Date: July 6, 1978

Project Title: Oxygen, Sulfur, and Carbon Chemisorbed on Iron Using Angle Resolved Photoemission

Project No: G-41-671

Project Director: Dr. Keith O. Legg & Dr. Martin W. Ribarsky

Sponsor: National Science Foundation, Washington, D.C. 20550

Agreement Period: From 6/1/78 Until 11/30/80*

*Includes 6 month flexibility period

Type Agreement: Grant No. DMR 77-22851

Amount:
$68,090 NSF Funds (G-41-671)
 14,435 GIT Contribution (G-41-315)
$82,525 Total

Reports Required: Annual Summary Reports; Final Technical Report

Sponsor Contact Person (s):

Technical Matters	Contractual Matters
D.L. Mitchell	(thru OCA)
Solid State Physics	Ms. Mary Frances O'Connell
Division of Materials Research	Grants Manager - MPE/BBS/SE Branch
National Science Foundation	National Science Foundation
1800 G Street, N.W.	1800 G Street, N.W.
Washington, D.C. 20550	Washington, D.C. 20550
Phone: 202-632-7334	Phone: (202) 632-2858

Defense Priority Rating: n/a

Assigned to: Physics   (School/Laboratory)

COPIES TO:

Project Director
Division Chief (EES)
School/Laboratory Director
Dean/Director—EES
Accounting Office
Procurement Office
Security Coordinator (OCA)
Reports Coordinator (OCA)

Library, Technical Reports Section
EES Information Office
EES Reports & Procedures
Project File (OCA)
Project Code (GTRI)
Other

CA—3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: ___6/5/81___

Project Title: Oxygen, Sulfur, and Carbon Chemisorbed on Iron Using Angle Resolved Photoemission

Project No: G-41-671

Project Director: Dr. Legg & Dr. Ribarsky

Sponsor: National Science Foundation

Effective Termination Date: ___11/30/80___

Clearance of Accounting Charges: ___11/30/80___

Grant/Contract Closeout Actions Remaining:

___ Final Invoice and Closing Documents

_x_ Final Fiscal ~~Report~~ Accounting (FCTR)

_x_ Final Report of Inventions

___ Govt. Property Inventory & Related Certificate

___ Classified Material Certificate

___ Other _____

Assigned to: ___Physics___ (School/Laboratory)

COPIES TO:

Project Director
Division Chief (EES)
School/Laboratory Director
Dean/Director—EES
Accounting Office
Procurement Office
Security Coordinator (OCA)
Reports Coordinator (OCA)

Library, Technical Reports Section
EES Information Office
Project File (OCA)
Project Code (GTRI)
Other _____

CA–4 (1/79)

AN INVESTIGATION OF OXYGEN, SULFUR AND CARBON CHEMISORBED ON IRON

USING ANGLE RESOLVED PHOTOEMISSION

Keith O. Legg

Martin W. Ribarsky

Experimental

The spectrometer design outlined in our original proposal was upgraded to take advantage of new designs published in the literature.[1] This allowed us to use published lens data, obviating the need for detailed electron optical designs on our part. By employing a four element input lens this new design permits a constant image size at the entrance aperture of the analyzer even with retardation, so maintaining constant transmission. The mechanical positioning of the analyzer remains similar to that which we originally proposed, ensuring that the θ and ψ rotations are not coupled. (This is not the case for the design of Ref. 1.) Both the ultra-violet lamp and the analyzer have been constructed and are in the process of being thoroughly tested. Included with this report is a photograph of the analyzer, taken during initial assembly, before the wiring and complete rotation controls had been added.

We had planned, during the first year, to have already obtained initial results on the O/Fe system. Thus we are running somewhat behind schedule. We expect to make this up during the coming year, especially with the help of Mr. Efstathiou, a graduate student partially funded by this program (see "Personnel").

Since funding for most of the equipment obtained so far in this project has been made available from other Institute funds, the $10,000 Georgia Tech contribution to this project is to be used to add a minicomputer system for controlling and positioning the analyzer, for varying its pass energy and lens voltages and for data aquisition, storage and processing.

---

[1] C. L. Allyn, T. Gustafsson, E. W. Plummer, Rev. Sci. Instr. _49_, 1197 (1978).

The computer system we have in mind is a Heathkit DEC 16 bit PDP 11 compatible computer with floppy disk storage. The analyzer will be moved by stepping motors while its lens and hemisphere potentials will be controlled by programmable power supplies via 16 bit D/A converters. A PDP 11 - compatible system was chosen both for its D/A resolution and for compatibility with the data handling systems at the Wisconsin synchrotron. Although this system will greatly simplify and speed up data acquisition in the long run, it requires a large initial investment of time. For this reason we intend to aquire early data manually and phase in complete control slowly over the coming year.

To help in this effort we shall seek to employ a knowledgeable Co-op student during the coming year.

Theoretical

Some time during the past year was spent modifying and upgrading our SCF-UHF computer codes. We added a feature which allows us to force particular orbital configurations in the self-consistent calculation. With this feature we can search several configurations to find the lowest energy state. As a result we have significantly improved our ionization energy and excitation energy results in several cases. In addition we added the option to remove symmetry partially in our two-electron integrals list. Thus we can calculate symmetry-breaking ionizations and excitations without relaxing symmetry completely. This is an especially useful feature in our large cluster calculations where the time necessary to sort the large number of integrals and to input them at each SCF cycle is greatly reduced. These changes in the compute codes have made them a much more useful instrument for calculating these large

iron clusters.

We have also spent some time investigating the pseudopotentials which are essential to reduce the size of the calculation. In this regard we have done calculations on the Fe atom and the Fe-O systems which yield good results for the valence orbital energies when compared with the all-electron results. A study which parallels our large iron cluster calculations, a calculation for Si_5H_{12}, has yielded pseudopotential and all-electron results in excellent agreement. This study has also produced important information on the effect of the hydrogen saturator bond length on the calculated band gap.

Most of our calculations thus far have focused on the initial stages of oxidation on the Fe {001} surface for which an accurate LEED determination of the geometry exists.[2] We have finished a study of an Fe_5O cluster, a reasonable representation of the fourfold symmetric environment of the adsorbed oxygen, using a small basis in order to get an idea of the bonding and the most stable configuration. Our results indicate that the Fe 3d orbitals do not contribute very much to the oxygen bonding. This observation is compatible with UPS results[3] which show little change in the d band emission during the initial stages of oxygen chemisorption. We are now doing a calculation of the Fe_5O cluster with a much larger basis in order to describe the bonding accurately. In addition we will vary the oxygen distance and position to see if our most stable configuration is the same as that found with LEED. In this way we can make the most of an excellent opportunity to test the predictive

---

[2] K. O. Legg, F. Jona, D. W. Jepsen and P. M. Marcus, Phys. Rev. B <u>16</u>, 5271 (197

[3] C. F. Brucker and T. N. Rhodin, Surf. Sci. <u>57</u>, 523 (1976).

capability of our calculations against an accurately determined adsorption geometry.

Our work on final state effects has involved the modification of a procedure due to McGuire[4] to calculate continuum functions so that we may use our calculated potentials. With this procedure we will be able to calculate the effects of final state resonances which can greatly affect the angle resolved photoemission at certain energies and which, when present, provide a strong indication of the correct bonding configuration.

During the next year we will continue our cluster calculations investigating further stages of oxygen adsorption. We will also do similar sets of calculations for C and S using the Fe basis constructed previously. These calculations will be combined with our final state results to produce electron distributions that can be compared with ARPS results. We will construct an effective d-electron potential from the cluster results in order to study the effect of the surface environment on the cluster. All these calculations will allow the analysis of the ARPS results so that we may explain the process of chemisorption and film formation on iron surfaces.

Personnel

Some of the funding originally intended for employing a Co-op student has been applied to fund a graduate student, Mr. Efstathiou, to work on this project.

When the computer arrives, a Co-op student will be hired to aid in implementing the system.

---

[4]E. J. McGuire, Phys. Rev. 161, 51 (1967).

Conferences

Both Drs. Legg and Ribarsky attended the APS meeting in Chicago, in March 1979.

