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In this work we have carried out a number of joint chemical and physical studies of metal surfaces, of adsorbates on such surfaces, and their reactions. Several catalytic reactions were studied theoretically, as well as materials problems related to interfaces and overlayers.

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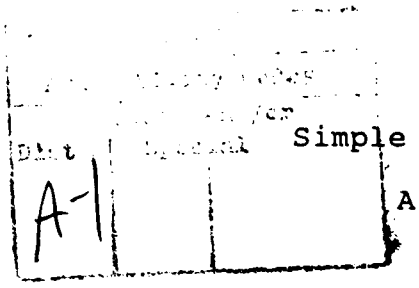

FINAL REPORT

Simple Adsorbates on Transition Metal Surfaces — A Joint Chemical and Physical Approach

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Roald Hoffmann and John Wilkins

The past three years have been exceptionally good for the collaboration of physics and chemistry that is the strong point of our work. The Wilkins and Hoffmann groups, in a series of joint group meetings, have established a central focus for theoretical studies of surfaces, one which has served the entire Cornell surface science community. We have also carried out a number of pioneering studies of the electronic structure of surfaces, of adsorbates on such surfaces, and of their reactions. Several significant catalytic reactions have been studied, as well as materials problems related to interfaces and overlayers. Our detailed achievements are described in the following pages.

Scattering from Surfaces

We have applied the formalism for calculating elastic and inelastic scattering probabilities of light atoms from surfaces to the case of H_2, D_2, HD, and He scattering from Cu. We are especially interested in the quantum mechanics of the process, both for the motion of the particle and the excitations of the lattice. The calculations use an interaction potential chosen to simplify the numerical calculations while retaining the essential physics of the interaction. The He scattering calculations show that these approximations quantitatively reproduce experimental results. Based on this success we consider how the scattering probabilities depend on details of the system such as the well depth and the steepness of the potential as well as the assumptions made to simplify the interaction potential. H_2 and D_2 inelastic scattering and trapping possibilities show strong enhancement by selective adsorption resonance and overall changes in scattering intensities due to the effects due to the rotational degrees of freedom. Temperature-dependent HD scattering probabilities show the effect of inelastic scattering on rotationally inelastic scattering and selective adsorption resonances.

Small Metallic Clusters

We have studied in detail how multiply charged metal clusters explode under the influence of electrostatic repulsion.

We have performed self-consistent calculations of the energetics of multiply charged Li clusters containing up to 40 atoms. While fragmentation of singly charged clusters has to be induced, the clusters containing two or more charges fragment spontaneously. For singly charged clusters, it is the largest fragment that carries the charge, while for multiply charged clusters, the charges are equally shared by the daughters. The fission products always contain the most stable singly charged cluster (i.e., a magic number cluster) unless forbidden by the conservation of mass in the fragmentation process — thus providing a unique way of looking for magic-number clusters.

Coadsorbates and poisoning

We have studied the influence of an S adlayer on CO adsorption on Ni(100). Tight-binding extended-Hückel calculations on a three-layer model slab indicated that the interadsorbate separation distance determines not only the mechanism but also the effect of the interaction. If the C-S distance is short, sulfur induces site blockage of CO chemisorption by means of a direct, repulsive interadsorbate mechanism. If the separation is increased beyond the normal S-C bond range, the sulfur adatoms work indirectly via modification of the electronic structure of the substrate. This is a form of through-bond coupling. It is consistent with the well-documented sulfur poisoning of CO adsorption and its usual explanation via relative electronegativities of adsorbates.

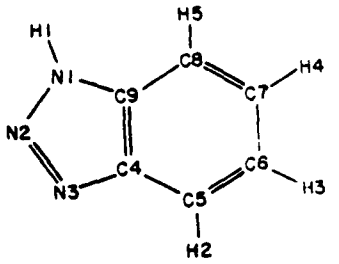
Metal carbide surfaces and their reactivity

Extended-Hückel tight-binding calculations were used to analyze the interactions of oxygen, carbon monoxide and methanol with the (100) and (111) faces of a representative rocksalt carbide, TiC. The (111) face has been experimentally shown to be the most active toward the adsorption, dissociation or decomposition of adsorbates, whereas the (100) face demonstrates very little activity. Our calculations suggest that the differential reactivity of the two faces is the result of the coordination of the atom in the active site and the presence of surface carbon. For CO on the (100) face the population of the $2\pi^*$ level increases if carbon vacancies are included in the calculation, and dissociation occurs. For the (111) metal-terminated face of TiC the population of the $2\pi^*$ level is nearly identical to that calculated for Ti(0001). Methanol dissociates into methoxy and a protic species on the (111) face but remains molecular on the (100). The calculations suggest that the molecular species is stabilized by interaction of the methanolic proton with the surface carbon.

