Metal Cluster Complexes and Heterogeneous Catalysis–A Heterodox View

MARTIN MOSKOVITS

Lash Miller Laboratories and Erindale College, University of Toronto, Toronto, Canada M5S 1A1

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The relationships among organometallic chemistry, metal cluster complexes, and chemistry at metal surfaces have lately been the subject of an explosion of interest[1] forming a part of the remarkable growth in general in surface science. No area in physics or chemistry has been more richly larded with new acronyms hailing new instrumental techniques than has surface chemistry. LEED, RHEED, UPS, XPS, SIMS, SPS, ELS—the list is endless—stand for various spectroscopic or diffractive electron, ion, and photon methods whose aim in most cases is to discover the geometry and location of molecular species adsorbed on metal surfaces, or of the bare surfaces themselves. The assumption is that the adsorbed species are either precursors to or intermediates in heterogeneously catalyzed reactions, an area of which a fundamental knowledge is, to a large measure, lacking.

The majority of these studies are undertaken on single-crystal faces, while most commercial heterogeneous catalysis takes place on oxide-supported metals or on oxides.[2,3] This complication, which is not often discussed as such, evokes questions relating, in the case of single-crystal surfaces, to the influence of crystal face and two-dimensional periodicity on adsorption and reaction at the metal surface; in the case of metal particles, to the modifications brought about by the oxide support and the size and geometry of the cluster; and in both cases to the electronic makeup of the metal. For clusters the roles of the support, cluster size, and electronic structure are not unrelated problems. Obviously the electronic structure of the cluster will depend on its size most dramatically for very small clusters, while the degree of contact with the support will likewise depend strongly on the number of atoms in the aggregate.

The recent entry of inorganic chemists and molecular orbitalists into the field has changed the complexion of surface chemistry and heterogeneous catalysis. The former group's interest arises from realization that both heterogeneous and homogeneous catalyses have a formal, procedural similarity in that both processes take place by bond-making of the adsorbate (ligand) to the metal, bond-making of a co-adsorbate such as hydrogen, reaction, rearrangement, and release of the product. There is also the fact that metal cluster compounds, dozens of which are now known, bear a similarity to molecules adsorbed on metal clusters. Hopes are still high that metal cluster compounds will be found which will act as efficiently as or more efficiently than commercial heterogeneous catalysts in hydrogenation, methanation, Fischer–Tropsch, and other reactions. Meanwhile theoreticians have attempted to understand adsorption on surfaces by approximating the surface with a small metal cluster and employing semiempirical molecular orbital methods.

Because both groups wish to model events on large metal surfaces with rather small metal fragments, there has been an enthusiastic campaign to emphasize the many similarities of the two systems, the differences often being ignored.

The main result of these investigations has been to change radically the language relating to surface chemistry. The terminology of coordination chemistry has now almost universally been adopted and the molecular orbital concepts common among inorganic chemists now provide the models for surface processes.

Modeling adsorption processes via small clusters requires localizing the interaction between adsorbate and adsorbent. This has resurrected in modified form the so-called local-bonding model. Originally the local-bonding model was the simple and, in all probability, justifiable assumption used by early surface spectroscopists[4] that the group frequencies observed for adsorbed molecules may be attributed to vibrating moieties similar to those in conventional molecules. So, for instance, if ethylene is adsorbed intact it will have carbon–hydrogen vibrations not dissimilar to those of ethylene complexes and adsorbed CO will vibrate with frequencies characteristic of carbonyls.

This original question has lately been enlarged to encompass a more subtle query, namely, how far-reaching is the interaction between an adsorbate molecule and the underlying metal, or between an adsorbate molecule bonded to one site and another bonded to a remote site. The success of the original model has produced an unjustified conclusion in the transformed version of the local-bond question, namely, that it suffices for the *spectra* of adsorbed molecules to resemble those of small metal cluster compounds or mononuclear complexes for one to conclude that the bonding is local. To my knowledge no argument has ever been put forward to show that an adsorbed layer of ethylene or CO which is engaged in *nonlocal* bonding would necessarily display an infrared, electron-loss, or UPS spectrum differing significantly from that of locally bonded molecules. Consequently the observation of infrared modes in the region of the spectrum in which metal carbonyls absorb or the observation of bands in UPS which one can assign to 4σ, 1π, and 5σ

Martin Moskovits was born in Romania in 1943. He received both the B.Sc. and Ph.D. degrees from the University of Toronto, where he is now Associate Professor of Chemistry.

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[1] (a) H. F. Schaefer III, *Acc. Chem. Res.*, **10**, 287 (1977); (b) G. A. Ozin, *ibid.*, **10**, 21 (1977); (c) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); **85**, 451 (1976).

[2] J. R. Anderson, "Structure of Metallic Catalysts", Academic Press, London, 1975.

[3] T. E. Madey, J. T. Yates, Jr., D. R. Sandstrom, and R. J. H. Voorhoeve, *Treatise Solid State Chem.*, **6B**, 1 (1976).