1)

G-41-671
physics

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology	Solid State Physics DMR	DMR77-22851
School of Physics	4. Award Period	5. Cumulative Award Amount
Atlanta, GA 30332	From 6-1-78 To 11-30-80	$68,090

Project Title

Oxygen, Sulfur and Carbon Chemisorbed on Iron using Angle Resolved

Photoemission.

PART II—SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

A coupled experimental and theoretical program for studying oxygen, sulfur and carbon adsorbed on the low index faces of iron was initiated. The main ingredient of this program was the bringing together of a combination of experiments designed to elucidate the mechanisms of the adsorption process, which is an intermediate step in many catalytic reactions. An angle resolved photoemission spectrometer of a new design was built to take measurements revealing the details of the surface bonding of the adsorbates. The combination of other experimental tools allowed these measurements to be made under precise and stable surface conditions. The theoretical effort was toward analyzing and explaining the complicated results of these experiments. Theoretical analysis of certain systems, especially oxygen on iron, indicated that calculations on small clusters containing the adsorbed atom and the nearest surface iron atoms in the appropriate geometry could yield the correct adsorbate position and bond length. Further calculations aimed at incorporating the small surface cluster into an environment appropriate for an extended solid showed that these important effects could be included using the very efficient methods already established for the cluster. This research has established the usefulness and, in some cases, the necessity of a joint experimental and theoretical program of this type, and it has developed experiments and calculational methods for continued investigations of the adsorption process on transition metal surfaces.

PART III—TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
Abstracts of Theses					
Publication Citations					
Data on Scientific Collaborators					
Information on Inventions					
Technical Description of Project and Results					31 May 19.
Other *(specify)*					

1. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Martin W. Ribarsky		15 May 19.
Keith Legg		

FINAL REPORT

NSF Grant # DMR77-22851

AN INVESTIGATION OF OXYGEN, SULFUR AND CARBON CHEMISORGED ON IRON USING ANGLE RESOLVED PHOTOEMISSION

By

Keith O. Legg
Martin W. Ribarsky

GEORGIA INSTITUTE OF TECHNOLOGY

SCHOOL OF PHYSICS
ATLANTA, GEORGIA 30332

1981

AN INVESTIGATION OF OXYGEN, SULFUR AND CARBON CHEMISORGED ON IRON

USING ANGLE RESOLVED PHOTOEMISSION

Keith O. Legg

Martin W. Ribarsky

Foreword

This report contains a summary of work completed under grant

No. DMR77-22851, during the two year grant period. Enclosed are descriptions

of the experimental and theoretical components of this research. The first

sections of the report describe new instrumentation built, and the last

sections deal with new results obtained.

Keith O. Legg
Principal Investigator

Martin W. Ribarsky
Principal Investigator

June 9, 1981

Analysis of Electron Energy Loss Spectra

The measurements described earlier were analyzed using the data analysis techniques outlined in the last section. The analysis showed that the movement to higher energy as the primary energy increases of the bulk plasmon peak at about 11 eV for E_p = 200eV, as shown in Fig. 6, was accompanied by a similar shift in the peak at 42eV; but the interband peaks remained nearly fixed in energy (a similar behavior occurs for oxidized Ti). The narrowing of the bulk plasmon peak as the oxidation proceeded was fit assuming a bulk plus surface component which reduced in size at the same rate as the surface peak during oxidation.

The movement of the bulk plasmon peak with primary energy is evidently related to the greater range of momenta of elastically scattered electrons which are detected at higher energies (a similar behavior occurs for oxidized Ti). Basic theory tells us that the plasmon dispersion is positive as one increases the momentum transfer. This dispersion can be several eV for materials such as Al, and if a corresponding dispersion occurs for Ti, the difference between the position of the bulk plasmon peak in reflection experiments, with primary energies usually under 300eV, and transmission experiments, with primary energies over 20,000eV,[10] would be explained. The resolution of this problem is of basic importance to understanding collective modes in transition metals since the transmission experiments put the plasmon peak near the free-electron value,[10] while the reflection peak is well below the free-electron value. Indeed, our results for oxidized Ti at higher primary energies are most like the transmission results which indicates the latter samples most probably were oxidized.

Angle Resolved Electron Energy Analyzer

An automated angle resolved electron energy analyzer has been constructed. Both the analyzer and its control electronics are more complicated and flexible than we originally envisaged in our project proposal. In the following sections we describe the analyzer and its control and data acquisition systems.

Electron Optics

The electron optical design was chosen to be similar to that used by Allyn et al.,[1] for a similar type of spectrometer. The instrument consists of a one inch radius hemispherical analyzer with a four element retarding input lens and a three element accelerating output lens. With this arrangement the spectrometer can be run at a constant pass energy (i.e. constant voltage between the hemispheres, and hence constant energy resolution) while the analyzing energy is swept by varying the potential on the Herzog plate (i.e. the average potential of the hemispheres with respect to the sample). At the same time the four element input lens holds the image size of the sample constant and focused in the analyzer. For a given pass energy, equations are given in Ref. 1 which relate the lens potentials to the analyzing energy. The output current is focused by an accelerating lens through a final aperture into a continuous electron multiplier.

A cone with two apertures at the input of the lenses defines an acceptance angle of 5°. Since the resolution of the analyzer is $\frac{\Delta E}{E} = 0.1$, a constant pass energy of 5eV gives 0.5eV resolution for all electron energies. Higher resolution is obtained by reducing the pass energy.

Control Instrumentation

A PDP-8E computer has been bought to provide accurate and flexible control of the lens and analyzer potentials. It has been interfaced to the analyzer

Fig. 1. Control Logic - Electron Energy Analyzer.

via D/A converters and programmable power supplies. The control logic is shown in Fig. 1. All the software has been developed to calculate lens potentials for a given pass energy and program the power supplies to apply the correct voltages to the lenses and the Herzog plate. Data can then be taken in the pulse-counting mode at each pass energy and stored on magnetic tape.

The computer has a dual magnetic tape drive and 35 k-bytes of core memory making it powerful enough for data reduction and analysis. Output is made either to magnetic tape, a display terminal or a point plotter. The interface boards for these units were designed and constructed at Georgia Tech. Fig. 2 shows the flow diagram for data acquisition and lens control. Software for all of these control functions has been developed and checked.

Mechanical Construction

All design and construction has been done at Georgia Tech to conform to the electron optical parameters used by Allyn et al.[1] The analyzer is shown without its magnetic shield in Fig. 3.

Magnetic fields are reduced to less than 20mG by the use of non magnetic materials and by surrounding the analyzer with a Mu-metal magnetic shield. The lenses and hemispheres are made of gold plated Everdur (a Cu-Si alloy) while all other parts are non-magnetic stainless steel, with beryllium-copper and sapphire ball races. In order to eliminate the noise associated with slip rings, all electrical connections are made by continuous wires, mostly running inside the analyzer supports, and "watch-spring" shaped tantalum connectors to allow rotation.

Mechanical motion consists of two orthogonal rotations about the sample, permitting the analyzer to rotate on a sphere with the cone 2 cm from

Fig. 2. Flow·Chart for Analyzer Control.

