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SECURITY CLASSIFICATION OF THIS PAGE

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. AD-A247 902			3. DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.		
2b. 			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Cornell University		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Ithaca, NY 14853		7b. ADDRESS (City, State, and ZIP Code)			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-89-J-1052	
8c. ADDRESS (City, State, and ZIP Code) Office of Naval Research, Chemistry Program Arlington, VA 22210		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.		PROJECT NO.	TASK NO.
				WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Simple Adsorbates on Transition Metal Surfaces; A Chemical and Theoretical Approach					
12. PERSONAL AUTHOR(S) Roald Hoffmann					
13a. TYPE OF REPORT FINAL		13b. TIME COVERED FROM 10/01/88 to 9/30/91		14. DATE OF REPORT (Year, Month, Day) 1992/02/26	
15. PAGE COUNT 20					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This final report summarizes research on the bonding and reactivity of molecules on surfaces supported by ONR Grant N00014-89-J-1052					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS					
21. ABSTRACT SECURITY CLASSIFICATION					
22a. NAME OF RESPONSIBLE INDIVIDUAL Roald Hoffmann			22b. TELEPHONE (Include Area Code)		
			22c. OFFICE SYMBOL		

**Simple Adsorbates on Transition Metal Surfaces;
A Chemical and Theoretical Approach**

FINAL REPORT

In the course of the three years of this grant we made great progress in understanding the way molecules bond to surfaces of metals and oxides, the way adsorbed molecules move around, the detailed mechanism of reactions on surfaces, especially those involved in catalysis.

Most importantly we have put into the hands of chemists and physicists a qualitative approach, a deeply chemical one, for looking at what happens on surfaces. This is frontier orbital theory, immensely useful for discrete molecules. In a number of specific papers, dealing with real systems we've shown how one can qualitatively move from bonds to bands, and, in the other direction, apply the analytical tools of quantum chemistry to discern in band structures the electron shifts and bond-forming processes critical for surface reactions.

The most important applications of our methodology have been to oxidation reactions, desulfurization catalysts, the chemisorption and reactions of hydrocarbons on surfaces, the deposition of aluminum, the reactivity of metal oxide surfaces and to some corrosion inhibitors and liquid crystal molecules interacting with surfaces.

Finally we have carried out the first simulated annealing study of a surface-subsurface rearrangement, of boron adsorbed on silicon.

The following pages describe in detail the achievements of

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this grant period. Not all of the subjects we have covered in our research are presented, only highlights. We refer to the papers published or submitted by their Technical Report (TR) number. The full list of Technical Reports is at the back of this Final Report.

Fundamental Theoretical Work

A book, "Solids and Surfaces, A Chemist's View of Bonding in Extended Structures" (Technical Report (TR 38)), was published by me. It is a pedagogical exposition of the frontier orbital perspective on the solid state. Chemists are introduced, gently, to band theory. And physicists can learn how chemists analyze orbital interactions.

Perhaps the Table of Contents of the book reveals the approach and style:

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That the book has sold over 5,000 copies and has been translated into German and Russian is some testimony to its success. Most importantly chemists and physicists are using this way of thinking.

A One-Electron Perturbation Theory of Chemisorption

Molecules reacting, a molecule interacting with a surface — these are systems quite naturally made up of two or more pieces or subsystems. We know their orbitals when they are separate, perhaps approximately. And we want to know their orbitals as they interact, the energetics and orientation of their reaction.

The natural language for the analysis of chemical reaction, the interaction of two chemical subsystems, is perturbation theory. The zeroth-order wave functions, presumably, if imperfectly, known, are those of the separate or isolated molecules. The perturbation is their interaction, weak or strong.

