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Binding and dissociation of CO on transition-metal surfaces

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There is a systematic trend across the transition-metal series as to whether a given first-row diatomic molecule prefers to adsorb in a molecular state or adsorb dissociatively. We use simple but well-defined methods to understand the physics and chemistry leading to the observed behavior. We perform calculations for CO on the 3*d* and 4*d* transition metals. These also elucidate the behavior of N_2, NO, and O_2 on transition-metal surfaces.

I. INTRODUCTION AND SURVEY OF EMPIRICAL RESULTS

In this paper we are concerned with understanding the empirical trends observed in the binding energy and the dissociation behavior of the diatomic molecules CO, N_2, NO, and O_2 on transition-metal surfaces. Brodén *et al.*[1] have noted the remarkable facts that: (1) For a given transition-metal (TM) series the further to the left a substrate metal lies, the greater is the tendency for such molecules to dissociate; (2) The approximate borderline for dissociative or molecular (D/M) adsorption moves to the left on going down from 3*d* to 4*d* to 5*d* metals; and (3) The borderline moves to the right in going from CO and N_2 to NO to O_2, i.e., in the same order as the bond strength in the free molecules, which are 11.1, 9.8, 6.5, and 5.1 eV, respectively. A diagram from Brodén *et al.*[1] replenished with some more data, providing the above facts for CO, N_2, and NO is shown as Fig. 1. O_2 seems to dissociate at room temperature on all TM. The D/M borderline, of course, depends on the temperature, due to kinetic reasons. The data in Fig. 1 are taken near room temperature. The main point of interest to us is that the total energies with molecular or dissociative adsorption cross over in the vicinity of the boundaries shown in Fig. 1.

The variation of dissociation behavior with the surface of a given metal is significant only for the borderline metals where under the right conditions both molecular and dissociative adsorption can be observed.[1] In general close-packed surfaces tend to be the least active in dissociation. There is also evidence that surfaces with steps and kinks may be extra active, as in the anomalous dissociation of CO by a high Miller index

CO	Sc	Ti a,b D	V c D	Cr	Mn	Fe D	Co b,d D/M	Ni M
	Y	Zr	Nb b,c D	Mo D	Tc	Ru M	Rh e M	Pd b M
	La	Hf	Ta b,c D	W b D/M	Re f D/M	Os	Ir M	Pt M

N_2	Sc	Ti g D	V	Cr	Mn	Fe D	Co	Ni h M
	Y	Zr i	Nb b D	Mo D	Tc	Ru	Rh h M	Pd b M
	La	Hf	Ta b,i D	W D	Re j D/M	Os	Ir b,h M	Pt b,h M

NO	Sc	Ti	V	Cr	Mn	Fe k D	Co ℓ D	Ni D/M
	Y	Zr	Nb	Mo	Tc	Ru D	Rh	Pd M
	La	Hf	Ta	W m ?D	Re j ?M	Os	Ir D/M	Pt M

FIG. 1. Room-temperature adsorption of the molecules CO, N_2, and NO. *D* means the molecule dissociates spontaneously. *M* means it remains in molecular form. Data are from Brodén *et al.* (Ref. 1), with extra data referenced by letters in the upper right-hand corner of each box.

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Pt surface.[2]

A related and important fact is that the binding energies for molecular adsorption, where available, vary much less across the TM series than the atomic binding energy to the TM of their constituents. The available data have recently been summarized by Toyashima and Somarjai.[3] The binding energy of atomic oxygen varies from about 8 eV for Nb to about 4 eV for Pd. On the other hand the binding energy of CO on all polycrystalline transition-metal surfaces is about 2 eV, within an error of about $\frac{1}{2}$ eV. It therefore follows that an understanding of the dissociation systematics follows simply if we can understand why the molecular binding energy is small and varies slowly across the TM series, compared to the atomic binding energy. The dissociation or molecular boundary would then be given when

$$\Delta H_{\text{bond}}(A)+\Delta H_{\text{bond}}(B)=\Delta H_{\text{bond}}(AB)+\Delta E_{AB}, \qquad (1)$$

where ΔE_{AB} is the dissociation energy in free space of the AB molecule. If the left side is lower, one has dissociative adsorption at equilibrium, and if higher, molecular adsorption.

