NBSIR 86-3304

Technical Activities 1985 Surface Science Division

C.J. Powell, Chief

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Chemical Physics
Surface Science Division
Gaithersburg, MD 20899

December 1985

Issued January 1986

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

ABSTRACT

This report summarizes technical activities of the NBS Surface Science Division during Fiscal Year 1985. These activities include surface-standards work, experimental and theoretical research in surface science, the development of improved measurement methods, and applications to important scientific and national problems. A listing is given of publications, talks, professional committee participation, and professional interactions by the Division staff.

Key words: surface chemistry; surface physics; surface science; surface standards

FOREWORD

This report is a summary of the technical activities of the NBS Surface Science Division for the period October 1, 1984 to September 30, 1985. The report was prepared as part of the Annual Report of the Center for Chemical Physics within the National Measurement Laboratory of NBS.

The technical work of the Division is separated formally into a task for the Development of Measurement Methods for Surface Properties and a Surface Competence task, as outlined briefly in the Introduction. The former task has two principal activities, a Surface Standards Program and a Surface Measurement Program. Work performed for these two programs is reported in Sections 2 and 3, respectively, of the report while work performed for the competence task is reported in Section 4. There are a number of separate technical projects for each activity. Information is given on project objectives, results obtained during the past year, and the nature of planned activities.

Sections 5 and 6 of the report contain listings of papers published, papers submitted for publication, and talks presented during the year. Talks presented at the Division's seminars at NBS are given in Section 7. The involvement of DIvision staff on professional committees is shown in Section 8 while internal and external scientific collaborations are described in Section 9. Visiting scientists who have worked in the Division during the year are identified in Section 10 and the Division staff is listed in Section 11.

Further information on the activities of the Division can be obtained by contacting the scientists identified in each project report or by writing Dr. C. J. Powell, Chemistry B-248, National Bureau of Standards, Gaithersburg, MD 20899 (telephone, 301-921-2188).

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SURFACE SCIENCE DIVISION

C. J. Powell, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1985

1. INTRODUCTION

A. Background

Over the last ten years, there has been a dramatic growth of surface science and its applications. At the national and local meetings of many professional societies, there are typically multiple sessions of papers concerned with the physical and chemical properties of surfaces. Similarly, many current professional journals and books are devoted in whole or in part to similar reports of recent advances in this field. These advances result from investigations of basic properties (such as composition, atomic structure, electronic structure) of surfaces and the dependence of many complex surface processes (such as molecular sticking, dissociation, diffusion, reaction, and desorption) on the basic properties and other variables relevant to catalysis, corrosion, thin-film systems, microelectronics, computer elements, and communications applications. Investigations of this type range from fundamental studies, at an atomic and molecular level, on clean single-crystal surfaces to similar studies on appropriately modified surfaces or structures and lead not only to the development of surface science but also to new materials, devices, and processes. Similar investigations, principally measurements of surface composition and of other needed properties, are frequently made of a large variety of materials (e.g., metals, polymers, semiconductors, oxides, glasses, etc.) after fabrication and at various time during their service life for quality control, process optimization, and failure analysis. The growth of surface science and its multidisciplinary impact on many important technologies have been documented in a recent article by H. D. Hagstrum [Frontiers in Science and Technology, W. H. Freeman and Co., New York (1983), pp. 113-134].

A large number of techniques are utilized for surface characterization. A choice of one or more techniques is made typically on the basis of the property to be measured, the specimen material, and the specific needs (e.g., spatial resolution, chemical information, sensitivity, degree of difficulty, and cost). The most common type of surface measurement is the determination of surface composition. Most surface analyses now are qualitative but there is a growing demand for quantitative analyses with improved accuracy. At the present time, there are very few standard procedures and limited reference data and reference materials. A variety of techniques is employed for the determination of surface atomic structures, surface electronic structure, and for investigations of surface processes such as reactions, diffusion, segregation, etc. Theories of the measurement process need to be developed for the newer techniques. For all techniques, there is a need for relevant procedures, tests to establish measurement reliability, and applicable reference data. In most cases, the measurement science needs to be developed since knowledge of the key concepts and parameters is often extremely limited.

The techniques utilized in surface science have generally been applied to characterize surfaces in an ultrahigh vacuum environment. The solution of many scientific and technical problems often requires removal of liquid- or gas-phase material prior to surface examination and/or the removal of solid-phase material to expose a region of interest. While this approach has often been successful, artifacts of many different types can arise during the removal of one or more phases. There is therefore a growing need for improved measurement methods that can be used for the in situ characterization of solid-solid, solid-liquid and solid-gas interfaces with the sensitivity, elemental specificity, and spatial resolution comparable to those attained with the current surface-characterization methods.

B. Goal, Objectives and Division Program

The goal of the Surface Science Division is to improve the quality of existing surface-characterization measurements and to extend the present capability. Specific objectives of the Division are:

(1) Perform experimental and theoretical research in surface science to provide a scientific base for surface-measurement methodology;

(2) Develop measurement methods and provide properties data for the physical and chemical characterization of surfaces and surface processes to meet identified needs of industry, government, and other groups;

(3) Develop standard procedures, calibration data, and reference materials in cooperation with national and international standards organizations; and

(4) Develop expertise in selected new areas of science in order that NBS can provide measurement services where needs are anticipated in the near future.

Objectives (1) through (3) are met organizationally through an NBS task titled "Development of Measurement Methods for Surface Properties" (Task 15502). The Division's program for this task is divided into two principal activities, a Surface Standards Program and a Surface Measurements Program. Work performed during the year in these two areas is reported in Sections 2 and 3, respectively. This work is supported by

NBS resources (including some funds transferred through the Office of Standard Reference Data) and by contracts with two Federal agencies (Department of Energy and Office of Naval Research).

Objective (4) is met through the Surface Competence Program (Task 26117). This task was established in October, 1984 and represents a new focus by the Division in two areas, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". A separate report on these activities is given in Section 4.

C. Technical Output and Professional Interactions

Sections 5 and 6 of this report contain listings of the publications and talks, respectively, for the past year by Surface Science Division staff and for projects supported by the Division.

Many members of the Division staff hold leadership positions in professional societies and groups, as listed in Section 8. These interactions not only reflect the professional esteem in which these staff members are held but provide useful mechanisms for both disseminating the results of NBS work and for learning of significant measurement problems being faced by those using surface-characterization equipment.

Interest in surface science and surface characterization at NBS continues to grow. The Division has had an active Seminar program, as indicated in Section 7, and these seminars have been attended by other NBS staff. The Division staff also participates in an informal weekly lunch meeting, attended by scientists from a number of NBS organizational units, at which developments in surface science are discussed. Members of the Division staff are frequently consulted on a wide range of NBS problems.

Much of the Division's work is carried out in collaboration with other scientists within NBS, within the U.S.A., and internationally. The nature of these collaborations is shown in Section 9. These collaborations are considered important because they enable a relatively small Division staff to work synergistically with other experts, they enable us to have access to unique facilities or expertise, and they enable our expertise to be extended to a larger range of important scientific and technical problems.

The Division has been fortunate in having thirteen visiting scientists work at NBS for varying periods during the past year, as indicated in Section 10. These scientists enrich our staff and our projects. A further enrichment of our programs comes from Postdoctoral Research Associates who hold 1- to 2-year appointments; four Postdoctoral Research Associates worked in the Division during FY 1985.

2. SURFACE STANDARDS PROGRAM

G. P. Chambers, W. F. Egelhoff, Jr., N. E. Erickson
J. Fine, Y. Hashiguchi, R. D. Kelley, C. J. Powell

The term "surface standards" is intended to cover a broad range of activities that are directed to improving the quality of surface-characterization measurements through: (1) development of needed reference data and standard reference materials; (2) leadership in standards-committee activities, the development of standard practices, and other actions to improve the accuracy and reliability of surface-analysis measurements; and (3) publication of review articles and books that enable scientists to make surface-characterization measurements of the needed quality.

A. Reference Data

We describe here results of projects in which needed reference data are being generated. Section 2.C includes recent review articles by Division staff that summarize and evaluate data required in a number of surface spectroscopies.

