

The close ties between organometallic chemistry, surface science, and the solid state

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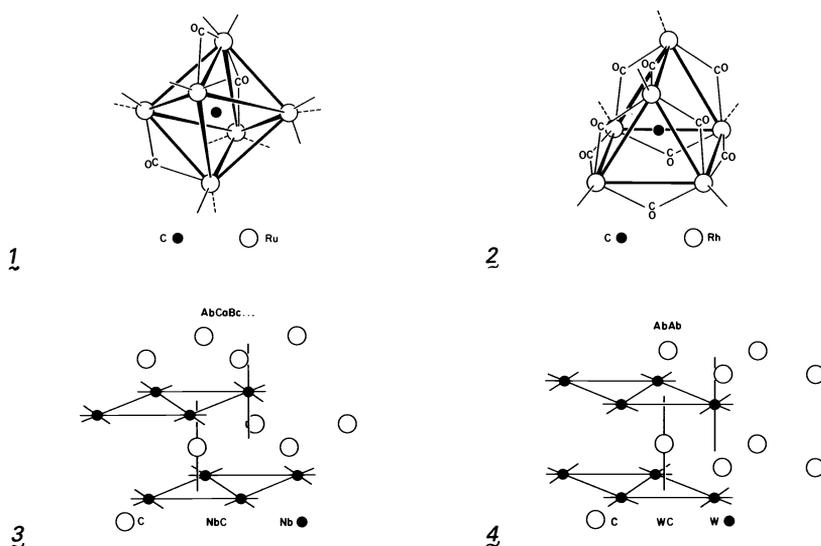
Abstract—There can be no real divergence between the bonding in a discrete molecule and that in an extended two- or three-dimensional solid. Translational symmetry introduces some complications, a different language, but also some simplifications. The essential continuity of bonding descriptions between organometallic chemistry, surface science and the rich world of three-dimensional extended systems becomes evident when one uses the language of density of states and various partitions thereof. Examples drawn from bulk interstitial carbides and CO on surfaces will illustrate these ideas.

INTRODUCTION

Transition metal organometallic chemistry is so exciting today - every new issue of our favorite journal brings news, from Novosibirsk or Mülheim or College Station, of a dozen new structures, twice as many reactions. Not only can we make molecules, and often see their structures, but we begin to understand the intricate, beautiful patterns in which they move, what is easy and difficult for them to do.

Heady times, these. In such marvelous days, when knowledge comes easy and we are caught in the flux of discovery, it is easy to forget that there are other fields of inorganic chemistry, or even not chemistry at all, that deal in significant ways with transition metals and carbon. Let me name two such areas, and give examples of problems in them that are closely related to our enterprise.

First there is solid state chemistry. While we correctly marvel at transition metal carbonyl clusters encapsulating carbides¹, molecules such as octahedral $Ru_6(CO)_{16}C^{2-}$, 1, or trigonal prismatic $Rh_6(CO)_{15}C^{2-}$, 2 out there in the (slightly more) real world there is a multimillion dollar industry making refractory carbides such as NbC, 3, or WC, 4.² The structures of these extended materials are not unrelated to the discrete clusters: in NbC each carbon is



octahedrally surrounded by six metal atoms, in WC by a trigonal prism. There are no carbon-carbon bonds, but there is of course in these conducting and sometimes superconducting substances a three-dimensional network of metal-metal interactions. These are simple-structures of cementite Fe_3C and Hägg's carbide, Fe_5C_2 , show a resplendent complexity.

Or take surface science. Carbon monoxide, our favorite ligand, chemisorbs on most clean transition metal surfaces³. It binds, upright on Ni(111),⁴ apparently lies down on Cr(110) and Ru(001)⁵, dissociates on most early transition metal faces.³ Whether it is bound upright or bent, on-top (the analogue of mono-hapto or terminal) or doubly or triply bridged is a function of the metal, the specific crystal face exposed, the coverage, adventitious coadsorbates (i.e. dirt) and temperature. A congeries of lettered spectroscopies has sprung into use, allowing the surface chemist to approach the very chemical problems of structure and reactivity on metal and other surfaces.

Clearly there is organometallic chemistry in both solid state chemistry and surface science. Yet I don't perceive much knowledge or use of information from these fields in our literature. Aside from the notion of a surface-cluster or solid-cluster analogy - usually operating in the direction "I know a molecule in which X binds just the way it does on your surface" or "Isn't it interesting how the atoms Y in this Y_nL_m cluster begin to assemble the structure of bulk Y"-beyond that there is little. Sometimes I have the distinct feeling that organometallic chemists think of both solid state chemistry and surface science as the other side of the moon.

But actually we have seen the other side of the moon. It is much the same as the side we see. and the same laws of physics and chemistry that shaped the side tidal forces hold toward us, the same principles apply. So it is with these neighboring fields of our science. They are governed by the same laws that guide our molecules, the strong dictates of electronic and geometrical structure - of orbitals, symmetry, overlap. Moreover we had better care about these other fields - not only are they economically important, but the intellectual activity in them is such that they are about to explode, have exploded, are about to overtake us.

So why don't we know more about solid state chemistry or physics, or surfaces, a two-dimensional subfield of the former? In part there is some fear - the structure of cementite looks awfully complicated. But is it really more complicated than solutions to the Enskog equation, or the synthesis of a molecule with nine asymmetric centers? Intellectual fear often derives from laziness - we are comfortable with the complexity we have learned, fear or dislike or consider uninteresting the complexity we have not yet learned. It is not difficult to learn to look at and love complicated three-dimensional structures, it only takes some practice.