Recently,[4] the systematic trends in the chemisorption energy of hydrogen and oxygen on TM's have been understood and related to the fundamental parameters characterizing the TM electronic structure on the basis of calculations employing simple but well-defined methods. These calculations are not of the *ab initio* variety but are based on models incorporating the various physical parameters. In this paper we extend these models for calculation of the trends in the diatomic binding and dissociation on TM.

As in Ref. 4, we will explicitly calculate the binding energy $\Delta H_{\text{bond}}(AB)$ of CO with the whole series of $3d$ and $4d$ TM's. Our values can be compared to the experimental data[3] obtained at low temperature and at very low coverage. Since we do not take into account specific CO–metal-atoms bonding configuration (geometry of the TM surface, site specificity, orientation of the molecule, etc.), our theoretical results may be compared to the experimental data,[3] which are relatively insensitive to such details.

At this point, it is worth remarking on the famous correlation often drawn,[3,5] for example, for the heat of adsorption of CO in TM with the heat of formation of transition-metal carbides and oxides. Toyashima and Somarjay[3] have noted that the two are proportional to each other for a lot of metals but independent of each other for others (see Fig. 2). A look at Fig. 2 and comparison with Fig. 1 reveals that the correlation exists when the adsorption is atomic and breaks down when it is molecular. The significant point therefore is that the physics and chemistry of atomic adsorption is akin to that of compound formation, but that of molecular adsorption is not. The methods of Ref. 4 can also be used to calculate heats of formation of compounds; the only change from the surface problem occurs in the absolute value of the numbers, due to change in coordination number and to a lesser extent in the hybridization parameters, with the trends remaining the same. This reflects the similarity in the bonding mechanism in the two cases. The positions of the orbitals of the molecule, which are important in molecular adsorption, with respect to the TM electronic structure is, however, so completely different from those of the constituent atoms (for the cases we are considering) that the bonding mechanism is quite different.

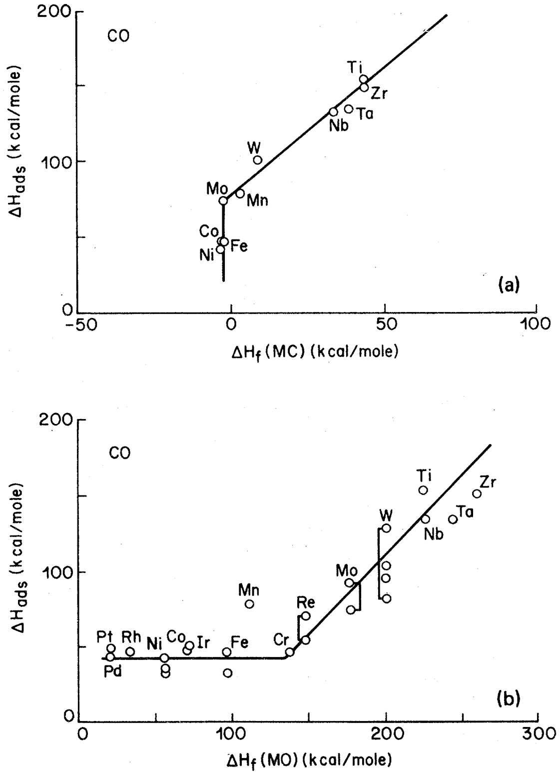

FIG. 2. (a) Heats of adsorption of CO on TM surfaces as a function of the heats of formation of the TM carbides (MC) (per metal atom); (b) Heats of adsorption of CO on TM surfaces as a function of the heats of formation of the TM oxides (MO) (per metal atom).

The bonding mechanism of CO adsorbed on TM surfaces has long been related to the chemical bonding in TM carbonyls. The correlation between the heat of adsorption and the heat of formation of gaseous carbonyls seems to be quite poor.[3]

However, the main features of photoelectron spectra of chemisorbed CO are found to be strikingly similar[6] to those of a carbonyl complex with a small number of metal atoms.

An interesting characteristic is exhibited by photoemission spectra[6,7] of molecularly adsorbed CO: they seem to be unaltered by the properties of the metal surface. In particular, the level associated with the 5σ orbital of the free molecule always occurs at $7\sim 8$ eV below the Fermi energy.

No clear systematics has been recognized in the vibrational spectroscopy[8] of adsorbed CO, except for a decrease of the C–O stretch mode frequency from its gas value, which is common to all TM surfaces. The other vibrational modes seem to be particularly sensitive to the bonding configuration.

