# ELECTRONIC STRUCTURE AND CATALYSIS ON METAL SURFACES

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■ Abstract The powerful computational resources available to scientists today, together with recent improvements in electronic structure calculation algorithms, are providing important new tools for researchers in the fields of surface science and catalysis. In this review, we discuss first principles calculations that are now capable of providing qualitative and, in many cases, quantitative insights into surface chemistry. The calculations can aid in the establishment of chemisorption trends across the transition metals, in the characterization of reaction pathways on individual metals, and in the design of novel catalysts. First principles studies provide an excellent fundamental complement to experimental investigations of the above phenomena and can often allow the elucidation of important mechanistic details that would be difficult, if not impossible, to determine from experiments alone.

# INTRODUCTION

First principles quantum mechanical calculations are fast becoming an indispensable tool in the fields of surface science and heterogeneous catalysis. Qualitative and oftentimes quantitative insights into surface chemistries can be obtained with first principles techniques.

In this review, we give a brief overview of the state-of-the-art computational techniques that are making the above investigations possible, and we discuss the application of these techniques to several classes of problems. The review is not intended as exhaustive, and readers interested in additional information should consult previous reviews on these subjects (1–8). First, we describe several areas in which first principles calculations have been used to successfully explain unusual experimental phenomena. Next, we examine the successful elucidation of chemisorption trends across the transition metals for specific adsorbates. Then, we consider the detailed exploration of certain classes of reactions on individual

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metal surfaces. We conclude with two examples of how fundamental computational methods have allowed researchers to progress beyond the information-gathering stage of research to the design of improved catalytic materials.

# **OVERVIEW OF FIRST PRINCIPLES TECHNIQUES**

# The Time-Independent Schrödinger Equation

The fundamental equation upon which electronic structure theories are based is the Time-Independent Schrödinger Equation (TISE),

$$\mathbf{H}\boldsymbol{\psi} = \mathbf{E}\boldsymbol{\psi}, \qquad \qquad 1.$$

where H is the Hamiltonian (total energy operator), E is the total energy of the system, and  $\psi$  is the wavefunction, a function of space thought to contain all knowable information about the system. Solution of this equation yields fundamental information about the system, including probability distributions for all particles within it and energetic information about particular particle configurations.

For systems of interest to surface physicists and chemists, the full TISE is simplified by the Born-Oppenheimer Approximation. This approximation relies on the fact that atomic nuclei move thousands of times more slowly than electrons. In effect, this approximation allows the TISE to be split into nuclear and electronic structure calculations that can be performed separately. The electronic problem, which is of primary concern here, may be visualized as fixed configurations of nuclei surrounded by an "electron gas." The electronic structure of this gas is determined by solution of the electronic TISE, and the resulting total energy is interpreted as a potential energy for the nuclei. Solution of the TISE for many different nuclear arrangements permits the construction of potential energy surfaces (PES's) for the nuclei. In practice, it is often only the ground-state PES that is of interest in chemical analyses; this PES can be used to analyze the nuclear dynamics either in a classical (molecular dynamics, classical Monte Carlo, etc.) approximation or in a full quantum formalism. The former approximation is by far the most commonly used in the surface science and catalysis communities.

#### **Electronic Structure Methods**

The solution of the electronic structure problem for given configurations of nuclei is an extremely difficult problem. Analytical solutions are not possible for systems of chemical interest, and approximate numerical schemes must be used. A large fraction of these schemes is based on the solution of the electronic TISE in terms of one-electron orbitals. In the following paragraphs, the simplest technique for the calculation of these orbitals, the Hartree Fock Self-Consistent Field (HFSCF) approach, is described (9). More elaborate approaches are also discussed.

In the HFSCF approach, the full, many-electron wavefunction for the system is written as a product of one-electron wavefunctions that contain adjustable parameters. The number of one-electron orbitals is equal to the number of electrons in the system. The full wavefunction is constructed so as to be antisymmetric with respect to electron exchange. Using this approximate wavefunction, the full TISE is separated into many one-electron equations,

$$-\frac{\hbar^2}{2\mathrm{m}}\nabla^2\psi + \mathrm{v}\psi = \varepsilon\psi, \qquad 2.$$

where  $\hbar$  is Planck's constant, m is the rest mass of an electron,  $\nabla^2$  is the Laplacian, v is an effective one-electron potential energy function, and  $\varepsilon$  is a one-electron eigenvalue. The one-electron potential energy function (v) is calculated from the exact electrostatic attraction of the nucleus for the electrons and from an average electron-electron electrostatic interaction energy. An iterative scheme is used to solve Equation 2. It involves the choice of initial guesses for the one-electron wavefunctions (usually written as linear combinations of basis functions), the calculation of an average electron-electron interaction energy (which depends on all of the one-electron orbitals) from these wavefunctions, the insertion of this interaction energy term as part of v in Equation 2, and the solution of Equation 2 for improved one-electron orbitals. This process is repeated until orbital convergence (self-consistency) is obtained. Full self-consistency in the HFSCF method requires  $\sim N^4$  calculations, where N is the number of basis functions used.

Although this solution technique is appealing in its simplicity, the HFSCF approach gives very inaccurate molecular energies. The problem stems primarily from the lack of explicit electron correlation effects in the technique. Only correlation effects imposed by the antisymmetric wavefunction are accounted for; the neglect of other correlation energies can give very poor results (6). Good methods of correcting for this deficiency do exist, but they are generally extremely computationally expensive. Configuration Interaction (CI) methods make use of unoccupied (virtual) states to account for correlation effects. The mechanics of the technique are very similar to the HFSCF technique, but additional (unoccupied) one-electron wavefunctions are used to construct the total wavefunction. This procedure essentially allows the incorporation of excited electron configurations into the wavefunction (10). The result of CI calculations is an accurate solution of the TISE but at extreme computational cost (the HFSCF method requires ~N<sup>4</sup> calculations per basis function, while CI methods can require more than N7 calculations per basis function) (6). Typically, excitations beyond the triple excitation level are infeasible, and the method is truncated at that point.