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of CO does not imply anything about the bonding save that one is dealing with metal to which undissociated CO is bonded.[5]

The properties of clusters which we have investigated in our laboratory combined with the work of others indicate, in fact, that (a) the reactivity of metal clusters toward adsorbate may show very dramatic size dependence, so that what is learnt with one size cluster is not necessarily transferable to another, (b) the spectra of adsorbates on small clusters may differ markedly from those on single-crystal surfaces, (c) certain collective phenomena may contribute in subtle ways to the observed frequencies, intensities, and bandwidths of spectra of molecules which, if interpreted as a local phenomenon, may lead to erroneous conclusions, and (d) the geometries of small clusters are often different from the bulk, hence the "surfaces" presented by clusters will differ from those of single-crystal surfaces even if no surface reconstruction takes place on the latter.

Structure of Bare Clusters vs. That of Bulk

Several examples have been reported to indicate that small cluster geometries differ from those of the bulk. Allpress and Sanders[6] found that electron micrographs of gold microcrystallites on mica showed obvious fivefold symmetries, a symmetry impossible in periodic structures. This was subsequently rationalized by Burton[7] who showed that a 13-atom cluster held together by a pairwise Lennard-Jones potential would not have a cuboctahedral geometry characteristic of fccub crystals but rather an icosahedral structure which contains fivefold rotation axes. Likewise Kimoto and Nishida[8] report that small chromium particles do not have the bccub structure of the bulk metal. Electron microscopic studies by the same authors on Fe and V clusters lead them to similar conclusions.

Yokozeki and Stein[9] have produced large aggregates of Bi, Pb, and In in beams by allowing metal atoms to recombine in an Ar atmosphere. Using electron diffraction, they witness a change in the structure of the cluster from that of the bulk in the neighborhood of 40–50 Å. Indium is particularly noteworthy, changing from a tetragonal to an fccub geometry with decreasing cluster size.

Electron microscopy of metal films on silica produces even more dramatic results. Prestridge and Yates[10] report a flat ring structure for Rh_6 on silica. This contrasts with the octahedral structure reported for Ag_6 trapped in cavities of zeolite A.[11] Even more astounding is the report that ruthenium and osmium rafts of essentially monatomic thickness and with diameters as large as 60 Å form on silica.[12]

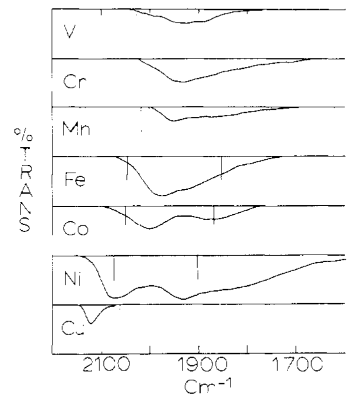

Figure 1. Superposition of the primary CO stretching (Cotton–Kraihanzel) force constants expressed as CO frequencies (vertical bars) of the species $M_2(CO)_x$ where x = 10, 9, 8, 7, and 6 for Mn, Fe, Co, Ni, and Cu, respectively, superimposed on Blyholder's spectra of CO adsorbed on supported aggregates of the metals indicated.[71] The force constants were obtained from ref 38 for $M_2(CO)_{10}$ and from ref 24 for $Cu_2(CO)_6$ and calculated from spectra reported in ref 72 for $Fe_2(CO)_9$ and ref 73 for $Co_2(CO)_8$ in its low-temperature form.

The above examples make the oft-repeated statements that cluster complexes contain bulklike metal skeletons on one hand and that they model surfaces and heterogeneous catalysts on the other hand somewhat inconsistent, since the bare clusters themselves do not adopt the bulk geometry in general, and the geometries seem to be strongly directed by the nature of the substrates on which they rest.

Ligands on Clusters vs. Adsorbate on Clusters

Small-cluster carbonyls have been known for some time. High-nuclearity metal carbonyl neutrals and anions and metal carbonyl carbides and hydrides have been produced over the past 10 years or so largely through the work of Chini and co-workers and summarized in his review.[13] Group 8 looms largest in this area, and clusters as large as $[Rh_{15}(CO)_{28}C_2]^-$[14] and $[Pt_{18}(CO)_{36}]^{2-}$[15] are reported. One of the prettiest compounds is $[Rh_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}H_3]^{2-}$,[16] which has a hexagonally close-packed core consisting of an atom and its 12 nearest neighbors.

Many similarities have been noted between these carbonyls and CO adsorbed on the same metal. For instance, ^{13}C NMR has shown that the CO's are fluxional in many of these clusters[17] with a very small activation energy, as with adsorbed CO. Both terminal and bridging carbonyls exist, and occasionally multiply bonded CO's, as in $[Fe_4(CO)_{13}]^{2-}$[18] and in $Co(CO)_{14}^{4-}$.[19]

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(5) The UPS spectrum of CO adsorbed on Pd (111) is remarkably similar to that of $Rh_6(CO)_{16}$ (for that matter all UPS spectra of CO adsorbed on metals are extremely similar) (H. Conrad, G. Ertl, H. Knözinger, J. Küppers, and E. E. Latta, *Chem. Phys. Lett.*, **42**, 115 (1976)). The chemistry and catalytic properties of these systems, on the other hand, are vastly different, implying that this form of spectroscopy is rather insensitive to the details which affect the chemistry most profoundly. To the extent that these studies indicate the bonding to be local, they imply that the spatial extent of the bonding is not the salient characteristic determining the chemistry of surfaces.

