process at a surface is allowed.

(i) From the bulk band strucutre of the solid, the wave functions for the surface are determined.

(ii) The wave functions (crystal orbitals) so determined are expressed in terms of a linear combination of Bloch functions $b_i(\vec{k})$:

$$\phi_{\vec{k}} = \sum_i C_i(\vec{k})\, b_i(\vec{k}). \qquad (3)$$

The Bloch functions are taken as a linear combination of atomic orbitals:

$$b_i(\vec{k}) = N \sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu}\, \chi_i(\vec{r}-\vec{R}_\nu), \qquad (4)$$

where $\chi_i(\vec{r}-\vec{R}_\nu)$ is an atomic orbital of type i centered at the point $\vec{R}_\nu$ and the sum is over all equivalent lattice sites.

(iii) Only those $\phi_{\vec{k}}$ which have eigenvalues close to the Fermi energy and are in a high-density-of-states region are explicitly considered. These one-electron states are the orbitals $\{\phi_o\}$ and $\{\phi_u\}$ mentioned above. From the band structure and the use of Eqs. (2) and (3), the symmetry properties of these orbitals are determined in terms of atomic orbitals.

(iv) The symmetry properties of the molecular orbitals ϕ_o and ϕ_u for the molecular reactant under consideration are determined (or the corresponding atomic orbitals in the case of an atomic reactant).

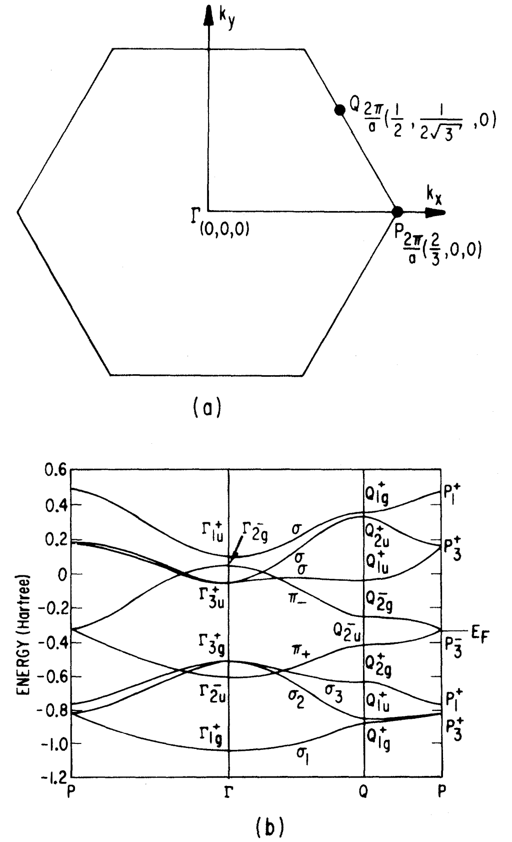
(v) Simple chemisorption or dissociative chemisorption will occur only if the wave functions $\{\phi_o\}$ and ϕ_u or $\{\phi_u\}$ and ϕ_o are such that, at a given site on a given plane of the solid, they transform locally according to the same irreducible representation of the appropriate symmetry group (i.e., they must have a net positive overlap).

In order to illustrate this procedure, we apply it to some atomic and diatomic adsorbates on a graphite surface.

III. APPLICATION TO CHEMISORPTION ON GRAPHITE

We illustrate the above rules with a consideration of the dissociative chemisorption of some simple diatomic gases (H_2, N_2, O_2, and F_2) and chemisorption of their constituent atoms (H, N, O, and F) on a graphite basal surface. Chemisorption on graphite has been the subject of a series of MO calculations.[9-11] It is a particularly straightforward example of the orbital-symmetry rules since the graphite band structure in the vicinity of the Fermi surface is very simple.

With the use of a two-dimensional representation of the material, a calculation of the energy bands[12] along the symmetry lines of the Brillouin zone shows that graphite has occupied and unoccupied states close to the Fermi level along the lines Γ-Q-P-Γ (see Fig. 3). The two relevant bands are degenerate at the point P with symmetry P_3^- and consist of p_z orbitals oriented perpendicular



(a)

(b)

FIG. 3. (a) Brillouin zone and (b) band structure of Painter and Ellis (from Ref. 12) of two-dimensional graphite.