Quantum Monte Carlo (QMC) techniques (11–14) present an alternative to CI methods for the incorporation of electron correlation effects into electronic structure calculations. These techniques use random sampling approaches to calculate energies for many-electron systems. In the Variational Monte Carlo method, for example, random sampling is used to evaluate integrals that arise naturally during CI calculations (15). In the Diffusion Monte Carlo method, on the other hand, the Schrödinger equation is recast into an integral Green's function form, and the Green's function is approximated by successive Monte Carlo sampling (15). QMC

techniques are computationally expensive, but they are beginning to be applied to realistic solid-state systems (16–18). These techniques have many attractive features; they offer the possibility of obtaining exact solutions to the TISE, and they are well suited to describe systems where electronic interactions are particularly important, such as superconductors, materials with large low-temperature-specific heat coefficients, and systems where van der Waals forces play a significant role (14).

The computational burden of the exact calculation of correlation effects makes it highly desirable to use an approximate scheme for evaluating such effects. This scheme, known as Density Functional Theory (DFT), is widely used in chemical computations. The methodology of DFT is substantially similar to that described for the HFSCF method, but an additional term is added to the effective one-electron potential energy functions v (see Equation 2) that are used in HFSCF (7, 19-21). This extra term is called the exchange-correlation (XC) energy and represents a heuristic, but highly efficient, way to account for these effects. By incorporation of these extra exchange-correlation terms, DFT can yield accurate total energies with comparable computational effort, as the number of calculations scales with  $N^{3}$  (6), which is a substantial improvement over CI methods. Although many XC energy expressions have been developed, all share the property of being explicit functionals of the electron density. The LDA (Local Density Approximation) uses an XC functional that depends only on the electron density itself and takes the XC energy to be the exact XC energy for a homogeneous electron gas (22, 23). The GGA (Generalized Gradient Approximation) incorporates density gradient terms into the XC functional. LDA calculations often produce poor estimates of binding energies and molecular structures (24, 25). State-of-the-art GGA calculations (together with suitable models for the surface structure, discussed below), however, can give much better values. Bond lengths and solid lattice constants, for example, are reproduced to within several hundredths of an angstrom (7, 26), and vibrational frequencies are calculated with an accuracy of  $\sim 5\%$  (4, 6, 7). Comparison of calculated adsorption energies with experimental values (which are obtained most accurately from Single-Crystal Adsorption Calorimetry) (27) demonstrates that these energies can be found to within  $\sim 0.15 \text{ eV} (7, 28-30)$ .

## **Core Electron Representations**

When implementing one of the above electronic structure calculation techniques, it is important to choose an appropriate method to represent core electrons. These electrons could certainly be treated with the same quantum techniques as valence electrons, but because the core electrons are located in the innermost shells of atoms, they do not generally play an active role in chemical bonding. Hence, it is often not necessary to explicitly include the core electrons in the quantum calculations, and their behavior can be treated approximately to reduce computational burdens. One approximation that retains almost all of the important features of the core electrons but reduces computational time (31, 32) is the Frozen Core Approximation (FCA). In the FCA, the one-electron wavefunctions for the core electrons

are not recalculated during every self-consistent iteration; they are simply fixed in the functional form that the isolated atomic orbitals would have. Another corelevel approximation is the pseudopotential method in which the core electrons are completely removed from the problem. Their effect is felt only through an effective core potential energy function (33, 34). Although this technique represents a rough approximation of the core states, the current generation of ultrasoft pseudopotentials (35) yields accurate energies with great computational efficiency.

# Models of Surface Structure

Other factors not directly related to the electronic structure determination problem can have significant effects on the accuracy of theoretical models in surface science and heterogeneous catalysis. One of the most critical issues is the representation of the surface structure. Cluster calculations use finite ensembles of metal atoms to model surfaces; these calculations are computationally convenient because they employ atomic or molecular orbital basis sets to satisfy the boundary condition of zero electron density at infinite distance from the cluster. Such basis sets have long been used by theoretical chemists to model isolated molecules, and hence no significant modifications are required to apply theoretical chemistry codes to surface cluster calculations. Unfortunately, the electronic structure of clusters can be quite different from the corresponding structure of semi-infinite surfaces (36), and thus the clusters may not in all cases be suitable models for heterogeneous catalyst surfaces. Slab calculations, on the other hand, use periodic boundary conditions to model extended surfaces. These models avoid the electronic structure artifacts that sometimes trouble cluster calculations. The slab models require the use of a periodic basis set to match the boundary conditions; plane waves are often used for this purpose. This basis works well for periodic systems, although convergence can be slow where there are sharp electron density gradients. The inclusion of some atomic orbitals (exactly represented with plane waves) has been shown to speed convergence for some systems (37).

## SYNERGY BETWEEN THEORY AND EXPERIMENT

Experimental investigations in surface science and catalysis often raise intriguing questions that cannot be easily answered by the experiments themselves. In such situations, it is sometimes possible to explain the resulting puzzles by attacking the problem with ab initio simulation methodologies. First principles calculations have a number of features that allow them to make important contributions to these types of investigations. First, the simulations can be performed at almost any degree of spatial resolution, thus making it possible to accurately determine the geometries, energies, electronic structures, and site preferences of adsorbates on well-defined solid surfaces. Such data are not easily accessible in experiments. Second, the inputs to simulations can be easily controlled, eliminating concerns about the effects of contaminants or other unknown variables. Finally, the results

of simulations are generally easier to interpret than are the results of experiments; although wavefunctions and other outputs from theoretical simulations can be quite complex, it is usually possible to create software to analyze these numerical data quickly and efficiently.

Below we discuss several areas of current interest to the surface science and catalysis communities to which substantial contributions have been made by theoretical methods. Our goal is to describe the fruitful and fascinating interplay between experimental and theoretical analyses that has allowed recent progress to be made in these areas.

## Site Preferences and Vibrational Spectroscopies

On single-crystal transition metal surfaces, vibrational spectroscopies (either EELS, HREELS, or RAIRS) can provide important qualitative information about the chemical structure of adsorbed species. These techniques are used both for the identification and classification of surface species and for the determination of site preferences and adsorption geometries of these species. Often, however, it is difficult to conclusively assign a specific structure to a measured vibrational spectrum, and without a reliable means of doing this, the vibrational spectra are of limited use.

Lately, theoretical techniques have been increasingly used to aid in the determination of physical and chemical structures from measured vibrational spectra. An illustration of this procedure comes from the surface oxametallacycle literature. These cyclic reaction intermediates incorporate metal surface atoms into their rings (Figure 1a) and are likely intermediates in epoxidation reactions and in other reactions involving oxygenate molecules (38). Unfortunately, the oxametallacycles are difficult to isolate on metal surfaces, and prior to the work described here, spectroscopic standards for the molecules did not exist. Jones et al. (38) overcame this difficulty by comparing a theoretical vibrational spectrum for an iodoethanolderived oxametallacycle attached to a silver cluster with an experimental HREELS spectrum taken on  $Ag\{110\}$ . The remarkable agreement between the theoretical and experimental spectra allowed the authors to conclusively identify the oxametallacycle and its exact structure (involving two metal atoms in the ring) on the indicated surface (Figure 1b). The same approach has also been used to identify oxametallacycles derived from 1-epoxy-3-butene on Ag{110} (39, 40) and from a tert-butoxy species on  $Pt\{111\}$  (41).