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In the former compound, two semibridged CO's have been observed. Each is bonded to two metal atoms in such a way that the carbon is closer to one than to the other. This variability in bonding site geometry is similar to what must exist for CO's adsorbed on single-crystal surfaces after compression takes place.[20]

The differences are more pronounced. The catalytic activity of the cluster carbonyls is markedly lower than that of heterogeneous catalysts containing the same metal.[21] For instance, CO is not reduced with great efficiency despite the presence of dissociated H in some of these entities and carbon in others. The structures of the metal skeletons are variable, often bearing no resemblance to the bulk metal (compare, for instance, $[Pt_9(CO)_{18}]^{2-}$[15] or $[Rh_2(CO)_{30}]^{2-}$[22] with bulk Pt and Rh), and have metal–metal distances that are strongly ligand-dependent.[13]

Furthermore, the vibrational spectra of CO adsorbed on metals are not clarified by comparison with those of cluster carbonyls save to indicate that in the former one probably has both terminal and bridging carbonyls. This is shown in Figure 1 where, superimposed on the spectra of CO adsorbed on various first-row transition metals, one has the primary force constants of the binary carbonyls $M_2(CO)_x$ including $Ni_2(CO)_7$ prepared in an argon matrix.[23] The CO force constants have been expressed as CO frequencies in order to remove the influence of the CO–CO interaction force constant while at the same time allowing a direct comparison of spectra. One notes neither trends nor similarities in the two sets of spectra, except perhaps in the case of Ni. In Cu the adsorbed species absorb at a higher frequency than does CO in $Cu_2(CO)_6$,[24] while in Mn the reverse is true. CO adsorbed on Mn has sensible absorption at very low frequencies, suggesting bridging CO, while $Mn_2(CO)_{10}$ has no bridging CO's. The CO stretching force constant for the terminally bonded CO's in $Fe_2(CO)_9$, $Co_2(CO)_8$, $Ni_2(CO)_7$, and $Cu_2(CO)_6$ are almost equal, while the peak of the high-frequency envelope of the adsorbed CO recedes in frequency on going from Cu to Fe.

Catalysis by Cluster Carbonyls vs. CO Adsorbed on Metal Clusters

For a given metal, the number of metal atoms which forms a viable cluster carbonyl appears to be restricted to certain "magic numbers". Attempts to make clusters of intermediate sizes either result in the cleavage of the cluster to smaller ones or the agglutination of clusters to larger ones.[13] The geometry of the metal skeleton and the values of these magic numbers, we propose, are largely directed by the ligands.

This principle is illustrated by the following example. Theoretical calculations predict the Cu_3 and Cu_4 have stable structures close to linear.[25] Our spectrum of Cu_3[26] does, in fact, appear to be consistent with this conclusion and that of Cu_4 is not inconsistent with it. (Recent Raman evidence, moreover, suggests that Ag_3 does not possess D_{3h} symmetry.[27]) Cu_4CO, on the other hand, which we have also made,[28] appears to have a square-planar Cu_4 skeleton and a μ_4-CO bonded to it. The CO, then, has brought about a marked change in the geometry of Cu_4.

Here we might have an explanation for the reluctance of stable cluster carbonyls to catalyze in the manner of heterogeneous catalysts. In the latter, metal clusters prepared in the absence of the ligand will have the geometries characteristic of the bare cluster, modified somewhat by the presence of the support.[12] When adsorbate interacts with the catalyst it finds cluster sizes and geometries quite different from those "perferred" by the stable cluster compounds formed by the metal with the adsorbate as ligand. In general the modifications in geometry and size required to form the stable compound will require breaking of energetic metal–metal bonds; consequently the adsorbate forms a compromise bond with the cluster, causing "strain" in the metal cluster as the aggregate attempts to attain a more favorable shape. The adsorbate–metal system is therefore more active than analogous stable clusters. It will, moreover, tend to remain coordinatively unsaturated since the preformed aggregate will not possess the needed electronic structure to support a full complement of ligands.

All this ensures three things: first, that sites are available for a co-adsorbate such as hydrogen needed to carry the reaction forward to its goal; second, that the metal still has sufficient electronic flexibility to dissociate the hydrogen if required; and, third, that the adsorbate–metal bond will not have its maximal strength because of strain in the cluster, favoring, thereby, transformation and release as product. The amount of strain will also obviously depend on the metal cluster geometry and size, which might explain the remarkable variability manifested by metal catalysts with preparation conditions and other like parameters.

Catalysis on single-crystal faces or unsupported polycrystalline metals is likewise constrained. The geometry of metal atoms in the surface is highly directed by the rest of the metal bulk and cannot easily accommodate the "wishes" of the adsorbate alone. (Adsorbate-induced surface reconstruction is a well documented phenomenon which maintains two-dimensional periodicity, however. Clearly, then, the geometrical changes do not come about in order to attempt to form a cluster compound.)

Type of Adsorption and Cluster Size

The reactivity of small, bare clusters toward certain ligands may also depend markedly on cluster size. We have shown,[29] as has Barrett, that N_2[30] will combine with Fe_2 but not with Fe to form dinitrogen species. When iron is deposited in argon under suitable conditions, one records the spectra of Fe, Fe_2, Fe_3, and higher clusters. Under the same conditions in N_2, only the spectrum of Fe atoms appears, while those of Fe_2

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(20) J. C. Tracy and P. W. Palmberg, *J. Chem. Phys.*, **51**, 4852 (1969), and ref 36.

