

Toward A Coherent Theory of Chemisorption

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Heterogeneous catalysis is crucial in the production of most industrial chemicals and therefore has become a focus of intense efforts in both industry and academia. Although recent developments in catalysis are impressive, they fall short of chemists' expectations. Catalyst development is still a matter of trial-and-error efforts, intuitive assessments, and, of course, a great deal of luck. The reason for this is that the course of a catalytic reaction is determined by many factors, both thermodynamic and kinetic, and the composition and structure of a catalyst may be critical. An important point is that all heterogeneous processes, whether simple or complex, have chemisorption as a necessary first step. Thus, the dissection of catalytic processes into primary events amenable to scientific inquiry must begin with an understanding of chemisorption.

Tremendous advances in describing chemisorption phenomena have led to the acquisition of an enormous amount of diverse information (1-5), but understanding has not kept pace with the accumulation of facts. Having encountered some troublesome examples in our practical work and failing to find coherent explanations within the current theoretical models, we searched for a better explanation of the paradoxical chemisorption phenomena. In this article, we describe some of our theoretical results, which concern the most fundamental aspects of chemisorption. Specifically, we describe relations among seemingly disparate aspects of chemisorption, such as adsorbate bond activation, the heat of chemisorption, adsorbate registry and stereochemistry, barriers for adsorbate surface migration and for adsorbate (molecular) dissociation, work-function changes, and core binding-energy shifts. Our approach combines, in a complementary fashion, both analytical and computational facets.

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New Theoretical Developments

Periodic regularities of the heat of chemisorption. The heat released on chemisorption (Q) determines the course of surface reactions, so that knowledge of the variations of Q —especially its periodic behavior—is a primary theoretical target. For atomic radicals such as H, O, and N, the values of Q monotonically

Summary. Studies of chemisorption phenomena, the cornerstone of heterogeneous catalysis, have become the central part of contemporary surface science. As a result of the great variety of the available experimental techniques, a backlog of information, some of which conflicts with current theoretical constructs, has accumulated. New models that combine analytical and computational facets have now begun to appear, revealing intrinsic relations among seemingly disparate chemisorption phenomena. Among the major findings are (i) the crucial role of antibonding adsorbate orbitals in bond activation and in the heat of chemisorption, (ii) adsorbate-induced surface polarization leading to a decrease of the metal work function and to an increase of the surface core binding energy, and (iii) important differences between atomic and molecular adsorbate modes of bonding and surface migration.

decrease from left to right along a particular series of the periodic table and typically down a column. This decrease is not significant for monovalent H but becomes quite apparent for divalent O and especially trivalent N, although the values are not simply proportional to the number of unpaired valence electrons. The periodic regularities for molecules are less pronounced and more complex. In particular, for strong acceptors such as CO and NO, Q changes only slightly and rather nonmonotonically, showing even a reverse trend compared with adatoms. Some representative data are given in Table 1. The current theoretical models are able to describe the monotonic atomic patterns (6-8) but fail to reproduce the nonmonotonic molecular behavior (7).

In an attempt to achieve a more coherent understanding, we developed a simple model of Q (5, 9, 10). This model is based on perturbation theory and uses the constant d -density approximation, which is effective in treating the cohe-

sion energy regularities for transition metals and their alloys (11). The notations used are given in Fig. 1.

The major feature of the metal band structure is the presence of a huge reservoir of electrons and electronic states and the presence of the Fermi energy E_F separating the occupied part of the d band of width W^{occ} from the vacant part of width W^{vac} ($W = W^{occ} + W^{vac}$). The Fermi energy does not change significantly under chemisorption. The value of Q includes a contribution from the direct metal-adsorbate interaction, similar to that in coordination compounds, and a contribution from the redistribution of electron density required to maintain the constant E_F specific for chemisorption bonding. As a result, the structure of Q appears to differ for donor, acceptor, and radical adsorbates, as do their periodic variations.

Within the Hückel-type approximation, the first-order perturbation results are as follows:

1) For a lone-pair donor adsorbate, Q^D is roughly proportional to the metal d -hole count $N_h = 10 W^{vac}/W$ and inversely proportional to $E_F - \epsilon_A$, namely

$$Q^D \propto \frac{\beta^2 N_h}{E_F - \epsilon_A} \quad (1)$$

where β is the Hückel resonance integral and ϵ_A is the lone-pair energy. Because $|E_F|$ increases only slightly from left to right along the transition series but N_h decreases significantly, one can expect Q to decrease monotonically in this direction and to be especially small for the late transition metals (N_h is very small, so that the bonding situation is similar to that in the He dimer).