Another reason for shying away from the solid state may be traced to the jargon of the trade - of necessity the language of solid state physics, of reciprocal space, Brillouin zones for hexagonal lattices, charge density waves and Peierls transitions. These terms are not part of our education. But in fact they are not difficult to learn, and the essential concepts often have a one-to-one correspondence with chemical ideas we know. I would like to show you in this paper how we can use some of the concepts of solid state physics, especially densities of states, to become comfortable with solid state chemistry and surface science, and to see the basic similarities between these fields and molecular organometallic chemistry.

CLUSTER AND EXTENDED CARBIDES

The most important theoretical contribution to inorganic chemistry in the seventies was the polyhedral or skeletal electron pair theory of Wade and of Mingos.⁷ These remarkably useful rules tell us that for a cluster of six metal atoms and associated ligands the appropriate electron count for an octahedron is 86, but for a trigonal prism it is 90. If a carbon atom is centered in the polyhedron, then one can still maintain these electron counts formally, if one deduces the C of all of its four electrons, and uses them in cluster binding. Thus $\text{Ru}_6(\text{CO})_{16}\text{C}^{2-}$ has 86 electrons and is octahedral, but $\text{Rh}_6(\text{CO})_{15}\text{C}^{2-}$ has four more electrons and the metal atoms form a trigonal prism.

Let us examine the bonding in an idealized octahedral complex, $\text{Ru}_6(\text{CO})_{18}\text{C}^{2+}$, in some detail.⁸ In Figure 1 we show an interaction diagram for the octahedral cluster $\text{Ru}_6(\text{CO})_{18}^{2-}$ (itself having been built up from 6 $\text{Ru}(\text{CO})_3$ fragments) with a C^{4+} at right. Let us describe qualitatively the $\text{Ru}_6(\text{CO})_{18}^{2-}$ orbitals. Each $\text{Ru}(\text{CO})_3$ fragment brings in three mainly metal-centered " t_{2g} " orbitals and three hybrids, pointing "away" from the three carbonyls. The d

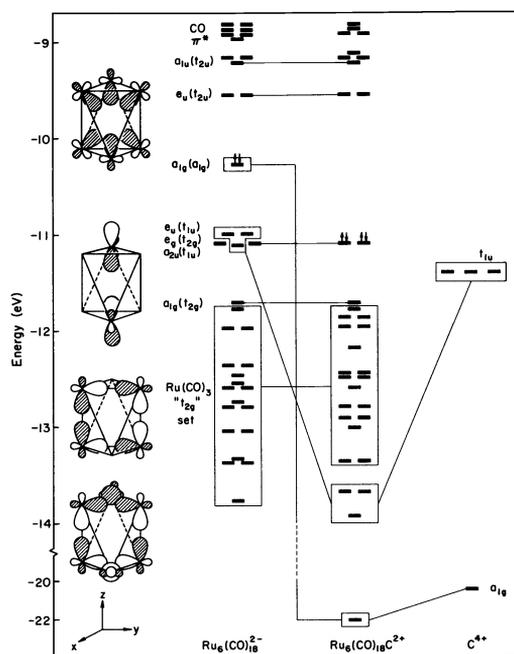


Figure 1. Interaction diagram for the formation of $\text{Ru}_5(\text{CO})_{18}\text{C}^{2+}$ from $\text{Ru}_5(\text{CO})_{18}^{2-}$ and C^{4+} . The metal framework is octahedral. The boxed frontier orbitals drawn interact with the carbon s, p_x , p_y , and p_z (top to bottom).

orbitals interact weakly⁹, to give a band of $6 \times 3 = 18$ orbitals spread in these calculations over ~ 2 eV. They are so close together that we, when we wrote the paper on which this lecture is based, desperately trying to avoid cluttering the figure, just put a black band for the 18 orbitals. We will return to this in a moment. Just above the t_{2g} band are the seven filled orbitals characteristic of a six-vertex closo cluster.⁷ These are responsible for metal-metal bonding. Above these are some unfilled, metal-metal antibonding orbitals, and still higher many CO π^* levels.

Now we bring in the carbon. The major interaction of carbon 2p is with the occupied t_{1u} , and carbon 2s with occupied a_{1g} . This is a crucial point, as it implies that no new occupied orbitals are introduced on carbon incorporation, if it is considered as C^{4+} (a formalism, of course). The 86-electron rule holds. Four of the seven framework orbitals, those interacting with carbon, fall below the t_{2g} block.

This is a small cluster, only six metal atoms. The creative community of organometallic chemists out there is cooking up bigger nuggets - cluster sizes up to 30 atoms are not uncommon. If the number of orbitals in Figure 1 is manageable, it will quickly not become so in these larger clusters. And think ahead to the extended solid - a tiny crystal of WC will have some 10^{20} levels in this energy range. A line for each level will not do for bulk WC, and it barely does for the six metal cluster. So let's anticipate the solid by drawing another representation of the energy level diagram of $\text{Ru}_5(\text{CO})_{18}\text{C}^{2+}$, a histogram in which we lump together all the energy levels that appear in a 0.2 eV range. This is the left side of Figure 2. Please do not look at the right side yet.

Suppose we wanted to trace the metal to carbon bonding in this cluster in some more detail. On the left side of Figure 3 all orbitals which were more than 5% carbon have been plotted; the length of the line drawn for an orbital is proportional to the percentage of carbon in the orbital. We see the three orbitals previously referred to lying just above -14 eV; these are the longest lines. We also see three orbitals at the top of the fragment t_{2g} set, as well as some others deeper down. The top three orbitals shown are empty, and we suspect metal-to-carbon antibonding.