Chemisorption should be analyzed, in principle, in a many-electron framework. In practice, a one-electron perturbation

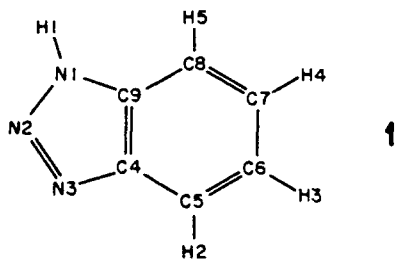
theory approach is often adequate. More than that, a one-electron perturbation theoretic approach lends itself to an analysis of trends as a function of atom or ligand electronegativity, donor or acceptor character, etc., i.e. nothing more or less than a *chemical* analysis.

In TR 50, Mikhail Basilevsky, Russia's best theoretical chemist, and I have developed such a perturbation theory. The explicit formalism has been used already by R. E. van Santen and others.

Studies of a Corrosion Inhibitor

It's not that far from a general theory to a study of the mechanism of action of a corrosion inhibitor.

Copper surfaces are commonly treated with benzotriazole (BTA), 1, to inhibit corrosion. $H1^+$ is thought to be lost 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 coordinate through the nitrogen lone pair. It is, however, unclear whether BTA^- lies parallel or perpendicular to the copper surface.

Marja Zonnevylle's study (TR 37) finds that a perpendicular orientation of these adsorbates is favored, and find strong indications for a role of coadsorbed oxygen.

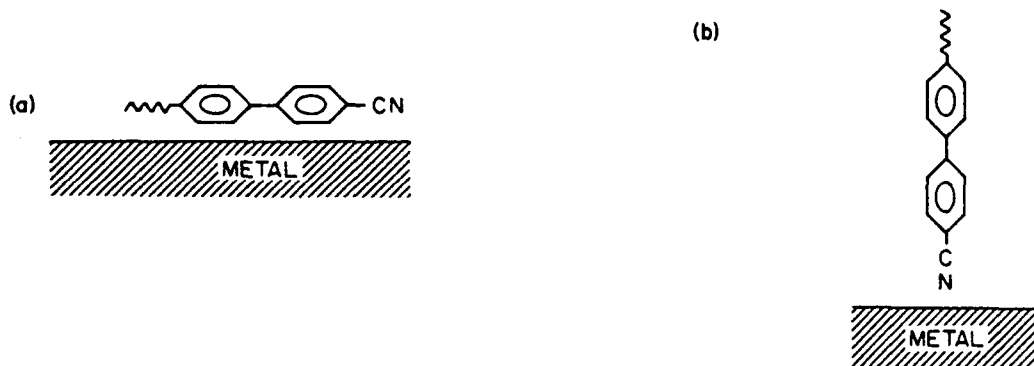
Liquid-Crystal Alignment at Metal Surfaces

In another quite applied study (TR 39) we have collaborated with an IBM group to look at liquid crystal forming molecules at surfaces.

Since 1970, studies of liquid-crystal (LC) surface interactions and alignment have proceeded actively, and several reliable methods of producing structurally inhomogeneous surfaces have been found that are effective in controlling the alignment and orientation of a LC at solid surfaces. Recent studies have shown that variable oblique alignment of a nematic liquid crystal (NLC) can be achieved by the interaction of NLC's with compositionally and microscopically inhomogeneous but macroscopically homogeneous surfaces. However, in spite of the great effort being devoted to the study of alignment of LC's, the molecular interactions with, and alignment by surfaces, remain among the least understood areas of LC physics and chemistry.

Our studies (TR 39) can distinguish between arrangements **a** and **b**, and why a perpendicular (homeotropic) induced alignment

was observed for Cu and Ag boundary layers, whereas parallel alignment was observed for Cr and Au.



Fundamental Distinctions in Chemisorption

Sometimes one has to look in detail at the most frequently studied and fundamental systems, to see if one can properly make sense of them as well as more applied cases of the type I mentioned above.

One of the most extensively studied adsorbates is carbon monoxide. Its interaction with surfaces has constituted the model systems for molecular chemisorption for many years. The reason for this is manifold. CO is the reactant for some important catalytic processes, for example, Fischer-Tropsch synthesis. Secondly it is ubiquitous, binding spontaneously to many surfaces. C-O bond stretching usually gives rise to an intense and sharp infrared absorption peak. From the frequency of this band, the location of the adsorbate at the on-top, 2-fold, 3-fold, or 4-fold adsorption site can be deduced.