1. Sputtering Yield Data Compilation
(J. Fine and G. P. Chambers)

Sputtering techniques for depth-profile analysis are presently being used in conjunction with a number of surface analytical methods to analyze compositional changes of materials at surfaces and at interfaces. Many of these techniques have now progressed to the point of being able to provide quantitative sputter-depth-profile information yet the necessary sputtering yield data is not readily available in easy-to-use, evaluated form.

We are preparing a compilation of evaluated sputtering-yield data for those parameters that will have specific use in surface analysis and depth profiling. This work is supported by the NBS Office of Standard Reference Data. Our compilation will be in tabular form for those ion species (Ne, Ar, Kr, Xe, O_2, N_2, Cs) and energies (0.5 to 20 keV) and angles of incidence used in surface characterization. The compilation will contain sputtering yields for elemental targets only.

The HP-1000 Data System in the Center for Chemical Physics is being used for the data compilation. Dr. D. Neumann and members of his group have provided guidance as well as technical assistance with the software development.

Two interactive data-base management programs were developed this past year to handle the specific needs of the data compilation. The structure developed allows easy data entry into one of these data bases;

information can then be transferred to the second data base for rapid access and searching. Additional software has been written to sort and tabulate the searched data in a format suitable for publication.

Sputtering yield papers are being compiled; data has been abstracted and entered into the data-base system. Initial tests indicate that the system is operating properly. Work also is progressing on our on-line abstract searching capability so that we can collect and enter additional references and data directly from the computer search into our data base.

In the coming year we intend to complete the data searching and data entry, to evaluate the data set, and to compile sputtering-yield data of interest to the surface-analysis and sputter-depth-profiling community on elemental targets.

2. Characterization of the Imaging Properties of a Double-Pass Cyclindrical-Mirror Analyzer.

(N. E. Erickson, C. J. Powell)

Knowledge of the specimen area being analyzed is important in surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS), particularly when inhomogeneous specimens are being examined and experimental conditions are being varied. We have characterized the imaging properties of a commercial double-pass cylindrical-mirror analyzer (CMA) used for AES and XPS with extensions of a method developed elsewhere. These extensions have yielded more quantitative analyzer characterization than was possible previously. This work was motivated also by the need to evaluate the analyzer imaging properties on the binding-energy measurements described in Section 2.A.5 below.

The electron beam from the coaxial electron gun of the CMA was rastered across a test surface and the intensity of elastically scattered electrons detected by the analyzer was stored in a computer as a function of beam position on the specimen and other experimental parameters. The intensity data could be later plotted to give "three-dimensional" images that showed clearly the imaging properties of the CMA. Elastic-peak images have been obtained for a typical specimen orientation (in our case at an angle of 60° to the CMA axis) and for typical measurement conditions (electron energies of 100, 500, and 1000 eV; analyzer pass energies of 25, 50, and 100 eV; selection of small or large apertures intended for AES or XPS measurements, respectively; and for selected analysis energies ranging between 1.5 eV above the incident energy and up to 5 eV below the incident energy). We have investigated how the images were modified as the specimen was translated along the CMA axis about its optimum position. Finally, we have obtained absorbed-current images to ensure that the test specimen was sufficiently smooth to prevent significant artifacts occurring in the elastic-peak images.

Figure 1 shows examples of elastic-peak images recorded with the specimen at its optimum position and with use of the AES aperture. Figure 1(a) shows images at a fixed pass energy of 50 eV and for incident energies of 100, 500, and 1000 eV; Figure 1(b) shows images for an incident energy of 500 eV and pass energies of 25, 50, and 100 eV. It is clear that the specimen area contributing to the detected signal is changing as these operating parameters are varied.

Comparisons have been made of observed image widths for particular operating conditions with those expected from a simple analysis. Semi-quantitative agreement has been obtained although there are differences in trends (as a function of electron energy or analyzer pass energy) that can be associated with non-uniformities of grids on the inner-cylinder apertures, with lack of sphericity of the retarding grids, and with simplifications of the analysis. Asymmetries in the measured images, for example at high retardation ratios or when the specimen is moved from its optimum position, are due to specific imperfections in our instrument.

Substantial changes are seen in the elastic-peak image shapes as the specimen is translated along the analyzer axis to simulate accidental misalignments. Similar changes are obtained in the image shapes as an offset voltage is applied to the electron gun so that the analyzer detects electrons on the high-energy side of the elastic peak or electrons that have been inelastically scattered in the specimen. The latter changes can be qualitatively interpreted in terms of the known coupling between detected signal and source position, angle of emission, and electron energy. These results indicate that sharp peaks in an energy distribution come from a smaller specimen area than for broad peaks or for inelastically scattered electrons.

We have also measured changes in the posiiton of the elastic peak as the incident beam is deflected to representative points on the specimen in the field of view of the analyzer. Changes of up to ±0.15 eV in peak position were found and these were not symmetrical about the vertical as would be expected for an ideal instrument.

It is planned to draft a Recommended Practice for Characterization of the Imaging Properties of Electron Energy Analyzers for ASTM Committee E-42 on Surface Analysis based on the above methods.

3. Energy Dependence of Electron Attention Lengths
(C. J. Powell)

The attenuation length (AL) of low-energy electrons in solids is an important parameter in surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). The AL determines the surface sensitivity of AES and XPS (and other electron-spectroscopic techniques of surface characterization) and is required for quantitative surface analysis by AES and XPS. Accurate AL