‡ F IS ONLY VALID IF BUZY FLAG
IS SET. MONITOR WILL REJECT

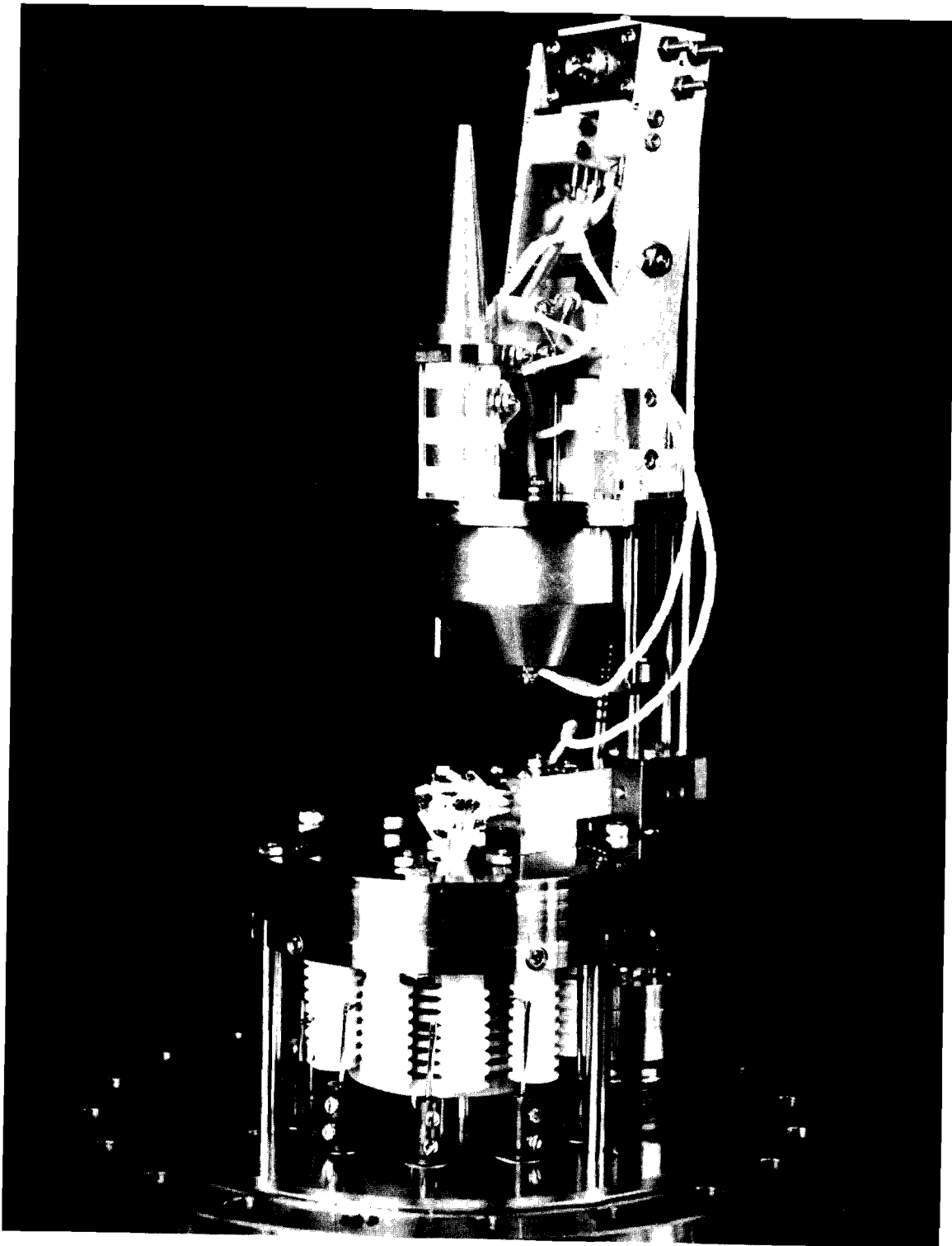† SCAN RECORDING ARE BUILT IN DEFAULT
VALUES DVM IS USED

-9-

Fig. 3. Analyzer with Drive Ring and Magnetic Shields Removed.

the sample surface. In this design, unlike that of Allyn et al., the two motions are independent. One motion is obtained via a direct manipulator rotary drive, while the other is effected with a linear drive. This latter motion was originally transferred rotation via a pulley and spring. However, this method was too imprecise and required too much force. The motion is now transferred via a rack and gear mechanism.

Ultra-Violet Lamp

The U.V. Lamp is a differentially pumped windowless type, illustrated in Fig. 4, designed and manufactured at Georgia Tech. It uses a Sampson capillary discharge lamp with capillary tubes to act as light guides and to permit adequate differential pumping. Pumping is by a trapped rotary pump and a liquid nitrogen trapped diffusion pump charged with Santovac 5 fluid. During operation the chamber pressure remains in the low 10^{-9} Torr region.
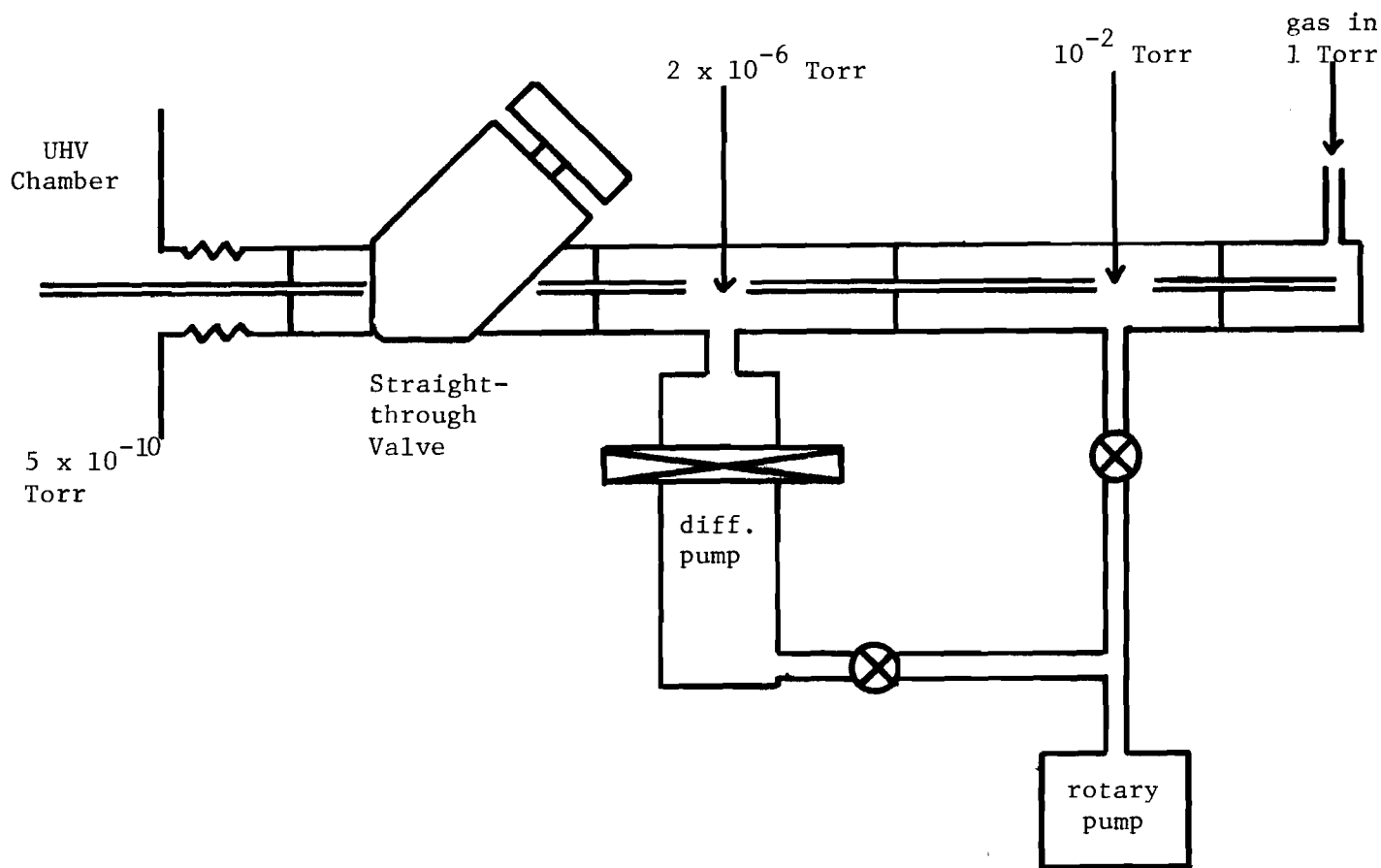
UHV
Chamber

2 x 10^{-6} Torr

10^{-2} Torr

gas in
1 Torr

Straight-
through
Valve

5 x 10^{-10}
Torr

diff.
pump

rotary
pump

Fig. 4. Schematic Diagram of Differentially Pumped u.v. Lamp.

