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REPORT DOCUMENTATION PAGE

REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
DECLASSIFICATION / DOWNGRADING SCHEDULE	
ERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): ARO 23011.6-CH
NAME OF PERFORMING ORGANIZATION: Lawrence Berkeley Lab. / 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office
ADDRESS (City, State, and ZIP Code): 1 Cyclotron Road, Berkeley, CA 94720	7b. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211
8a. NAME OF FUNDING / SPONSORING ORGANIZATION: U. S. Army Research Office / 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: ARO MIPR 121-86, 102-88
8c. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
The Structure Determination of Molecular Adsorbates with Large Unit Cells or Lattice-Gas Disorder on Metal Surfaces

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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 12/4/85 TO 6/30/89	June 1989	5

16 SUPPLEMENTARY NOTATION
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Molecular Adsorbates, Metal Surfaces, Lattice-Gas Disorder, Electron Scattering, Disordered Surfaces, Kinetic Electron Energies

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

For the purpose of structural determination of molecular adsorbates with large unit cells or lattice-gas disorder on metal surfaces, a novel method was developed to handle multiple scattering of electrons by surfaces. The method is particularly suitable for complex and disordered surfaces. It enables a great increase in computational efficiency for the determination of surface structures. In particular, a method of treating electron scattering by chains of atoms (these chains are to be thought of as components of a surface) was developed. These new methods were applied to the interpretation of experimental data, thereby extracting structural information about simple but non-trivial surfaces.

The key to the approach is twofold: first, use kinetic electron energies above a few hundred electron volts, so as to obtain forward focusing by atoms; second, treat the surface as a cluster of atoms without regard to periodicity, thereby allowing complex and disordered surface structures.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

ARO 23011.6-CH

Final Report

1. ARO PROPOSAL NUMBER: 23011-CH

2. PERIOD COVERED BY REPORT: 17 December 1985 - 30 June 1989

3. TITLE OF PROPOSAL: The Structure Determination of Molecular Adsorbates with Large Unit Cells or Lattice-Gas Disorder on Metal Surfaces

4. CONTRACT OR GRANT NUMBER: MIPR 121-86 , MIPR 102-88

5. NAME OF INSTITUTION: Lawrence Berkeley Laboratory

6. AUTHORS OF REPORT: Dr. M.A. Van Hove

7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP, INCLUDING JOURNAL REFERENCES:

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"Automated Structure Search with Tensor LEED Applied to Carbon and Sulfur Adsorption on Mo(100)", P.J. Rous, D.G. Kelly, M.A. Van Hove and G.A. Somorjai, in preparation.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED:

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Dr. R.F. Lin,

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Dr. M.L. Xu,

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BRIEF OUTLINE OF RESEARCH FINDINGS

For the purpose of structural determination of molecular adsorbates with large unit cells or lattice-gas disorder on metal surfaces, we have developed a novel method to handle multiple scattering of electrons by surfaces. The method is particularly suitable for complex and disordered surfaces. It enables a great increase in computational efficiency for the determination of surface structures. In particular, we have developed a method of treating electron scattering by chains of atoms (these chains are to be thought of as components of a surface).

We have successfully applied these new methods to the interpretation of experimental data, thereby extracting structural information about simple but non-trivial surfaces.

The key to our approach is twofold: first, we use kinetic electron energies above a few hundred electron volts, so as to obtain forward focusing by atoms; second, we treat the surface as a cluster of atoms without regard to periodicity, thereby allowing complex and disordered surface structures.

A theory called "Near–Field Expansion in Clusters" was developed. It selects only important scattering events in such a way that the computing effort is proportional to the electron wave number. Conventional LEED-style methods scale as at least the fourth power of the wave number. This removes the most serious barrier to the analysis of electron diffraction at higher energies. In the case of Low– and Medium–Energy Electron Diffraction, this approach enables a better understanding of the multiple–scattering events that occur at surfaces.

The method was next extended to emphasize chain effects, namely to investigate how chains of atoms focus electrons in the chain direction. It has been applied to several techniques involving diffracted electrons. With Medium–Energy Electron Diffraction we found definite chain–focusing effects. These were modulated by strong interference effects. Both types of effect could be used to determine surface structures. In fact, the best application is for disordered surfaces, our main goal. However, we found a helpful simplification if we took

electrons generated in a different way, such that incoherent emission from each surface atom can be assumed. This situation applies to the techniques of angle–resolved x–ray photoelectron emission, of angle–resolved Auger electron emission and of angle–resolved inelastic electron scattering ("Kikuchi-like" electron emission). Disorder is easily treated with these techniques as well.

Previous experimental work with these techniques exists in the relevant energy range. Simple calculations by others have predicted some of the main observed features, but point to the necessity of including multiple scattering effects. Our theory is perfectly designed to do this and we have been able to reproduce experiment for the first time within the experimental uncertainty. More important is the finding that observed peaks of electron emission indeed are directed along chains of surface atoms, but that some of those peaks are interference effects that only indirectly indicate the direction of atomic chains. We have thereby established that our approach gives an excellent structure–sensitive tool. Two advantages over other methods stand out: relatively fast computations and no need for synchrotron radiation.

The technique which we have applied has gained much popularity as an effective method of surface structure determination. This illustrates its potential which could be developed further for different applications.

In the next phase of the work, we have dealt more specifically with structure determination from "diffuse LEED" for disordered surfaces. The theory has been programmed by us and experimental data obtained by the group of Professor Somorjai in Berkeley.

The theory is based on the successful "beam–set neglect" method of LEED calculations. It was introduced in the past by us to tackle complex surface structures, in particular for molecular overlayers. It now finds a new application in the case of disordered overlayers. The soundness of the method has been checked against a more exact but much more computer–intensive method. Computing efficiency is of the utmost importance in structure determination, since one normally has to check out many different candidate structures, and each one requires a full computation.

The experiment (not part of this ARO grant, but crucial to its success) involves a novel type of position–sensitive LEED detector. It combines a "wedge and strip" detector with multichannel plates, and involves real–time microcomputer data processing. This study is its first application. The new detector is ideally suited to the task of measuring the relatively weak diffuse intensity due to disordered surface structures. In addition, the new detector allows ultra–weak electron beams to be used, which eliminates the customary high risk of beam–induced damage to molecular layers.

The surface chosen for our study is carbon monoxide on Pt(111), which provides an excellent and realistic prototype for disordered molecular overlayers. We were extremely pleased that we could, for the first time in surface crystallography of disordered molecular adsorbates, determine their detailed bonding arrangements: bond lengths, bond angles, adsorption sites, and even the distribution among different, simultaneously occupied adsorption sites. We could compare the new results with previous results for the ordered case, and we found very good agreement, thereby reinforcing our confidence in this new approach.

We have also analyzed the structure of disordered benzene adsorbed on the Pt(111) surface. The structure that we obtained is very satisfactory, as it fits our expectations in various ways. We have found that to obtain details of the distortions within the benzene, however, our experimental data base was not quite sufficiently large. The experimentalists are therefore at present extending their measurements and a final analysis is about to take place.

It is already clear from our most recent work that the technique will be able to deliver the desired information. That was exactly the purpose of this project. We know this also from recent analyses of atomic adsorbates (obtained by molecular decomposition). Specifically, we have studied the structure of sulfur atoms adsorbed on Mo(100) (a very useful model for the important MoS_2 catalyst). They present disorder and induce relaxations in the metal lattice itself. We have been able to analyze these details in large part through the development of an automated structural search technique (previously, one had to laboriously fit each unknown structural parameter to the experimental data).