2) For a vacant-orbital acceptor adsorbate, Q^A may depend on how close the orbital energy ϵ_A^* is to E_F and the value of the resonance integral β^* . In particular, for moderate acceptors where $\beta^*/(\epsilon_A^* - E_F) \leq 1$, we have

$$Q^A \propto \frac{\beta^{*2} N_d}{\epsilon_A^* - E_F} \quad (2)$$

that is, Q^A is proportional to the d occupancy $N_d = 10 W^{\text{occ}}/W$, which is just opposite to the dependence of Q^D on N_d in Eq. 1 because $N_h = 10 - N_d$. For strong acceptors with $\beta^*/(\epsilon_A^* - E_F) \gg 1$, the dependence of Q^A on N_d and N_h appears to be nonmonotonic and may show parabolic character analogous to classic cohesive energy behavior (11), namely

$$Q^A \propto \beta^* N_d N_h \quad (3)$$

Such a behavior is typical for CO (Table 1).

3) For a radical adsorbate, in which a singly occupied orbital lies below the Fermi level ($\epsilon_A < E_F$), there can be significant charge transfer, so that some self-consistent adjustment of the initial energy ϵ_A and of the resulting occupancy of the chemisorption levels must be made. The resulting heat of chemisorption Q^R for a k -valent radical is

$$Q^R = (E_F - \epsilon_A)^2/2U_A + kn\beta^2[\ln(W^{\text{vac}}W^{\text{occ}}/\beta^2) + 3/2]/W \quad (4)$$

where U_A and n are scaled parameters (10). Quantitative estimates made with Eq. 4 are highly accurate, errors being typically less than 5 to 10 percent (10). Because $|E_F|$ increases monotonically from left to right within groups VI through VIII of the periodic table, the E_F -dependent term in Eq. 4 decreases in this direction. We can also foresee that Q^R will increase as k increases but at less than the first power, because only the second term in Eq. 4 is k -dependent. Thus, all the major periodic trends in Q mentioned above can be understood in terms of Eqs. 1 to 4 [for computational details, see (5, 12)].

The crucial role of the antibonding adsorbate orbitals in bond activation. Saturated molecules such as H_2 or CH_4 and lone-pair molecules such as NH_3 have very high energy vacant antibonding σ^* orbitals well above the vacuum level. For this reason, the σ^* ligand orbitals in transition-metal complexes are commonly neglected in descriptions of bonding, and saturated or lone-pair molecules are considered to be exclusive donors. For example, recent theoretical analyses (13) of hydrogen addition to or elimination from transition-metal complexes have not explicitly considered the d - σ^* interactions.

But even when these molecular rules of the game are applied, they may fail in the case of chemisorption. First, the Fermi level that separates occupied metal states from vacant states becomes an analog of the molecular frontier orbitals, highest occupied and lowest vacant. The Fermi energies and the frontier orbital

Table 1. Heats of chemisorption for some atomic and molecular adsorbates. Examples are given for ordered transition metal surfaces of high atomic density with the stated Miller indices. The first three metal entries compare changes within a column, and the latter three compare changes across the 5d series (3-5, 10).

Metal surface	Heat of chemisorption (kcal/mol) for				
	H	O	N	CO	NO
fcc Ni(111)	63	130	135	27	25
fcc Pd(111)	62	87	130	34	31
fcc Pt(111)	60*	85	127	32	27
fcc Ir(111)	63	93	127	34	20
bcc W(110)	68	104-129	155	27	D†

*From R. J. Madix (37).

†Dissociated.

energies differ significantly. Typical values of $|E_F| = 4.5$ to 5.5 electron volts, as defined by the transition-metal work function, can be contrasted with the atomic d -orbital ionization potentials ranging from 8 to 12 eV. Thus, metal surfaces are better electron donors than metal complexes or clusters and interact more significantly with σ^* and π^* adsorbate vacant orbitals. Second, the antibonding σ^* and π^* orbitals overlap with the metal d orbitals more strongly than do their bonding σ and π counterparts. The reason, which went unnoticed until recently (14), is that the normalized LCAO-MO coefficients are larger in $\sigma^*(\pi^*)$ than they are in $\sigma(\pi)$ (LCAO-MO is a linear combination of atomic orbitals representing a molecular orbital). For example, the bonding ψ and antibonding ψ^* LCAO-MO for a homonuclear molecule X_2 , such as H_2 , N_2 , or O_2 , are

$$\begin{aligned} \psi &= [2(1 + S)]^{-1/2} (\chi_1 + \chi_2) \\ \psi^* &= [2(1 - S)]^{-1/2} (\chi_1 - \chi_2) \end{aligned} \quad (5)$$