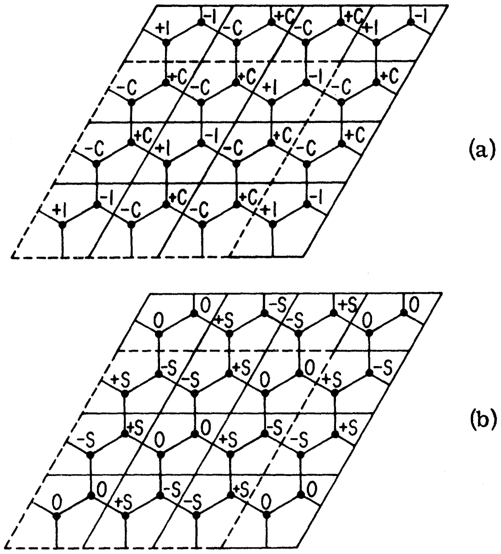


FIG. 4. (a) Real and (b) imaginary parts of the coefficients of the p_z orbitals which comprise the wave functions of the π_- band at the P point in the Brillouin zone. The coefficients at various sites in a 3×3 representation are shown. C and S are, respectively, the cosine and sine of 60°.

to the surface plane. The conduction band which has Γ_{2g}^- symmetry at the center of the Brillouin zone consists of an antibonding combination π_- of orbitals on the two sites in a unit cell. The valence band, which has Γ_{2u}^- symmetry, consists of a bonding combination π_+ of orbitals on those two sites. The other bands are further from the Fermi level and, in addition, have no lobes pointing out of the surface. When interaction between the two-dimensional planes is included, semimetallic behavior is obtained. The number of holes in the valence band and electrons in the conduction band is small, however, compared to the number of electrons and holes, respectively, in those bands.

We thus confine our attention to the results of a two-dimensional calculation. The π_- and π_+ bands, in the vicinity of the Fermi level, correspond, respectively, to the $\{\phi_u\}$ and $\{\phi_o\}$ states characteristic of the substrate. In order to consider their symmetry properties, we plot the phase of the p_z orbital at each site for the symmetry point P of the Brillouin zone, since the relevant electron states have their wave vectors in the vicinity of that point. Figures consisting of 3×3 unit cells are, in general, sufficient to show all distinct sites. There are two figures (corresponding to the real and imaginary parts of the wave function) for each of the two bands. Figures 4(a) and 4(b) show the phase maps for the π_- conduction band. Figures 5(a) and 5(b) are for the π_+ valence band.

We consider adsorbate species approaching the surface along paths perpendicular to the points α—at a carbon atom, β—between two nearest-neighbor carbon atoms, and γ—at the center of a six-carbon-atom ring. There are 18 α sites, 27 β sites, and 9 γ sites within the 3×3 representation.

For concerted dissociative adsorption of diatomic species, two surface sites must be involved since the carbon atoms of the substrate can form, at most, one bond each. Thus no such adsorption occurs over an α site. In addition, no dissociative adsorption occurs at a β or γ site when the diatomic axis is perpendicular to the surface plane.

A study of the behavior of the atomic species requires an examination of s and p atomic orbitals; comparable treatment of the diatomic species requires examination of $\sigma(s)$, $\sigma^*(s)$, $\sigma(p)$, $\sigma^*(p)$, and π^* orbitals. The orbitals are shown schematically in Fig. 2. The orientations of some typical orbitals above the three types of sites are shown in Fig. 6. Only the lobe(s) in the plane closest to the surface are considered in determining matching symmetry. Above position β, when two lobes are in the plane, they are assumed to point toward the two carbon atoms. Above position γ, we consider the six distinct symmetric orientations for such orbitals.

The criteria used for assigning a matching or nonmatching symmetry of the adsorbate and surface wave functions is quite simple. Above an α site, a single adsorbate lobe is always able to adjust its phase to allow matching symmetry. For

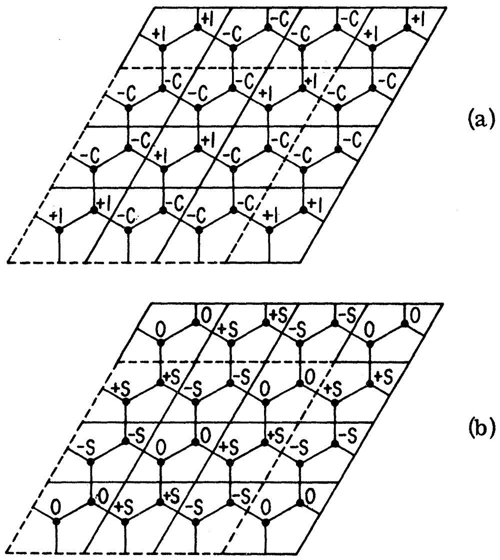


FIG. 5. (a) Real and (b) imaginary parts of the coefficients of the p_z orbitals which comprise the wave functions of the π_+ band at the P point in the Brillouin zone. The coefficients at various sites in a 3×3 representation are shown. C and S are, respectively, the cosine and sine of 60°.