(21) A. K. Smith, A. Theolier, J. M. Basset, R. Ugo, D. Commereuc, and Y. Chauvin, *J. Am. Chem. Soc.*, **100**, 2590 (1978), and references therein.

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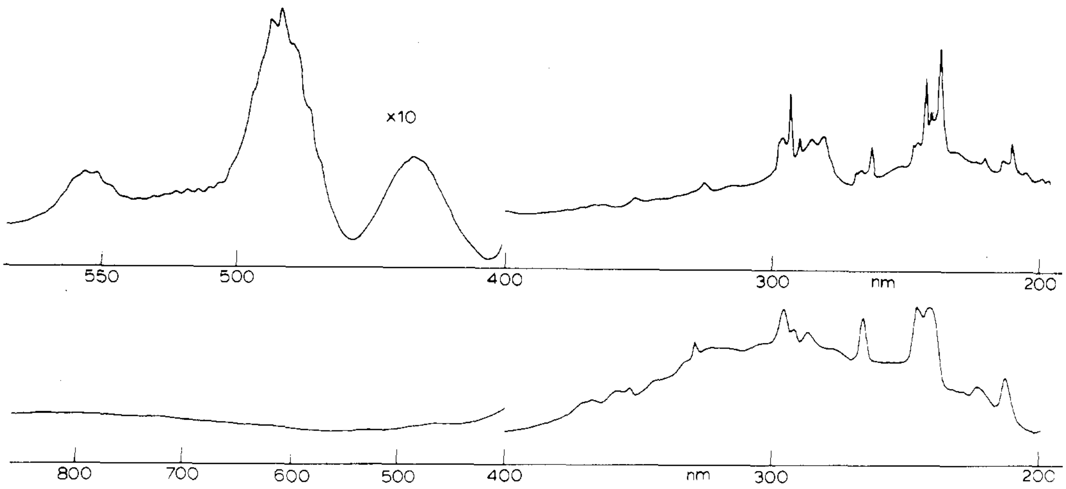

Figure 2. Portions of the UV–visible spectra of iron isolated in Ar (upper trace) and N_2 (lower curve) at 11 K. Features carried by Fe_2 and Fe_3 are visible in the top curve. They are absent in the lower curve in which absorptions by Fe atoms and colloidal Fe particles are discernible, the latter in the form of a broad band between 200 and 350 nm. (Note scale change in the lower trace.)

and Fe_3 have disappeared (to be replaced by much weaker absorptions belonging to Fe–dinitrogen complexes) (Figure 2). This fact has been confirmed by infrared analysis of these systems which shows that dinitrogen complexes form when iron is placed in N_2. The persistence of the spectrum of Fe atoms in the UV–visible spectrum and analysis of the IR spectra indicate that none of the IR bands belong to mononuclear species.[30]

For very large Fe clusters, one observed UV–visible absorptions characteristic of the bulk metal and a gradual disappearance of the NN modes in the infrared, suggesting that the bonding of N_2 to bulk Fe clusters is weak, a fact known from adsorption studies.[31] N_2, then, reacts with small clusters of iron but not with iron atoms or large clusters. In the language of adsorption, it chemisorbs on small clusters but physisorbs on bulk metal. Clearly, any conclusion one obtains from studying mononuclear species is not necessarily applicable to small clusters, nor are conclusions obtained from studying small clusters applicable to bulk metals.

Single-Crystal Surfaces vs. the Surface of Small Clusters

The spectra of molecules adsorbed on single-crystal faces also differ in important ways from those of molecules adsorbed on large clusters which in turn are not always similar to the spectra of the same molecules bonded to small clusters. So, for instance, the CO stretching vibration in the series of molecules Cu_nCO (n = 1 to 4) quickly approaches that of CO adsorbed on large, supported Cu clusters.[28] This is shown in Figure 3. The peak in the envelope of bands obtained with CO on copper particles supported in solid argon comes at a frequency close to that observed with silica-supported copper,[32] implying that the nature of the support does not affect the major features of the spectrum.

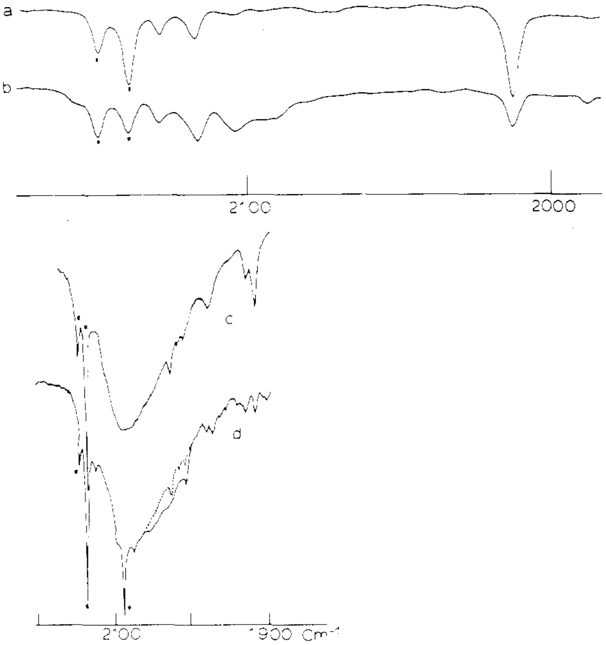

Figure 3. (a) Portion of the IR spectrum of a matrix containing Cu/CO/Ar in the approximate ratio 1:10:4000. (b) The spectrum of the same matrix after warmup to 35 K. (c) The spectrum obtained with a matrix approximately 50 times richer in Cu. Asterisks mark uncoordinated CO absorptions. (d) Same as (c) but with a roughly equimolar mixture of ^{12}CO and ^{13}CO. Cross-of-Lorraine marks absorption by uncoordinated ^{13}CO. The dotted line is the low-frequency edge of spectrum c drawn to emphasize the small change in the spectrum of CO "adsorbed" on large Cu clusters brought about by the addition of ^{13}CO. Note frequency scale contraction in (c) and (d).