where S is an overlap integral between the interacting atomic orbitals χ_1 and χ_2 . Thus, in a linear fragment $M-X_{(1)}-X_{(2)}$ we have for the interacting metal orbital $\chi_M(d_{z_2} \text{ or } d_{xz})$

$$\begin{aligned} \beta &= \langle \chi_M | H | \psi \rangle \\ &= [2(1 + S)]^{-1/2} (\beta_1 + \beta_2) \end{aligned} \quad (6)$$

$$\begin{aligned} \beta^* &= \langle \chi_M | H | \psi^* \rangle \\ &= [2(1 - S)]^{-1/2} (\beta_1 - \beta_2) \end{aligned} \quad (7)$$

where H is the Hamiltonian. Assuming $|\beta_1| \gg |\beta_2|$, since the resonance integral is a strong function of the metal-adsorbate distance, we have

$$\beta^*/\beta \approx (1 + S)/(1 - S) \quad (8)$$

Thus, for typical values of $S = 0.3$ to 0.6 , $(\beta^*)^2/\beta^2 \approx 2$ to 4 . Because typically $E_F - \epsilon_A \gg$ both the numerator and the denominator favor acceptor bonding when we compare Eqs. 1 and 2.

Table 2 illustrates the metal-adsorbate (M-A) charge transfer found by straight-

forward calculations for H, Cl, CH_4 , CO, and NH_3 on an fcc(111) surface of a five-layer metal film (15). Even CH_4 and NH_3 behave as acceptors. The predominant role of σ^* in chemisorption was further corroborated in a subsequent comprehensive study (16).

Adsorbate-induced surface polarization. The energy required to remove an electron from a metal to vacuum is the work function ϕ . It is a common practice to explain changes in the metal work function $\Delta\phi$ induced by chemisorption solely through formation of an M-A electrostatic dipole moment (I). If the work function decreases ($\Delta\phi < 0$), the adsorbate A is deduced to be more electropositive than the metal M, or if the work function increases ($\Delta\phi > 0$), A is considered to be more electronegative. The behavior of $\Delta\phi$ found experimentally for various adsorbates and surfaces is rather bizarre if the explanation described above is universally true. For example, for a given metal M, adatoms such as H, N, S, and Cl often give $\Delta\phi < 0$ on highly dense surfaces but $\Delta\phi > 0$ on low-atomic-density surfaces (17, 18). Moreover, the sign of $\Delta\phi$ for a given surface may depend upon the adsorbate coverage. For example, $\Delta\phi < 0$ at low coverage of Cl on Pt(111) and $\Delta\phi > 0$ at high coverage (18).

The conventional explanation of the reversal of the sign of $\Delta\phi$ is the reversal of the M-A electrostatic dipole moment, $M^{\delta-}-A^{\delta+}$ ($\Delta\phi < 0$) or $M^{\delta+}-A^{\delta-}$ ($\Delta\phi > 0$), respectively. But it is hard to comprehend how adsorbate atoms that are more electronegative than the metal surfaces may become electropositive. It appears that the conventional interpretation of the work-function change under chemisorption is strongly deficient, and non-electrostatic factors must be considered.

An explanation of this behavior comes from the fact that, for a particular metal, its surfaces have different values of ϕ , which are larger for densely packed surfaces than for loosely packed surfaces. This anisotropy in ϕ may be as large as 1

eV and often exceeds $\Delta\phi$ caused by chemisorption. The only source of the anisotropy in ϕ is surface polarization leading to formation of the intrinsic surface dipole moment (19), because clean metal surfaces are electrostatically neutral. We therefore assumed that this surface dipole moment is affected by chemisorption as well. The adsorbate-induced change $\Delta\phi$ consists of two contributions, $\Delta\phi_{\text{ext}}$ from the external electrostatic dipole moment and $\Delta\phi_{\text{int}}$, the new term due to internal polarization dipole moment

$$\Delta\phi = \Delta\phi_{\text{ext}} + \Delta\phi_{\text{int}} \quad (9)$$

We have analyzed this new $\Delta\phi_{\text{int}}$ term within the LCAO-MO tight-binding approximation, both analytically by first-order perturbation theory (20) and computationally by straightforward metal-film calculations (15). We found that all atomic and molecular adsorbates cause uniform changes in surface polarization, shown schematically in Fig. 2c. More precisely, all adsorbates decrease the surface d density and induce the out-of-phase d - p orbital rehybridization, leading to formation of the surface dipole moment directed to the bulk and therefore decreasing the metal work function ($\Delta\phi < 0$). This uniform pattern for adsorbates as diverse as H, Cl, NH_3 , CO, and CH_4 is illustrated by metal-film calculations (Table 2).