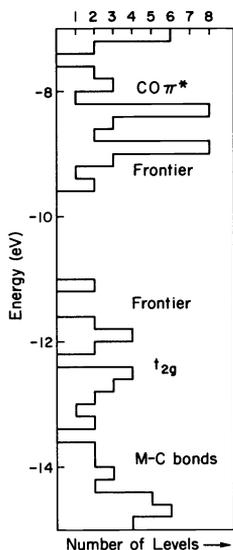


Figure 2. A "density-of-states" diagram for the Ru_6 cluster. All the levels in a 0.2 eV range are grouped together.

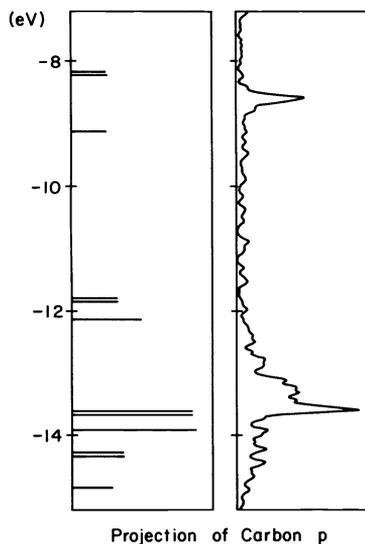


Figure 3. Projection of carbon p orbitals as described in the text. On the left is the octahedral cluster; on the right is NbC.

In figure 4 at left we show the same orbitals, now weighted by their contribution to the metal-to-carbon overlap population. The interpretation of this figure is simple: orbitals to the right of the vertical center-line (+) are metal-to-carbon bonding; orbitals to the left of that line (-) are metal-to-carbon antibonding.

If we try to use a similar plot to describe metal-to-metal bonding, we run into difficulties, since there are many orbitals involved in metal-to-metal bonding. Instead, in Figure 5, at left we have constructed a histogram of step size 0.2 eV. All orbitals within a step are weighted according to their contribution to the metal-to-metal overlap population, and the weights are added up.

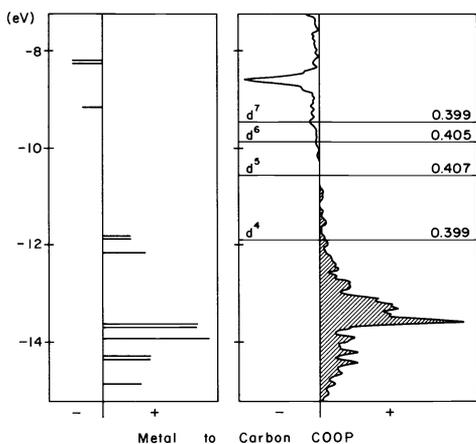


Figure 4. Metal-to-carbon crystal orbital overlap population (COOP); left, cluster; right, solid. The numbers on the solid-state curves are the integrated overlap populations for the Fermi levels indicated. It is clear from the relative sizes of the bonding and antibonding components that most antibonding orbitals are off-scale.

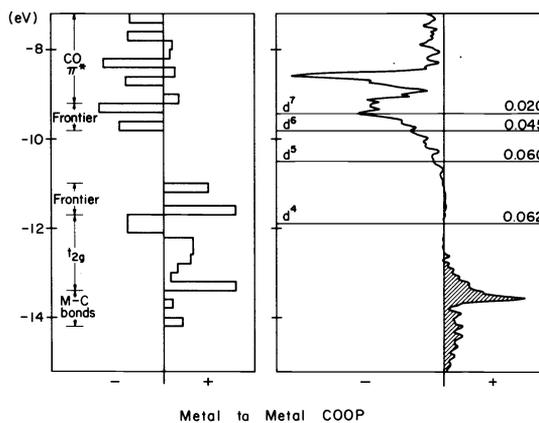


Figure 5. Metal-to-metal COOP: left-cluster; right-solid. The difference between the two curves lies in the occupation of antibonding " t_{2g} " orbitals in the cluster.

In order to interpret Figure 5 more easily we divided up the energy range according to the notation used in Figure 1. The lowest orbitals shown are the metal-to-carbon bonds which are seen to also be metal-to-metal bonding. Next is the fragment t_{2g} set; the lower end of which is bonding, the upper end antibonding. Above the t_{2g} set lie the bonding frontier orbitals, a HOMO-LUMO gap, and the antibonding frontier orbitals. Finally, we have the band labeled $CO \pi^*$, within which are buried metal-to-metal antibonding frontier orbitals.

To sum up, the left hand sides of Figure 3-5 are useful pictorially in showing the bonding in situations where many orbitals are involved. They prepare us for applying similar methods of analysis to the solid state, where the number of orbitals is infinite, or nearly so.

Next we jump - it's a big jump, but not as big as one thinks - to the solid, specifically the NbC structure depicted in 3. The calculation is of the extended Hückel type, and in the trade it would be called a tight-binding band calculation. The product of such a calculation is shown in Figure 6 - a band structure and a density of states. We have landed smack in the middle of some solid state jargon, so let us step back and discuss what is being shown here. To do so it is convenient to move to a model one-dimensional system.