Moreover, we know that the spectrum of Figure 3c involves large particles whose surfaces are locally flat enough to cause vicinal CO's to be almost parallel to one another, as deduced from the spectrum obtained with equimolar $^{13}CO/^{12}CO$ which gives the indicative band-intensity asymmetry.[33] Since the CO absorption of Cu_xCO ($x \geq 4$) occurs at approximately the same frequency as that of CO on bulk copper, one might conclude that the bonding of CO to Cu is so local that four metal atoms suffice in establishing an adsorption site. This may indeed be true for small clusters provided that the CO–metal stoichiometry is kept small as with adsorbed molecules. The spectra of CO adsorbed on single-crystal faces of copper, on the other hand, show a marked dependence on Miller index[34] and,

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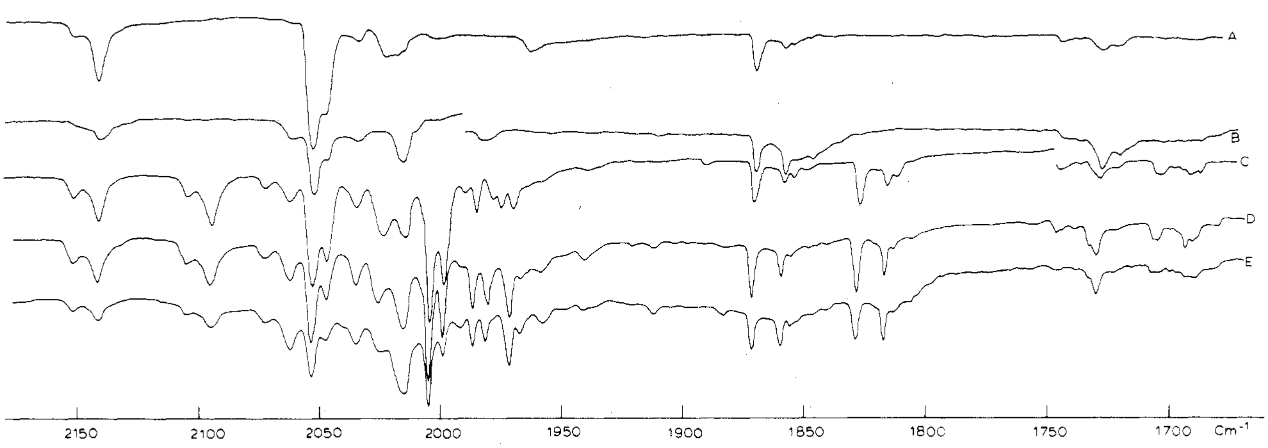

Figure 4. (A) Portion of the IR spectrum of Pd atoms condensed with CO/Ar = 1:500 molar ratio mixture on a surface cooled to 11 K. (B) Same as (A) but after warming to 35 K for 10 min. (C) Spectrum obtained with a $^{12}CO/^{13}CO/Ar$ mixture in the molar ratio 1:1:500. (D), (E), after successive warmups to 35 K.

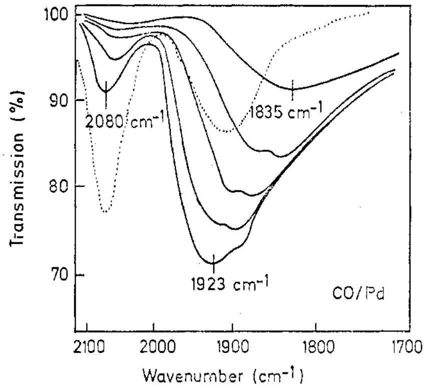

Figure 5. Portions of the IR spectra of CO adsorbed on silica-supported Pd cluster for various coverages[4] (solid line). Dotted line is the spectrum obtained after warming a Pd/CO/Ar matrix at ~40 K for 15 min.

except in the case of high-index faces, have CO frequencies quite different from those observed on clusters.

A more spectacular example is that of CO on Pd. Palladium cluster monocarbonyls (containing 4 Pd atoms or fewer) have been produced in solid argon.[35] The portion of a typical set of infrared spectra showing the CO stretching region is reproduced in Figure 4. With ^{12}CO in argon, bands occur in three regions of the spectrum: 2000–2500 cm^{-1}, 1840–1870 cm^{-1}, and 1720–1750 cm^{-1}. The three regions likely arise from linearly bonded, μ_2-bridging, and μ_3-bridging carbonyls. On warming this composition, one obtains a spectrum consisting of two broad envelopes of bands centered around 2080 and 1910 cm^{-1} (Figure 5) which, except for a difference in relative intensity, appears quite similar to spectra of CO adsorbed on silica-supported Pd (Figure 5). In contrast with copper, the spectra of the small Pd cluster carbonyls in which the CO/metal stoichiometry is small do not resemble that of CO adsorbed on large Pd clusters, in which little trace is left of the bands near 1720 cm^{-1} and the band at 2080 cm^{-1} (at high coverages) is higher in frequency than the CO stretching modes of any of the small cluster carbonyls of Pd. Moreover, the shift in low-frequency band of the adsorbed molecules from 1835 cm^{-1} to 1923 cm^{-1} (for CO on Pd/silica) with increasing coverage is not easily understood in terms of the knowledge gleaned from the study of small clusters.