As indicated above, most adsorbates behave as acceptors on metal surfaces. Thus, in Eq. 9 the two terms typically have opposite signs ($\Delta\phi_{\text{ext}} > 0$, whereas $\Delta\phi_{\text{int}} < 0$) so that the resulting sign of $\Delta\phi$ is determined by a balance of these opposite contributions. Our model predicts that the electrostatic term $\Delta\phi_{\text{ext}} > 0$ will be the least positive and the polarization term $\Delta\phi_{\text{int}} < 0$ will be the most negative on the most densely packed surface. These surfaces are prone to show a decrease in work function ($\Delta\phi < 0$) under chemisorption. This conclusion, based on our model, makes understandable the seemingly bizarre patterns of $\Delta\phi$ mentioned above. Most recently, our model has gained further support from the ab initio band-structure calculations for sulfur adsorbed on Rh(100) (21), which revealed an unexpected decrease in work function despite the conventional charge transfer $\text{Rh}^{\delta+}-\text{S}^{\delta-}$, and this decrease ($\Delta\phi < 0$) was due to the surface polarization (rehybridization).

The core binding energy of an atom is the energy required to ionize a core electron of the atom. The core binding energy of atoms on the surface differs from that in the interior of transition

Table 2. Effective charge q and polarization dipole change $\Delta\mu$ under chemisorption. Results are typical calculations for an fcc(111) surface of a five-layer metal film of a late transition metal (15). See text.

Ad-sorbate	q (atomic units)	$\Delta\mu$ (Debye)
H*	-0.37	-0.05
Cl*	-0.54	-0.14
CH_4^*	-0.08	-0.22
$\text{CH}_4^\dagger$	-0.17	-0.04
CO^*	-0.30	-0.19
$\text{NH}_3^\dagger$	-0.03	-0.15

*On-top site. † Hollow C_{3v} site.

metals. The peak of the core binding energy on the surface may be shifted by the presence of adsorbates. Our model allows an explanation of these shifts in terms of surface rehybridization rather than charge transfer. It is commonly accepted (22–24) that for late transition metals with more-than-half-occupied d bands, the local d density increases as the number of the metal nearest neighbors decreases; the opposite behavior is found for early transition metals with less-than-half-occupied d bands. For example, it has been shown experimentally (22) and theoretically (23, 24) that, for metals on the right half of the 5d transition series such as W, Ir, and Pt, the $4f_{7/2}$ core binding energies decrease from the bulk to surface metal atoms. Again, no charge separation can be invoked to explain this behavior for clean metal surfaces, but rather a d - sp rehybridization

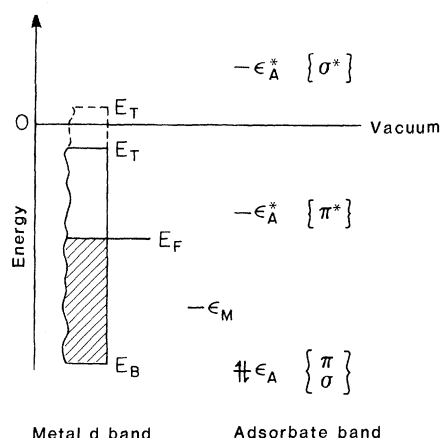


Fig. 1. Energy diagram of the metal-adsorbate band-structure interactions. The metal d band is spread out (E_B is the bottom energy, E_T is the top energy, which may be either below or above vacuum; E_F is the Fermi energy). The adsorbate bands at least for low coverage are very narrow (almost degenerate). Shown are typical positions of the adsorbate levels, occupied ϵ_A (σ or π) and vacant ϵ_A^* (π^* below vacuum but σ^* above vacuum), as well as a position of an atomic metal d orbital ϵ_M .

affecting the Coulomb potential in the metal core. We saw above that the persistent pattern of chemisorption is a decrease of the surface d density. Thus, our model predicts that all adsorbates will increase core binding energy.

We tested our polarization mechanism by experimentally measuring surface $4f_{7/2}$ core shifts for ordered Pt surfaces chemisorbing diverse adsorbates such as CO, NH_3 , and K (25). For each adsorbate, the $4f_{7/2}$ surface core binding energy increases. Final-state relaxation effects, which are often discussed in photoemission (24, 26), cannot explain the direction of the shift. We conclude that chemisorption phenomena such as the surface core shifts and work-function changes are primarily determined by the adsorbate-induced surface polarization or rehybridization but not the adsorbate-surface charge transfer.