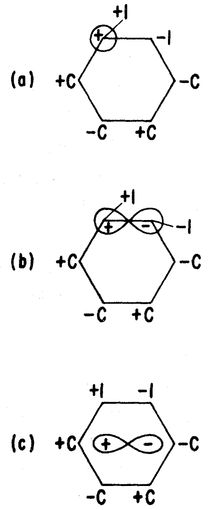


FIG. 6. The adsorbate lobes closest to the substrate plane for (a) an atomic *s* orbital above point α, (b) a π^* orbital above point β, and (c) a π^* orbital above point γ, the other possible orientations of which can be obtained by performing a series of 30° rotations on the π^* orbital about point γ. The substrate phase diagram is associated with the real part of the π_+ wave function at the *P* point in the Brillouin zone. *C* represents the cosine of 60°.

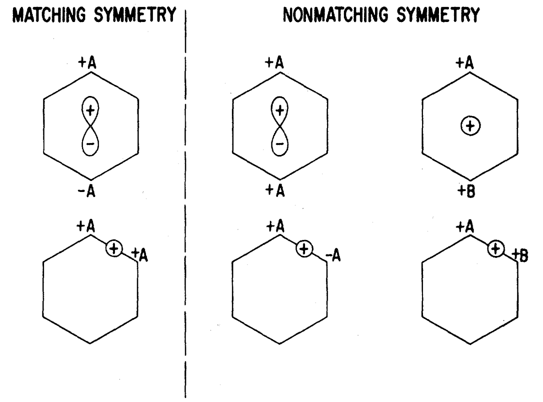


FIG. 7. Some symmetry configurations at the three types of substrate sites for typical orbitals. The letters *A* and *B* represent the coefficients of the real (or imaginary) part of the substrate wave function.

matching symmetry above a β or γ site, we demand that the relevant surface orbitals *all* have the signs and magnitudes required for matching with the adsorbate lobes (remembering, of course, that only the relative signs of the adsorbate lobes are meaningful). A schematic representation of some examples of these criteria is shown in Fig. 7. Figures 6(a)–6(b) are also all examples of matching symmetry.

The number of sites of a given type within a 3×3 representation at which matching symmetry exists with respect to either real or imaginary parts of the wave function is given in Table I. The diatomic axis and the atomic *p* orbital are assumed to be parallel to the surface plane. Note that the interatomic separation in F_2 (1.435 Å) is such that the two *p*-like parts of the $\sigma^*(p)$ orbital lie directly above carbon atoms when F_2 is over position β, hence the entry of "zero" under point β for $\sigma^*(p)$ in Table I. When the adsorbate orbital gains electrons, its symmetry must match that of the substrate orbitals $\{\phi_o\}$—i.e., the wave functions of the π_+ band. When the adsorbate orbital loses charge, its symmetry must match that of the substrate orbitals $\{\phi_u\}$—i.e., the wave functions of the π_- band.

Figure 2 gives the orbitals involved in electronic charge transfer for all the adsorbate species considered. Only atomic chemisorption and dissociative chemisorption of diatomics are considered here; single-site adsorption of diatomics is ignored. Consideration of the orbitals in Fig. 2 leads to the conclusion that O_2 and F_2 may dissociatively chemisorb only by a gain of electronic charge. The underlined orbitals in that figure are the ones which electronegativity arguments indicate are relevant for adsorption of the various species on graphite.

TABLE I. Symmetry matches at adsorption sites.