Among the possible bonding configuration, CO prefers either terminally bonded M–C–O ligands or bridge bonding, depending on the particular conditions of the metal surface. In the former cases, where very accurate LEED data are now available,[9] the molecule is almost perpendicular to the surface and the bonding to the metal is done through the carbon atom. This is easily understood because both molecular orbitals involved, namely the 5σ and the 2π orbitals, are mainly localized on the C atom.

The decrease in C–O stretching frequency indicates an increase of the C–O separation with respect to the free molecule, and, in turn, a weakening of the molecular bond. Brodén *et al.*[1] argued that an appropriate measure of this effect is the change of the splitting of the 4σ and 1π levels $\Delta(4\sigma - 1\pi)$, which are bonding with respect to C and O. They also found a strong correlation between Δ and the tendency to dissociate (shown in Fig. 1).

In the following we will try to justify some of the above empirical facts. There have been other theoretical approaches to the chemisorption of CO on TM surfaces[10,11,12,13] which have focussed on specific surface geometries and especially on Ni, Pd, and Pt, in an attempt mostly to understand the features of photoemission spectra.

II. PROCEDURE OF THE CALCULATIONS

For details of the general procedure, please see Ref. 4, which we will refer to as I from now on. We briefly summarize it here for application to diatomic molecules.

The calculation is done with a *self-consistent* phenomenological tight-binding method. The starting point for the calculation is an expression for ΔH_{bond}, the bond energy in terms of the change in the local density of states (LDOS) of the admolecule and the transition-metal atoms, upon adsorption. Let $n_{i\alpha}(\epsilon)$ be the LDOS of any orbital α on an atom or molecule i involved in the adsorption, before adsorption, and $\tilde{n}_{i\alpha}(\epsilon)$ be the corresponding quantity after adsorption. Let $C_{i\alpha}$ and $\tilde{C}_{i\alpha}$ be their respective first moments. Then it can be shown in a self-consistent one-electron approximation (like the density-functional approximation) that

$$\Delta H_{\text{bond}} \cong \sum_{i,\alpha} (E_{i\alpha} - \tilde{E}_{i\alpha}) - \tfrac{1}{2} \sum_{j} (D_{i\alpha j\beta} + \tilde{D}_{i\alpha j\beta}) \Delta N_{j\beta}, \tag{2}$$

where

$$E_{i\alpha} = \int_{-\infty}^{\epsilon_F} d\epsilon (\epsilon - C_{i\alpha}) n_{i\alpha}(\epsilon), \tag{3}$$

$$\tilde{E}_{i\alpha} = \int_{\infty}^{\tilde{\epsilon}_F} d\epsilon (\epsilon - \tilde{C}_{i\alpha}) \tilde{n}_{i\alpha}(\epsilon), \tag{4}$$

$$\tilde{D}_{i\alpha j\beta} = C_{i\alpha} - C_{j\beta}, \tag{5a}$$

$$\tilde{D}_{i\alpha j\beta} = \tilde{C}_{i\alpha} - \tilde{C}_{j\beta}, \tag{5b}$$

and $\Delta N_{j\beta} = \tilde{N}_{j\beta} - N_{j\beta}$ is the change in the total charge in $j\beta$.

The first term in Eq. (2) is evidently a covalent or metallic-type bonding term and the second is an ionic-type term. Note that for $\tilde{n}_{i\alpha} = n_{i\alpha}$, i.e., for the adatom far from the metal surface, $D = \tilde{D} = (\mu - \epsilon_F)$, where μ is the chemical potential of the adatom. In this case $\Delta H_{\text{bond}} \cong (\mu - \epsilon_F)\Delta N$.

To calculate ΔH_{bond} into Eq. (2), we need to specify the LDOS of the relevant orbitals of the adatoms and of the relevant transition-metal atoms before and after adsorption. By relevant we mean here the orbitals that change their shape in adsorption (through hybridization) and/or change their total occupation. For carbon and oxygen only $2p$ orbitals are relevant. For the molecule, the relevant orbitals are the 5σ orbital and the 2π orbital, which are completely filled and empty in the free molecule, respectively. The orbitals lower in energy than the 5σ have very weak hybridization to be important-this is generally accepted. In considering the d orbitals at the TM surface, it is convenient, as in I, to perform calculations in terms of the set of group orbitals which couple to the orbitals of the molecule rather than to the atomic orbitals. One must also consider the set of group orbitals with which the orbitals of the molecules do not (or very weakly) hybridize, but to which they can transfer charge. From now on the labels (i, α) will refer to these two kinds of group orbitals at the TM surface and to the 5σ

and 2π orbitals of the molecule concerned.