Electron Energy Loss Measurements

Our understanding of the ARPS spectra and of the surface electronic structure which produce them is enlarged by using other experimental probes. One of these is electron energy loss spectroscopy (EELS) which gives us information about the conduction band structure of our materials, especially for excitations from localized bands like the d-bands. Coupled with ARPS which measures the electron distribution in the filled valence bands, these experiments give us a complete picture of the electronic states in the region of the Fermi energy. The EELS is also quite sensitive to changes in surface states, and we and other people[2] have observed large changes in surface – induced states for certain transition metals upon adsorption of only a fraction of a monolayer of gas. Changes in these states due to hydrogen adsorption have been noted,[3] and this can be quite useful for studying the effects of hydrogen since its effects are hard to see directly with the usual spectroscopic techniques.

We have used EELS on samples of clean and oxidized Ti and Fe. The samples were polycrystalline, cleaned by argon bombardment and not annealed. The samples were analyzed under high vacuum at a base pressure of 10^{-10} torr using the internal electron gun on a single pass CMA. The inelastically scattered reflected electrons were collected in the N(E) mode with direct counting. The clean surfaces were maintained by sputtering while the data was taken so there was no nitrogen from the pumps or carbon or sulfur and less than 1/4 monolayer of oxygen. The oxidized surfaces were measured at 1/2 monolayer, 1 monolayer, and at intervals after successive oxidations until the samples were heavily oxidized. Spectra were also taken for a range of primary energies from 100eV to 1000eV.

Some of the results for our clean and oxidized Ti surfaces are presented in Figs. 5 and 6 . The results clearly show a surface peak at about 5eV which
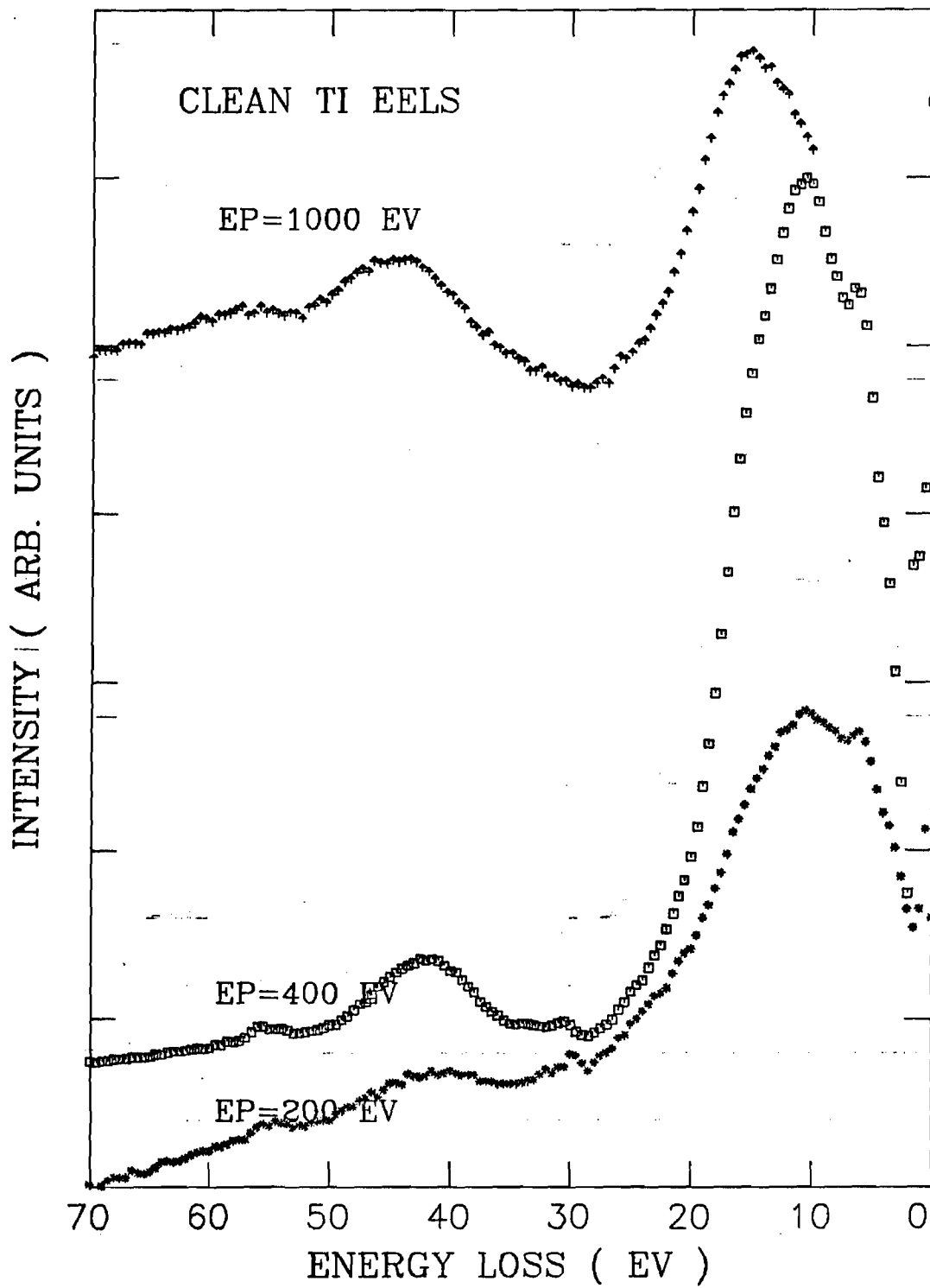
Fig. 5. A comparison of Ti loss spectra for different
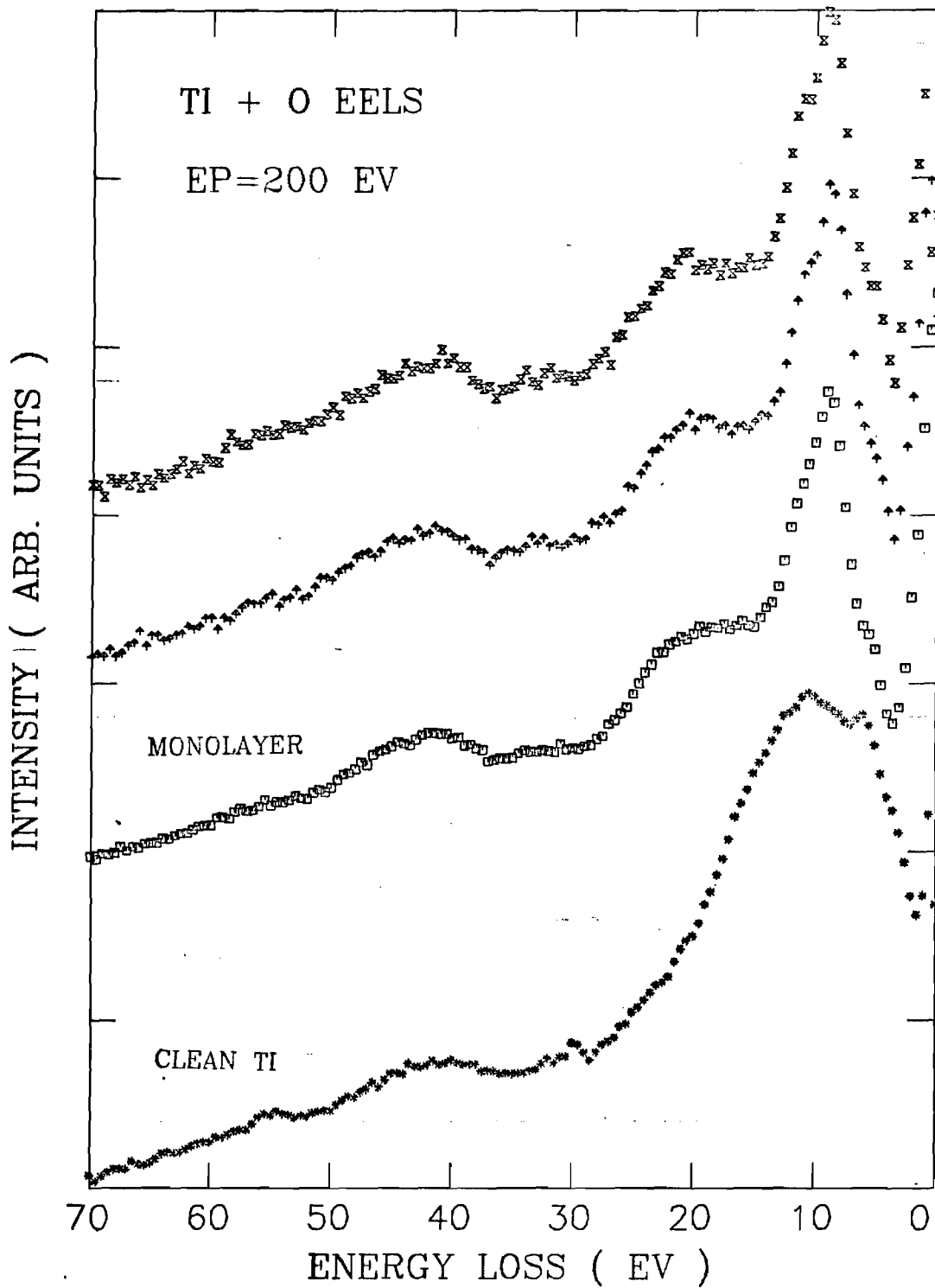   primary energies.