Surface migration and dissociation of adsorbates. Surface migration phenomena involving lateral motion of an adsorbate along a metal surface are potentially rate limiting in desorption of dissociated species in many catalytic processes (2). Experimental observations show that the migration activation barrier ΔE^* typically equals 10 to 25 percent of the heat of chemisorption Q (1–3), but there were no specific theoretical arguments explaining this experimental range.

Migration and dissociation of adsorbates involves changes in the coordination mode of the metal site $\text{M}_n\text{-A}$, where n is the coordination number of adsorbate A, and in the M–A distances. Thus, it is crucial to choose a potential for the M–A interaction that can reproduce the equilibrium minima as well as other points on the potential energy curves. We have chosen the simplest potential, namely, the Morse potential (Eq. 10), following the “Occam’s razor” philosophy. More specifically, we describe each two-center M–A interaction by Eq. 10, where the total energy $E(r, x)$ relates to the bond order x (Eq. 11), which is an exponential function of the M–A distance r . Here a is a screening parameter, and Q_0 and r_0 are the bond energy and distance at equilibrium

$$E(x) = Q_0(x^2 - 2x) \quad (10)$$

$$x = \exp[-(r - r_0)/a] \quad (11)$$

where $x = 1$, by definition. Some justification of the Morse potential curve comes from its similarity to the universal binding-energy plots recently demonstrated numerically (27) and analytically (28) for various cases of metallic binding. We have further assumed that the multi-

center M_n -A interactions are pairwise additive and that the total M_n -A bond order is normalized to unity and conserved along a migration path up to the dissociation point. One can add that bond-order conservation for various gas-phase three-center interactions is known to be a very accurate criterion (29).

In the analytical model we have limited the M_n -A interactions to nearest metal neighbors. In the straightforward computations, we have treated a five-layer metal film for which the number of metal atoms involved exceeded 1000. Also, in the film computations, an energy-minimization criterion along with bond-order conservation was examined. The analytical results are rigorous (29) and fully consistent with the computational analyses for a broad range of the relevant parameters (30). Since the atomic migration patterns might differ greatly from the molecular migration patterns, we describe them separately. Because the model does not explicitly take into account the adsorbate-adsorbate interactions, all of the results, strictly speaking, should be assigned to low (zero) coverage.

Atomic Migration

The M_n -A bonding energy Q_n is a monotonic function of the coordination number n for atomic adsorbates A

$$Q_n = Q_0(2 - 1/n) \quad (12)$$

where Q_0 is the two-center M-A bond energy in the on-top position. On highly symmetric surfaces with regular unit meshes M_n such as equilateral triangles, $n = 3$ for fcc(111), or squares, $n = 4$ for fcc(100), the hollow positions of the highest coordination should always be preferred, in full agreement with experiment (1, 4). The relevant value of Q_n (Eq. 12) can be identified with the heat of chemisorption Q_A . Migration on such surfaces is always confined to the hollow $\rightarrow$ bridge $\rightarrow$ hollow path with the barrier

$$\Delta E^* = k_n Q_n, \quad k_n = \frac{n-2}{4n-2} \quad (13)$$

where the proportionality coefficients k_n fall well within the experimental range of $k = 0.1$ to 0.3 (1-3). For the first time, theory explained the interrelation between the migration barrier and the heat of chemisorption mentioned earlier. A typical energy profile computed for atomic migration on a fcc(111) surface is shown in Fig. 3.

Molecular Migration

A diatomic molecule AB interacts with a metal surface separately through the A and B ends within the pairwise additive scheme. Thus, the heat of molecular chemisorption Q_{AB} includes two atomic contributions, Q_A and Q_B , which may have the same or opposite signs. The former case ($Q_A > 0$, $Q_B > 0$) corresponds to a donor AB, with the in-phase LCAO-MO, σ or π , being responsible for the M-AB bonding. The latter case

($Q_A > 0$, $Q_B < 0$) corresponds to an acceptor AB, for which the M-AB bonding involves primarily the out-of-phase LCAO-MO, σ^* or π^* (29-31). Similar results were found for the cases of the fixed and varied A-B bond order. Atom-like migration patterns are predicted (29, 31) for strong donor molecules for which ΔQ monotonically increases with n . This leads to a preferred hollow site and a migration activation barrier identified with the hollow-bridge energy difference. A migration energy profile for a