Another instance in which experimental surface spectra have been analyzed with the help of ab initio techniques involves the adsorption geometry of NO. The adsorption and dissociation of NO have been heavily studied on a wide variety of transition metal surfaces (42), but for the sake of brevity, the present review details NO adsorption geometry on only two such surfaces, Pd{111} and Rh{111}. On Pd{111}, site assignments have been made using a combination of vibrational frequency information from gas-phase nitrosyl compounds and LEED patterns (43, 44). The conclusions from these studies are that NO prefers either top-site or bridge-site binding (or a combination of the two), depending on coverage. These



Figure 1 Surface oxametallacycles: (*a*) an oxametallacycle derived from iodoethanol and (*b*) comparison of theoretical and experimental oxametallacycle vibrational spectra on  $Ag\{110\}$  with the corresponding peak assignments. [Reprinted with permission from (38); Copyright 1998. Am. Chem. Soc.]

conclusions are contradicted, however, by a periodic DFT study of NO chemisorption on Pd{111} (45). In that work, it is shown that theoretical frequencies from hollow sites provide the best match with the experimental data at low coverages, and a combination top/hollow site occupation gives good agreement with experiments at high coverages. On Rh{111}, HREELS and LEED studies (46) are again taken to indicate that NO adsorption occurs on bridge and top sites. This interpretation is contradicted by DFT calculations that favor hollow sites at moderate coverages and a combination of top and hollow sites at high coverages (45). These theoretical corrections to the experimental vibrational results are confirmed by Temperature Programmed Static Secondary Ion Mass Spectroscopy (TPSSIMS) (47) and X-ray Photoelectron Diffraction (XPD) (48) studies. Brown & King (42) conclude from the above theoretical considerations that re-evaluation of the site-vibrational frequency relationship for NO is necessary to obtain accurate site assignments from experimental vibrational spectra.

#### Effect of Surface Defects

Another area in which there has been fruitful interaction between first principles calculations and experimental investigations involves the effect of defects on surface chemistry. It has long been speculated that defects and, more specifically, steps are more reactive than terraces, but it has not been until relatively recently that quantitative descriptions of the relationship between these defects and surface reactivity have been developed. Periodic DFT calculations indicated that N<sub>2</sub> dissociation at steps on  $Ru\{0001\}$  is activated by 0.4 eV, while dissociation on terraces is activated by ~1.9 eV (Figure 2). These predictions helped in the interpretation of detailed experiments by Dahl et al. (49). The authors measured the activation barrier for dissociative adsorption of N2 on both clean and goldpassivated Ru $\{0001\}$ . The clean surface barrier was  $\sim 0.4$  eV, whereas the barrier on the passivated surface was  $\sim 1.3$  eV. The experimental findings, together with the theoretical calculations, demonstrated convincingly that nitrogen dissociation on clean  $Ru\{0001\}$  is completely dominated by steps, while the same reaction on gold-passivated  $Ru\{0001\}$  (where steps and other defects have been saturated by gold) occurs on terraces. Even the gold-passivated sample may not show the true terrace barrier but rather the sum of the step barrier and the energy required to remove gold from the step.

#### **Reactions with Subsurface Species**

In recent years, the effect of subsurface hydrogen on hydrogenation reactions has received considerable attention. In particular, the case of the hydrogenation of methyl to methane over nickel has been thoroughly studied. Johnson et al. (50) performed a pioneering study of this system in which they showed unambiguously that subsurface hydrogen is the active species in this reaction. Although they speculated that the reaction was  $C_{3V}$  symmetric, occurring via the combination of a hydrogen atom in an octahedral subsurface site with methyl adsorbed directly





above it, they could not provide definitive descriptions of the microscopic pathways by which the reaction proceeded. More recently, two periodic DFT studies (51, 52)have been performed to elucidate these microscopic pathways. Both studies confirmed that surface hydrogen has a high barrier to methyl hydrogenation, and both showed that the symmetric  $C_{3V}$  pathway proposed by Johnson et al. (50) is highly energetically unfavorable, presumably due to strong Pauli repulsive forces along this pathway (52). Both studies found that the reaction mechanism involves a composite pathway consisting of hydrogen resurfacing from the bulk (accompanied by perturbations to the surface methyl structure), followed by recombination of the hydrogen with the surface methyl. It appears that the reaction barrier is highly sensitive to the exact location of the resurfacing event. Thus, small differences in the chemical environment (e.g., the subsurface hydrogen coverage) that change the preferred resurfacing site may also change the reaction barrier. The calculations also show that while subsurface hydrogen is more reactive than surface hydrogen, the difference in the reaction barrier is simply a result of the higher potential energy of the subsurface hydrogen. This means that under steady-state reaction conditions subsurface hydrogen is no more important than surface hydrogen for the overall reaction rate.

#### High- and Low-Pressure Reactivity

The pressure gap is an important issue at the interface between surface science and heterogeneous catalysis. It is sometimes found that surface science experiments on well-defined surfaces in ultra-high vacuum (UHV) conditions yield results that are different from results obtained in high-pressure catalytic reactors. An illustration of this effect can be found in the case of CO oxidation on ruthenium. In this system, at a total pressure of ~10 torr, the rate of CO oxidation on Ru{0001} is higher than on any other transition metal surface (53, 54). The oxidation rate is highest for a combination of high surface coverages of oxygen and extremely low coverages of CO. In stark contrast to these results, Ru{0001} is among the poorest of CO oxidation catalysts under UHV conditions (55).