Fig. 6.   A comparison of loss spectra for clean and successively
          oxidized surfaces.

is greatly affected by even a small amount of oxidation. The plasmon peak is located at about 11eV at E_p=200eV and moves to higher energy as the primary energy increases. The split Ti 3p level is evident at 35eV, but there is also a broad, unexplained maximum at about 42eV. This maximum also persists in the oxidized Ti data. The growth of the O 2s peak in the oxidized Ti spectra is clearly seen. The clean and oxidized Fe data show the surface and bulk plasmon peaks, but do not show the broad structure above the 3p peak in either the clean or oxidized spectra. The loss structure below 10eV is more complicated than for Ti due to the fact that the peaks due to the 3d levels are sharper and more pronounced. In the section on data analysis, we will discuss these resutls further.

Theoretical Effort and Analysis

Our theoretical effort was toward analyzing the complicated results of the ARPS and other experiments, and toward developing models to explain the bonding of the adsorbates on the iron surface and, hopefully, to predict adatom positions. To carry out these objectives we have implemented various calculational methods and used them to study especially the oxidation of iron surfaces. Our results indicate that predictions of adatom positions are indeed possible and that the bonding states and d-band states in the adsorbate-metal complex are quite localized.

SCF - UHF Calculations

Some time during the first year of this project was spent modifying and upgrading our SCF - UHF computer codes. We added a feature which allows us to force particular orbital configurations in the self-consistent calculation. With this feature we can search several configurations to find the lowest total energy, which is a necessary option for systems with high spin states and many close-lying d-levels as is the case for our transition metal clusters. As a result we have significantly improved our ionization energy and total energy
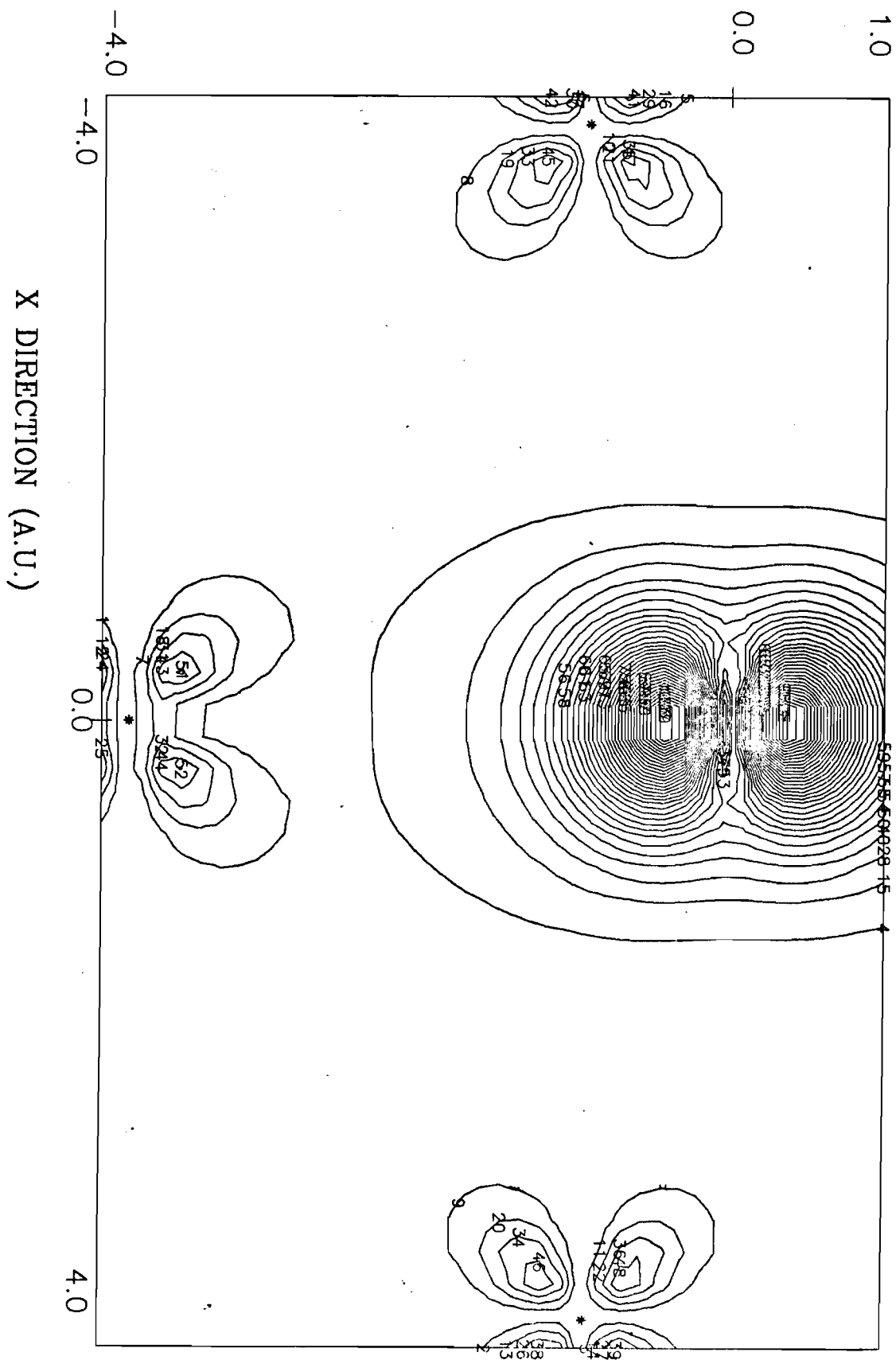
Fig. 7. Charge density for symmetry orbital 1 of Fe_5O viewed in the x-z plane.

calculations in several cases, and we have been able to force our systems into particular excited state configurations in order to calculate excitation energies.

O Adsorbed on Fe Surfaces

Our first set of calculations focused on the initial stages of oxidation on the Fe{001} surface using the SCF-UHF theory. An accurate determination of the geometry from LEED exists for this system, and this was one of the systems we wished to study using ARPS. The calculation is described in detail in Appendix I. We studied clusters representing oxygen and the nearest neighbor irons on a relaxed iron surface for three oxygen adsorption sites: four-fold, bridge and head-on. In summary the result was that the four-fold site had the lowest energy, in agreement with LEED, and the equilibrium oxygen position was also in agreement with the LEED result. These calculations were performed with a 2s, 2d optimized valence basis set on each iron, but we also did a parallel set of calculations with a minimal s,d basis set. Although the binding energies differed greatly in the two calculations, the shapes of the potential energy curves in the two cases were quite similar.