One of our basic assumptions, fully discussed in I, is that the bond to the adatoms is primarily through the d electrons, with the sp electrons primarily screening charge imbalances and renormalizing the Coulomb repulsion parameters, etc., so that the band through the d electrons is most effective.

Another basic premise of I, which was justified through detailed calculations in II (see Ref. 4), was that the systematic features we seek to explain depend on some general features of the d-electronic structure and not on the details. We determine the general feature of the LDOS from their first few moments evaluated in the tight-binding (TB) method. These moments depend on $C_{i\alpha}-C_{j\beta}$ and $V_{i\alpha j\beta}$, the hybridization matrix elements in the TB matrix set. The further constraints on the LDOS imposed are that their first moment be self-consistent with the charge transfer and the associated Coulomb interactions, i.e.,

$$\tilde{C}_{i\alpha}=C_{i\alpha}+\sum_{(j\beta)\neq(i\alpha)} U_{i\alpha j\beta}\Delta N_{j\beta}, \tag{6}$$

where $U_{i\alpha j\beta}$ are the Coulomb-repulsion parameters. In practice, we will only consider, the U parameter on TM denoted by U_m, a common parameter U_{am} for interaction between charges on any orbital of the molecule and of any *relevant* group orbital of the TM surface, and a common parameter U_a for interaction between charges on any different orbital of the molecule. This is, of course, a considerable simplification. However, we think, on the one hand, that nothing new is gained in understanding the broad general trends by introducing more parameters, and on the other hand, that these are the minimum number necessary to characterize the essentials of the problem. How these parameters are determined is discussed in the next section.

An additional important constraint we impose is that the system be locally charge neutral, i.e.,

$$\sum_{i\alpha j\beta} \Delta N_{i\alpha j\beta}=0. \tag{7}$$

Here, "locally" means the molecular orbitals and the group orbitals formed from TM atoms in the immediate vicinity. Local charge neutrality is brought about in real life through the long-range nature of the Coulomb interactions which in metals leads to screening lengths of atomic size. Within the context of our model, we can use condition (7) to determine the parameter U_{am}.

The calculation proceeds in the following steps. First, the parameters of the surface atoms of the TM (moments of their LDOS, and charge on them) are determined insofar as they differ from the bulk. The known bulk electronic-structure parameters[14] and U_m are used in this calculation. Next, the moments of LDOS on the orbitals of the adatoms and the surface group orbitals which couple to them are self-consistently determined using the free-molecule energy levels $\epsilon_{5\sigma}$, $\epsilon_{2\pi}$, the hybridization matrix elements $V_{5\sigma}$, $V_{2\pi}$ (for 5σ orbital and the corresponding metal group orbital and the 2π orbital and the corresponding metal group orbital, respectively), the molecular Coulomb parameter U_a, the metal Coulomb parameter U_m, and the molecule-metal Coulomb parameter U_{am}. The moments are used to form a canonical LDOS of the form given in Ref. 4. These are integrated up to the Fermi level to find the charge in each orbital. The moments of the LDOS and the charge are required to be self-consistent through Eqs. (6). Local charge neutrality [Eq. (7)] is required and is used to determine U_{am}.

III. CHOICE OF PARAMETERS

The parameters used in the calculations are constrained sufficiently by a variety of information that they have very good qualitative and some quantitative predictive ability. We wish to emphasize that our aim is only to understand the general trends in the experimentally observed adsorption and dissociation behavior, and to understand the bonding processes involved. Toward this limited end the model is rich enough and the parameters in it constrained enough to be meaningful. Copious information on TM electronic structure is available through *ab initio* calculations. We have used the calculations of Watson *et al.*,[14] which have been summarized in Table I of I. The d-d on-site Coulomb repulsion parameter appropriately screened by the reverse flow of sp electrons is known to have a value of about 3 eV. As discussed in I, we believe that at the surface of a TM, the screening is to a large extent from the overflow sp electrons at the metal surface.