Corrosion inhibition of copper surfaces by nitrogen heterocycles

Copper surfaces are commonly treated with benzotriazole (BTA) to inhibit corrosion. BTA is thought to lose a proton at N1 to the oxide coating, which is present on commercially

available copper, through the formation of water. BTA^- is proposed to bind to the surface through the nitrogen lone pairs, rather than through the π orbitals of the rings. By analogy to organometallic copper chemistry, pyridine ligands (as examples of nitrogen containing aromatic rings) show a marked preference to



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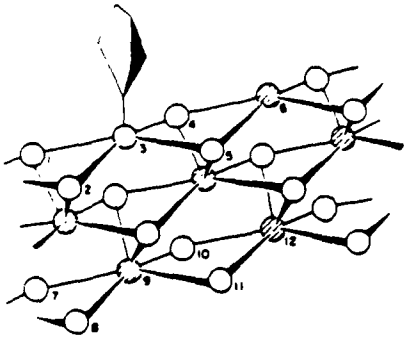
coordinate through the nitrogen lone pair. Hundreds of examples of N-bound copper-pyridine complexes exist, but only a few π-bound species have been found. It is unclear whether BTA^- lies parallel or perpendicular to the copper surface, and this formed the focus of our study, which also looked at the effect of coadsorbed oxygen.

Hydrodesulfurization

The removal of sulfur in the form of H_2S from petroleum, is a crucial step in the industrial refinement process. Using the extended Hückel tight binding method, we have examined the nature of the active site and the mechanism of desulfurization in the case of thiophene on MoS_2.

Adsorption geometries such as **2** and **3** were compared. The η^5



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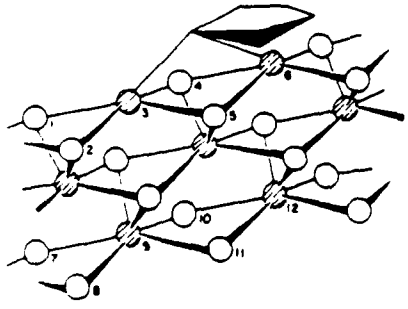

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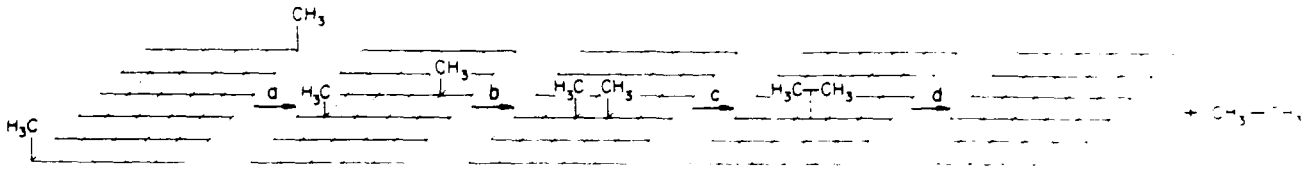
-bound sites, in which the thiophene ring lies parallel to the surface, are particularly advantageous to weakening the S-C bond. η^1-bound sites are less active. The removal of surrounding surface sulfurs increase the HDS potential of the η^5 geometry, but is ineffective at promoting the poorer adsorption modes. Surface reconstruction has also been examined; the possibility of Mo-Mo pairing is suggested. The effect of poisons and promoters is considered. The role they play in HDS catalysis may be determined by the position they occupy in the MoS_2 lattice. Metals which replace a surface molybdenum tend to poison HDS, whereas those which "pseudo-intercalate" between the S-S layers can serve to promote the reaction.

<u>The Fischer-Tropsch Synthesis</u>

The reductive oligomerization of CO over a heterogeneous catalyst, described over 60 years ago, is of tremendous actual and potential importance. In a very long paper, which I feel will stand as a paradigm for theoretical studies in surface chemistry, we have looked at the late stages of this reaction, the bonding and coupling of C_1 fragments on metal surfaces.