We have also studied the distribution of charge and the bonding for our clusters. Typical results are shown in Figs. 7 and 8 for Fe_5O. In both cases the plane viewed is the X-Z plane through the oxygen and three iron atoms. For symmetry orbital 1 in Fig. 7, the main contribution comes from the s and p_z orbitals on O and the orbitals on Fe. As one can see, the Fe-O bond is quite localized and the xz orbital is localized on the iron centers. The molecular orbital in Fig. 8 contains p_z from the O with some s and d from the Fe and shows the character of the metal bond.
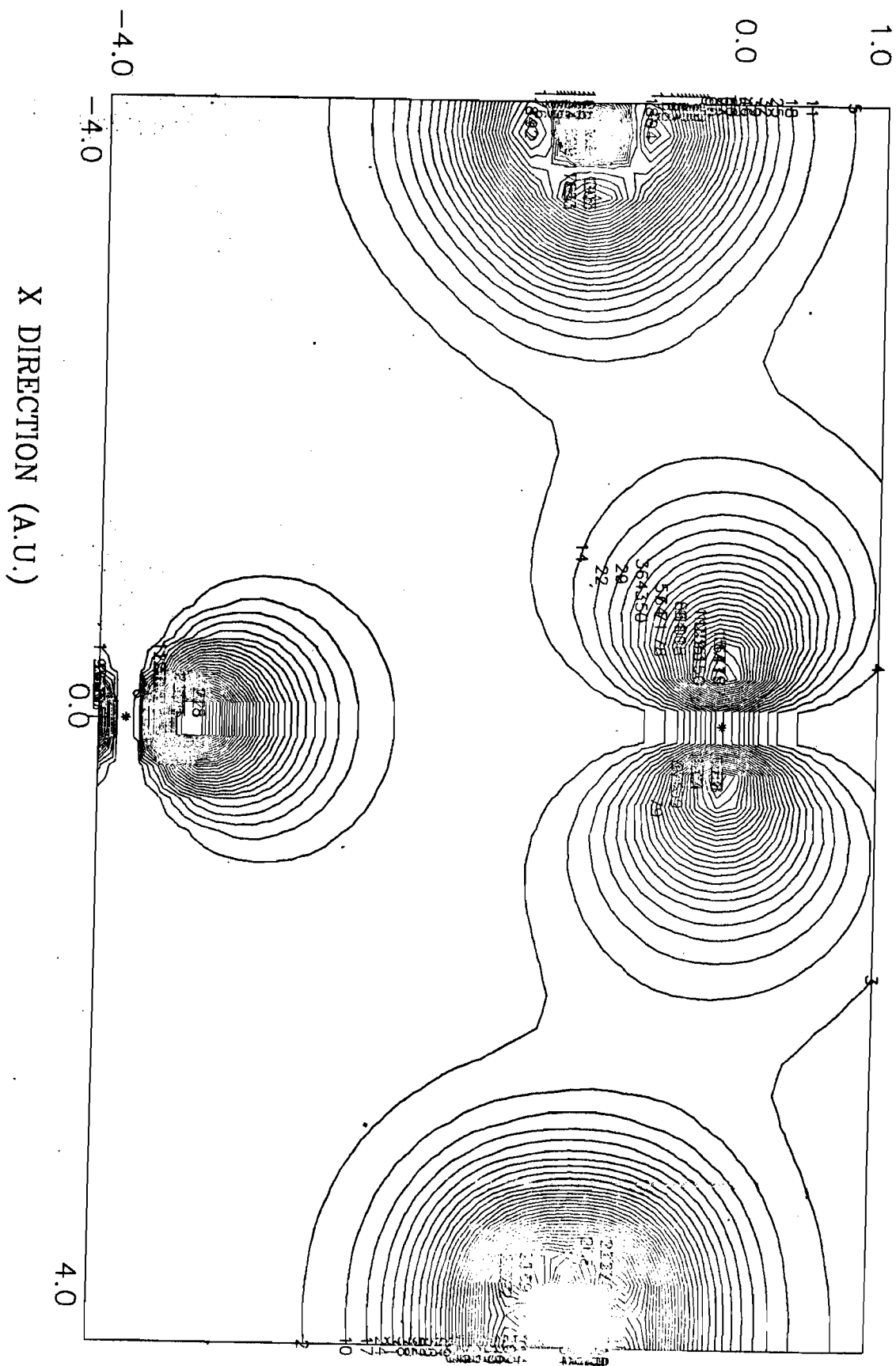
Fig. 8. Charge density for symmetry orbital 2 of Fe_5O viewed in the x-z plane.

LCAO X-α Calculations

The SCF-UHF procedure is limited to small clusters of transition metal atoms, even when the core pseudopotential is used, due to the number of four-center integrals one must compute and then use to construct the Fock matrix at each iteration of the SCF cycle. An alternative is to use a local density approach, such as X-α, and thus avoid the four-center integrals. We have implemented here an LCAO-Xα procedure developed by Dunlap et al.,[5] which does away with the muffin-tin approximation of the multiple-scattering X-α model.[6] Since the Dunlap model uses a basis set expansion in gaussians, its results can be compared directly to the UHF results. The LCAO-Xα procedure has given good results on small molecules for binding energies and equilibrium positions, results which are sometimes better than HF.[7] We have extended the calculations to our larger clusters and looked at the resulting charge densities for the first time. Since the SCF-UHF and LCAO-Xα calculations can be run in parallel with the same basis set, we have been able to compare the results of the two methods. Our finding is that the two methods produce consistent results, and in the future we will use the LCAO-Xα method to study larger clusters than we can now.

Data Analysis

To interpret our experimental results, we have developed a variety of analysis techniques. Some of these are appropriate for implementing on the PDP-8E computer so that the complicated results of the ARPS and other experiments can be partly analyzed immediately. One such technique is a 2n+1 point interpolative data smoothing procedure which allows noise reduction and also provides a derivative of the spectrum which can be adjusted to remove a slowly varying background and then re-integrated.

Another technique, based on the Van-Cittert iterative deconvolution method,[8,9] allows the removal of the effects of an instrument resolution function or

characteristic energy loss structure from the spectrum. One may obtain the
usual Van-Cittert approximate solution iteratively by solving the following
recursion formula:[9]

$$W_{n+1}(y) = W_n(y) + [S(y)-A(y,x) * W_n(x)] \qquad (1)$$

$$n = 1,2,3...$$

$$W_o(y) = S(y)$$

where the unfolded solution is

$$W(y) = \lim_{n \to \infty} W_n(y) \qquad (2)$$

In these equations $S(y)$ is the original, convoluted spectrum, $A(y,x)$ is the
resolution function, and

$$A(y,x) * W_n(x) = \int_{-\infty}^{\infty} A(y,x) \, W_n(x) \, dx. \qquad (3)$$

The resolution function is normalized and normally depends only on y-x, thus

$$\int_{-\infty}^{\infty} A(y-x)dx = 1. $$

This method is easily amenable to computer programming and usually converges in
less than 10 cycles. A discussion of its accuracy may be obtained from Ref. 9.

The problem we must solve is slightly different than above. The width of
our resolution function depends on the energy of the scattered electron. Thus
the function becomes $A(y,x-y)$. However, if all the electrons are transmitted
by the instrument, it still must be true that

$$\int_{-\infty}^{\infty} A(y,x-y)dx = 1. \qquad (4)$$

-18-

Now the usual shape of the resolution function is gaussian, and if we include the correct energy dependence of the width, the function will be

$$A(y,x-y) = \frac{\alpha(y)}{\sqrt{\pi}} e^{-\alpha^2(y)(x-y)^2} . \qquad (5)$$

Eq. (5) will satisfy Eq. (4) and also satisfies the stability condition

$$\int_{-\infty}^{\infty} W_n(y)dy = \int_{-\infty}^{\infty} S(y)dy.$$

We have coded and tested this procedure for unfolding experimental spectra and find that it gives good results. It allows us to remove energy-dependent extrinsic effects in spectra taken over a large range of electron energies or at widely different primary energies as in the energy loss spectra discussed below.

We have also developed non-linear least-squares fitting computer codes for analyzing the lineshapes in the tabulated spectral data. These codes allow us to find peak positions, widths and heights quite accurately by fitting the entire lineshape in the region of the peak, and we then have accurate information on changes in the peak as the emission angle, primary electron energy or other factors are varied. We use a linear combination of gaussian and lorentzian functions to fit each peak which gives a measure of the lifetime and instrumental or random statistical effects in the lineshape.[10] With these curve-fitting procedures, we are able to get information even about peaks which overlap so much that they are not individually distinguishable.