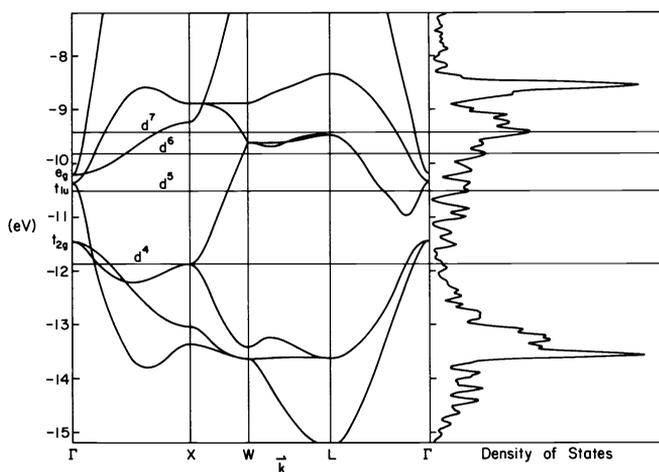
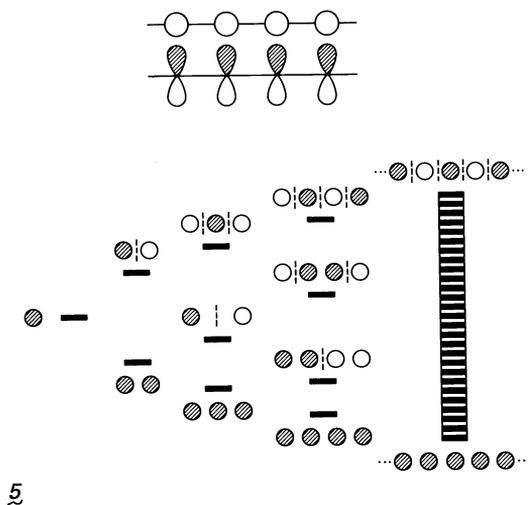


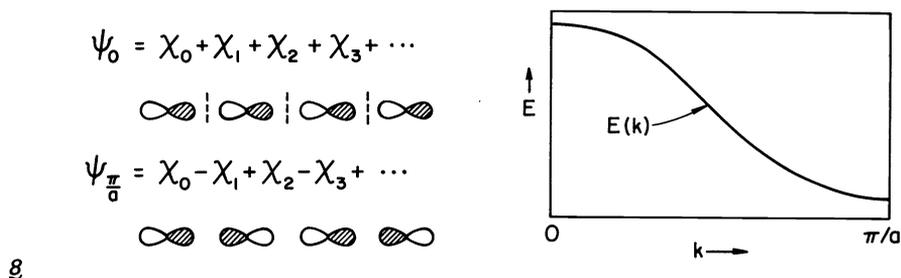
Figure 6. Band structure (left) and density of states (right) for the solid with the NaCl structure (NbC). The wide bands and absence of a band gap are typical of a metal.

Consider a chain of hydrogen atoms (or the isomorphic problem of the π orbitals of a polyene with no bond alternation). We all know the orbitals of the oligomers, shown in 5.



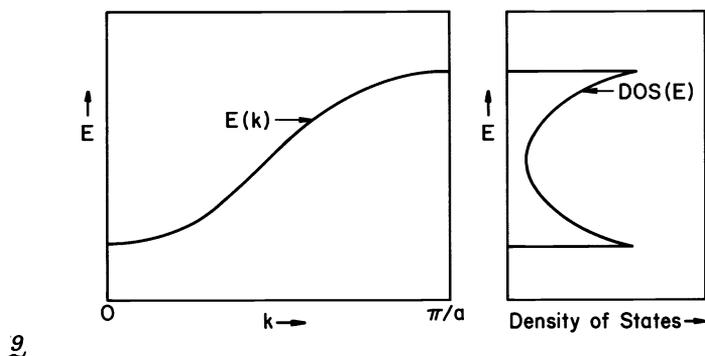
The number of allowed values of k is the number of translations in the crystal, hence there are as many values of k as there are microscopic unit cells in the macroscopic crystal - so let us say infinity, give or take a few. There is an energy level for each value of k (actually two for every value of k because of that $E(k)$ and $E(-k)$ degeneracy mentioned above) and they are equally spaced in k space. So the band at the right of 5 is drawn by solid state physicists as in 7. The space of k is reciprocal space (remarkable k is not only a symmetry label, a node counter, but it is also a wave vector, and so related to momentum); the range of unique k ($0 \leq |k| \leq \frac{\pi}{a}$) is called the Brillouin zone; the difference between the most bonding level and the most antibonding one in the band is called the dispersion of the band; and the energy of the highest occupied crystal molecular orbital (if we fill the levels - so far we have just generated them) is the Fermi level. There is a good part of the jargon.

In Figure 6 we see not one line but many lines. And we see some letters at bottom. Each line is a band. After all NbC in a rock salt structure is more complicated than a line of H atoms. The Brillouin zone is three-dimensional and the letters label special points in that zone. Some bands run "up", some "down". This is a consequence of the topology of orbital interactions. For a chain of hydrogen orbitals the topology is such that the $k = 0$ combination is the most bonding one and the $k = \frac{\pi}{a}$ combination is the most antibonding one. So the band "runs up" from $k = 0$ to $k = \frac{\pi}{a}$. But suppose we had a chain of 2p orbitals instead of hydrogens, 8. Then the $k = 0$ combination is the most antibonding one, and $k = \frac{\pi}{a}$ the most bonding one. The band would "run down" in energy.



Each band of NbC in Figure 6 is an ordered multitude of levels. It is difficult to deal with these infinities (recall it was difficult to do so even with the hexanuclear cluster) and so a way must be devised to speak of bunches of levels and the behaviour of these bunches. We come to the language of densities of states.

A natural way to group orbitals is by energy. The density of states, $DOS(E)$, is simply the relative number of levels in a given energy interval. For the simple band of a chain of hydrogen atoms, 7, it takes the shape of 9. Note that because the levels are spaced equally along the k axis, and because of cosine shape of $E(k)$, there are more states at the top and bottom of the band. In general $DOS(E)$ is related to the inverse of the slope of $E(k)$ - obviously the flatter the band the greater the number of levels at that energy. The shapes of DOS curves are thus predictable from the band structures; note in this context the DOS curve of NbC in Figure 6, and how it relates to the band structure at left.