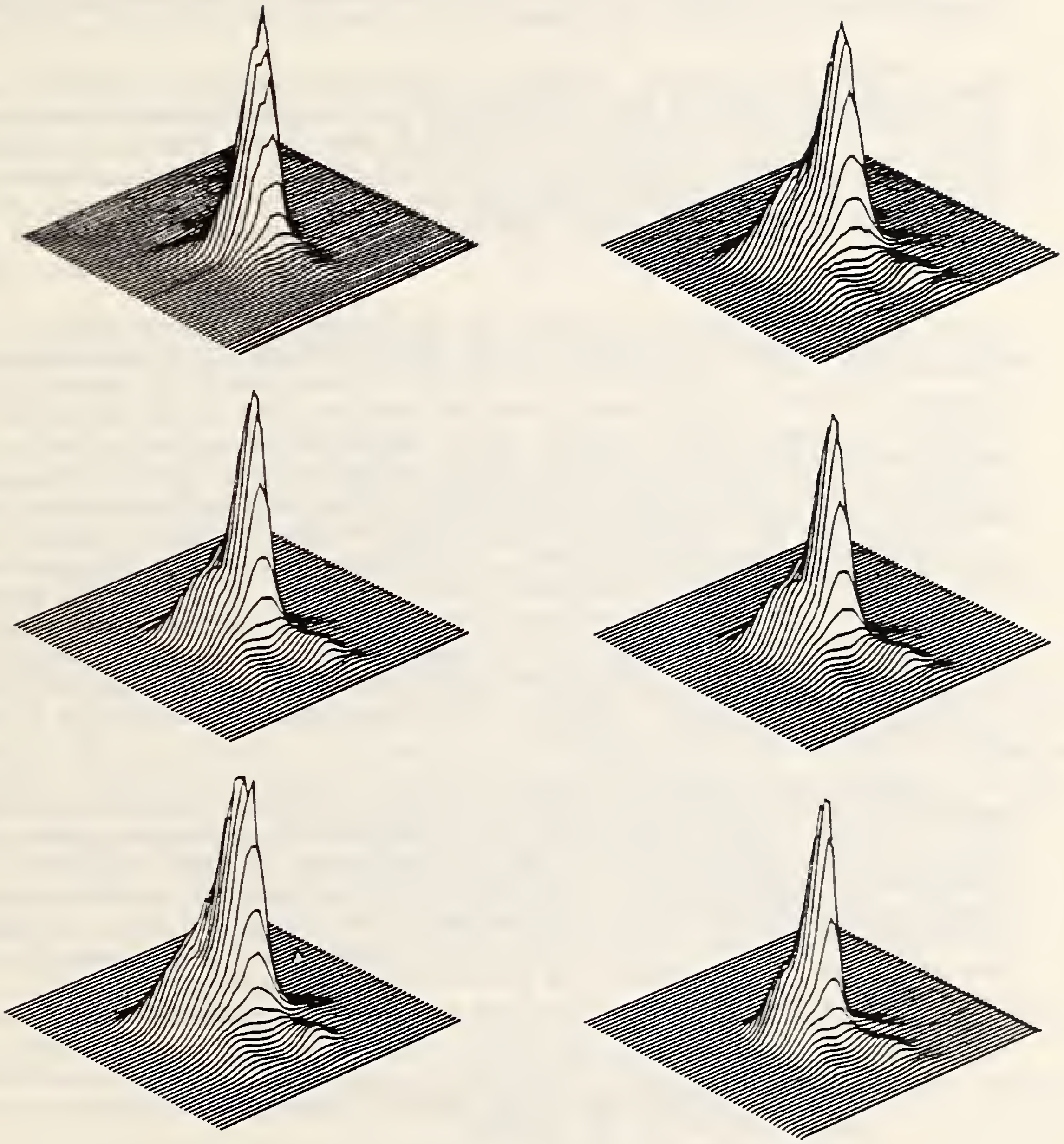


Fig. 1 Elastic-peak images recorded with a double-pass cylindrical-mirror analyzer, the AES aperture, and a test specimen at its optimum position. Left: Images recorded with an analyzer pass energy of 50 eV and incident energies of 100 eV (top), 500 eV (center), and 1000 eV (bottom). Right: Images recorded with an incident energy of 500 eV and analyzer pass energies of 25 eV (top), 50 eV (center, and 100 eV (bottom). The horizontal (bottom left to right) distance scanned by the electron beam on the specimen is 13 mm and the vertical distance is 15 mm.

measurements are difficult in the electron energy range of practical interest but relative AL measurements are useful since they give the AL energy-dependence which is needed in one method of quantitative analysis.

The Bethe theory of inelastic electron scattering in matter has been very successful and it was thought useful to test whether it was valid also for AL data in solids. According to the Bethe theory, AL values λ would be given the by formula, $\lambda = AE/b\ln(cE/\Delta E)$, where E is the electron energy, ΔE the most probable excitation energy for the material, A a term containing material and other constants, and b and c parameters of order unity.

AL measurements for Al, Au, Si, Ge, Al_2O_3, SiO_2, NaF, NaCl, and KI have been successfully fitted to the Bethe formula for E typically between 100 and 1500 eV. The quality of these fits was generally superior and the electron energy range greater than for earlier fits to an empirical formula. It was found, however, that the parameter b was higher and the parameter c much lower than the values expected from theory. These deviations are similar to those found in other tests of the Bethe theory where the electron energies were not high enough for the parameter values to reach their asymptotic values. Nevertheless, it is useful empirically that the Bethe equation adequately describe those AL data which exist for a representative group of materials over a substantial energy range. Although the derived values of the parameters are material-dependent, good estimates of the ratios of ALs at different electron energies can be obtained from the Bethe equation using the average value of $c = 0.4$ and the average value of $\Delta E = 20$ eV.

A separate investigation has shown that electron inelastic mean free paths (IMFPs) can be calculated from experimental dielectric data. IMFPs calculated for eight materials agreed reasonably (within 50%) with available AL measurements (which had been obtained with a model in which elastic electron scattering was assumed to be insignificant). Since it is difficult to measure ALs with accuracies much better than about 50%, it is useful to obtain IMFP data from another base of experimental data. It is planned to extend these calculations using optical data for additional materials.

4. Atomic Layer-by-Layer Analysis of the Source of Angular Anisotropies in XPS and AES

(W. F. Egelhoff, Jr.)

Attenuation lengths of low-energy electrons in solids, important for quantitative surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS), have been frequently measured from the characteristic decay or growth of an AES and XPS signal as a film of increasing thickness is deposited on a substrate. A fundamental complication for such measurements is the enhancement of an AES or XPS peak intensity along crystal axes in single-crystal samples. These enhancements along nearest-neighbor directions are due to forward scattering of the emitted electrons by lattice atoms. An example of the angular anisotropy is shown in Figure 2(a) for epitaxial Cu layers on Ni(100).

In order to deepen the understanding of the depth dependence of this forward-scattering phenomenon, single-scattering electron-diffraction calculations have been performed in collaboration with Dr. R. A. Armstrong of the National Research Council, Ottawa. Figure 2(b) shows an example of these calculations for conditions appropriate to the data in Figure 2(a). The comparison between the calculations and the data reveal several important points.

(1) Since all observed peaks are accounted for in the calculations, single-scattering events must be the dominant mechanism for the observed peaks.

(2) The observed thickness at which each of the four peaks first appears is in accordance with predictions of the calculations. This result confirms the original interpretation, namely that the intensity of the peaks is due mainly to constructive interference in the forward scattering direction by nearest-neighbor and next-nearest-neighbor atoms in the lattice.

(3) The calculated enhancement in the peak intensities continues to grow for Cu thicknesses greater than 3 ML whereas in the data there is very little increase beyond a thickness of 3.3 ML. (Compare, for example, the peak at 45° in Figures. 2(a) and (b).) This comparison reveals an important result. The first (single) scattering event enhances the intensity along a nearest-neighbor direction (e.g. at 45° in Figure 2(c)) but subsequent (multiple) scattering events wash out this enhancement. The single-scattering calculations thus predict a continued growth in the peaks which is not observed experimentally. As a consequence, the measured peaks are due more to short-range order, or nearest-neighbor axes, than originally thought.

This combined theoretical and experimental analysis has deepened the understanding of the phenomena involved in electron attenuation-length measurements with single-crystal materials. Such measurements will have to be made in the future for specific angles of electron emission.

5. Measurement of Core-Level Binding Energies

(N. E. Erickson and C. J. Powell)

Accurate reference values of the binding energies of core-level electrons are needed for the commonly used technique of x-ray photoelectron spectroscopy (XPS) and for other surface-characterization methods. These values are needed for the calibration of instrumental energy scales. For this application, data are required for a limited number of pure materials that adequately cover the range of common measurements.

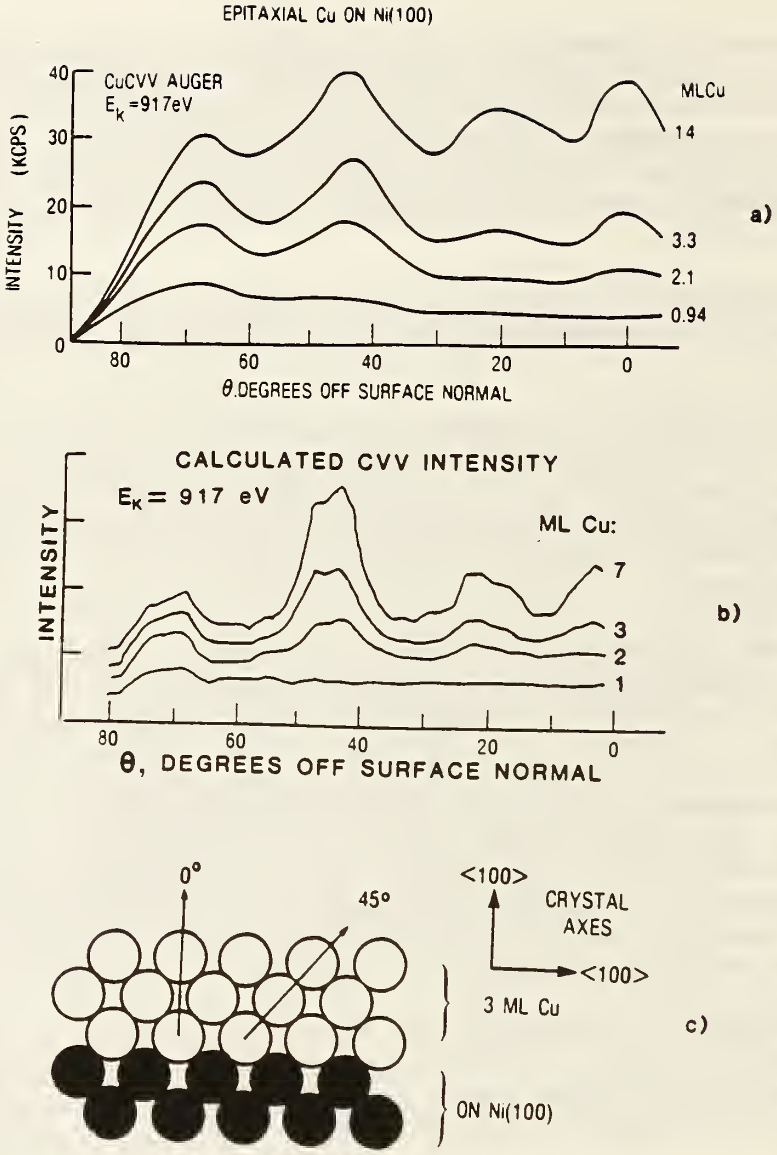


Fig. 2. (a) Measured intensities of the x-ray-induced Cu L_3VV Auger intensity as a function of polar angle of emission for various thicknesses (in monolayers) of Cu on Ni(100). (b) Corresponding calculated intensities. (c) Schematic illustration of the surface profile.