For simplicity, all intramolecular Coulomb relusion parameters U_a are taken identical. It is important that U_a be screened by the image effects. Starting from a bare atomic value of about 14 eV, the screened U_a at a distance of 1 Å from the surface has a value of about 6 eV. A bare U_a gives an altogether incorrect position of the chemisorption level for the molecules as it does for the atoms.[4] A variation of ± 2 eV about 6 eV affects the molecular binding energy by 0.5 eV and the chemisorption level $E^*_{5\sigma}$ by a constant amount of ± 0.3 eV. The effect is counterbalanced by the systematic variation of the molecule–surface-atom repulsion parameter U_{am}, which is determined here, as in Ref. (4), by requirements of local charge neutrality. U_{am} is found to have reasonable values lying between 0.2 and 1 eV.

Next, we discuss the hybridization parameters V_σ and V_π. V_σ can be adjusted by comparing the sharp molecular-level-derived features in our LDOS with the corresponding features in the photoemission data.[7] A molecular state which hybridizes weakly with the metal atoms (like the 4σ and the 1π states) shifts its energy on adsorption by $\Delta E \approx U_a \Delta N_{\rm mol}$, where $\Delta N_{\rm mol}$ is the total change in the charge on the molecule upon adsorption. Experimentally, for CO on Ni, $\Delta E_{4\sigma} \approx \Delta E_{1\pi} \approx 3$ eV, and their splitting in the adsorbed state remains about the same as in the gas phase. The 5σ level is raised up by a smaller amount, $\Delta E_{5\sigma} \approx 1.5$, because hybridization due to V_σ alone pushes this level further below the band.

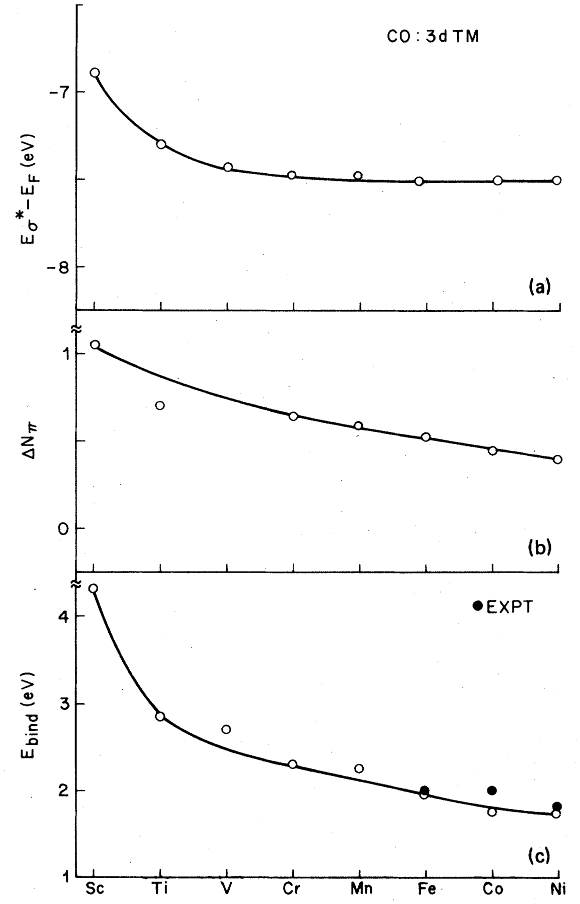

FIG. 3. Theoretical results for CO adsorbed on TM surfaces of the $3d$ series. (a) Chemisorption level (corresponding to the 5σ level of the free molecule) referred to the Fermi energy of each metal; (b) Charge transfer from the metal surface to the fourfold-degenerate 2π level (empty in the free molecule). Bonding energies ($E_{\rm bind} = -\Delta E_{\rm CO}$) of CO to the TM surfaces. The values are compared to experimental data of the heats of adsorption in the cases of molecular adsorption.

We find, in our calculations, that, with $U_a \cong 6$ eV and with V_π to be discussed below, a value $V_\sigma \cong 2$ eV gives $\Delta E_{5\sigma} \approx 1.3$ eV for CO on Ni, compared to a change $\Delta E_{4\sigma} = \Delta E_{1\pi} \cong U_a \Delta N_{\rm tot} \cong 2$ eV. If, as is reasonable, the Coulomb repulsion of the charge in the outer orbitals with the charge in the core orbitals 4σ and 1π was taken larger than U_a, corresponding layer values of $\Delta E_{4\sigma}$ and $\Delta E_{1\pi}$ would be obtained.