Now we can see that the histogram we constructed for the Ru_6 cluster in Figure 2 was a primitive DOS curve, for a molecule.

The molecular orbitals of the NbC solid can be analyzed in some detail.⁸ But let us see if we can gain some understanding by just doing some detective work on the DOS, without looking at the wave function in detail. To do this we need just two more concepts. One is that of projections or decompositions of densities of states, sometimes called local densities. These are just like decompositions of electron densities. If in Figure 3 left we are plotting the part of the discrete cluster orbital that is on carbon, so in Figure 3 right we are interrogating all the levels in a given energy range and plotting that part of them which is on C (and not on Nb). Still another use of these projected DOS curves is given below, in Figure 7. Each metal atom in NbC is surrounded octahedrally by 6 carbides (and has additional metal-metal contacts). So it should exhibit a local t_{2g} below e_g splitting. We can ask what part of the DOS in the extended structure is derived from t_{2g} or e_g sets on each Nb.

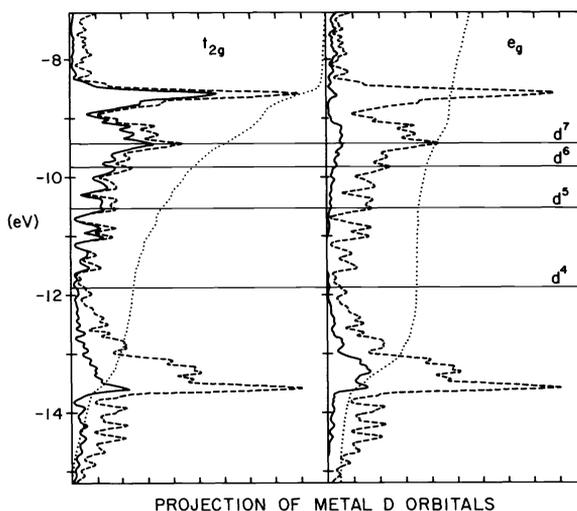


Figure 7. Projection (solid curves) of metal t_{2g} and e_g orbitals for NbC. The total DOS (dashed) is provided for reference. The dotted curve is the integral of the projection on a scale of 0-100% full.

Note the t_{2g} levels are spread over the entire range - clearly metal-metal interactions are very important, delocalizing these orbitals.

Finally we have the solid state analogue of the overlap population. This is called a COOP curve (for crystal orbital overlap population), and one such is shown for metal-carbon bonding in Figure 4, right and for metal-metal bonding in Figure 5. The COOP curve simply interrogates the myriad levels in a given energy interval and inquires whether they are bonding or antibonding in a specific bond. Thus the bottom of the d band in NbC is both NbC and Nb-Nb bonding; the top is strongly Nb-Nb antibonding.

Let us compare the bonding in the cluster and the interstitial bulk carbide. We will use Figures 2-7. Each contains some aspect of the DOS of the system, and we will find some parallels. The reader must keep in mind, however, that the left and right-hand sides of each drawing do not refer to the same system, one is $\text{Ru}_6(\text{CO})_{18}\text{C}^{2+}$, the other is NbC. The parallels are accidental, as similar as they may appear one is not a model for the other. The differences will become clear only in the end. With this caveat, let us proceed.

In both cases metal-to-carbon bonding is strong, and the metal-to-carbon bonding orbitals are pulled down deep, away from the Fermi level and into the range -13-14 eV (Figure 3). In the cluster, bonding to the carbon atoms as well as to the carbonyl ligands is accomplished through metal d^2sp^3 hybrids. This means that only two of the fragment d orbitals, the e_g set are involved. Since the local environment of a metal atom in the solid-state compound is six carbon atoms arranged in an octahedron, ligand field arguments indicate that again only the e_g set of metal orbitals is involved in bonding to carbon.

We can now understand in broad terms the difference between the clusters and the extended solids. In Figure 8 (left) we show in a schematic diagram the construction of the cluster levels. An ML_3 fragment is hexamerized, creating a t_{2g} band and some framework levels. Some of these are M-M bonding, some nonbonding, and some antibonding. The carbon atom interacts with some of the framework levels to give a set of M-C bonding orbitals and a corresponding antibonding set. In the composite cluster carbide all M-C and M-M bonding levels are filled, and this occurs for electron counts greater than d^6 , around d^8 .

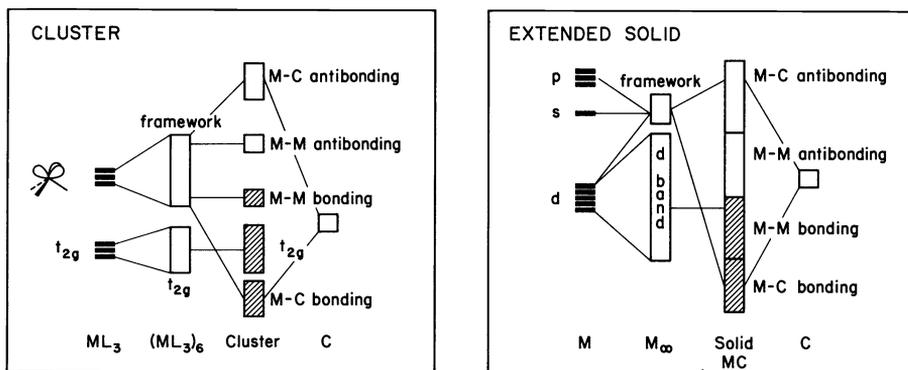


Figure 8. A schematic diagram of bonding in a discrete cluster and an extended carbide, explaining why the former allows d electron counts much greater than the latter. See text for discussion.