We have made measurements earlier of the core-level binding energies by XPS for the principal peaks of Ni, Cu, Ag, and Au. The accuracy of these measurement, however, was limited severely by voltage drifts in our XPS system. To improve the accuracy and precision of the measurements, we have installed programmable power supplies and digital multimeters for the control and measurement of the voltages applied to the cylindrical-mirror analyzer. The experimental measurements are under computer control. Programs have been written to set and step the analyzer voltage suppliers and to read the multimeters. Least-squares peak-fitting routines have been evaluated for determining peak positions. These tests have shown that fits using a quadratic or a quartic to the top 20-50% of a peak are about equally satisfactory.

Stability checks have been made to assess the short-term (several hours) and long-term (ca. 1 month) stability of the upgraded system. The short-term reproducibility in the location of peaks is now about 4 meV and is limited by the counting statistics of typical scans. The long-term stability is approximately 10 meV and is within the instrumental specifications for electronic drift.

A certified calibration of the voltage-measuring instruments is scheduled to be made shortly. We will then make new high-accuracy measurements of the Ni, Cu, Ag, and Au XPS peaks and compare these with recent independent measurements at the U.K. National Physical Laboratory (NPL). We will initially use a beam of elastically scattered electrons from a gun with a thermionic cathode as an energy reference, as we have in our preliminary measurements. We will then use a gun with a field-emission cathode to compare results from the two types of electron sources and to resolve an apparent discrepancy in a recent measurement of the Au $4f_{7/2}$ binding energy made using a field-emission reference source. After completion of these XPS binding-energy measurements, we will make similar measurements of the kinetic energies of Auger electrons from Cu, Ag, and Au and compare these results with similar measurements now in progress at NPL.

6. Reference Data for X-ray Photoelectron Spectroscopy and Auger-Electron Spectroscopy

(C. J. Powell and N. E. Erickson)

A project was initiated in FY 82 with funding by the NBS Office of Standard Reference Data to prepare compilations and evaluations of core-electron binding energies and of the kinetic energies of selected Auger electrons for a wide range of elements and compounds. In particular, data are being compiled of the "chemical shifts" that can give useful information on the chemical state of a particular element. Data of this type are now scattered throughout the scientific literature but there is a need both for a convenient single source and for evaluation of the sometimes conflicting data. The reference data are being compiled by Dr. C. D. Wagner, a contractor to NBS, and the Surface Science Division is providing technical review. Dr. Wagner has currently generated over 10500 data entries in his files from 600 papers and the compilation is approximately half-completed. During the past year, progress has been significantly delayed by illness but it is expected that the project should be completed next year. The reference data will be included in a report for the Journal of Physical and Chemical Reference Data.

7. Algorithm for Fitting Sputter-Depth-Profiles at Interfaces
(J. Fine, G. P. Chambers, and Y. Hashiguchi)

The determination of interface widths from sputter-depth-profiles is presently accomplished by means of graphical methods. Since the shapes of such interface profiles are generally not symmetric and since there is no accepted method of measuring interface widths, accurate width determination as well as intercomparison of results is often difficult to accomplish. One solution to this problem is to fit numerically the interface profile shape to an appropriate analytical expression from which one can obtain a factor proportional to different definitions of the interface width.

In collaboration with Dr. W. H. Kirchhoff of the NBS Chemical Thermodynamics Division, a fitting analysis for Auger-electron sputter-depth profiles has been developed using a logistic function of the form:

$$I = [A + a(T-T_o)]/(1 + e^{-t}) + [B + b(T-T_o)]/(1 + e^{t})$$

where I is the peak intensity of the Auger spectrum of the sputtered atom as a function of time T. A is the intensity from a totally covered surface, B is the background intensity from a completely uncovered surface, and a and b empirical parameters which can account for additional time dependence of instrumental effects. T_o is the apparent midpoint of the transition region and t is a dimensionless, reduced time defined as $(T-T_o)/D$. The scaling factor, D, is the characteristic time for sputtering through the interface region. Asymmetry in the depth profile can be accommodated by allowing D to vary with time.

A least-squares fitting program has been written which fits the measured Auger spectral intensities to the above equation within measurement error. All currently used measures of the interface width are proportional to D. The statistics associated with the least squares fit allow confidence limits to be placed on the measured widths of interface regions and on the widths of surface layers of dissimilar materials.

8. Needs for Reference Data

The growth of surface science and its applications has led to needs for expanded reference data. These needs can be summarized in the following three categories.

(a) Surface Analysis

Four techniques are now in common use for surface analysis: Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS), and ion-scattering spectroscopy (ISS). With each technique, there is need for the following reference data:

- evaluation of spectra from pure elements for common conditions of measurement
- evaluation of chemical or matrix effects on spectra
- benchmark data for the calibration of the energy and intensity scales of instruments
- reference data on line positions in compounds
- reference data for key parameters in quantitative analysis (e.g., ionization cross sections (AES, XPS), ion scattering cross sections (ISS), electron inelastic mean free paths and attenuation lengths (AES, XPS), electron backscattering (AES), ion neutralization cross sections (SIMS, ISS), and multiple ionization (SIMS)
- algorithms for data analysis (e.g., determination of background due to multiple scattering (AES, XPS, ISS) and fragments (SIMS, ISS), deconvolution to obtain source lineshape (AES, XPS, ISS), inelastic scattering (AES, XPS), and double scattering (ISS))
- data for ion sputtering yields in elements, alloys, and compounds as a function of ion type, ion energy, and bombardment geometry
- data for radiation damage rates during analysis, including cross sections for desorption from surfaces and decomposition of surface layers.

(b) Surface Science

Many techniques are in common use for the determination of surface properties and processes. Data are needed in the following areas:

- reference data on vibrational energies and intensities for molecular species on surfaces (as measured by electron energy-loss spectroscopy, infrared spectroscopy, Raman scattering, neutron inelastic scattering)

- reference data for determination of surface structures by low-energy electron diffraction and other techniques (e.g., library of basic data, algorithms to compute surface structure)

- reference data for absolute determination of surface coverages (atoms/cm^2) on surfaces of different structure and atomic composition

- reference data for surface processes (kinetic data for catalytic and surface reactions, desorption, diffusion, segregation)

- Ion-surface interactions are of importance in sputtering and ion scattering spectroscopy. Reference data are needed to characterize the electron and photon spectroscopy of scattered and sputtered ions, as well as of excited neutral species leaving the surface.

(c) Interface Science

There is rapid development now of techniques that can be used for the in situ characterization of solid-solid, solid-gas, and solid-liquid interfaces. A variety of techniques (e.g., Rutherford backscattering spectroscopy, infrared spectroscopy, Raman spectroscopy, extended x-ray absorption fine structure, neutron inelastic scattering, particle-induced x-ray emission) are being utilized and reference data and algorithms will be required for their effective application.

The Division is providing reference data to meet some of the above-mentioned needs through the projects described in this Section and through the publication of the review articles listed in Section 2.C. Other current Division projects, not described in detail in this report, are:

- comparison of core-level excitation energies by different spectroscopic techniques

- calculation of electron inelastic mean free paths from experimental optical data

- measurement of electron attenuation lengths in condensed molecular films

The Division will coordinate its efforts with the data activities that have been initiated recently through the Surface Chemical Analysis activity of the Versailles Project on Advanced Materials and Standards (VAMAS), as described in Section 2.D.2. There will also be coordination with the NBS Office of Standard Reference Data and the Standard Reference Data Subcommittee of ASTM Committee E-42 on Surface Analysis.

B. Reference Materials

1. Development and Production of Standard Reference Materials for Sputter-Depth Profiling

(J. Fine)

The objective of this project is to develop standard reference materials (SRM's) that will allow convenient determinations of ion-beam sputter-removal rates in commonly used surface-analysis instrumentation. Thin-film reference materials of known thickness will be used to calibrate ion-gun current densities for particular operating conditions. This information together with sputtering-yield data for a range of materials will establish depth scales in the measurement of depth profiles.