This interesting puzzle was recently analyzed by Stampfl & Scheffler (56, 57) using periodic DFT calculations. Motivated by the fact that, under high-pressure conditions, high-coverage (1 × 1)-O overlayers can be created by O<sub>2</sub> dissociation on Ru{0001} (58, 59), the authors examined CO oxidation under these conditions. They describe an Eley-Rideal (E-R) mechanism for the reaction in which fast CO molecules approach the oxygen-covered surface directly above adsorbed oxygen atoms; after reaction, CO<sub>2</sub> desorbs. The thermochemistry of this reaction is highly favorable ( $E_{rxn} \sim -1.95$  eV), although the kinetic barrier is quite high [~1.1 eV with respect to CO(g) and O(a)]. The oxidation rate calculated from this barrier (with a pre-exponential estimated from gas-phase kinetic theory) is much lower than the experimentally measured rates, so it is unlikely that the E-R mechanism alone could be responsible for the measured high-pressure oxidation rates. However, the E-R reactions (in conjunction with thermal fluctuations) open up vacancies

in the  $(1 \times 1)$ -O adlayer. These vacancies can be filled by CO molecules (the equilibrium CO coverage is estimated to be 0.0003) that are then oxidized in a Langmuir-Hinshelwood-type reaction. The estimated reaction barrier for this process is ~1.5 eV. Although this barrier is quite large, the authors estimate that the close proximity of the CO and O adspecies will lead to a very high attempt frequency (pre-exponential) for the reaction, thereby giving a high rate of CO oxidation via this mechanism.

#### **Polymerization Catalysis**

Theoretical techniques have made many contributions to the fields of heterogeneous and homogeneous polymerization chemistry over the past several years. The most well-known of the heterogeneous polymerization catalysts are the Ziegler-Natta (ZN) catalysts. Since their discovery in the 1950s (60), the ZN catalysts have been in widespread industrial use. In spite of their importance, however, the detailed mechanisms governing their operation are still not well understood, owing in large part to the difficulty of experimental studies of the extremely rapid surface polymerization reactions (61, 62). Hence, the use of first principles calculations to probe in detail the structure and energetics of reactants, catalyst, and products can provide valuable insights into the ZN polymerization chemistries. Boero et al. (62-65) have conducted extensive calculations to analyze olefin polymerization on MgCl<sub>2</sub>-supported TiCl<sub>4</sub>. Analyzing the dynamics on the  $MgCl_{2}$  {110} facet, they determine that a Ti atom coordinated to three surface Cl atoms and two free Cl atoms is an excellent candidate for an active site precursor. To fully activate the active site, one free Cl atom must be replaced with a chain-terminating group (e.g., a methyl group). Then, an ethylene molecule spontaneously complexes to the Ti center and is later inserted between the Ti and the methyl chain termination group (Figure 3). This last process is found to have a barrier of  $\sim 0.28$  eV, in excellent agreement with experimental results. The insertion process is apparently facilitated by so-called agostic interactions where hydrogen atoms, bonded either to the methyl chain-termination group or, later, to the growing polymer chain, interact with the Ti center, thereby destabilizing the Ti-C bond.

Boero et al. (65) considered the possibility that other MgCl<sub>2</sub> facets may be active in polymerization. They analyzed polymerization on the  $\{100\}$ ,  $\{104\}$ , and  $\{110\}$  facets and concluded that the  $\{110\}$  facet described above is, indeed, the most suitable facet for the ZN reactions. They also extended their polymerization analyses to include propylene polymerization and determined that their proposed Ti active complex on MgCl<sub>2</sub>{110} can produce isotactic polypropylene with a high degree of stereoselectivity, in agreement with experimental observations of ZN catalyst activity.

Single-site organometallic catalysts for homogeneous polymerization have emerged as interesting alternatives to the ZN catalysts since their discovery 25 years ago (66). Many of these catalysts consist of a metal ion sandwiched between



Figure 3 Ethylene insertion into a TiCl<sub>4</sub> ZN catalyst. Ethylene is seen to approach the Ti center from the right in the first and second images. One of the ethylene carbon atoms begins to bond with the Ti-coordinated methyl group, leading to a weakening of the methyl-Ti bond and eventually to complete insertion of the ethylene between methyl and Ti. [Reprinted with permission from (62); Copyright 1998. Am. Chem. Soc.]

two or more ligands (67, 68). Polymer chains are formed at the metallic ion site in an activation/complexation/insertion mechanism similar to the ZN mechanism (69). Metallocene catalysts, consisting of metal ions bonded to two ligands, are a particular class of organometallic polymerization catalysts that have attracted the attention of theoretical investigators. Ziegler and co-workers have performed extensive DFT investigations on these catalysts (69-72) and found, for example, that a wide variety of first-row transition metals can be active in metallocene chemistry. Complexation and insertion energies for ethylene vary depending on the *d*-orbital occupancy of the metallic ion, but all high-spin first-row transition metals with up to four *d*-electrons can be expected to have some catalytic activity (69). They have also considered the effect of various spectator species on the polymerization reactions. Co-catalysts (used to activate the metallocenes by converting them to cations), unactivated metallocenes, and solvent molecules could form ion pairs or so-called dormant complexes with the activated cation. The presence of ion pairs or dormant complexes would be expected to have an effect on the polymerization reactions. The authors predict that such species could well be present in typical polymerization conditions and that they lead to substantial changes in the polymerization chemistry (70, 71). Finally, they have examined the interaction of polar co-monomers with Ni and Pd-based catalysts (72). Ni, experimentally observed to be inactive for incorporation of polar co-monomers into polymer chains, is found to bind the co-monomers through their carbonyl oxygen atoms, thus precluding polymerization. In contrast, Pd binds the co-monomers through their olefinic functionalities, thereby facilitating polymerization in agreement with experimental results.

#### Catalysis with Zeolites

Zeolite chemistry is extremely important in the petrochemical industries where these catalysts are used for alkane aromatization, methanol-to-gas conversion, reactive separations, and other processes. Ion-exchanged zeolites, in which Si atoms in the silica framework have been replaced with Al atoms, have an excess of negative charge. This charge can be neutralized by a combination of protonation (resulting in solid acid sites) and metal cationic insertion. Zeolites resulting from Zn insertion in this manner are active for alkane dehydrogenation and aromatization (73, 74). Unfortunately, in spite of the industrial importance of these catalysts, little is known about the nature of the catalytically active Zn sites. Theoretical analysis has proved useful in providing more information about these catalytic centers. For instance, Barbosa et al. (75) have used cluster DFT calculations to simulate the interaction of methane probe molecules with Zn sites. They determined equilibrium structures and vibrational frequencies for methane interacting with bare Zn(II) cations, ZnO solid, and [Zn-O-Zn]<sup>2+</sup> in 4T and 5T rings. None of these models yielded methane vibrational frequency shifts (with respect to gas-phase methanol) as large as experiments had suggested. Shubin et al. (76) studied Zn<sup>2+</sup> active sites in 4, 5, and 6-membered rings. They found that Zn<sup>2+</sup> is least stable in 4-membered rings, indicating that these configurations should be the most reactive. This result was confirmed by calculations of heterolytic ethane dissociation over Zn<sup>2+</sup> active sites; in these calculations, the reaction barrier was smallest in 4-membered rings. Barbosa et al. (77) performed a similar study using periodic DFT calculations in chabazite with a Si/Al ratio of 5.0. They, too, found that  $Zn^{2+}$  cations are less stable (and hence more reactive) in 4-membered rings. Probe molecules will generally bind to these sites with a chemisorption energy proportional to the stability of the site if the probes interact weakly with the zeolite lattice, as is found for methane. However, if the probes interact strongly with the lattice, they can cause significant deformations that may obscure the stability trends of the cationic sites.