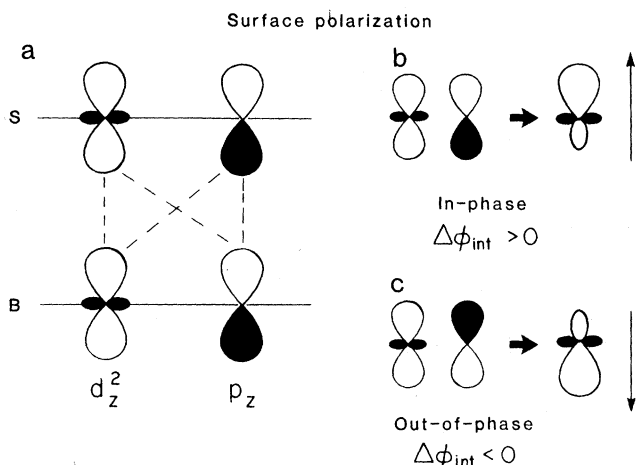


Fig. 2. (a) Mutual orientation of d_{z^2} and p_z atomic orbitals for the surface and bulk layers. The dashed lines show how the atomic orbital lobes interact. Formation of the surface dipole moment for the (b) in-phase $S_d + S_p$ and (c) out-of-phase $S_d - S_p$ mixing is also shown [from (20)]. The out-of-phase mixing always prevails. See text.

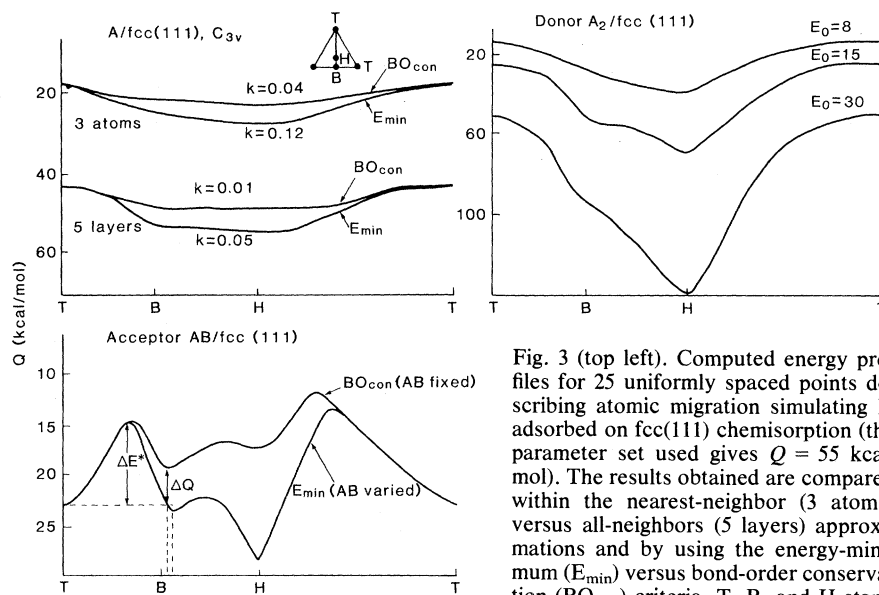


Fig. 3 (top left). Computed energy profiles for 25 uniformly spaced points describing atomic migration simulating H adsorbed on fcc(111) chemisorption (the parameter set used gives $Q = 55$ kcal/mol). The results obtained are compared within the nearest-neighbor (3 atoms) versus all-neighbors (5 layers) approximations and by using the energy-minimum (E_{min}) versus bond-order conservation (BO_{con}) criteria. T, B, and H stand for the on-top, bridge, and hollow sites, respectively. The M_n -A bond energy increases monotonically as the effective coordination number n increases along the series $T < B < H$ for both E_{min} and BO_{con} procedures, the latter giving a shallower curve. The values of $k = \Delta E^*/Q$ are also shown (31). Fig. 4 (top right). Computed energy profiles for 25 uniformly spaced points describing a homonuclear donor molecule A_2 on a five-layer fcc(111) film. The upright geometry is kept throughout the migration path. The results (within the E_{min} procedure) were obtained for fixed values of r_0 (1.9 Å) and a (0.43 Å) with E_0 varied. The patterns are rather atom-like (see Fig. 3) (31). Fig. 5 (bottom left). Computed energy profiles for 25 uniformly spaced points describing a heteronuclear acceptor molecule AB (upright configuration) on a five-layer fcc(111) film, where A and B are different. Both the energy minimum (E_{min}) and bond-order conservation (BO_{con}) procedures were used. The parameters for atom A are $a = 0.271$ Å; $r_0 = 1.9$ Å, and $Q_0 = 80$ kcal/mol. The parameters for atom B are $a = 0.901$ Å, $r_0 = 1.0$ Å, and $Q_0 = 3812$ kcal/mol. Nonmonotonic energy barriers are found for fixed A-B bond length (1.178 Å) or variable A-B bond length (31).