CO also exhibits a rich variety of bonding modes. For Pt(111) only, three adsorption sites have been reported. The molecular axis of the chemisorbed carbon monoxide can be parallel, perpendicular, or tilted with respect to the surface. At one-third coverage of carbon monoxide, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ low-energy electron diffraction (LEED) pattern has been observed on Ni(111), Pd(111), and Pt(111). Interestingly, the C-O stretching frequency indicates three completely different adsorption sites: a 2-fold bridge site for Ni(111), a 3-fold site for Pd(111), and an on-top site for Pt(111). As the coverage increases to one-half, a $c(4 \times 2)$ LEED pattern appears. For Ni(111) and Pd(111), the adsorbate seems to prefer the 2-fold site. On Pt(111), half of the chemisorbed CO sits on the on-top site while the other half is located at the 2-fold site. Further increase in coverage results in tilted CO molecules on Pt(111) and adsorption of CO at the on-top site of Ni(111) and Pd(111).

In a study that I think will be a classic theoretical analysis, Yat-Ting Wong and I have explained these preferences (TR 42).

The Chemisorption of Ethylene

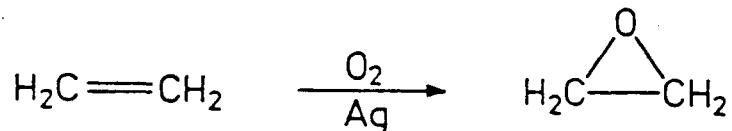
Heterogeneous catalysis on metal surfaces implies enhanced reactivity. Facilitation of a reaction may occur in any of the many steps of a surface mechanism, e.g. chemisorption, reaction, migration on the surface, further reaction, desorption. If we are to understand these reactions, we have to understand them in

detail for one metal, and, most importantly, how they vary as we pass from one metal to another.

The common crystal forms of the group 10 elements Ni, Pd and Pt are face-centered cubic. The hexagonal (111) face is a close-packed plane, likely to be minimally reconstructed. For a given adsorbate, we might expect a smooth, gradual change in adsorbate-surface interaction as we go from Ni(111) → Pd(111) → Pt(111). Consider now specifically ethylene. Electron energy loss scattering (EELS) showed that ethylene is more strongly bound and more distorted on Ni(111) and Pt(111) than on Pd(111). Comparison of the vibrational spectra also suggested a different adsorption site on Pd(111).² This is inconsistent with the simple idea of a gradual change and poses a puzzle, which we have explained, we believe, in TR 51.

Oxygen Transfer to Ethylene Catalyzed by the Ag(110) Surface:
Possible Adsorption Sites for Molecular and Atomic Oxygen and A
Model for the Oxygen-Transfer Step