Prototype thin-film structures were initially fabricated in order to evaluate their usefulness as depth profiling SRM's and to develop appropriate characterization techniques. These structures were made by sputter deposition as part of a joint US/Yugoslavia program between NBS and Dr. B. Navinsek at the J. Stefan Institute in Ljubljana. Analyses of these prototype materials at NBS and by members of ASTM Committee E-42 on Surface Analysis were done using Auger-electron spectroscopy, x-ray fluorescence, secondary-ion mass spectroscopy, Rutherford backscattering spectroscopy, and proton-induced x-ray emission. The results were satisfactory and a stock of similar thin-film SRM's were fabricated in 1982 using the sputter deposition facility at the J. Stefan Institute in Ljubljana. Production and characterization of the Ni-Cr thin-film SRM was supported by the NBS Office of Standard Reference Materials.

The preliminary analyses obtained on the nickel-chromium multilayered thin-film structures indicate that this material should be of considerable benefit as a depth-profiling SRM. Work on its characterization and calibration has now been completed. We have determined the uniformity and periodicity of the thin-film layers, absolute film thicknesses, sputtered interface depth resolution, and structural stability. Measurement methods used to characterize this Ni-Cr SRM include N(E) Auger sputter profiling, Rutherford backscattering spectroscopy (RBS), and neutron activation analysis (NAA). These measurements have resulted in the following certified values for this Ni/Cr structure that has recently been issued as NBS Standard Reference Material 2135.

(a) Total Cr and total Ni thicknesses

The total thickness of the five Cr layers and the total thickness of the four Ni layers were determined by NAA using a gravimetrically calibrated reference and are given below.

Element	Total Thickness	Uncertainty
Cr	191 μg/cm^2	± 8 μg/cm^2
Ni	235 μg/cm^2	± 9 μg/cm^2

The uncertainty stated is based on our best judgement of all factors involved and corresponds to about two standard deviations of the average.

(b) Individual layer uniformity and Ni+Cr bilayer uniformity (periodicity).

Layer thickness uniformity was determined by measuring the ion bombardment time required to sputter-remove a single layer. This time was obtained by monitoring the surface composition by Auger spectroscopy during sputter erosion. The uniformity of Ni+Cr bilayer removal also was determined in a similar way.

Type of Layer	Relative Layer thickness uncertainty*	Number of profile measurements (9 layers each)
Single Cr layer	± 4.8%	6
Single Ni layer	± 4.6%	6
Bilayer of Ni and Cr	± 3.0%	6

*This uncertainty is two relative standard deviations.

(c) Individual layer thicknesses

The average thickness for a single layer of a given element was obtained from the total layer thickness for that element and the number of layers present. The relative uncertainty of this average layer thickness was determined by combining the uncertainties in the total thickness and in the single layer uniformity for that element.

Element	Single layer thickness	Relative layer thickness uncertainty*
Cr	38.2 μg/cm^2	± 2.3 mg/cm^2
Ni	58.8 μg/cm^2	± 3.5 μg/cm^2

*This uncertainty is two standard deviations

The following additional information has been provided about SRM 2135; this information is uncertified.

(a) Layer thicknesses in units of length

The certified layer thicknesses could be converted into units of length (nm) if the densities of the layers were known. As these densities are not known, an approximate thickness in nm can be derived by using the known bulk densities for Cr (7.19 g cm^{-3}) and Ni (8.9 g cm^{-3}); the values so obtained are 53 nm for Cr and 66 nm for Ni.

(b) Layer thickness and uniformity

Measurements of SRM 2135 using RBS give information on the single-layer thickness and uniformity of each of the Cr and Ni layers. RBS measurements of the single-layer uniformity confirm the uncertainties obtained from the sputter removal times for single layers. Layer thickness measurements obtained by RBS depend on the value of the stopping power used to calculate thickness. A 5 to 10% uncertainty in thickness can result from the uncertainty in currently available stopping-power data and can limit the accuracy of this technique. Single-layer thickness determined by RBS confirm the values certified, providing that a 5 to 10% uncertainty is assumed in the RBS measurements. The RBS result obtained for the average thickness of a single Cr layer is 8.5% smaller than its certified value, while the RBS single Ni value is 5.4% smaller than that certified.

(c) Relative sputtering rates and yields of Ni and Cr using argon ion bombardment

Ion Energy (keV)	Ni/Cr Rate	Ni/Cr Yield
1.0	1.03	1.12
2.0	1.07	1.17
3.0	1.09	1.20
4.5	1.09	1.20

Rate is expressed in units of length/time.
Yield is given as number of atoms sputtered per incident ion.

Future work includes characterizing and certifying additional Ni/Cr structures similar to SRM 2135 as well as a "marker" layer-type sputter depth profile SRM which we have recently fabricated in production quantities. This material also was fabricated in Dr. Navinsek's laboratory and consists of eight Cr layers (~ 40 nm each) separated by about 2 monolayers of Cr_2O_3.

2. Quantitative Sputter Depth Profiling of Interfaces

(J. Fine, Y. Hashiguchi)

Determination of composition-versus-depth at virgin solid/solid interfaces is at present difficult to achieve with sputter-depth-profiling techniques. This is due, to a large extent, to a lack of understanding of bombardment conditions (i.e., ion beam energy, species, angle of incidence, current density, and sputtered depth). A careful evaluation of such factors which affect interface resolution is not available for any given interface system. A consistent set of such measurements obtained for various ion beam parameters, all done on the same material, would significantly enhance our ability to assess the abruptness of interfaces before sputter-profile analysis took place and would be of value in determining optimum sputter-profile conditions.

Our development of the Ni-Cr thin-film depth-profile SRM 2135 with known layer thickness and periodicity (as described above) makes it both possible and practical to examine systematically the dependence of interface resolution on ion beam parameters. Use of the computer controlled, sequential-mode N(E) Auger data system which has been previously developed allows us to obtain reliable and accurate measurements of the interface depth resolution for the Ni-Cr material.

In collaboration with Dr. P. A. Lindfors of the Perkin Elmer Corporation, Physical Electronics Division and Dr. D. F. Mitchell of the National Research Council of Canada, Ottawa, we have examined the dependence of Ni-Cr interface broadening an ion beam energy, ion current density, and angle of incidence, all as a function of sputtered depth. Our results indicate that much narrower interfaces are observed when profiling with low-energy ions; for example, the interface widths with 1 keV argon ion bombardment at a particular ion-beam angle of incidence are about half those for 3 keV bombardment. We also find that narrower interfaces can be obtained by bombarding at more oblique (grazing) angles. Our narrowest interfaces (~ 5 nm) resulted when the ion beam was incident at 70° with respect to the surface normal.

Preliminary measurements of interface-width dependence on ion-beam current density indicate this this parameter may affect interface resolution. We plan to explore this dependence by examining the relationship between ion current density and ion energy.

3. Needs for Reference Materials

The following needs for additional reference materials have been identified.

(a) Depth-Profiling SRM's

Surface analysis is frequently combined with ion sputtering to measure composition versus depth and to investigate solid-solid interfaces. It is believed that sputter-depth-profiling applications will continue to grow and, with the development of new techniques for deposition of materials (e.g., molecular-beam epitaxy), the development of better depth-profiling techniques, and demands for better accuracy, use of new materials, and desire for sharper interfaces, there will be an increased demand for suitable SRM's to ensure the reliability of the relevant measurement system.

NBS has recently developed a multi-layer periodically-modulated SRM consisting of alternate layers of Ni and Cr (Section 2.B.1). Similar structures consisting of Ni/Ag and Cr/Cr_2O_3 have been fabricated but remain to be characterized. We have also fabricated films of Ta_2O_5 on Ta and these also have to be characterized.

There are needs for similar SRM's involving other types of materials in high-technology industries, for example, SiO_2 on Si, epitaxial modulated-thickness films of GaAs/GaAℓAs, thin layers of metals on semiconductors (Schottky barriers), and polymer films on metal substrates.