strong donor A_2 on an fcc(111) surface is shown in Fig. 4. The similarity to the atomic migration profile in Fig. 3 is remarkable. The analytical model, in contrast, predicts (29, 31) for acceptor admolecules a nonmonotonic ΔQ versus n energy profile. The preferred site will be typically of low coordination number, and the activation barrier may be much larger than the energy difference between the total energy minima, which may not necessarily correspond to symmetric sites. This explains why CO usually prefers the on-top or bridge sites but seldom the hollow sites on flat surfaces. This puzzling observation is a reversal of the atomic behavior. Figure 5 shows that the M_n -CO energy varies nonmonotonically with n on an fcc(111) surface and that a significant barrier exists between the deepest minima. Furthermore, one of the minima corresponds to a nonsymmetric site. This behavior, discussed above as a qualitative possibility, is consistent with experimental data recently obtained for CO migration on Pt(111). The energy difference between the preferred on-top adsorption site of the up-right geometry and bridge site was estimated to be less than 1 kcal/mol (32), but the migration barrier is 7 kcal/mol (33).

Dissociation of Adsorbates

A catalytically important chemisorption process is molecular dissociation on a surface. Thermodynamically, for a diatomic molecule AB to dissociate, the heat of chemisorption of atomic constituents A (Q_A) and B (Q_B) must exceed the gas-phase dissociation energy D_{AB} . Too often, this necessary thermodynamic condition is not sufficient because the dissociation process has a large activation barrier ΔE_{AB}^* that makes the reaction rate too slow at common temperatures. Again, no theoretical model has explicitly related ΔE_{AB}^* with $Q_A(Q_B)$ or D_{AB} , or with other observables.

Within our Morse potential approach based on M_n -AB bond-order conservation, the dissociation activation barrier ΔE_{AB}^* reads as follows (34)

$$\Delta E_{AB}^* = D_{AB} - (Q_A + Q_B) + \frac{Q_A Q_B}{Q_A + Q_B} \quad (14)$$

where D_{AB} is the gas-phase dissociation energy and $Q_A(Q_B)$ is the heat of atomic chemisorption. In the homonuclear case A_2 ($A = B$), we have

$$\Delta E_{A_2}^* = D_{A_2} - kQ_A \text{ for } k = 3/2 \quad (15)$$

that is, $\Delta E_{A_2}^*$ is linearly dependent on Q_A , with slope $k = 3/2$. For H_2 , O_2 , and N_2

on various surfaces of Fe, Ni, Co, W, and Pt, the experimental values of k lie within the range 1.4 to 1.7 (3, 35) close to the theoretical value of 1.5. Unfortunately, almost no experimental data on heteronuclear ΔE_{AB}^* are available, so that Eq. 14 cannot be directly verified.

Equations 14 and 15 predict atomic heats of chemisorption to be the only variable components of the dissociation barrier. Thus, periodic regularities of ΔE_{AB}^* can be deduced from the periodic regularities of Q_A (Q_B), discussed in detail above. The results correlate well with the experimental observations (1-3, 34, 35).

The value of ΔE_{AB}^* (Eq. 14) does not explicitly depend on the molecular heat of chemisorption Q_{AB} . Although Q_{AB} may somehow affect ΔE_{AB}^* [which may be the reason for the observed 1.4 to 1.7 range for k (3, 35) rather than the constant value of 1.5 (Eq. 15)], the Q_{AB} contribution appears to be minor. We stressed above that molecular heats of chemisorption (unlike atomic ones!) vary slightly from left to right along the transition series. Moreover, they vary nonmonotonically and can even increase (Table 1), which shows no correlation with the periodic trends in ΔE_{AB}^* .

Atomic versus Molecular Chemisorption

It is common to talk about the gas-solid phase interactions without specifying the atomic or molecular state of the adsorbate. One tacitly assumes that the general regularities of the metal-adsorbate interactions are qualitatively similar for the atomic and molecular species. As a result, many generalizations about chemisorption phenomena have been made (and are still being made) by extrapolating atomic chemisorption findings to molecular chemisorption, and vice versa. We saw, however, that differences between the atomic and molecular chemisorption patterns are typical, whereas similarities are rather exceptional. Examples we have discussed are periodic changes of the heat of chemisorption, adsorbate registry, the migration energy profile, and the nature of the migration barrier. Although this pattern was well known from experimental work, its importance was underestimated because there was no theoretical explanation for the occurrence of such differences.