The binding energy of the molecule to the surface is found to be quite insensitive to the value assumed for V_σ. This point is discussed later on. The binding energy is, however, quite sensitive to V_π. We fix V_π by equating our calculated binding energy with the measured value for CO in Ni. As explained in Sec. I, we have taken the value of $\Delta H_{\rm ads} \sim 1.7$ eV which is obtained[3] at low temperature on polycrystalline surfaces. We consider the data of calorimetic measurements to be the most reliable ones, as suggested also in Ref. 3. The value so found is $V_\pi \approx 1$ eV. This value for V_π reproduces the measured binding energy for CO on Co and Fe as well. We leave the coupling parameters V_σ, V_π unchanged throughout a given TM series, just as we did for atomic oxygen ad-

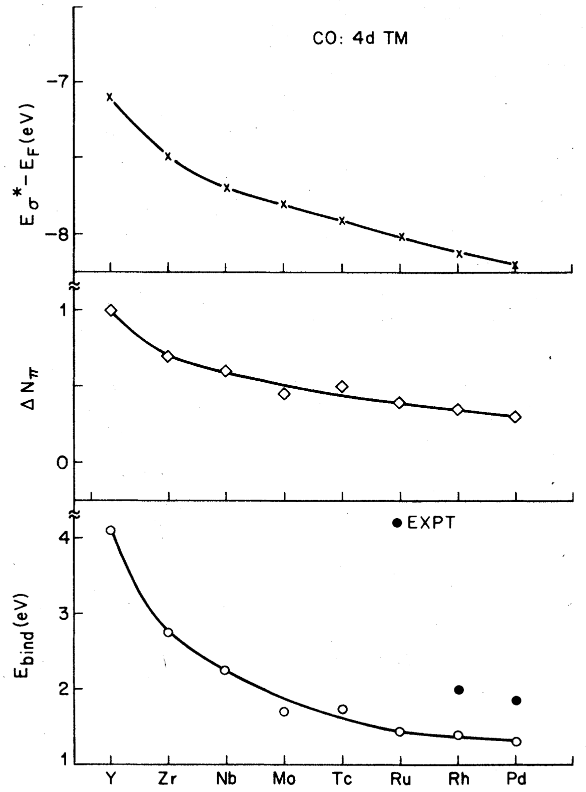

FIG. 4. Same as Fig. 3 for $4d$ series.

sorption for transition metals where we had fair justification. Our justification here is simply that it is a working hypothesis with which we can determine how the basic properties of the substrate metal affect the chemisorption process and, *a posteriori*, that we can obtain the right binding energy in all cases known. The parameters in the calculation needed to reproduce both the features in photoemission and the binding energy are interdependent to some extent. We have not made any particular effort to fine tune our parameters—that would be inconsistent with our broad aims.

It remains only to discuss the molecular levels. They are simply taken from the measured ionization energies of the various levels and including the image correction as in the Coulomb-repulsion parameter. We are also ignoring any change in the CO bondlength on adsorption and the consequent change of the position of the 5σ and the 2π levels. For CO on Ni this quantity has been measured[9] and is very close, ≈ 1.15 Å, to the gas-phase value, ≈ 1.13 Å.[15]

IV. RESULTS AND DISCUSSION

With the parameters constrained as discussed in the last section, the calculated binding energy, the charge transfer to the 2π orbital, and the position of the 5σ-derived chemisorption level $E^*_{5\sigma}$ with respect to the Fermi level for CO adsorbed on the $3d$ TM's are shown in Fig. 3. Results of similar calculations for $4d$ TM's are shown in Fig. 4. We find the charge transfer out of the 5σ orbital, in all cases, to be much smaller ($< 0.1e$) than the charge transfer to the 2π orbitals.

Our calculations indicate that in the range of molecular adsorption the photoemission feature $E^*_{5\sigma}$ is nearly constant throughout a given series and changes only slightly from the $3d$ to the $4d$ series. We find $E^*_{5\sigma} \sim 7.5$ eV and ~ 8 eV below the Fermi energy of the $3d$ the $4d$ TM series, respectively. This is in agreement with photoemission data. This result gives us some confidence in our assumption of constant V_σ and V_π across a given series. Note that ΔN_π is changing significantly in the range where $E^*_{5\sigma}$ is constant. We find that the change ΔN_π is clearly correlated to the binding energy ΔE. ΔE is almost proportional to ΔN_π, with a proportionality factor of ~ 4 eV throughout both $3d$ and $4d$ TM series.