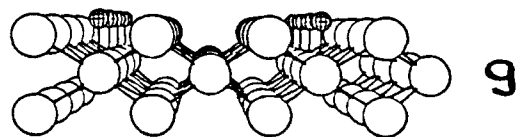
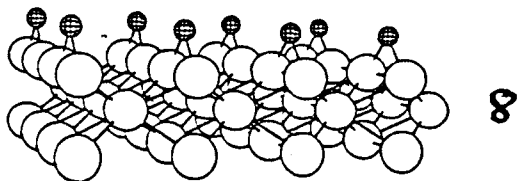
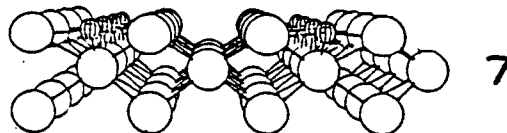
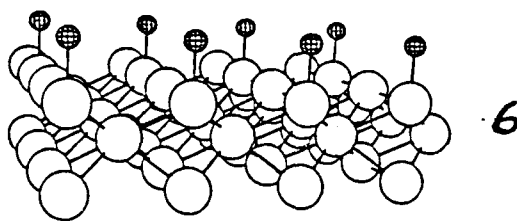
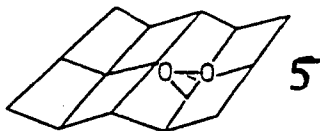
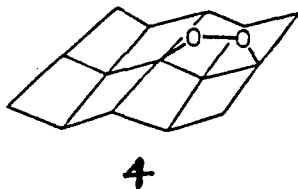
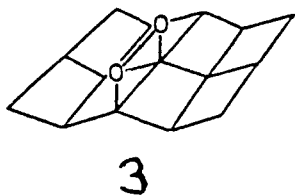
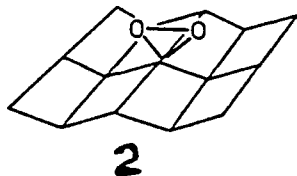
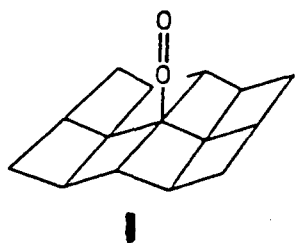
The transfer of an oxygen atom from a silver surface to an ethylene is an important industrial reaction — a process driving a several billion dollar industry.



How does this reaction proceed? How does one avoid a competing process, combustion to CO₂ and H₂O? What is the effect, on the

microscopic level, of electronegative moderators and electropositive promoters?

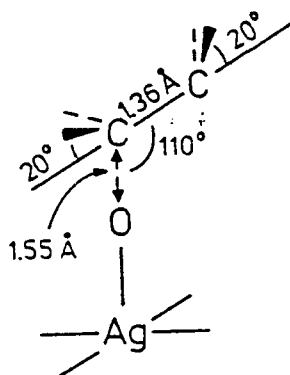
Not enough is known about the location and even the stoichiometry (atomic or molecular) of O_2 on silver surfaces. Alternatives are shown below.



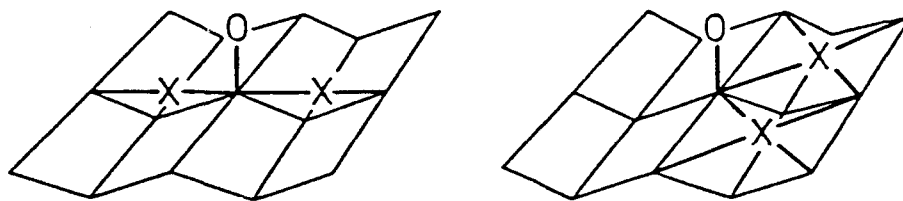
Our computed preference (TR 43, with Karl Anker Jørgensen) is for 3 (in agreement with experimental work of Madix and Bradshaw),

and for 6 and 8.

Among many possible oxygen transfer geometries, the calculations favor that shown below. This opens up the possibility of rotation around the CC bond, needed to explain the experimental results.



We think that chlorine increases the yield of ethylene oxide (reducing combustion) by adsorbing in the grooves of the Ag surface, as shown. The Ag-O bond is weakened as a result.



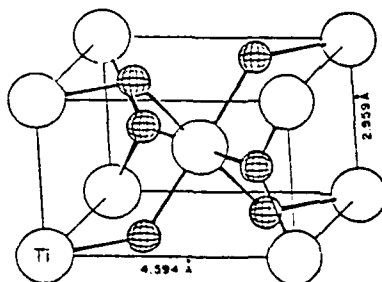
Adsorption of Organo-Rhodium Species on Metal-Oxide Surfaces:

Theoretical Aspects

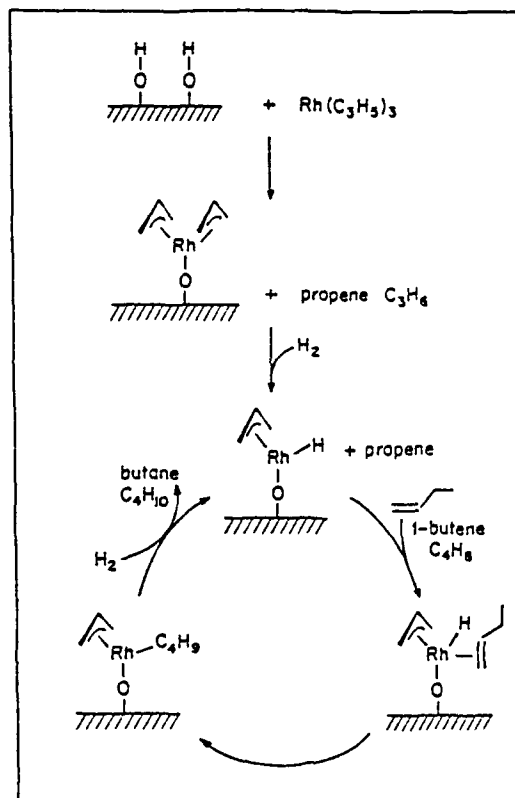
Most transition metal catalysts are dispersed on oxide supports. The detailed mechanism of the catalysis is not very well understood. Metal atoms or compounds sit down in specific

sites on oxide surfaces and effect reactions which would not go the surface itself nor on the metal compound in solution by itself. What happens? How do the metal containing molecule and oxide surface interact? What are basic steps in the catalytic process?

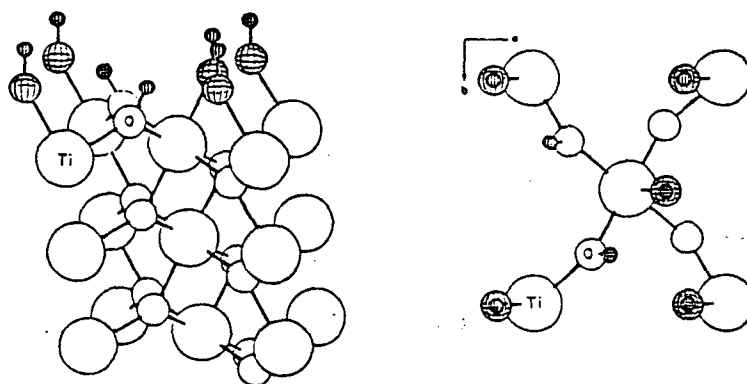
The system studied theoretically by us (TR 40) involves a typical oxide (titania or rutile, TiO_2) shown below, exposed as a single crystal face surface.



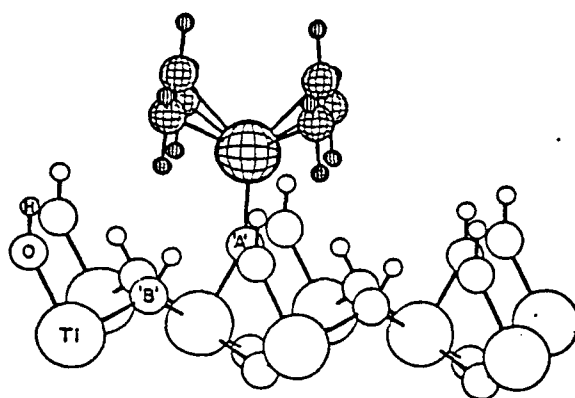
Recently, Smith, Bernasek, Schwartz and McNulty have reported that tris(allyl)rhodium reacts on hydroxylated metallic oxide surfaces (titania and alumina) to produce a bis(allyl)rhodium surface species. Upon subsequent reaction with hydrogen, an (allyl)rhodium hydride complex is formed. This hydride species, when anchored on the oxide surface, exhibits unusual catalytic activity for hydrogenation of alkenes and arenes, as shown below.