The bonding of CH_3, CH_2, and CH fragments to Ti(0001), Cr(110), and Co(0001) metal surfaces was examined with extended Hückel band calculations on two-dimensional slabs of metal and adsorbate. A local chemical viewpoint was sought through fragment analyses, decompositions of the density of states, and overlap population studies. All fragments tend to restore their missing C-H bonds when bound to these surfaces — CH_3 prefers the on-top, CH_2 the bridging, and CH the capping geometry. CH_3 anchors more strongly to the on-top site of a metal surface of higher d band filling since the antibonding feature at the top of the d band destabilizes sites of higher coordination. Similar conclusions hold for other fragments. Thus, the mobility of these fragments is reduced on metal surfaces of higher d band filling. The mobility patterns of CH_3, CH_2, and CH are examined. In general, on the way to products there are barriers to migration on the surface, a proximity or crowding effect which makes it costly for two fragments to approach on the surface, a barrier, small or large, to the reaction with each other, and finally a desorption barrier. These are illustrated

schematically in drawing **4** for two methyl groups.



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When two C_1 fragments couple, the C-C σ^* orbital rises from below the Fermi level. It is initially filled and then empties as the reaction proceeds. Hence the lower the Fermi level (for metals at the right side of the transition series) the smaller the reaction barrier. The theoretically expected decrease of the mobility of the organic fragments or one hand and the higher coupling rate on the other, as the metal is changed from the left to the right side in the Periodic Table, may be two of many reasons that are responsible for metals in the middle of the transition series having higher reactivity in Fischer-Tropsch catalysis.

A new approach to the orbitals of truncated crystals and surfaces

Large clusters and small crystallites are a form of matter intermediate between discrete molecules and infinite solids. At the same time as they are structurally intriguing, they are difficult to treat by using conventional orbital methods. A

Linear Combination of Crystal Orbitals (LCCO) method is described for calculating the orbitals of large, finite systems such as clusters, crystallites, or thin films from a band calculation on the corresponding infinite solid. Our analysis breaks the problem into two parts: (1) choosing k points where orbitals of the solid resemble cluster MO's and (2) performing a perturbation calculation to include the effects of truncating the crystal and of adding the end atoms omitted from the band calculation. The reciprocal space of the finite crystal and its relation to the reciprocal lattice of the infinite solid provide a fundamental connection between cluster MO's and crystal orbitals of the solid. Wannier functions localized within a large unit cell corresponding to the cluster make the connection explicit and guide the choice of k points for the band calculation. In the final step, the perturbation calculation is accomplished by using a matrix diagonalization algorithm introduced by Davidson to solve the CI problem for small molecules.

Ralph Wheeler, a talented graduate student who developed this method, tested it on linear polymers, simple and complicated. But the LCCO approach is general and can be used with any orbital method. The approach is also valid for other systems perturbed from perfect translational symmetry, such as surfaces, interfaces, and defects.

The frontier orbital analysis of bonding at surfaces

It's taken some time, but from detailed studies such as

those mentioned above, I have assembled the elements of a general theoretical approach to surface structure and reactivity that is within the framework of solid state theory, yet strives for chemical ways of interpretation. One begins then from highly delocalized band structures, but introduces interpretational tools (density of states decompositions, crystal orbital overlap populations) that allow a tracing of local, chemical acts. It is quite feasible to construct interaction diagrams for surfaces, and to make frontier orbital arguments, just as for molecules. There are some interesting ways in which the surface-adsorbate interaction differs from simple molecular binding — in particular, in the way that two-orbital four- and zero-electron interactions can turn into bonding. The surface and bulk acting as a reservoir or electrons or holes at the Fermi level are important in this context. Chemisorption emerges as a compromise in a continuum of bonding whose extremes are dissociative adsorption and surface reconstruction.

The paper which describes this work has had an instructive history. It was commissioned by Accounts of Chemical Research. it turned out to be too big for that excellent journal, and so was submitted to the Journal of the American Chemical Society. From which it was rejected, not because of the content, but because of the overly pedagogical style. With the active help and advice of John Wilkins, the paper was modified to make it clear to physicists, and has just been accepted by Reviews of Modern Physics.

This history is not a tale of woe, but is viewed by me positively, as testimony to the ability of our work to cross the borders between physics and chemistry in ways that I think few people can.

The work described here has been integrated with a still longer account of our solid state research into a book that has just been published by VCH. It is entitled "Solids and Surfaces: A Chemist's View of Bonding in Extended Systems."

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Principal Investigators	1985-86	1986-87	1987-88
R. Hoffmann	x	x	x
J. Wilkins	x	x	x
Postdoctoral Associates and Visitors			
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R. J. Nieminen		x	x
K. W. Jacobsen			x
S. Jansen	x	x	
Graduate Students			
M. Zonnevylle	x	x	x
Y. Hu	x	x	
M. Stiles	x		
C. Zheng	x		
D. Sullivan		x	x

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Due to our error some reports were filed twice. The above represents a corrected list.