A popular model for molecular chemisorption, the Blyholder model,[16] relies on the notion of molecular charge neutrality and requires $\Delta N_{5\sigma} \approx -\Delta N_{2\pi}$. For the case of TM carbonyls this assumption has been criticized by Johnson and Klemperer,[17] who in extensive calculation of $\mathrm{Cr(CO)}_n$ complexes find $|\Delta N_{2\pi}| \gg |\Delta N_{5\sigma}|$, in spite of a weaker coupling matrix element. ($V_\pi < V_\sigma$ in our language.) We find even smaller $|\Delta N_{5\sigma}|$ for surface adsorption. There are two reasons for this and the relative insensitivity to V_σ in our calculations. First, the antibonding continuum of the 5σ level with the TM density of states lies mostly below the Fermi level for TM's to the right of the series, i.e., where the covalent interactions are relatively large. To the left of the series, the covalent interactions themselves are small since the band lies far above the 5σ level. The second reason is that one will always pull up antibonding states above the chemical potential in small complexes for moderate values of V_σ, but not at the surface of TM's where one has a continuum density of states. Consequently, charge transfer out of the 5σ orbital for a given V_σ will be larger for a small complex than for adsorption. We find an antibonding pole appearing above the continuum only for unreasonably large values of V_σ. Only for further increase in V_σ, we find large and rapidly increasing $|\Delta N_{5\sigma}|$ as also a rapidly varying binding energy.

The dominant binding mechanism in our calculations is the hybridization of the 2π orbital with the TM surface density of states and the consequent increase in the charge of the 2π bonding-derived continuum. The mean energy of this continuum is always below the mean energy of the TM continuum from where this charge comes from. The antibonding 2π-TM surface feature lies above the d-electron density of states and is a δ function in our approximation. Our calculations give its position as ~ 2 eV above E_F for Ni. This feature should in principle be observable in energy-loss spectroscopy, if not obscured by interband transitions.

The qualitative differences in the bonding of adsorbed CO and TM carbonyls that we have discussed above seem to give some insight into the experimental facts mentioned in Sec. I. Indeed, the similarity of the spectra does *not* imply correlation between the binding energy of the former and the heat of formation of the latter (ΔE is dominated by V_π).

In Fig. 5 we plot the molecular binding energy to the TM surface plus the dissociation energy of the molecule in the gas phase together with the sum of the atomic chemisorption energy of the constituents. For oxygen the latter are the same values as calculated in I; for carbon they have been calculated by similar methods using the same hybridization parameter of the p orbitals with the TM orbitals as for oxygen. The molecular curve varies much more slowly across the TM series than the atomic curve so that the two sets of curves cross near Fe for CO on $3d$ series and

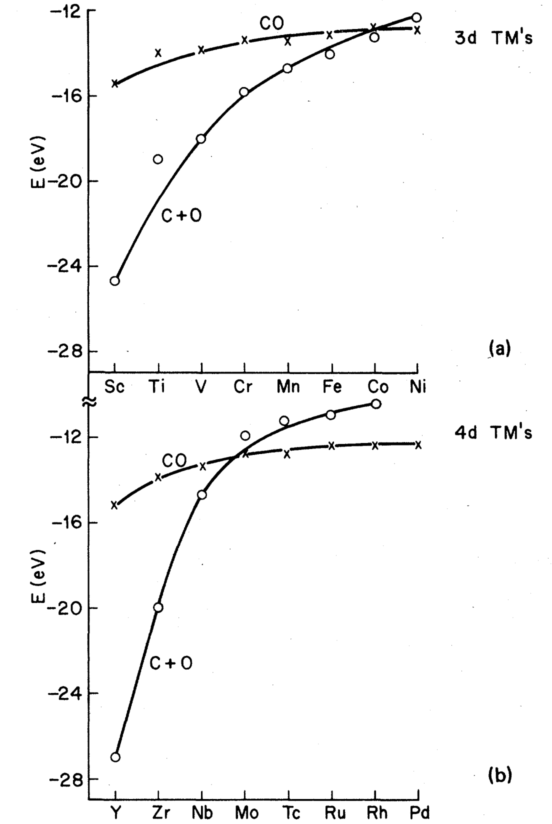

FIG. 5. Energy gain in molecular (CO: $\Delta E_{\text{CO}} + D_{\text{O}}$) and in atomic (C+O: $\Delta E_{\text{C}} + \Delta E_{\text{O}}$) adsorption for CO or $3d$ (a) and $4d$ (b) TM surfaces. Note that the crossing point shifts to the left on passing from (a) to (b).

near Mo for the $4d$ series.