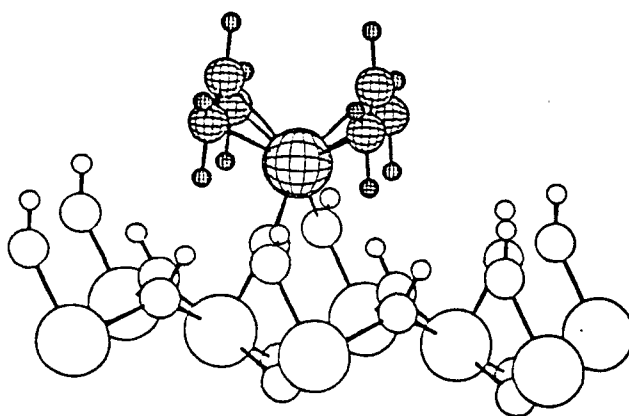
The rutile surface is probably hydroxylated.



The rhodium-containing molecule can bond to this surface in a number of ways, through one oxygen atom.



or through two



We examined various sites for bonding, carefully comparing molecular and solid state alternatives.

There are similarities, and differences. Crucial to the role of the oxide support is its partial reduction, through defect structures, and resonances between support and adsorbate energy levels. The oxide support not only serves to immobilize the organometallic adsorbate, but might also act as an electron reservoir or electron sink, depending upon the electronic requirements of the adsorbed complexes. Pouring electrons into rhodium-allyl antibonding levels is necessary to activate this reaction.

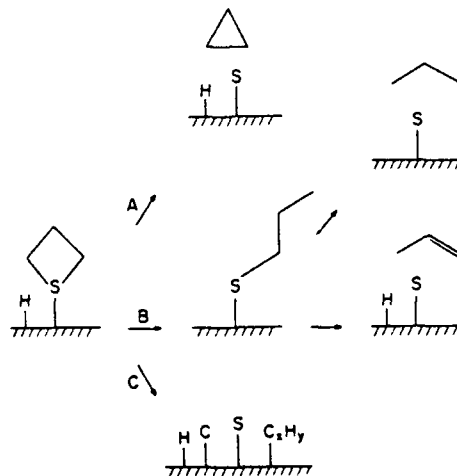
This is the first detailed theoretical study of an oxide-

supported metal catalyst.

Adsorption and Reaction of Cyclic Sulfides

Hydrodesulfurization is a widely used process by which fuel feedstocks react with a molybdenum sulfide catalyst to afford hydrocarbons with lower sulfur content. Several kinds of sulfur derivatives, both aromatic and aliphatic, are found in the raw materials, and considerable effort has been dedicated toward understanding how the reactions occur. Often, simple models than the actual catalyst are used for that, namely single-crystal transition-metal surfaces.

The molybdenum(110) face has been chosen, due to its stability toward reconstruction, by Friend and co-workers to study systematically the reactions of cyclic sulfides and linear thiols. With the help of several complementary experimental techniques such as temperature-programmed desorption, X-ray photoelectron, and high-resolution energy loss spectroscopy, they have been able to establish three distinct reactivity patterns. These three pathways are indicated in 1, depicting how trimethylene sulfide reacts after adsorption onto the Mo(110) face.

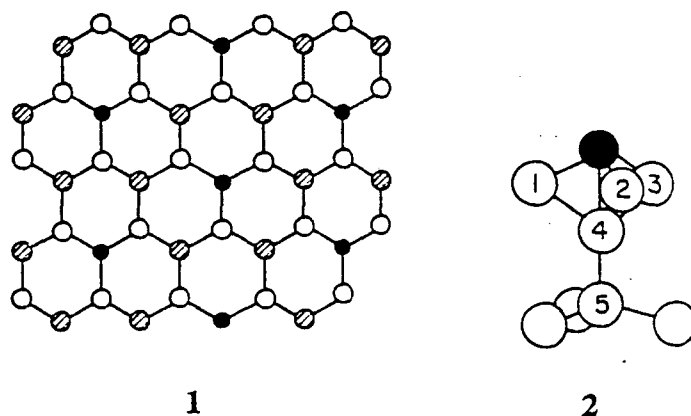


In a study with M. J. Calhorda and C. Friend (TR 42), we have been able to explain why for small rings pathway A is favored, but for larger rings there is a switch over to B.