In addition to active site characterization, theoretical studies are useful to elucidate the chemistry of particular reactions in zeolites. For example, the hydrolysis of acetonitrile has been examined with DFT cluster calculations on Zn-substituted 4T model zeolites (78). The reaction was found to proceed via activation of either water or acetonitrile, depending upon conditions. Interestingly, the active Zn(II) sites in the model zeolite behaved in a remarkably similar way to biological enzymatic Zn(II) sites that catalyze  $CO_2$  hydrolysis. Another theoretical study, employing periodic DFT methods, has considered the isomerization of toluene and xylenes in an acidic mordenite zeolite (79). This reaction was found to be highly structure sensitive, with steric constraints from the zeolite cage structure exerting a strong influence on the reaction. Periodic DFT calculations have also been employed to study the conversion of methanol to dimethyl ether (a candidate for the first step in the methanol-to-gas reaction) in chabazite (80). Two possible pathways are found for this conversion: One pathway involves direct condensation of methanol molecules in the zeolite pores to form dimethyl ether; the other proceeds through a zeolite-bound methyl intermediate. Carbene and ylide species are found to be unstable in the zeolite matrix and hence are not likely reaction intermediates.

## CHEMISORPTION TRENDS

One of the principal objectives of surface science is to develop a detailed, fundamental understanding of the factors that influence the chemical reactivity of surfaces. To this end, the determination of chemisorption trends across the periodic table is crucial. First principles calculations provide a convenient, accurate, and efficient means of studying these trends. It is straightforward to perform tests on a wide variety of metal surfaces because these tests do not require the purchase and preparation of a large number of samples (as would be the case for experimental periodic studies). In recent years, a body of literature on theoretical calculations has accrued that permits the analysis of chemisorption trends for many adsorbates and across a variety of transition metal surfaces. Here, we briefly summarize some of those trends and the methods used to determine them.

#### A Simple Model for Periodic Trends

Hammer & Nørskov (7, 81) have developed a simplified theory of adsorbate bonding on transition metal surfaces. The theory, based on the assumption that the interaction of a relatively few adsorbate orbitals with surface *sp*- and *d*-bands will determine periodic trends in the chemisorption energy of the system, has great explanatory and predictive power. For atomic adsorbates (where only a single type of adsorbate orbital interacts to an appreciable extent with the surface), the model is particularly simple:

$$E_{d-hyb} = -2(1-f)\frac{V^2}{|\varepsilon_d - \varepsilon_a|} + 2(1+f)\alpha V^2,$$
 3.

where  $E_{d-hyb}$  is the energy gained from hybridization of the adsorbate orbital with the metal *d*-bands, f is the fractional metal *d*-band filling, V is a Hamiltonian matrix element that describes the coupling between the metal *d*-band states and the adsorbate orbital,  $\varepsilon_d$  is the first moment of the metal *d*-band density of states (the *d*-band center),  $\varepsilon_a$  is the adsorbate orbital energy (renormalized by the metal *sp*-bands), and  $\alpha$  is a constant that is independent of the metal and depends weakly on the identity of the adsorbate (7). Interactions of adsorbates with metal *sp*-bands generally depend only on the nature of the adsorbate, and so  $\varepsilon_a$  is essentially constant from metal to metal. Also, constant *sp*-band interaction energies imply that changes in  $E_{d-hyb}$  for given adsorbates on various metals are nearly identical to corresponding changes in the full chemisorption energies ( $E_{chem}$ ) of these adsorbates. This fact, in combination with Equation 3, leads to the major conclusion of the Hammer-Nørskov model; namely, that changes in adsorbate chemisorption energies ( $E_{chem}$ ) over different metals are simply related to changes in the metal *d*-band centers.

This simple model accounts well for trends in atomic chemisorption energies on transition metals. It can, for example, predict trends in atomic oxygen and sulfur chemisorption energies to a high degree of accuracy (7) (Figure 4*a*). A similar model developed for molecular adsorbates works equally well, as evidenced by the remarkable parity plot of the model's predicted CO chemisorption energies versus full DFT-GGA chemisorption energies in Figure 4*b* (82).

In addition to describing periodic trends in atomic and molecular adsorption on pure metal surfaces, the model captures changes in chemisorption energies on pseudomorphic overlayers as well. Pallassana et al. (83) showed that this model could be used to describe trends in hydrogen chemisorption energies over Pd{111}, Re{0001}, and pseudomorphic overlayers of these two elements. For these systems, they demonstrated that the  $E_{chem}$  versus  $\varepsilon_d$  relationship is linear. In a subsequent paper, the same authors (84) developed an extension of the Hammer-Nørskov model to Pd and Re systems with alloyed surface layers. The extended model, using a weighted surface *d*-band center, again showed a linear relationship between the hydrogen chemisorption energy and the weighted *d*-bound center.

The Hammer-Nørskov model is also useful for describing periodic trends in dissociation energies. For example, this model accurately predicts changes in the energy of dissociative adsorption of dihydrogen on metals with a wide variety of *sp*- and *d*-state properties (81).

A compilation of a wide variety of applications of the Hammer-Nørskov model to systems of interest in surface science and heterogeneous catalysis is shown in Figure 5. This figure, from Mavrikakis et al. (85), includes



**Figure 4** Hammer-Nørskov model analyses. Full DFT-GGA predictions versus model predictions. (*a*) Atomic oxygen chemisorption. [With kind permission from Kluwer Academic Publishers (7).] (*b*) CO chemisorption. [Reprinted with permission from (82); Copyright 1996. Am. Phys. Soc.]

correlations of chemisorption and dissociation energies with *d*-band centers ( $\varepsilon_d$ ) for various metals, single-crystal metal facets, defect structures, bulk alloys, pseudo-morphic overlayers, and strain levels. The remarkable quality of these correlations underlines the potential use of  $\varepsilon_d$  as an important catalyst design parameter.