	Adsorption sites (adsorbate loses electrons)			Adsorption sites (adsorbate gains electrons)		
Adsorbate orbitals	α	β	γ	α	β	γ
s	18	6	0	18	15	0
$\sigma^*(s)$, π^*, *p*	0	15	9	0	6	3
$\sigma(s)$, π, $\sigma(p)$	18	6	3	18	15	9
$\sigma^*(p)$	0	0	9	0	0	3

Hence, from the information of Fig. 2, together with the number of matching sites of a particular type from Table I, a prediction of the relative probability of the binding of a given species at the α, β, and γ sites is permitted. The fraction of sites of a given type at which a particular species will chemisorb is given in Fig. 8. For atomic N, O, and F, the result given in Fig. 8 is obtained by taking the union of allowed *s* and *p* matching sites obtained from Table I, since a *p* orbital perpendicular to the graphite plane has the same symmetry, for its lower lobe, as an *s* orbital.

The information is specific in predicting the relative probability of adsorption of particular dia-

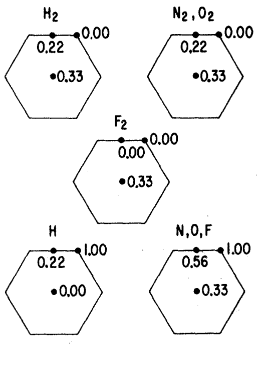


FIG. 8. Fraction of sites of a given type at which a particular adsorbate binds in the 3×3 representation.

tomics at definite graphite surface sites: (i) None of the diatomics dissociatively chemisorb directly over a carbon atom and (ii) F_2 will not dissociatively chemisorb over the midpoint between two nearest-neighbor carbon atoms.

The hydrogen atom is predicted to favor the site directly above a carbon atom and never approach the center of a carbon ring. Atomic N, O, and F have allowed sites between nearest-neighbor carbon atoms and in the center of carbon rings. These observations are in accord with the detailed atomic chemisorption calculations presented previously.[10]

More detailed predictions might be made by comparing the electron affinities (and ionization potentials) at the adsorbate with the graphite work function (~4.38 eV). For example O_2 has an electron affinity of ~0.43 eV, while N_2^- is not stable. Thus, O_2 dissociative adsorption should be favored in accord with Eq. (2) compared to N_2 dissociative adsorption even though the percentage of allowed sites (Fig. 3) is the same for the two species.

Predictions based on the overlap of "charge clouds" would be very different than those above. Charge-cloud reasoning[13] would, for example, predict hydrogen to bind at the center of carbon rings.

Again, we should emphasize that the above predictions (summarized in Fig. 8) concerning dissociatiave chemisorption of diatomics on graphite are not saying that such reactions take place—they are only saying that if such reactions do take place, that they will occur as specified above. There is, at present, a lack of good quality experimental information on these systems with which to compare our results although, experimentally, atomic species do appear to adsorb more readily than diatomics.[14]

It is interesting to speculate on the significance of wave-function patterns such as in Figs. 4 and 5 for the understanding of low-energy-electron-diffraction (LEED) results of chemisorbed species on metals. It is known that LEED gives results which can be interpreted as a definite pattern of chemisorbed species repeated periodically. Since wave-function patterns such as Figs. 4 and 5 also have a definite periodic pattern, it is possible that the wave-function nodes are responsible for the nonuniform coverage on the surface and for the corresponding pattern that is produced. Much more work along these lines is obviously needed before any definitive statements can be made.

We now consider the effect of changes in the Fermi level on adsorption predictions. In the present graphite example, these changes are small. If the π_- conduction band is partially filled then reactions, which involve charge transfers to the adsorbate, have their electrons originate in that band rather than in the π_+ conduction band; i.e., the wave functions of the π_- band rather than those of the π_+ band serve as the $\{\phi_o\}$ for the graphite substrate. The number of favorable symmetry matches for a given type of site (Fig. 8) is sometimes changed, but the number of "yes" or "no" predictions is not. Thus, for example, from Table I, when the π_- band is partially filled there are 15 rather than 6 favorable sites in the 3×3 representation for N_2 or O_2 dissociation at a β site when the molecular axis is parallel to the surface.

In other situations, binding changes associated with shifts of the Fermi level may be more dramatic. For example, in a one-dimension chain of atoms each with a single *s* orbital, the phase variation along the chain changes radically as the band is filled. The evaporation of doped thin films on a substrate and the subsequent investigation of binding phenomena might allow an investigation of Fermi level effects.

Although our predictions for chemisorption on graphite are rather specific, they depend somewhat on the particular matching criteria chosen. More detailed investigations of adsorption on a series of transition-metal surfaces will allow the further development of this approach.

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