(b) Calibration of Surface Analysis Instruments

There is a growing need for the characterization and calibration of surface-analysis instrumentation, particularly since the newer computer-controlled instruments require greater system stability and reproducibility than before. Until recently, most surface analyses have been qualitative but there is increasing demand for quantitative analyses of defined accuracy. These developments require SRM's for instrument calibration (e.g., of the instrument transmission functions for Auger-electron spectrometers (AES) and x-ray photoelectron spectrometers (XPS) and for the determination of instrument performance (e.g., the detection of trace constituents).

Pure elemental and multicomponent materials can be utilized for calibration of the energy and intensity scales (and instrument transmission functions) of AES and XPS instruments. A suite of pure elements (e.g., Cu, Ag, and Au) could be used for both purposes. Liquid alloys (e.g., Ga-Sn or Ga-In) can be cleaned readily to generate two-component surfaces of known composition for checks of instruments and algorithms for analyses. Multicomponent materials with known quantities of trace elements are needed for determining the ability of an instrument to detect trace species. Suitable materials could include ion-implanted impurities in silicon (with a specified depth distribution and maximum concentration) and multi-component liquid alloys (with homogeneous compositions or with segregation of trace species at the surface).

(c) Surface Science

There is a need for SRM's that would lead, with the user following a prescription, to surfaces of known composition (e.g., to known coverage of a chemisorbed layer of molecules on a metal substrate or to a monatomic layer of a metal on a substrate). A single-crystal SRM (e.g., Ni) could be cleaned and exposed to different gases (e.g., O_2, N_2, H_2, CO, H_2S) to establish known surface coverages of such gases. Such an SRM would enable calibration of AES and XPS equipment now used for measurements of surface coverages. Another use of the SRM could be through the deposition of several monolayers of a metal (e.g., Ag), again after cleaning, with appropriate thermal treatment to remove all but a monolayer of the deposit. This process could also be used for the calibration of AES and XPS equipment used for investigations of novel properties of ultrathin metal films.

The Division will coordinate its activities to produce and characterize SRM's with related efforts that have been initiated in other countries through the Community Bureau of Reference of the Commission of the European Communities and, more recently, the Surface Chemical Analysis activity of the Versailles Project on Advanced Materials and Standards (VAMAS), as described in Section 2.D.2. Plans for producing additional SRM's at NBS will also depend on sales of SRM 2135 (Section 2.B.1) and the results of a needs survey of the ASTM Committee E-42 on Surface Analysis.

C. Review Articles and Books

1. Review Articles

The Division staff authors many review articles and book chapters that provide information on measurement methods, relevant reference data, reference materials, theories of the measurement process for many surface spectroscopies, and surface standards.

Division staff members have authored 24 review articles recently. The titles and abstracts of review articles published since 1984 are listed below:

(a) "Instrumentation for Photon Stimulated Desorption," R. Stockbauer, Nucl. Instr. Meth. 222, 284 (1984).

Photon stimulated desorption (PSD) refers to the ejection of ions, atoms or molecular fragments from a surface initiated by the absorption of single photons; to date, most studies have concentrated on detection of ions. The properties of PSD which make it attractive as a surface characterization tool are its extreme surface sensitivity, the ions being ejected only from the topmost layer and the rapidity with which the ions are ejected. Since the desorption is fast ($\sim 10^{-14}$ s), with respect to molecular vibrations ($\sim 10^{-12}$ s), the ion trajectory reflects the initial bonding geometry of the particle to the surface.

To study the ion desorption process, one would like to know the mass, kinetic energy distribution, angular distribution and the yield (desorption rate vs. photon energy) of the desorbing ions. Time-of-flight (TOF) analyzers are used where the time between the light pulses from the synchrotron light source is on the same order as the flight time of the ion from the surface to the detector. One can measure easily ion mass and yield but not kinetic energy or angular distributions with this class of analyzer. Electrostatic deflection analyzers are used to measure ion yields and kinetic energy distributions and, in some instruments, ion angular distributions. In general, they are useful where the time structure of the synchrotron light is too short to allow TOF analysis. Optical methods have recently been applied to the detection of excited states of neutral Li seen in PSD of LiF.

(b) "Inelastic Scattering of Electrons in Solids," C. J. Powell, in Electron Beam Interactions with Solids for Microscopy, Microanalysis, and Microlithography, D. F. Kyser, H. Niedrig, D. E. Newbury and R. Shimizu, eds. (SEM Inc., Chicago), 19-31 (1984).

The principal mechanisms and available data for the inelastic scattering of electrons in solids are reviewed. The processes relevant for electron-probe microanalysis, electron energy-loss-spectroscopy, Auger-electron spectroscopy, and x-ray photoelectron spectroscopy are described and examples of relevant electron energy-loss data are shown. The discussion is based on the dielectric description of inelastic scattering and treats processes important in the excitation of both core electrons and valence electrons. Information is given on the cross sections for ionization of core levels, inelastic mean free paths of Auger electrons and photoelectrons in solids, and radiation damage.

(c) "Non-adiabatic Effects in Elementary Surface Reactions: State-to-State Molecular Beam Experiments as a Probe," J. W. Gadzuk, in Many-Body Phenomena at Surfaces, D. Langreth and H. Suhl, eds. (Academic Press, N.Y.), 517 (1984).

A theory of elementary chemical reactions at solid surfaces is described in terms of surface-induced diabatic transitions between "reactant" and "product" potential curves. it is then shown how the internal vibrational state distribution of a diatomic molecule scattered from a surface could provide unique dynamical information required as input to the diabatic transition theory.

(d) Early Applications of Vacuum, from Aristotle to Langmuir," T. E. Madey, J. Vac. Sci. Tech. A2, 110 (1984).

Highlights of the development of vacuum science and technology from ancient times to the early twentieth century are reviewed. The view of the Greek philosophers that vacuum was an impossibility hampered understanding of the basic principles of vacuum until the mid 17th century. Verifiable vacua were first produced in Italy by Berti and Toricelli; von Guericke's dramatic experiments vividly demonstrated atmospheric pressure. Piston-like "air pumps" were widely used in England and the European continent through the 18th and early 19th centuries to produce and characterize the properties of vacuum (lack of sound transmission, inability to support life, gas discharges, etc.). The Industrial Revolution was made possible through the genius of Newcomen, who designed huge atmospheric engines (based on condensation of steam to form a vacuum beneath a piston, which was then driven by the pressure of the atmosphere). A system of "atmospheric railways" propelled by vacuum pistons was built in England in the mid 19th century. Serious scientific developments of the 19th century which necessitated vacuum included Crooke's and Faraday's gaseous discharge measurements, the first sputtering experiments by Grove, and isolation of the rare gases by

Ramsey, the standards work of Miller, the discovery of the electron by Thomson and of X-rays by Röntgen. The development of the incandescent light by Edison provided a background for the remarkable achievements of Langmuir in vacuum and surface science at the dawn of the 20th century. An appendix is included which lists museums containing vacuum-related exhibits.

(e) "Laser Studies of Surface Chemical Reactions," R. R. Cavanagh and D. S. King, Chemistry and Physics of Solid Surfaces V, Springer-Verlag Series in Chemical Physics 35, 141 (1984).

A review of laser studies of surface chemical dynamics with emphasis on thermal desorption processes is presented. The correlation of gas-phase and liquid-molecular dynamics with analogous surface processes is demonstrated with primary emphasis on experimental techniques for monitoring relevant quantum state populations. Recent results for the desorption of NO from Ru(001) and NO from oxidized Ru crystals are compared in terms of rotational populations, and velocity and angular flux distributions.

(f) "Characterization of Surfaces Using Electron and Photon Stimulated Desorption," T. E. Madey, D. E. Ramaker, and R. Stockbauer, Ann. Rev. Phys. Chem. 35, 215 (1984).

We review various mechanisms of electron- and photon-stimulated desorption of ions and neutrals from surfaces. Examples include desorption from ionic surfaces, from covalent adsorbates on metal surfaces, and from layers of physically adsorbed atoms. The use of the electron stimulated desorption ion angular distribution (ESDIAD) method for determining local structures of surface molecules is described.

(g) "Inelastic Mean Free Paths and Attenuation Lengths of Low-Energy Electrons in Solids," C. J. Powell, Scanning Electron Microscopy/1984, IV, 1649 (1984).