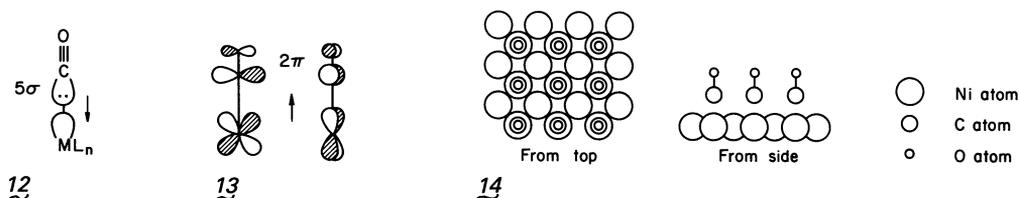
Contrast the extended carbide. The metal orbitals interact strongly with each other, creating a relatively wide d band, and some framework orbitals, four of which point toward the cavity to be occupied by the carbon. The carbon interacts with these orbitals to give M-C bonding and antibonding combinations. If M-C and M-M bonding is to be maximized, only the bottom of the t_{2g} band can be filled for the top is M-M antibonding. Only low d electron counts allow this, and high counts, such as those observed for the discrete clusters, would be disruptive of all bonding.

Otherwise, every aspect of the interaction with carbon in Figure 1 has its analogy in the solid-state compound. For example, carbon increased the HOMO-LUMO gap in the cluster. We recall that the equivalent of the gap in the cluster is a dip in the density of states between bonding and antibonding orbitals in the solid. Both experiment and theory indicate that this dip is neither as deep nor as broad in the transition metal as it is in the carbide.

We have now explored the bulk carbide and the cluster side by side. The similarities and differences are noted; the important thing that we have learned is that we have a common language for discussing both discrete molecules and extended structures. Let us use that language in a seemingly different field.

CARBON MONOXIDE ON METAL SURFACES

We know very much about the way that CO bonds, and does so well, in discrete transition metal complexes. The beautifully extended carbonyl lone pair, 5σ , 12, donates electron density to an appropriately directed acceptor orbital of any transition metal fragment. And the Lewis acid character of CO, displayed through its 2π or π^* orbital, 13, accepts electron density from the metal. This two way charge transfer makes CO one of our favorites.

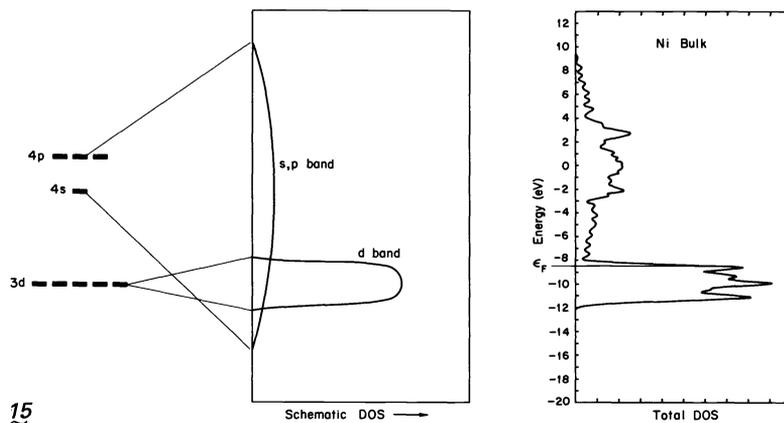


Surely something like this must happen when CO chemisorbs on a metal surface. Let's look at that process.^{10, 11} One must choose a surface and a coverage. Let's take Ni(100) and a coverage of $\frac{1}{2}$ corresponding to the observed $c(2 \times 2)$ configuration of CO.⁴ The geometry of the system is shown in 14.

A true surface is not easy to calculate. In two dimensions it is characterized by translational symmetry, which simplifies calculations immensely. But in the third dimension, perpendicular to the surface, it is not periodic. And it is no great joy to diagonalize semi-infinite matrices. The way theoreticians deal with that problem is to calculate a film, a slab of finite thickness. The number of layers of metal atoms in the slab is usually chosen for reasons of computational economy but justified by appeals to a proper approach to both bulk and surface properties. In our case we chose a four layer slab, and we put CO on one side of it only.

Let's construct an interaction diagram for the metal slab and its CO overlayer, just as we would for any transition metal complex L_nM-CO , partitioning it into L_nM and CO. First the metal slab. A metal slab, or a true surface is just a hefty piece of bulk metal. The orbitals of that slab should in their gross features resemble those of bulk nickel. There will be differences between inner and surface layers, and we will soon return to these. But first let's see what the electronic structure of any bulk transition metal, not just Ni should be like.

We don't even need a band structure for that, we can move directly to the density of states. Each metal atom has nd and $(n+1)s$ and p valence orbitals. Whatever the metal structure, hexagonal or cubic close packed, these levels will spread out into bands. The dispersion of the bands will be a function of the overlap of the respective orbitals, and the diffuse s and p orbitals overlap more than the tighter d functions. The net result for the DOS of a bulk transition metal, bypassing the detailed band structure, is shown in 15. At right in the same drawing is an extended Hückel DOS for the specific case of Ni. Please mark that 15 is schematic, and important, very important fine structure, crucial differences for magnetic systems, all that is not present in this picture. But it will do for our purposes.



The wide s, p band penetrates the narrower d band. For Ni, 10 electrons, per metal atom, the filling of states at the Fermi level leads to a configuration such as $d^{9.2}s^{0.6}p^{0.2}$, with related configurations for other elements. Let us in fact anticipate an important result about other metals, namely a rough indication of their Fermi levels. This will turn out to be crucial to the behavior of CO on different metal surfaces, or for that matter to the surface chemistry of all molecules.