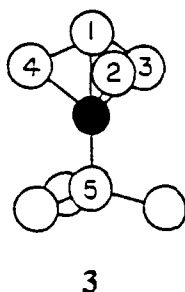
Investigation of the Si(111)-($\sqrt{3}\times\sqrt{3}$)R30'-Boron Surface
Reconstruction by Simulated Annealing

In Monte Carlo and molecular dynamics simulations, millions of geometrical configurations are explored. A quick calculation of the energy of a many-body system is crucial. Of all the computational techniques in quantum chemistry, the extended Hückel method is one of the most economic. Although simplistic, it often gives valuable qualitative results in appropriately selected applications. It can be modified to give reasonable geometries of molecules. A combination of molecular dynamics and Monte Carlo simulations with the extended Hückel method has been developed, which should be useful in studying dynamic phenomena near surfaces and in the solid state. The first application of this method (Tr56) is to the reconstruction of the Si(111) ($\sqrt{3}\times\sqrt{3}$)R30'-Boron surface structure.

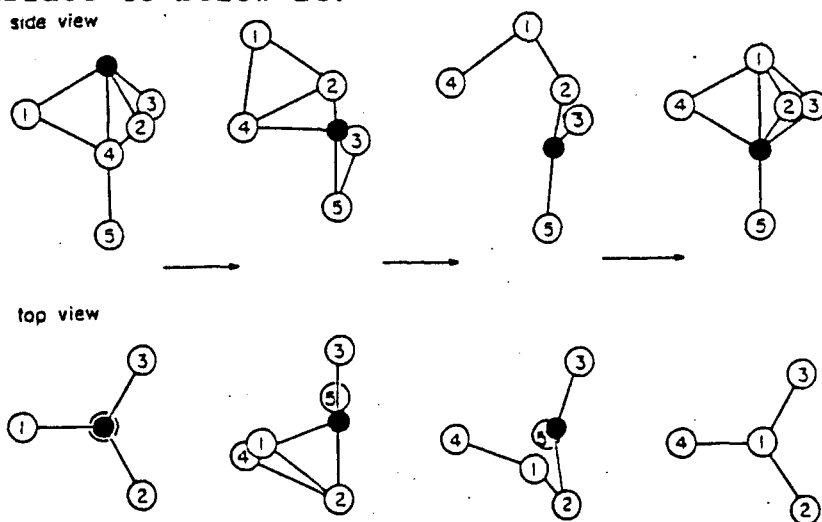
On Si(111), at low temperatures, the boron adatom sits on top of a second-layer silicon atom and is bonded to three other silicon atoms of the top layer, as indicated in the top view 1 and local side view 2. (The empty, dashed and solid circles represent the top-layer silicon atoms, second-layer silicon atoms and the adsorbate, respectively.) Note the unusual, propellane-like bonding situation.



On annealing at 1000°C, the boron atom substitutes for a second-layer silicon atom. The new silicon adatom is directly over the boron atom, 3. Now the boron atom is bonded to five silicon atoms.



This is the first well-established case for subsurface substitutional doping of a semi-conductor. It is also a unique situation where atoms originally adsorbed on top of a surface are finally embedded under two layers of a the host material. Here is what the calculations predict about the way the boron migrates from the surface to below it:



The computer simulation suggests that the reconstruction involves a three-atom rotation inside a silicon matrix instead of a simple exchange of positions between two atoms. We hope that our proposed mechanism will be tested in the near future by isotopic labelling. To our knowledge, this is the first study of surface reconstruction by simulated annealing.

I think much useful research has been done, of value to the scientific and engineering communities. I am grateful to the Office of Naval Research for its support of this work.

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56. Investigation of the Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Boron Surface Reconstruction by Simulated Annealing, *Y.-T. Wong, B. Schubert and R. Hoffmann*,

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