Why does the molecular binding energy vary so slowly compared to that of the atoms? In I it was shown that the primary binding mechanism of, for example, oxygen to the transition metals is the transfer of d electrons of the metals to the partially empty oxygen p-metal d-bonding states which lie below the d band. If the hybridization parameters of the adatom to the TM atoms were very small, the TM parameter determining the charge transfer would be the Fermi level. The hybridization of the atomic p level with the metal d band is, however, strong enough that the LDOS on the transition metals is significantly altered throughout the d band. In this case the trends in the charge transferred and the binding energy are determined by the gross parameters of the metals, i.e., the position of the center of gravity of the d band with respect to the atomic level and to a lesser extent to the d-band width. The hybridization parameter, and to a much lesser extent the Coulomb parameters, set the energy scale for the binding energy. (The Coulomb parameters are quite important for getting the right photoemission level, however). In the extreme limit where one considers only the center of gravity C as important as far as the metal parameters are concerned, and ignores Coulomb interaction, the binding energy due to charge transfer to a doubly degenerate level, which is only singly filled, is given by

$$[\tfrac{1}{4}(\epsilon_a - C)^2 + V^2]^{1/2} . \qquad (8)$$

This expression describes the zero-order trend in the binding energy of adatoms on TM.

For the adsorption of first-row diatomic molecules on TM's, the 5σ level has been found by us not to be important. The 2π level hybridizes with the TM d band, and the LDOS on the molecule acquires an image of the d band which is of the bonding type (and an antibonding level above the d band). Charge is transferred to this bonding continuum. The average of the occupied part of this continuum will in general be below the average of the occupied part of the d bond. This is the primary mechanism of molecular bonding to the TM's. For the molecular case also, the hybridization with the d band is strong enough that only the salient features of the d-electronic structure are relevant. If we use the grossly oversimplified model which gave Eq. (8) for a binding of an atom with an unfilled level below the d band for the binding of a molecule with an empty level above the d band, the binding energy is

$$\tfrac{1}{2}(\epsilon_m - C) - [\tfrac{1}{4}(\epsilon_m - C)^2 + V^2]^{1/2} . \qquad (9)$$

This is much more slowly varying as a function of $(\epsilon_m - C)$ than Eq. (8) is as a function of $(\epsilon_a - C)$. Also, note that as we go the right of the TM series, $(\epsilon_a - C)$ decreases while $(\epsilon_m - C)$ increases, so that although (9) is much more slowly varying than (8), its variation is in the same direction as that of (8). Also, for V of similar magnitude in Eqs. (8) and (9) and molecular binding energy $E(AB)$ of similar magnitude as the atomic binding energy, $E_{\text{mole}} + E(AB)$ is likely to cross $E_A + E_B$ somewhere in the TM series, with the crossover point moving to the right as E_{AB} decreases. On the right of the crossover, the adsorption is molecular; to the left it is atomic.

The definition of the borderline is obviously delicate both from an experimental and a theoretical approach. However, if we compare our results with the pattern in Fig. 1, we see that we have actually succeeded in obtaining the basis for the observed behavior. In particular, for CO on Mo, it is found that[17] at $T = 77$ K CO is molecularly adsorbed and at room temperature it has already dissociated. The shift of the borderline to the left on passing from the $3d$ to the $4d$ TM series is understood in our model. This is due to the corresponding decrease of the binding energies of both molecule and atoms; this, according to (1), shifts the crossing point toward the left. The success of our theoretical scheme in reproducing experimental trends shows that the basic properties of the chemisorptive bond and the driving mechanism for the dissociation of the molecule are both essentially determined by the gross features of the TM substrate.

From our calculations on CO, we can make qualitative remarks about the dissociation patterns of other first-row diatomic molecule. The molecule N_2 has energy levels close to that of CO. Being a symmetric molecule, however, it may prefer to lie on the side on TM surfaces. The dissociation energy of N_2 in the gas phase, ΔE_{N_2}, is about 1.3 eV higher than that of CO. The dissociation systematics of N_2 (Fig. 1) are observed to be similar to that of CO.

The movement to the right of the molecular or dissociated line when going from CO to NO to O_2 seems primarily due to the lower dissociation energy ΔE_{AB}. The chemistry of the adsorption of NO and O_2, we expect, is similar to that of CO, involving primarily the 2π orbitals.

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