Two factors compete in setting the way the Fermi level of metals varies as one sweeps across transition series, say from left to right. Though the s band penetrates the d band, most of the electrons are in d orbitals. So let us focus on the d band. The center of the d band follows the energy of the atomic d function. This falls, moves to lower energy as one goes from left to right in the periodic table, from Ti to Ni. The d band spreads around this level, and since the d functions are more contracted as the nuclear charge increases, the bands are narrower for Ni than for Ti. This is the first factor, and it can be seen in the schematic diagram 16.

The second factor is simply the filling of this d band with electrons. The two factors compete. The experimental (and theoretical) fact is that the first factor, the atomic orbital energy,

wins out, the energy of the Fermi level decreases, the work function of transition metals increases as one moves from Ti to Ni. This is a very important result.

Returning to Ni(100) and the specific 4 layer slab we use to model that surface, let us see if there is a difference between the surface and inner (bulk-like) layers of the slab. Figure 9 shows the total DOS (compare to the schematic 15) and its decomposition into surface and inner layer contributions.

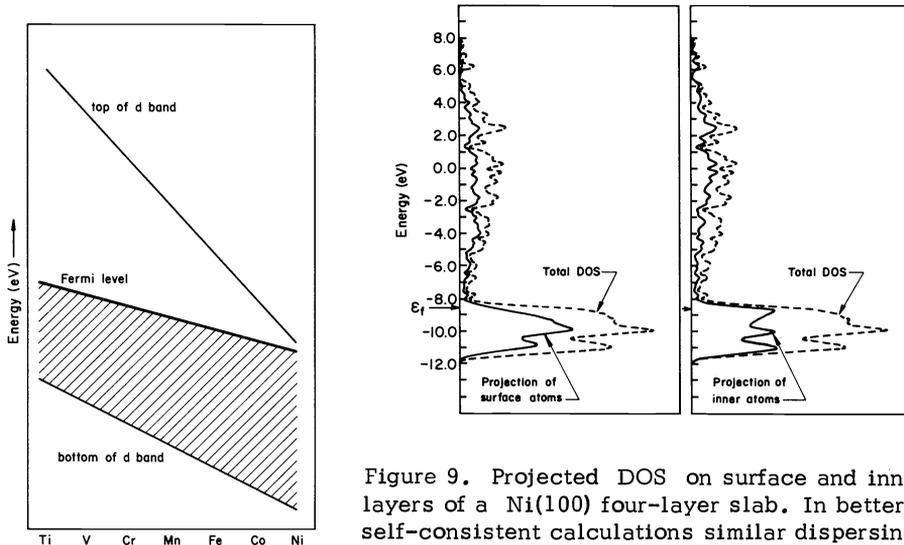


Figure 9. Projected DOS on surface and inner layers of a Ni(100) four-layer slab. In better, self-consistent calculations similar dispersing effects are observed, but the surface states are more skewed toward the Fermi level.

Note the surface layer DOS is more peaked, less dispersed than the inner layer one. This is true both for the s, p and the d bands. Why is this so? Dispersion or bandwidth is a function of overlap with neighboring unit cells, neighboring atoms. The inner layer atoms simply have more neighbors than surface layer atoms. An important consequence of this is that for high d electron counts the surface should be more electron rich than the bulk.

We are almost ready to assemble the chemisorbed system. All we need are the bands and DOS of the CO layer. Because the CO's are relatively far apart, this is easy - each CO molecular orbital will give rise to a relatively narrow band, a peaked DOS at just about the energy of the free molecule's orbitals.

Now let us see what happens when the $c(2 \times 2)$ CO-Ni(100) system is assembled. At left in Figure 10 is the DOS of the naked slab, at right the isolated CO layer, and in the center the composite surface plus overlayer. The electron-density changes are best indicated in tabular form (Table I).

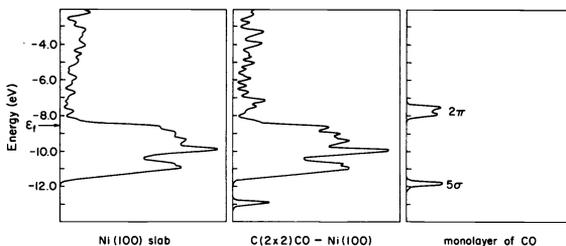


Figure 10. Total DOS of a Ni(100) slab, a $c(2 \times 2)$ CO-Ni(100) system, and a monolayer of CO.

Table 1. Some Results on $c(2 \times 2)$ CO-Ni(100)

Overlap Populations	
M-C	0.84
C-O	1.04(1.21 in free CO)
CO Electron Densities	
5σ	1.62(2 in free CO)
2π	0.37 (0 in free CO)
Electron Density Changes on Surface Atoms with CO on top.	

Δs	-0.05
Δp_{σ}	0.17
Δp_{π}	0.04
Δd_{σ}	-0.50
Δd_{π}	-0.50
Δd_{δ}	0.03
total	-0.80

The total DOS of the composite system shows that the 5σ band (narrow, as expected) has been pushed down in energy. And something has happened to the 2π band. But we need some further detective work to trace down the details of what has transpired.

First the σ interaction: Figure 11 shows the computed DOS of d_{z^2} of a clean surface layer (left), the d_{z^2} part of the composite chemisorbed system (middle) and the CO 5σ contribution in the composite system. Clearly 5σ and d_{z^2} (and not only d_{z^2} ; s and p_z as well) have interacted as the chemisorbed system formed. The net result as far as charge transfer is concerned is both loss of electrons from CO 5σ and from d_{z^2} of the surface. The latter conclusion follows from the fact that $5\sigma - d_{z^2}$ antibonding combinations rise above the Fermi level.