REFERENCES

1. C. L. Allyn, T. Gustaffson and E. W. Plummer, Rev. Sci. Instr. 49, 1197 (1978).

2. G. W. Simmons and E. J. Scheibner, J. Appl. Phys. 43, 693 (1972); K. O. Legg and M. W. Ribarsky, to be submitted.

3. M. R. Barnes and R. F. Willis, Phys. Rev. Lett. 41, 1729 (1978).

4. M. W. Ribarsky, Solid State Comm., to be published.

5. B. I. Dunlap, J. W. D. Connolly and J. R. Sabin, J. Chem. Phys. 71, 3396 (1979).

6. J. C. Slater and K. H. Johnson, Phys. Rev. B5, 844 (1972).

7. B. I. Dunlap, J. W. D. Connolly and J. R. Sabin, J. Chem. Phys. 71, 4993 (1979).

8. P. H. Van Cittert, Z. Phys. 69, 298(1931).

9. H. H. Madden and J. E. Houston, J. Appl. Phys. 47, 3071 (1976).

10. G. K. Wertheim, M. A. Butler, K. W. West and D. N. E. Buchanan, Rev. Sci. Instrum. 45, 1369 (1974).

11. C. Wehenkel and B. Gauthe; Phys. Stat. Sol. B64, 515 (1974).

Publications and Presentations

During the period of this grant the following paper was accepted for publication:

"Ab-Initio Cluster Calculations of the Equilibrium Distance and Geometry of Oxygen on the Fe{001} Surface", M. W. Ribarsky, Solid State Comm., to be published.

and work on the following paper was completed:

"Analysis of Energy Loss Spectra of Clean and Oxidized Titanium and Iron", to be submitted.

The following presentation was made:

"Ab-Initio Cluster Calculations of Oxygen Chemisorbed on Iron", M. W. Ribarsky, March Meeting, A.P.S., New York, N.Y. (March 1980).

Abstracts of the publications are presented in Appendix I.

Professional Personnel

The following personnel have been partially compensated by funds provided in the grant for conduct of this research during the period June 1, 1978 to November 30, 1980.

Dr. Keith O. Legg - Senior Research Scientist and Principal Investigator.

Dr. Martin W. Ribarsky - Research Scientist and Principal Investigator.

Mr. Leo Efstathiou - Ph.D. Candidate.

AB INITIO CLUSTER CALCULATIONS OF THE EQUILIBRIUM DISTANCE AND GEOMETRY OF OXYGEN ON THE Fe {001} SURFACE*

M.W. Ribarsky

School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

We present the results of Spin Unrestricted Hartree–Fock cluster calcu-
lations of oxygen at the four-fold, bridge and head-on surface sites. The
four-fold site is the lowest energy configuration, in agreement with a
LEED structure analysis, and the equilibrium distance above the surface,
0.38 Å, is close to the LEED result, 0.48 Å. These results indicate that
cluster calculations may be used to corroborate the LEED analysis and in
some cases to predicts independently the correct adsorption geometry.

WE PRESENT IN this paper results for cluster calcu-
lations of three possible binding sites for oxygen on the
Fe {001} surface. Cluster calculations for adsorbate
substrate complexes are a direct way of determining
localized electronic properties of these systems. Recent
calculations for oxygen on the Li {001} surface [1] and
sulfur on the Ni {001} surface [2] suggest that small
clusters consisting of the adsorbed atom and the nearest
neighbor metal atoms provide an adequate model for
several properties of the chemisorption system. The
studies for oxygen on lithium [1] are similar to the
present study and indicate that the clusters we use give
binding energies and equilibrium positions close to the
values for larger clusters, except for the top position
cluster which is discussed below. Unfortunately, no
experimental results to compare with the calculations
exist for oxygen on lithium. The Ni_5S clusters [2] in the
four-fold geometry proved quite useful in interpreting
angle-resolved photoemission spectra and especially
final state resonance structures.

One of the most effective methods for investigat-
ing the surface structure of materials undergoing chemi-
sorption has been through the analysis of LEED data
[3, 4]. In some cases highly accurate determinations of
adatom-substrate geometry are possible [3], but the
LEED structure analysis is complicated because it
requires optimization of theoretical results for several
diffracted beams. Thus in many cases workers have
been unable to determine the surface structure
of chemisorbed systems unambiguously from LEED
data. Our results for oxygen on iron suggest that cluster
calculations to find the most stable adatom geometry
can be used to corroborate LEED results and in some

cases to predict independently the correct chemisorption
structure.

We decided first to look at localized systems which
had been successfully LEED analyzed. Thus we chose to
study the initial oxidation of the {001} face of body-
centered-cubic iron for which Legg et al. [3] obtained
good LEED results. Their results are presented in a hard
sphere model in Fig. 1(a) which shows that the oxygen
rests on top of the second layer iron atom in the four-
fold symmetric hollow on the substrate surface and that
there is a 7.5% expansion of the first interlayer spacing
with respect to the bulk. To reproduce the geometry in
the region of the oxygen atom [1], we considered a
cluster consisting of the oxygen and its five nearest
neighbor irons, that is, without the bottom layer Fe
atoms in Fig. 1.

The calculations are in the Spin Unrestricted
Hartree–Fock (SUHF) model with frozen cores on the
oxygen and irons represented by Kahn's effective core
model [5]. We have done test calculations on Fe_2 which
give valence molecular orbitals energies in close agree-
ment with energies obtained in an all-electron calcu-
lation. The cluster orbitals are expanded in a represent-
ation of contracted Cartesian Gaussians with a $2s$, $2p$
set on the oxygen and a $2s$, $2d$ set on the iron. For
economy no p Gaussians were placed on the irons
because calculations on Fe_2 indicated that the added
p function lowered the total energy by only about 0.01
Hartree, and the effect of optimizing the second d func-
tion was much greater. For the iron valence basis set, we
used a $3d$ function contracted from the Roos et al. [6]
$4d$ set optimized for the iron atom and a $4s$ function
contracted from Topiol's [7] $3s$ set optimized for the
frozen core iron. For oxygen we used a contracted set
of 4 primitives [7] for the $2s$ state and 5 primitives for
the $2p$ state [8], except that in the latter case we only

983

(a)

(b)
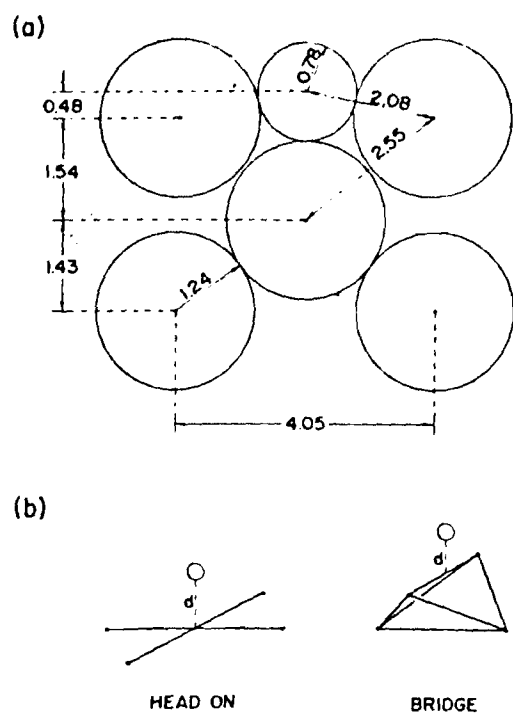
HEAD ON   BRIDGE

Fig. 1. Binding site geometries used: (a) Hard sphere model of the four-fold site distances in angstroms. The bridge site (b) and the head-on site (c) were calculated with the same substrate spacing as (a).
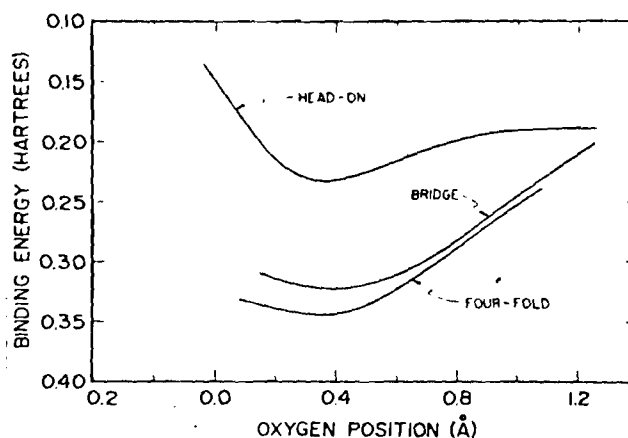

Fig. 2. Calculated binding energy curves for oxygen. The horizontal axis gives the distance above the iron surface of the oxygen atom when 1.24, 0.45 and 0 Å are added to the head-on, bridge and four-fold scales, respectively. The vertical axis gives the energy difference between the clusters with and without the oxygen atom.

contracted the 4 tightest primitives and replaced the loosest one with an uncontracted orbital with $\alpha = 0.2$ in order to describe bdoning. Likewise we added an additional function with $\alpha = 0.2$ to the s orbital set. It proved worthwhile to optimize the additional iron s and d functions with calculations for Fe_2 and FeO set at the appropriate separations. The optimal exponents turned out to be rather loose with $\alpha = 0.05$ and $\alpha = 0.0929$ for s and d respectively. In fact the optimal d exponent gave an energy 0.03 Hartrees lower than a calculation with $\alpha = 0.2$.