The disparity between the spectra of small Pd cluster carbonyls and those of CO adsorbed on single-crystal faces of Pd is even more striking. The spectra are strongly face-dependent.[36] On the (100), (111), and (210), the low-coverage absorptions come at 1894, 1823, and 1878 cm^{-1}, respectively. LEED data indicate that, at low coverages, the CO is μ_2-CO on all three crystal faces.[36] Thus a μ_2-CO on Pd can absorb at least at the three frequencies above, depending on which crystalline face it finds itself on. Two of these are substantially different from the CO stretching frequency of $Pd_2(\mu_2\text{-}CO)$, which absorbs at 1868 cm^{-1}.

The coverage dependence of the absorption spectra of CO adsorbed on the three faces is even more remarkable. The frequency of maximum absorption shifts to higher frequencies with increasing coverage in the case of all three crystalline faces. The amount of shift, however, depends markedly on the face. At half coverage the stretching frequencies of CO on Pd(100), Pd(111), and Pd(210) have attained values of 1948, 1936, and 1985 cm^{-1}, respectively. In two cases the shift exceeds 100 cm^{-1}. Between the low- and half-coverage extremes the CO vibration is found to broaden, then narrow again.[36]

Both the shift in CO frequency and the broadening and narrowing effect have been adequately explained by invoking CO–CO vibrational coupling.[33] In order to product a 100-cm^{-1} shift, however, one has to use a CO–CO interaction force constant greater than 0.5 mdyn/Å,[37] five times larger than the largest reported CO–CO interaction force constant across the metal–metal bond of neighboring metal atoms in multinuclear carbonyl.[33,38] Similar CO frequency shifts, though

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[35] M. Moskovits and R. Smith, in preparation.

[36] A. M. Bradshaw and F. M. Hoffmann, *Surf. Sci.*, **72**, 513 (1978). These authors attribute the large change in frequency in the Pd(111) case as opposed to that encountered with Pd(100) to a change of site from μ_3-CO to μ_2-CO. We have been able to reproduce the spectra including the broadening effect using a calculation as described in ref 33 by assuming μ_2 bonding throughout. A. M. Bradshaw (personal communication) states that the LEED pattern cannot distinguish in this case between the two possibilities. Our argument, however, is equally valid in either instance, since the CO frequency observed at low coverages on Pd(111) (1823 cm^{-1}) would be at odds with that of CO in the molecule, $Pd_3(\mu_3CO)$ (1720 cm^{-1}), on one hand, and with the CO stretching frequencies of CO adsorbed on (100) and (110) on the other.

[37] This value was obtained when CO–CO interactions were limited to those between nearest neighbors. More conventional values could be obtained if one assumed sizable interactions between more remote neighbors, slowly decreasing with increasing separation. Either way, the calculation suggests the existence of important through-metal CO–CO coupling.

[38] H. Haas and R. K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967).

smaller, have been reported for CO adsorbed on supported Pt particles,[39] and the shift from 1835 to 1923 cm^{-1} shown in Figure 5 may also be due to such coupling. Evidently the "communication" between adsorbate molecules is much more pronounced than that between ligands in cluster carbonyls. This enhanced interaction may be through the intermediary of the conduction electrons, perhaps by coupling to plasmon polaritons, as was proposed recently by Metiu[40] to explain the infrared bandwidth of absorbed CO at low coverages. If so then the infrared spectra of adsorbed molecules partly reflect nonlocal phenomena, although group frequencies will occur in the usual regions of the spectrum. Even here one is not entirely on safe ground. For instance, vibrations of ethylene and cyclohexane adsorbed on Ni(111) and Pt(111) that do not absorb at any of the usual hydrocarbon group frequencies have been observed.[41] These have been attributed to metal–hydrogen-bonded C–H stretching vibrations. All this does not guarantee that the chemistry need be described in terms of nonlocal models. It does say, however, that the spectroscopy as a probe of the chemistry will include contribution from nonlocal effects.

Collective Phenomena

Other optical properties of adsorbed species that suggest that coupling to conduction electrons is somewhat pervasive have recently been reported. Greatly enhanced Raman scattering has been observed for several heterocycles adsorbed on electrochemically roughened silver electrodes.[42] Although the exact mechanism for intensity enhancement is not agreed upon, it appears that plasmons,[43] and in particular collective oscillations in metal bumps on the surface,[44] play a part.