A review is given of calculations of inelastic mean free paths and measurements of attenuation lengths of low-energy electrons in solids. The emphasis of the review is on the systematics of the dependence of these quantities on material and electron energy. Calculations of inelastic mean free paths from experimental dielectric data indicate that different dependences on electron energy occur in different materials and that deviations from simple theoretical or empirical expressions are to be expected.

(h) "On Vibrational Lineshapes of Adsorbed Molecules", J. W. Gadzuk and A. C. Luntz, Surf. Science 144, 429 (1984).

The possible information content in lineshapes observed in vibrational spectroscopy of molecules adsorbed on surface is considered by drawing analogies with similar situations in other spectroscopic areas where the systematics are more completely understood. When possible, simple physical models are introduced which illustrate the points to be stressed. Particular emphasis is placed on the relative roles of T_1 (dissipative decay) vs. T_2' (pure dephasing) processes in determining linewidths, on the roles of substrate electron-hole pairs, phonons, and photons in T_1 processes, and possible ways to establish which broadening mechanism is operative in a given situation. A particular kind of dephasing that is important for vibrational lineshapes in molecular crystals, so called exchange-coupling, is suggested as playing a significant role for molecular adsorbates as well. Some recent experimental studies are analyzed in the light of concepts introduced in this paper.

(i) "The Thermal Desorption of Adsorbed Species," J. T. Yates, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.), 425 (1985).

The experimental and theoretical basis of thermal desorption spectroscopy as a tool for surface characterization is described. Methods of analysis of thermal desorption spectra to obtain kinetic information (desorption energies, desorption order, coverages of adsorbed species) are included, together with numerous examples of desorption of small molecules from single-crystal metal surfaces.

(j) "Experimental Methods in Electron and Photon Stimulated Desorption," T. E. Madey and R. Stockbauer, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.1985), 465 (1985).

We review experimental techniques and applications of electron stimulated desorption (ESD) and photon stimulated desorption OPSD) of atomic, molecular, and ionic species from surfaces. The physical principles of these methods, as well as details of experimental measurements and data analysis are discussed. We close with a discussion of beam damage in surface analysis.

(k) "Innershell Ionization Cross Sections," C. J. Powell in Electron Impact Ionization, T. D. Märk and G. H. Dunn, eds. (Springer-Verlag, N.Y.), 198 (1985).

A review is presented of cross sections for the ionization of inner-shell electrons by electron impact. Calculations, measurements, and empirical formulas are described and compared. Recommendations are given for the selection of cross-Section data. Finally, applications of inner-shell ionization cross-Section data to materials and surface analysis problems are described.

(l) "The Coordinated Development of Standards for Surface Chemical Analysis", M. P. Seah and C. J. Powell, NBS Internal Report NBSIR 85-3120 (March, 1985).

This report is based on a proposal to the Steering Committee of the Versailles Project on Advanced Materials and Standards (VAMAS) for the coordinated development amongst the VAMAS member states of standards for surface chemical analysis. VAMAS was established following a meeting of the Heads of State or government at Versailles, France in 1982 that agreed on a number of projects relating to technology, growth, and employment. Specifically, VAMAS was organized to promote international coordination in the development of standards in a wide range of advanced material sectors. Surface chemical analysis was approved as a VAMAS Technical Working Area in June, 1984.

The report describes the growth and diversity of surface analysis in the development of advanced materials in modern technologies and the use of surface analysis for improved films and coatings. The principal techniques of surface analysis in common use are identified and the technical limitations to accurate surface analyses pointed out. Accurate surface analyses require: (i) knowledge of the principles of the measurement method, (ii) knowledge of the behavior of the measuring instrument, and (iii) correct interpretation and expression of the final measured result. Standards for the measurement of surface composition with known accuracy and for the reliable determination of chemical state require: (a) a base of principles, definitions of terms, and suitable equations, (b) reference procedures for the measurement of intensities and spectral features, (c) procedures and data for instrument calibrations, (d) reference data for material parameters such as elemental sensitivity factors, matrix terms, chemical state spectra, ion sputtering rates, etc; and (e) standard methods for specifying an analysis. Specific needs are identified for the common methods of surface analysis, Auger-electron spectroscopy, x-ray photoelectron spectroscopy, and secondary-ion mass spectroscopy together with the needs for ion sputtering which is used to obtain composition versus depth information in films and coatings. Existing standards activities in the member countries of VAMAS are reviewed and suggestions are made for additional standards for surface chemical analysis.

(m) "Surface Harpooning", J. W. Gadzuk, Comments on Atomic an Molecular Physics, <u>16</u>, 219 (1985).

The principles involved in charge transfer/harpooning collisions between atoms or molecules and surfaces are presented in terms of concepts drawn from gas-phase atomic and molecular collision theory. As specific examples, the charge state of atoms and the vibrational excitation or dissociation of molecules which have experience harpooning while scattering from a surface are considered.

(n) "The Uses and Limitations of ESDIAD for Determining the Structure of Surface Molecules", T. E. Madey, in The Structure of Surfaces, Springer Series in Surface Science 2, M. A. van Hove and S. Y. Tong, Eds. (Springer-Verlag, N.Y.), 264 (1985).

The principles and mechanisms of electron-stimulated desorption (ESD) and photon-stimulated desorption (PSD), as well as the utility of the electron stimulated desorption ion angular distributions (ESDIAD) method as a tool for determining the structure of surface molecules, have been described in a recent book and several review articles. The present short paper is intended to provide a guide to the relevant literature, and to describe briefly some recent work relating to the uses and limitations of ESDIAD for determining the structure of surface molecules.

2. Review Articles in publication

We list below the titles and abstracts of review articles in the course of publication.

(a) "The Chemisorption of Carbon Monoxide by the Transition Metals," J. T. Yates, Jr., T. E. Madey, and J. C. Campuszano, The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, D. A. King and D. P. Woodruff, eds. (Elsevier).

A comprehensive review of the adsorption of carbon monoxide by transition and noble metals is presented. The systematics of CO adsorption and dissociation are discussed, along with detailed examinations of the surface structures, electronic and vibrational spectra, and kinetic behavior of adsorbed CO.

(b) "Final-State Resolved Studies of Molecule-Surface Interactions," D. S. King and R. R. Cavanagh in New Laser and Optical Investigations of Chemistry and Structures at Interfaces, Verlag Chemie.

Quantum state-specific diagnostics as applied to surface dynamics are discussed. The NO molecule is used as an illustration of the experimental determination of gas-surface interactions. Topics reviewed included beam-surface scattering thermal desorption, vibrational accommodation, Doppler profiles, and Fourier-transform infrared emission spectroscopy.

(c) "Core-Level Binding-Energy Shifts in Solids at Surfaces," W. F. Egelhoff, Jr., Surface Sci. Reports.

This review presents an overview of the theory and of various successful approaches to the interpretation of core-level binding-energy shifts observed in photoelectron spectroscopy. The theoretical background is presented at a level readily accessible to the general reader. Particular attention is paid to relative merits of the two basically different conceptual frameworks for interpreting core-level binding-energy shifts, the initial-state--final-state approach and the equivalent-core-Born-Haber-cycle approach.

(d) "Recent Advances Using ESDIAD: Applications to Surface Chemistry", T. E. Madey, C. Benndorf, N. D. Shinn, Z. Miskovic, and J. Vúkanic, Proceedings of DIET-II Symposium (Desorption Induced by Electronic Transitions), in Springer Series in Chemical Physics.

Recent applications of ESDIAD (electron stimulated desorption ion angular distributions) to surface chemistry are described. Examples include the influence of catalytic promoters and poisons on surface structure and reactivity, the evidence for a new structural form for adsorbed H_2O (i.e., H_2O dimers on Ni(110)), and the characterization of a new bonding mode for CO on Cr(110). Calculations of the perturbing influence of image force and reneutralization effects in ESDIAD are described.

(e) "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces", J. W. Gadzuk, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr., and T. E. Madey, eds., Vol. 4 of Methods of Surface Characterization (Plenum, NY).

An introduction to the theoretical basis of vibrational excitation mechanisms and processes relevant to vibrational spectroscopy of adsorbed molecules is presented.

(f) "Neutron Inelastic Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces", R. R. Cavanagh, J. J. Rush, and R. D. Kelley, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr. and T. E. Madey, eds., Vol. 4 of Methods of Surface Characterization (Plenum, NY).