In constructing our theoretical model, we tried to account for the differences in atomic and molecular chemisorption patterns. Our general conclusion is that strong donor admolecules may closely mimic adatoms in their relatively simple

behavior, but acceptor admolecules will typically show distinct and complicated patterns. Our model resolves many seeming contradictions with the prediction that on metal surfaces (unlike clusters!) most molecules, including even saturated molecules, will behave as effective acceptors.

Concluding Remarks

Although the conclusions based on our model are contrary to some commonly held perceptions, the picture as a whole fits experimental findings well. Our goal was a broad and coherent understanding of a variety of chemisorption phenomena with considerable relevance to heterogeneous catalysis (36). The new developments we have described constitute a first step in this direction. We hope that our findings will stimulate further theoretical and experimental analyses of this area of important industrial applications.

References and Notes

- See, for example: G. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell Univ. Press, Ithaca, N.Y., 1981); T. N. Rhodin and G. Ertl, Eds., *The Nature of the Surface Chemical Bond* (North-Holland, Amsterdam, 1978).
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36. Most recently, we have extended our bond-order-conservation model to treat various coverage and coadsorption (promoting and positioning) effects, in good agreement with experiment (E. Shustorovich and R. C. Baetzold, in preparation).
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38. We express our deep gratitude to the late Earl L. Muetterties, whose unique intuition often guided our choice of problems.

Electrically Conductive Metallomacrocyclic Assemblies

Tobin J. Marks

Until only a few years ago, the idea that a traditional organic or metal-organic substance could exhibit the electrical, optical, and magnetic properties of a metal seemed a complete contradiction in terms. Among other features, such substances lack the partially filled, spatially delocalized electronic energy levels (bands) which are an essential characteristic of a metal (1). This picture has, however, changed dramatically in the past several years, and the art of chemical synthesis has given rise to whole new classes of molecular (2-5) and polymeric (2-6) materials with properties analogous to those of metals having restricted dimensionality. The culmination is a new condensed matter field of study at the interface of chemistry, physics, and materials science that is stimulating breakthroughs in synthetic chemical strategy and methodology, in spectroscopic, structural, and transport analysis, and in the fundamental theoretical descriptions of how electrical charge is transported in the solid state of matter. Terms such as "molecular metal," "synthetic metal," "organic superconductor," "soliton conductor," and "bipolaron conductor" were unheard of only a few years ago. The application of this new knowledge to sensors, rectifiers, batteries, switching devices, photoresists, solar energy devices,

electrophotographic devices, static charge-dissipating materials, electro-magnetic shielding materials, chemoselective electrodes, and video disk coatings has also received a great deal of discussion (2-6).

Summary. The design, synthesis, and study of electrically conductive molecular and polymeric substances constitute a new scientific endeavor involving the interaction of chemists, physicists, and materials scientists. The strategies, developments, and challenges in these two closely related fields are analyzed via a class of materials that bridges both: assemblies of electrically conductive metallomacrocycles. It is seen that efforts to rationally synthesize tailored, "metal-like" molecular arrays lead logically to structure-enforced polymeric assemblies of linked molecular subunits such as metallophthalocyanines. The properties of these assemblies and fragments thereof provide information on the relationship between atomic-level local architecture, electronic structure, and macroscopic transport properties. Electrically conductive, processable polymeric materials also follow from these results.

Despite the impressive advances that have been achieved in the fields of molecular and macromolecular electrically conductive materials, it is fair to say that our current level of physical understanding of and chemical control over such systems is at a rather rudimentary level. From a synthetic chemical standpoint, the ability to tailor charge-transporting microstructures at the atomic level represents an exciting challenge and a key both to manipulating macroscopic prop-

erties and to testing theoretical predictions. A brief overview of these activities is given in this article.

To review in detail the recent chemical progress made by the host of excellent research groups working on conductive molecular and polymeric substances is not possible in the space available here. Thus, we have chosen to be selective and to illustrate current strategies, approaches, and problems by focusing on work performed in this laboratory on a new family of materials which is at the crossroads between molecular and polymeric conductors and which embodies characteristics of each. Our long-range goal has been to develop rational, flexible syntheses of low-dimensional, metal-like molecular assemblies and, through correlated physical and theoretical in-

vestigations, to understand the properties of these assemblies as a function of architecture and electronic structure. This approach leads quite logically from rather simple systems composed of aggregated single molecules to more elaborate, structure-enforced polymeric arrays of covalently linked molecular subunits.

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