As another example, resonance coupling between electronically excited molecules placed on or near a metal surface and surface plasmon polaritons has been demonstrated by Kuhn[45] and by Drexhage,[46] who showed that the fluorescence quantum yield of a Eu(III) complex changed as the distance from a silver surface was increased by inserting monolayers of fatty acid between the chromophore and the metal. The theory for such a process has been discussed by Morawitz and others.[47] More recently, Gordon and Swalen showed that the surface plasmon polariton resonance of gold could itself be shifted by adsorbing cadmium arachidate films on the surface.[48] Philpott[49] has considered the effect of coupling between exciton polaritons of a dye and plasmon surface polaritons of a metal on the electronic spectrum of a monolayer of dye molecules adsorbed on a metal or a fixed distance above the metal. He concluded that large enhancements would be observed in the absorption of the dye. Fluorescence lifetimes of molecules are also known to be affected by the presence of bulk metal though "leakage" via the plasmon channel.[50]

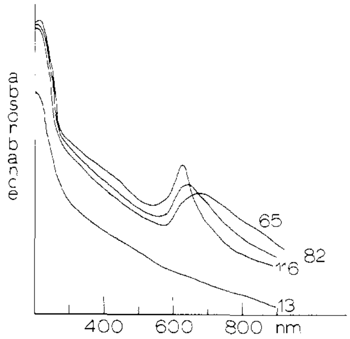

Figure 6. UV–visible spectra of colloid copper particles dispersed in a dielectric medium of refractive index 1.58, calculated as in ref 26 and 51 using copper optical constants of ref 74. Particle radii in Å are indicated. Note broadening and eventual disappearance of the feature at approximately 610 nm as the particle size is reduced.

It is an accepted fact that collective electronic processes such as plasma resonance are important aspects of the optical and spectroscopic properties of metal aggregates be they colloidal metal[51] particles or "island films".[52] Nevertheless, one can lose sight of the nonlocal nature of plasmons, as in a recent claim that an Xα molecular orbital calculation on a linear silver hexamer yielded features which showed incipient "plasmon" behavior.[53] Plasma resonance, a collective phenomenon, does not correlate with any molecular absorption in the limit of small particles. In fact Figure 6 shows that the resonance is damped to obscurity as the metal cluster is reduced in dimension below the electronic mean-free-path which in good conductors is of the order of 200 Å.[54]

Calculations and the Chemisorptive Bond

Although an extensive discussion of the vast theoretical effort made over the years in understanding the nature of the bond between adsorbed molecules and a metal substrate is clearly outside the scope and intent of this Account, one cannot entirely escape touching upon these studies in view of the great impact they have had on one's thinking regarding the nature of the surface chemical bond. The types of calculations performed fall roughly into three categories: band structure, molecular orbital, and other two-body and many-body interaction calculations.

The first,[55] exemplified by the work of Schrieffer[56] and others,[57] assumes a periodic adsorbent and a pe-

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riodic overlayer and makes use of relationships arising out of the periodicity to make the calculation tractable. The quantities presented are densities of states and energies of chemisorption. The language of these types of calculations has been for many years that of band theory, with the symmetries, types of orbitals, and charge distributions associated with them keeping a low profile. The results of these calculations were therefore not immediately assimilable by inorganic chemists, who think in terms of hydrogenic wavefunctions and molecular orbitals manufactured out of them.

The second type of calculation did a great deal to remedy this. A large number of MO calculations on "adsorbate"-bearing small metal clusters appeared, normally using approximate MO techniques such as Extended Hückel,[58] CNDO,[59] or Xα-SW. The last has become the most prolific, largely through the work of Messmer[60] and Johnson.[61] These calculations are cast in the familiar language of chemists, and their main benefit to date has been to establish firmly adsorption and related surface phenomena as a branch of chemistry. Several calculations have been reported as well which compare the results obtained via the two methods.[62]

Despite the apparent coming together of the solid-state physicist's and the chemist's points of view, differences exist and with these some confusion. For example, various, quite separate queries go by the name of the local bond question, among them: (a) how quickly the bond energy of an adatom or admolecule reaches a constant value as the cluster to which it is bonded increases in size, (b) the distance away from an adsorbed molecule at which the charge distribution on a metal atom (assuming throughout a metallic adsorbent) differs appreciably from the charge on that metal atom in the absence of the adsorbate both along the surface and into the bulk, and (c) the way in which one adatom (molecule) affects another one (its bond energy, its vibrational frequency, etc.) as a function of distance along the surface. The last two questions must be asked of single-crystal surfaces and clusters separately since the situation may differ in the two cases. Moreover, one must determine if collective behavior sets in as the adsorbate becomes a periodic overlayer on a single-crystal surface, a state of affairs clearly not possible with small metal clusters.

The extant majority opinion as I write this suggests that the largest part of the chemisorptive bond energy arises from "local" bonding, local in the sense used in point (a) above. However, the best estimates show (and this is by no means a settled question) that one needs clusters in which there exist at least third-neighbor interactions before convergence to the experimental bond energy is approached.[1a,63] This normally means aggregates containing 25–50 atoms. Needless to say, most calculations on clusters do not involve such large metal fragments because of the inordinate computer requirements. Calculations performed on smaller clusters (and indeed chemistry carried out on them) should then be considered as very crude approximations (over and above the approximations inherent in the calculational techniques) of a bulk surface. I cannot find any argument to support the notion that one or two metal atoms model a surface with any accuracy whatsoever. (In a recent paper,[1a] BeH was stated to be a good model for H chemisorbed on Be because of the similarity between the bond energy (D_e) of the diatomic (46.4 kcal/mol) and that of H bonded to a 22-atom cluster (55.1 kcal/mol), despite the fact the D_e varied between 19.1 and 71.3 kcal/mol for intermediate size clusters and for various bonding geometries.)