#### Trends in Segregation Energies and Surface Alloy Formation

It is well known that the elemental chemical composition at the surface of an alloy may differ from the composition in the bulk; one of the alloy components is effectively enriched in the surface region. This enrichment can be caused, for example, by differences in surface segregation energies between the alloy components. Such



Figure 4 (Continued)

compositional changes can have a dramatic effect on the reactivity of the surface and are therefore of first order importance in heterogeneous catalysis. In an effort to develop a more fundamental understanding of the properties of surface alloys, Ruban et al. (86) have performed an extensive analysis of the electronic properties of pseudomorphic metal overlayers and of surface metal impurities. Following the Hammer-Nørskov reactivity model, they assume that reactivity trends will follow trends in *d*-band center values of overlayer and impurity atoms. They present an extensive database of *d*-band center shifts for these systems, and they conclude that, when metals with small lattice constants are overlayed or alloyed on metals with larger lattice constants, the *d*-band center shifts up. The reverse is true when metals with larger lattice constants are alloyed on metals with smaller lattice constants. These trends appear to result from a combination of *d*-band bandwidth changes upon overlaying or alloying, followed by *d*-band shifts to maintain a constant local *d*-band filling. An important question in connection with alloy catalysis is determining the composition of the surface of the alloy. Christensen et al. (87) combine data from periodic DFT calculations with a detailed thermodynamic formalism describing surface compositions to produce phase diagrams for surface alloys. They find that this analysis provides a good description of many types of surface alloys, including random pseudomorphic overlayers, ordered overlayer structures, non-pseudomorphic structures, and systems where subsurface segregation occurs.

Finally, Ruban et al. (88) have created an extensive database of surface segregation energies for bimetallic systems (Figure 6). The database points to two important periodic trends in surface segregation energies, and the authors interpret this information using a combination of several theories of surface structure. First, in agreement with the observations of Aldén et al. (89, 90), a substantial portion of the surface segregation energy is determined by the difference in surface energies of the host and the impurity. This conclusion is reached by interpreting the surface segregation data with the theory of Friedel (91), wherein cohesive energies of the transition metals are related to the *d*-occupation numbers of the metals. This theory, in combination with the observations of Aldén, implies that no impurities in the middle of a transition series are expected to segregate to the surface of early or late transition metals, an implication that is strongly supported by the calculated segregation energies. Second, crystal structure differences between the host and the impurity can have a significant effect on segregation energies. Such differences alter the local d-state character around the impurities and can lead to changes in the surface segregation energy of up to 1 eV. These changes are particularly significant if either the host or the impurity comes from the beginning of a transition metal series.

#### Oxygen on Transition Metals

Oxygen chemistry on transition metal surfaces is of fundamental importance in numerous surface processes, from oxidation reactions on heterogeneous catalysts to corrosion processes. In an effort to gain a fundamental understanding of such processes, a number of first principles studies of oxygen adsorption and dissociation on transition metal surfaces have been undertaken. Calculations of binding energies for atomic oxygen on a variety of surfaces have been performed; they generally indicate that the absolute binding energy increases from right to left on the periodic table (Figure 4a). Other studies have focused primarily on the overlayer structures of chemisorbed atomic oxygen (58, 59, 92). On both Ru{0001} and Rh{111}, high-coverage states (up to 1 ML) exist; there are kinetic barriers to forming these states, and hence they are only observed under high-pressure conditions or under conditions where highly energetic atomic oxygen has been prepared. The binding energy of the O atoms on  $Ru\{0001\}$  is higher than that on  $Rh\{111\}$ , a result explained in terms of the higher *d*-band center of  $Ru\{0001\}$  surface metal atoms. Additionally, chemisorbed oxygen leads to an increased separation between the first and second metal layers for both  $Ru\{0001\}$  and  $Rh\{111\}$ . However, the expansion is much smaller for Ru{0001}, an observation that is explained by the higher cohesive energy of bulk Ru.

Other studies of oxygen on transition metals have focused on molecular surface states and dissociation pathways. Hafner and coworkers (93–95) have examined  $O_2$  adsorption and dissociation on Ni{111}, Pd{111}, and Pt{111}. Three molecular  $O_2$  precursors were identified in each of these cases, and a monotonic increase of the absolute value of the binding energy (with respect to gas-phase  $O_2$ ) with the metal *d*-band center energy was found [Ni{111} had both the largest binding energies and the highest *d*-band center, followed by Pd{111} and then Pt{111}]. This trend appears to extend to the work of Xu & Mavrikakis (96) on Cu{111}. The authors find an additional precursor state not present on Ni{111}, Pd{111}, or Pt{111}, but their results for precursor binding energies still fit nicely into the monotonic relationship of binding energy to *d*-band center mentioned previously.

#### CO on Transition Metals

CO chemistry on transition metal surfaces is of great importance in heterogeneous catalysis. Describing the full range of theoretical work that has been done in this area would be impossible in a brief review, so we focus on only four prominent contributions that first principles techniques have made to the understanding of CO chemistry on transition metals. First, we note that DFT calculations indicate that absolute binding energies for CO increase as one moves from right to left across the periodic table (Figure 4b). Second, we discuss a study of CO diffusion along the close-packed [110] directions of Pt{110}-(1  $\times$  1) (97). In these directions, CO chemisorbed on top sites has a binding energy about 0.02 eV stronger than does CO on bridge sites. A simple model of diffusion (in which the bridge site is arbitrarily assumed to be a transition state for the diffusion process) would suggest a diffusion barrier of this order, but calculations with a higher spatial resolution along the reaction coordinate show that the true diffusion barrier is  $\sim 0.13$  eV (Figure 7). A similar bridge-top diffusion barrier has also been computed on  $Rh\{100\}$  (98). These calculations demonstrate the important role that first principles techniques can play in the detailed description of diffusion on transition metal surfaces.