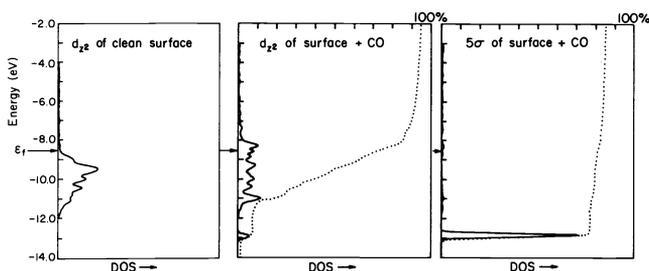


Figure 11. At left the d_{z^2} part of the DOS of surface metal atoms; in the middle, the d_{z^2} contribution to the DOS of those metal atoms which have CO bound to them in the surface-adsorbate composite; at right: the CO 5σ contribution to the DOS of the composite.

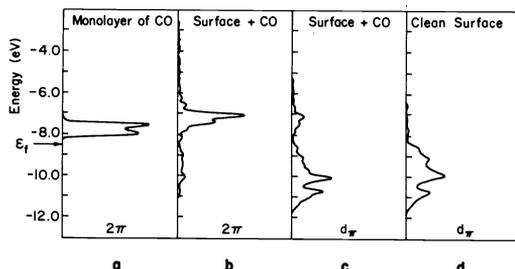


Figure 12. Projected DOS for (a) 2π of a monolayer of CO, (b) 2π of the same CO, adsorbed, (c) d_π levels of those surface atoms having adsorbed CO, and (d) d_π of the clean metal surface.

What happens with the 2π or π^* level is still clearer, and is shown in Figure 12. d_π refers to metal d_{xz} and d_{yz} . Local interactions dominate, and Figure 12 is about as close to a molecular interaction diagram as we can get - remember the surface is not one level but zillions of levels.

The net result of both interactions, just as in the molecular case, is donation from 5σ and back-donation to 2π of adsorbed CO. What is different from the molecular case is an important polarization induced in the surface by the adsorbate.

Another way to follow the involvement of the various orbitals is through the aforementioned COOP curves. In Figure 13 we saw in the d_π and 2π projections a build up of electron density in two regions, at -10 - 11 and around -7 eV. We would suspect that these regions correspond to metal - CO π -bonding and antibonding combinations, respectively. The lower set were shown locally in 13. Figure 13 shows the computed COOP curve for the surface

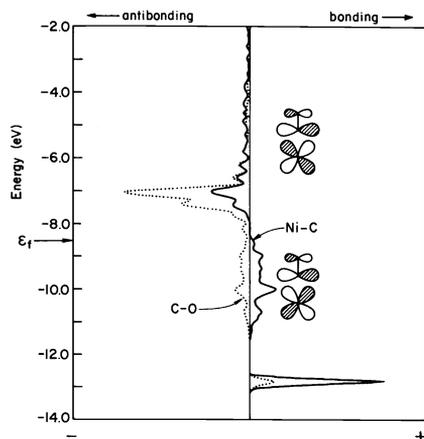


Figure 13. Crystal orbital overlap population in the $c(2 \times 2)\text{CO-Ni-(100)}$ chemisorption system.

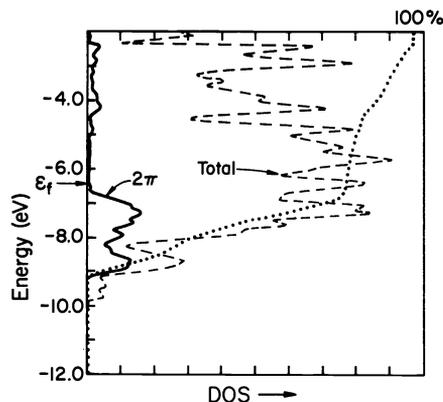


Figure 14. Projected DOS of 2π of CO on the Ti(0001) surface. The dotted line is the integrated DOS of 2π . The broken line is the total DOS of the chemisorption system.

plus adsorbate. Note that the curves, which are sums over all orbitals, nevertheless pick up the features of the 2π and $d\pi$ DOS and that signs of the overlap populations follow the above simple picture. Thus the region immediately below ϵ_F is M-C bonding and C-O antibonding, and that above the Fermi level is antibonding M-C and C-O.

Of many interesting points that remain, let us pick up one, the behavior of different metal surfaces. Figure 14 shows the calculated DOS of CO on Ti(0001). The whole d band of Ti is much higher in energy than that of Ni. Most of it lies above 2π of free CO. 2π is heavily populated (1.20 electrons vs. 0 in free Co, 0.37 on Ni (100)). The CO bond is much weakened and it is no wonder that it breaks up on that surface. It is also clear (see 16) that the further one moves to the left in the transition series the more one is likely to populate 2π in chemisorbed CO, and thus eventually dissociate the molecule.

This ends the carbonyl story. Both for the bulk carbides and for CO on surfaces there is more, but it is told elsewhere^{8,11} And to be sure there is greater richness, variety and therefore interest in the multitude of solid state structures and surface-adsorbate systems being made and studied around us. The point of the account we have given here is that the electronic structure (which in turn determines geometry, mobility and reactivity) of these extended systems is eminently accessible to a chemical analysis. Densities of states and crystal orbital overlap populations are the solid state analogue of levels, charges and bond orders. They allow a reduction of the fascinating complexity of the structure and bonding in the solid state to the potentially understandable.

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