A more important point is the fact that catalysis is the chemistry following chemisorption. What determines the strength of the chemisorptive bond need not be what governs its subsequent chemistry. And just as the vibrational spectra of molecules adsorbed on crystalline surfaces were in a general way similar to those of cluster complex analogues while their finer details were distinct from them as a result of subtle adsorbate–adsorbate and adsorbate–metal interactions, so I contend that the great variety of chemistry possible on metal surfaces is highly sensitive to subtle variations in bond strength arising from these types of interactions.

As a single illustration, Ta atoms adsorbed on W(110) tend to form islands while Re atoms repel each other,[64] despite similar adsorption bond energies. Island formation has also been reported for CO adsorbed on various metal surfaces.[65] The stability of these surface aggregates depends more critically on adsorbate–adsorbate interactions than on the usually much stronger chemisorption bond strength. One can easily surmise that effects such as these can affect catalytic activity by, for instance, aiding or hindering the coming together of co-adsorbed molecules or blocking adsorption sites. Moreover, indirect interactions have been found on occasion to be rather long range,[64] again implying a through-metal effect.

Theoretical work suggests that the agents mediating these long-range effects are the metallic electrons,[66] with plasmon-mediated interactions also taking some part.[67] Others have shown that shorter range interactions arising from phonon-mediated coupling can also exist.[68] The presence of conduction electrons may also produce what is classically spoken of as image charges[69] which contribute to the bonding energy in a way which would vary from metal to metal and with cluster size. (It will be almost nonexistent in very small clusters.) Moreover, the crystalline environment underlying the adsorbate may give rise to even subtler effects such as spd hydridization, creating localized states which take part in metal–metal bonding and adsorbate–metal bonding in different ways.[69]

The last-mentioned phenomenon suggests that the division between local and nonlocal phenomena is at

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times artificial. An admolecule may indeed interact most strongly with the surface atoms in the vicinity of the adsorption site; the electronic structure of the latter, however, may nonetheless be modified by the rest of the metal and hence the adsorbate–metal bond need not be the same as that between the same adsorbate and a gas-phase cluster approximating the geometry of the adsorption site. Consequently small metal cluster "models" for the localized bonding will not always mimic the interaction with the surface accurately.

The situation therefore, as I see it, is as follows: The gross features of the chemisorptive bond, as well as that between a molecule and a very small cluster, are adequately described by a local bond. However, the chemistry and the spectroscopy, especially vibrational spectroscopy, may respond to subtle effects which are not always accurately understood by analogy with single-metal-atom or very small, stable cluster complexes. Moreover, catalysis by small, supported-metal aggregates will in general be different from that by stable cluster complexes as a result of the existence of many "metastable" structures for the bare cluster. When large enough to achieve a crystalline aspect, further differences set in arising from substrate-mediated adsorbate interactions. On two-dimensionally periodic surfaces one might have additional collective effects as well.[70]

Much of the above is speculative. It is nevertheless clear that a great number of phenomena have been reported which are unique to bulk metals having no obvious local counterparts. While their role in surface chemistry is as yet uncertain, it behooves us to investigate it.

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New Transparent Ferromagnets

PETER DAY

Oxford University, Inorganic Chemistry Laboratory, Oxford, OX1 3Q, England

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This Account descibes a wide-ranging set of experiments to prepare and characterize a new series of transport ionic ferromagnets with the general formulae A_2CrX_4, where A is either an organic or an inorganic unipositive cation and X is a halide ion.

The large majority of ferromagnets are metallic conductors. Conversely, by far the largest proportion of ionic transition-metal or lanthanide compounds, including oxides, halides, sulfates, and many complexes, are antiferromagnets. In its simplest terms, ferromagnetism in metals arises from the coupling of localized electrons on neighboring centers, such as those in partly occupied 3d shells, via the mobile conduction electrons.[1] In insulators, the interaction between the unpaired electrons on neighboring cations is normally mediated by an intervening ligand bridge, usually an anion. In that case the sign of the resulting exchange integral depends on a variety of competing superexchange pathways involving delocalization of the unpaired spin on the metal toward the ligand as a result of covalency.[2] It turns out that in the great majority of cases the sum total of all the superexchange pathways is an antiferromagnetic coupling.

Are there then any ionic transition-metal salts which order as simple ferromagnets? The answer is very few. In fact, Table I contains close to an exhaustive list. A striking feature of this list[3-11] is how chemically disparate the various substances are, embracing simple cubic lattices, coordination complexes, and lanthanide and transition-metal compounds. Having such diverse crystal structures and ground-state electron configurations, it would be surprising if the superexchange pathways giving rise to the ferromagnetic ordering had very much in common. However, at least between the

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Peter Day was born at Wrotham, Kent, England, in 1938. His first degree and D.Phil. are from Oxford University, where he was a Scholar at Wadham College. At present he is a Science Research Council Senior Research Fellow and Fellow of St. John's College, Oxford, having, until 1977, been University Lecturer in Inorganic Chemistry. In 1971 he was awarded the Corday–Morgan Medal of The Chemical Society.

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