Third, we examine a periodic DFT study of the interaction of CO with potassium promoters on Co{1010} (99). In that analysis, it is confirmed that CO adsorbs through carbon in an orientation roughly perpendicular to the surface. Potassium increases the reactivity of this configuration by donating charge to the CO  $2\pi^*$ antibonding orbital. Furthermore, the potassium charge donation leads to a polarization of this orbital, with charge accumulating around the oxygen end of the molecule. These effects could facilitate either the dissociation of CO or the hydrogenation of the molecule to COH; either of these elementary pathways could be the first step in Fischer-Tropsch reactions on cobalt.

Lastly, we discuss a study of the investigation of localized demagnetization effects of CO on Ni $\{110\}$  (100). In this study, Ge et al. find that CO adsorption on the surface leads to a strong, highly localized surface demagnetization. The key



**Figure 7** Potential energy surface for diffusion of CO on Pt{110}- $(1 \times 2)$  along  $\langle 1\bar{1}0 \rangle$  directions. The reference energy state corresponds to the total energy of a gas-phase CO molecule at infinite separation from the platinum surface. Distances correspond to lateral displacements of the CO center of mass in angstroms. Atop and bridge refer to specific, stable surface sites for CO adsorption. The coverage is 0.25 ML. [Reprinted with permission from (97); Copyright 1999. Am. Inst. Phys.]

electronic contribution to this effect is a transfer of residual spin from the surface nickel atoms to the  $2\pi^*$  or  $1\pi$  orbitals of CO.

#### **REACTIVITY TRENDS**

First principles calculations are powerful tools for the analysis of reactivity trends on well-defined transition metal surfaces. Because of the ability of ab initio techniques to study transition states and reactive intermediates, the techniques can be used to generate large databases of chemisorption and activation energies for bond-breaking/bond-making events on given surfaces. From these energies, potential energy surfaces (PES's) for various reaction pathways can be developed that can be used to determine kinetically significant steps in the reaction pathways and to identify abundant surface species on the metal surfaces. In this section, we present several examples of systems in which theoretical techniques have been used to establish such trends on well-defined transition metal surfaces. Although these calculations are generally performed for specific surfaces, a comparison of reactivity trends on different metals can be extremely valuable, and we present some of these results below.

#### Hydrogenation-Dehydrogenation Reactions

Hydrocarbon hydrogenation and dehydrogenation reactions are crucially important to the chemical industry. They form the basis of isomerization reactions of alkanes and alkenes, syngas synthesis, and the Fischer-Tropsch synthesis, among other industrially important processes. A fundamental understanding of these processes is therefore extremely valuable, and many theoretical efforts have been made to determine hydrogenation/dehydrogenation trends on transition metal surfaces. Kua & Goddard (101), for example, have used DFT cluster calculations to study methane and ethylene fragments on Pt{111}. They find that  $CH_x$  species adsorb so as to maintain a tetravalent coordination for carbon. The binding energy of these fragments scales almost linearly with the number of Pt-C bonds. The CH radical is found to be the thermodynamic sink for the methane decomposition reaction on this surface.

The same authors have also performed a more general study of  $CH_{n-m}(CH_3)_m$ (n = 1, 2, 3 with m  $\leq$  n) species on Pt, Ir, Os, Pd, Rh, and Ru (102). For methane fragments, they find that a tetravalent carbon configuration is preferred for all fragments on all metals. Furthermore, CH is the thermodynamic sink on all metals, and fcc metals appear to bind methyl fragments more than hcp metals. For fragments of higher carbon numbers, steric interactions of methyl groups with the surface lead to lower binding energies. The authors synthesize all of their data for Pt{111} surfaces to design an elegant group contribution approach for the estimation of hydrocarbon binding energies to that surface.

Papoian et al. (103) have also studied the behavior of small hydrocarbon fragments on  $Pt\{111\}$ . Using periodic DFT calculations, they show that atomic hydrogen moves freely about the  $Pt\{111\}$  surface, whereas methyl and ethyl fragments are strongly bound to top sites through their carbon atoms. These results, consistent with the findings described above, are analyzed in detail using the Crystal Orbital Hamilton Population Theory (104, 105).

Additional methane hydrogenation/dehydrogenation periodic DFT studies have been performed on Ru{0001} (106) and Ni{111} (107). On Ru{0001}, it is found that all methane fragments prefer threefold binding configurations; this result apparently contradicts the results of the cluster calculations described above (102). In the case of CH<sub>3</sub>, at least, the authors attribute this result to reduced Pauli repulsion from the unfilled Ru *d*-bands leading to a preference for highercoordination sites. CH is found to be the thermodynamic sink for the methane dehydrogenation reaction, and all reaction steps (with the exception of C–H scission in CH) are found to be exothermic. On Ni{111}, it is found that all methane fragments prefer threefold sites, and CH is again the thermodynamic sink of the reaction. In this study, kinetic barriers were also calculated, and it was determined that, with the exception of CH<sub>2</sub> conversion to CH, these barriers are significant ( $\sim$ 0.85 eV for most steps). C–H bond scission occurs exclusively over top sites.

Michaelides & Hu (108) performed a detailed thermochemical and kinetic study of C, N, and O hydrogenation on Pt{111}, starting with the bare atoms and ending with CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O. Using periodic DFT calculations, they demonstrated that the transition states for hydrogenation reactions of all of these atoms possessed the preferred valency of the atoms themselves. Furthermore, the direction of approach of hydrogen atoms to the CH<sub>x</sub>, NH<sub>x</sub>, and OH<sub>x</sub> species during hydrogenation coincided with the directions of the molecular orbitals of these species (Figure 8). The same authors extended this analysis to more general diatomic recombination reactions of C, O, N, and H atoms on Pt{111} and Cu{111} (109), reactions in which all species involved could have well-defined valencies and site preferences. In these reactions, transition states were always of the hollowbridge or hollow-top form. The higher valency reactant was always found to occupy the hollow position. The lower valency reactant occupied the bridge position if its PES was highly corrugated and occupied the top position if its PES was smooth.

#### Partial Oxidation Reactions

Partial oxidation reaction pathways on transition metal surfaces can also be well described by theoretical techniques. For example, Greeley & Mavrikakis have studied the reaction pathway for methanol decomposition (partial oxidation) on both Cu{111} and Pt{111} surfaces using periodic DFT calculations (Figure 9). On Cu{111}, the authors find that the rate-limiting step (RLS) for this decomposition process is the conversion of methoxy to formaldehyde. The RLS for the reverse reaction, methanol synthesis from CO, is found to be the hydrogenation of CO to yield a surface formyl intermediate. For either the forward or reverse reactions, a high-pressure gas phase environment appears to be necessary to obtain a reasonable reaction rate. Three of the species in the pathway (methanol, formaldehyde, and CO) have higher reaction barriers than desorption barriers, making it likely that they will desorb before reacting in a UHV environment.