We did calculations on two other likely oxygen—iron configurations in addition to the four-fold geometry so that we could compare results. These are geometries for oxugen in the bridge position and in the head-on position with respect to the surface irons. As in the four-fold calculation, we included only nearest neighbor irons and used the same surface/substrate iron distances. Thus as shown in Fig. 1(b), we used an Fe_4O cluster for the bridge site and an Fe_5O cluster for the head-on site. Both these and the four-fold configurations were studied by Hermann and Bagus in their calculations of oxygen on lithium [1]. Their Li_4O bridge calculation gave a binding energy close to that for an Li_8O cluster, but their Li_5O head-on cluster remained unbound for all oxygen distances. Evidently this result was due to the poor RHF description of the Li—Li interaction at large

distances. Since we used UHF which dissociates properly for large interatomic distances, we had no trouble obtaining bound solutions for the head-on cluster. Except for the Li_5O head-on cluster, Hermann and Bagus' calculations [1] indicate that clusters which include the nearest neighbor substrate atoms give binding energies and absorbed atom positions close to those for larger clusters. In all these systems it was necessary to take care in finding the lowest energy electron configuration. This is especially true because the irons want a high spin state. Thus the lowest energy state for the four-fold cluster was spin $= 11$, for the bridge cluster spin $= 9$, and for the head-on cluster spin $= 11$. In order to compare binding energies we also had to do calculations for the iron clusters without the oxygen. Here the lowest energy states for the four-fold, bridge, and head-on configurations were spin $= 10, 7,$ and 8, respectively. Since in the SUHF model the calculated eigenstate is not an exact eigenstate of both $\hat{S}^2$ and $\hat{S}_z$, one must monitor the calculated spin. In our calculations the calculated ground state spin was well within 0.5% of the exact value except for the Fe_5 head-on cluster where it was 1.5% above the exact value.

To find the most stable oxygen position, we moved the atom up and down with respect to the iron clusters in all three geometries. We did not change the iron distances in any of the calculations. The resultant binding energy curves are given in Fig. 2. The head-on position is well above the other two curves, and the four-fold coordinated site indeed has the lowest energy. However, the energy difference between the lowest points on the four-fold and bridge curves is only about 0.55 eV. The effects of correlation and of the substrate

environment are neglected in this calculation even though spin polarization effects are included. Since these first two effects could be of the same magnitude as the energy difference between the bridge and four-fold curves, one cannot say with certainty that the four-fold site would remain the most stable calculated site when these effects are taken into account. Also, the use of effective core potentials tends to reduce calculated binding energies somewhat from the all-electron values, although we expect this trend to be systematic and not to affect our conclusions [5]. However, these results are encouraging, and, in addition, Fig. 2 shows an equilibrium position for oxygen at about 0.38 Å above the iron surface. This position is about 0.1 Å closer to the surface than the LEED analyzed result [1], and gives an effective oxygen radius, 0.68 Å, quite close to Pauling's covalent radius of 0.66 Å. By contrast the equilibrium position at the bridge site is 0.83 Å above the iron surface. Since the LEED analysis is strongly affected by the oxygen—iron surface distance [1], this result tends to corroborate further the choice of the four-fold site.

An improved study of the adsorbed oxygen geometry would require considering the effects of correlation and the substrate environment. One method which may improve the cluster energies while still remaining in the one-electron framework is to replace the non-local exchange potential in the SCF equations by the $X\alpha$ local exchange-correlation potential [9]. Recently developed LCAO $X\alpha$ models [10, 11] give a variational total energy and can use basis set expansions similar to the one used here so that a full comparison with the present calculations would be possible. Dunlap et al. [11], have shown that this $X\alpha$ method gives dissociation energies and equilibrium separations for several diatomic molecules which are closer to experiment than HF. We are currently making calculations on the oxygen—iron system and other systems using Dunlap's method in order to compare the results with the present calculation. We are also considering the problem of embedding the cluster in the substrate environment using Pisani's method [12], which includes in the cluster equations the part of the substrate potential outside the cluster.

The next step in the cluster calculations is to consider other adsorbates on the Fe {001} surface. We have begun calculations for both carbon and sulfur adsorbates. For sulfur there exist some LEED data [13], but no complete determinations of geometry exist for carbon. We are also studying the photoionization differential cross-section for the present systems with special emphasis on the final state resonance structures [14]. It would be important to learn whether these structures change significantly with different site geometry. We hope to compare our results with angle resolved photoemission spectra we are now taking for these systems.

REFERENCES

1. K. Hermann & P.S. Bagus, *Phys. Rev.* B17, 4082 (1978).
2. E.W. Plummer, B. Tonner, N. Holzwarth & A. Liebsch, *Phys. Rev.* B21, 4306 (1980).
3. K.O. Legg, F. Jona, D.W. Jepsen & P.M. Marcus, *Phys. Rev.* B16, 5271 (1977).
4. For a review of LEED theory and results, see J.A. Strozier Jr., D.W. Jepsen and F. Jona, *Surface Physics of Materials*, p. 1. Academic Press, New York (1975).
5. L.R. Kahn, P. Baybutt & D.G. Truhlar, *J. Chem. Phys.* 65, 3826 (1976).
6. B. Roos, A. Veillard & G. Vinot, *Theoret. Chim. Acta (Berlin)* 20, 1 (1971).
7. S. Topiol, Ph.D Thesis, New York University (1976) (unpublished).
8. T.H. Dunning, Jr., *J. Chem. Phys.* 53, 2823 (1970).
9. J.C. Slater, *Advances in Quantum Chemistry* 6, p. 1. Academic Press, New York (1972).
10. H. Sambe & R.H. Felton, *J. Chem. Phys.* 61, 3862 (1974).
11. B.I. Dunlap, J.W.D. Connolly & J.R. Sabin, *J. Chem. Phys.* 71, 4993 (1979).
12. C. Pisani, *Phys. Rev.* B17, 3143 (1978).
13. K.O. Legg, F. Jona, D.W. Jepsen & P.M. Marcus, *Surf. Sci.* 66, 25 (1977).
14. D. Dill & J.L. Dehmer, *J. Chem. Phys.* 61, 692 (1974).

Physics and Astronomy
Classification Scheme
Number 73

Suggested title of
session in which paper
should be placed
Chemisorption

Ab-Initio Cluster Calculations of Oxygen Chemisorbed
on Iron, M. W. Ribarsky, Georgia Institute of Technology.*
--We have made some self-consistent HF studies of iron
clusters bonded to a single oxygen which are designed to
simulate the initial stages of oxygen chemisorption on
iron. The method uses pseudopotentials to describe the
iron and oxygen core regions, and the results are both
reliable and computationally feasible. We compare our
results with very careful LEED measurements[1] of the oxygen
and iron atom positions. We also disouss what the
calculation tells us about bonding and about angle re-
solved and angle integrated photoemission experiments.
* Supported in part by NSF Grant No. DMR 77-22851
[1]K. O. Legg, F. Jona, D. W. Jepsen, and P. M. Marcus,
Phys. Rev. B 16, 5271 (1977).

( ) Prefer Standard Session

Signature of APS Member

Martin W. Ribarsky
School of Physics
Georgia Institute of
Technology.