On Pt{111}, the reaction pathway is completely different. The RLS for the methanol decomposition reaction is the abstraction of hydrogen from methanol to produce methoxy; the RLS of the reverse reaction is the hydrogenation of CO to formyl. CO is the thermochemical sink of this reaction pathway (in fact, the CO binding energy is so strong that this species is a poison for the catalyst surface). Finally, because of the weak binding of methanol to Pt{111}, a high-pressure environment is necessary to observe this reaction experimentally.







**Figure 9** Calculated potential energy surfaces for MeOH decomposition on Cu{111} and Pt{111} surfaces (J. Greeley, M. Mavrikakis, unpublished data). The zero of the vertical axis corresponds to the total energy of a methanol molecule at infinite separation from the corresponding metal surface. The \* indicates adsorbed species, whereas (g) is used to indicate species in the gas phase. T. S. represents local maxima in the reaction path, corresponding to the respective transition states. The broken arrow used for the adsorbed CO on Pt{111} indicates that the energy for that state is off with respect to the scale of the vertical axis.

# CONCLUSION: FROM THEORY TO INDUSTRIAL APPLICATIONS

In this review, we have attempted to both highlight some of the recent contributions that theoretical techniques have made to the fields of surface science and catalysis and to show the great potential of theory for advancing these fields in the future. We have described how first principles methods can provide significant insight into puzzles that cannot be explained by purely experimental means, how these methods are well-suited for identifying trends in reactivity across the periodic table, and how insight into detailed reaction pathways and mechanisms on particular surfaces can be obtained with these techniques. We would be remiss, however, if we failed to mention two case studies in which theoretical analyses played a major role in the

development of new catalysts, either directly through suggestions of new catalyst compositions based on explicit calculations, or indirectly through the development of concepts that have been used in catalyst development work. These examples epitomize the potential of theoretical methods in surface science and catalysis.

#### New Steam-Reforming Catalysts

In steam-reforming processes, hydrocarbons such as methane are converted to CO and  $H_2$  over nickel catalysts. Graphite formation is a problem over nickel, however, and can lead to catalyst deactivation. As a possible solution to this problem, Besenbacher et al. (112) considered a gold-doped nickel catalyst. They performed two sets of theoretical calculations for methane steam reforming. First, they calculated the change in the reaction barrier for hydrogen abstraction from methane (the RLS for steam reforming of methane) (113), when 0.25 ML of Au was substitutionally alloyed into the Ni surface layer. The barrier increased by  $\sim 0.31$  eV (compared with pure Ni) for methane dissociation over Ni atoms with two Au neighbors. Second, they determined the effect of the same Au doping on the binding of atomic carbon to the surface. 0.25 ML of gold completely destabilized carbon on three quarters of the threefold sites (the preferred binding sites of C on Ni) and led to a  $\sim 0.26$  eV decrease in the binding energy of C on the remaining two sites. The authors concluded that graphite formation would be substantially inhibited by Au doping and that methane dissociation would be only marginally affected. Extensive surface characterization confirmed that a stable Au/Ni surface alloy could exist under in situ reaction conditions and that the catalyst could effectively catalyze the reforming reaction without substantial graphite formation. The extra cost of this new catalyst is reasonable because Au stays on the surface of Ni; Ni and Au do not produce a bulk alloy. Thus, only a small amount of Au is needed. As a result, the Halder Topsøe corporation is presently replacing its traditional steam-reforming catalyst with a Au/Ni alloy catalyst, which has substantially improved lifetime characteristics.

#### New Ammonia Synthesis Catalysts

The RLS in the heterogeneously catalyzed synthesis of ammonia from  $N_2$  and  $H_2$  is known to be the dissociative adsorption of  $N_2$  (114). The transition state in this elementary step resembles adsorbed atomic nitrogen (115), and thus trends in the nitrogen dissociative chemisorption energy are strongly correlated with the reaction barrier and with the overall rate of reaction. For metals on which nitrogen is relatively weakly bound, decreases in the endothermicity of nitrogen chemisorption (corresponding to more strongly bound nitrogen) imply a lowering of the transition state energy and thus a higher rate of reaction. For metals on which nitrogen is strongly bound, however, increases in the strength of the metal-nitrogen interaction can lead to increased nitrogen surface coverage and thus to decreased catalytic activity. The net result of these two effects is a volcano plot

in which a maximum in the ammonia synthesis rate versus nitrogen chemisorption energy relationship is observed. Jacobsen et al. (115) showed that alloying can be used to make new structures with nitrogen chemisorption energies close to the optimum. They identified CoMo as a potential high-activity alloy catalyst (i.e., an alloy with a suitable nitrogen chemisorption energy) by simple interpolation between the corresponding pure-metal components on the volcano curve (Figure 10). Then, they confirmed with first principles DFT calculations that nitrogen does, in fact, have the required intermediate chemisorption energy on CoMo surfaces. They also calculated that the  $N_2$  dissociation energy on this alloy is intermediate between the dissociation energies on the pure metal components. Finally, they used a  $Co_3Mo_3N$ catalyst (synthesized by Jacobsen; 116) to demonstrate experimentally that this alloy has an ammonia synthesis activity comparable to that of the best industrial catalysts.

Theory-to-catalyst successes such as those described above are expected to become more common in the future. With continued improvement of electronic structure calculation techniques and concurrent increases in available computer resources, theoretical tools will play an increasingly important role in rational catalyst design in the coming years.



**Figure 10** Calculated turnover frequencies for ammonia synthesis as a function of the adsorption energy of nitrogen for various transition metals and alloys. [Reprinted with permission from (115); Copyright 2001. Am. Chem. Soc.]

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**Figure 5** Chemisorption energies and dissociation barriers for various atomic and molecular species on a variety of transition metal surfaces versus the clean metal *d*-band centers ( $\varepsilon_d$ ). The *top* panel summarizes trends in CO chemisorption energies; the *middle* panel provides similar information for atomic chemisorption energies; and the *bottom* panel shows trends in dissociation energies for various molecules. [Reprinted with permission from (85); Copyright 1998, Am. Phys. Soc.]



**Figure 6** Surface segregation energies of transition metal impurities (solutes) for the close-packed surfaces of transition metal hosts. [Reprinted with permission from (88); Copyright 1999, Am. Phys. Soc.]