An introduction to neutron scattering as a probe of adsorbates at surfaces is presented. Emphasis is placed on experimental aspects of triple axis and time-of-flight techniques along with a single-phonon model for the spectral features. Wilson FG methods for constructing molecular force fields relevant to the molecular modes of the adsorbate are presented. The applicability of neutron scattering for exploring rotational diffusion and adsorbate torsions is also examined.

(g) "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy", C. J. Powell, J. Vac. Sci. Tech.

An overview is given of recent developments in quantitative surface analysis by x-ray photoelectron spectroscopy and Auger-electron spectroscopy. The two major tasks of an analysis are the identification of the surface phases that are present and the determination of the concentrations of particular elements or compounds. Methods for accomplishing both tasks will be described together with the pitfalls and problems that remain. Particular attention is given to the following topics: identification of surface phases and reference data for the calibration of instrumental energy scales; reference data on inelastic mean free paths and attenuation lengths; effects of specimen crystallinity; intensity measurements; measurement of the imaging properties of electron energy analyzers; and the intensity-energy response functions of different instruments.

(h) "Surface Chemical Analysis - Report on the VAMAS Project," C. J. Powell and M. P. Seah, Surf. Interface Anal.

The VAMAS project on surface chemical analysis is a multi-national cooperation for the provision of standards data and materials for surface chemical analysis measurement and for the provision of the basic understanding necessary for these activities. This project is one of a rapidly growing suite of projects initiated as a result of decisions following the 1982 Versailles Summit Meeting of the Heads of State or Government of Canada, France, Germany, Italy, Japan, UK, USA and the Representatives of the Commission of the European Community. During the past year national representatives to this VAMAS project have been appointed and national committees established. This article summarizes the philosophy, scope, and organization of the project and describes specific activities that have been initiated. Information is given on how individuals, both within and outside the group of member states, may participate.

(i) "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra", J. W. Gadzuk, J. Electron Spectroscopy.

Extremely useful connections exist between the dynamics of adsorbed molecule vibrations, as revealed in spectroscopic lineshapes, and the dynamics of molecular processes at surfaces because in both cases, the constituent atoms of a molecule, solid, or combination of the two execute multi-dimensional motion over the same potential energy surfaces, undoubtedly sampling different regions of it.

In this paper, recent insights and advances in surface dynamics will be applied to the problem of vibrational lineshapes. Classical particle and semi-classical wavepacket dynamics will be used to address the issues of energy decay (T_1) vs. pure dephasing (T_2') overtones, and non-linear dynamics as they apply to lineshape analysis.

(j) "Field Emission Microscopy - Trends and Perspectives," A. J. Melmed, Chemistry and Physics of Solid Surfaces VI, Springer-Verlag

The author's view of the role of surface microscopies, in particular the field emission microscopies, is given. Brief outlines of the historical development and nature of field-electron emission microscopy (FEEM) and field-ion microscopy (FIM) are given and selected examples are presented to illustrate the scope of research in FEEM and FIM. Research trends are described and some projections for the future are made.

3. Books

(C. J. Powell, T. E. Madey)

While there are many books and review articles on different aspects of surface science and its applications, there is a dearth of information on how to make reliable surface-characterization measurements. There is, in essence, a large information gap between review articles in which the latest scientific advances are discussed and manufacturers' handbooks in which the operation of a commonly used surface-characterization equipment is described. Arrangements have been made with a commercial publisher to produce a series of books, "Methods of Surface Characterization," which will address this need. Two Division staff members (Powell and Madey) and three other scientists (A. W. Czanderna at the Solar Energy Research Institute; D. M. Hercules and J. T. Yates at the University of Pittsburgh) constitute an editorial board that will oversee the production. A series of four volumes in currently planned which will describe the principles, techniques, and methods considered important for surface characterization. It is intended to describe how important surface-characterization measurements are made and how to ensure that the measurements and interpretations are satisfactory (to the greatest extent possible). The approach of the series will be pedagogical or tutorial.

Volumes 1 and 2 of the book series will describe the techniques and methods for electron spectroscopy and ion spectroscopy, respectively, which are in widespread use for surface analysis. These volumes will be concerned largely with techniques for which commercial instrumentation is available. It is hoped that writing for both volumes will be completed shortly.

Volume 3 will describe techniques for specimen handling and depth profiling. For specimen handling and treatment, this volume will provide a compilation of methods that have proven useful. This volume will also address the common artifacts and problems associated with the bombardment of solid surfaces by electrons and ions. Finally, a description will be given of methods for depth profiling. Preparation of this volume should be completed in 1986.

Volume 4 will bring together a description of methods for vibrational spectroscopy of molecules on surfaces. Most of the techniques are currently under active development; commercial instrumentation is available for some techniques but this situation could change in the next few years. The current state-of-the-art of each technique will be described as will the relative capabilities. An important component of the volume will be the summary of the relevant theory. This volume is essentially complete.

D. Standards-Committee Activities

Three staff members of the Division hold offices on two ASTM Committees, the E-42 Committee on Surface Analysis and the D-32 Committee on Catalysts, and on the recently established Surface Chemical Analysis Working Party organized under the auspices of the Versailles Project on Advanced Materials and Standards. Participation in the activities of these groups provides an opportunity for leadership, for dissemination of NBS expertise, and to learn of significant measurement problems in relevant areas.

1. ASTM Committee E-42 on Surface Analysis
(C. J. Powell, J. Fine)

The ASTM Committee E-42 on Surface Analysis, founded in 1976, now has some 120 members; in addition, a large number of non-members, both within the U.S. and throughout the world, participate in Committee activities. The purpose of the Committee is to advance the field of surface analysis and the quality of surface analyses through the development of appropriate standards, standard practices, reference data, reference materials, round robins, symposia, workshops, and publications.

Committee activities of the past year have included development of the following documentary standards (which are at varying stages of approval):

- Additional definitions of terms for AES, XPS, SIMS, and Energetic Ion Analysis
- Guide to Depth Profiling in Auger Electron Spectroscopy
- Guide for Specimen Handling in AES and XPS
- Practice for Reporting Spectra in XPS
- Method for Calculating Data-Gathering Speed in XPS
- Guide to Steady-State Charge-Referencing Techniques in XPS
- Practice for Reporting Sputter Depth Profile Data in SIMS (secondary-ion mass spectroscopy)
- Guide to Determine the Depth Resolution in SIMS
- Guide for Specification of Ion Beams for Use in Surface Analysis
- Procedure for Sample Positioning with Cylindrical Mirror Analyzers in ISS (ion-scattering spectroscopy)
- Procedure for Approximate Energy Scale Calibration with Cylindrical Mirror Analyzers Used in ISS
- Proposed Guide for Data Reporting in ISS

The Standard Reference Data Subcommittee is conducting a survey of needs for reference data and of format requirements. A survey of the E-42 membership is being made to determine needs for new types of reference materials. Finally, a report has been submitted for publication recently of an ISS round robin involving comparisons of peak-position and peak-width measurements on a Cu-Ag-Au ternary alloy using seven cylindrical-mirror analyzers from the same manufacturer. This round robin showed that much of the spread in reported peak positions was associated with incorrect positioning of the specimen with respect to the analyzer.

The Committee has sponsored two symposia each year, one at the annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in the spring and the other at the National Symposium of the American Vacuum Society (AVS) in the fall. Papers presented at these symposia are published. After 1985, arrangements for the AVS Symposium will be made by the recently formed AVS Applied Surface Science Division. A workshop is held at each meeting to discuss particular measurement problems. At the 1984 AVS Symposium the topic was "Data Reduction for Quantification in Surface Analysis", and the topic at the 1985 Pittsburgh Conference was "Solving Industrial Problems with Surface Analysis".

The Committee is planning to prepare a booklet of E-42 surface analysis standards which will be published by ASTM. It is believed that many users of surface-analysis equipment will find the booklet to be a convenient compilation of terminology, guides, and recommended practices. The booklet will be updated roughly every two years and should be an effective means of disseminating E-42 standards.

2. Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards (VAMAS)

(C. J. Powell)

The "Versailles Agreement" arose from a meeting of the Heads of State or Government (Economic Summit) of industrialized nations at Versailles in 1982. The participants represented Canada, Federal Republic of Germany, France, Italy, Japan, United Kingdom, United States of America, and the Commission of the European Communities (CEC). A Summit Working Group on Technology, Growth, and Employment was established consisting of government science advisers. This group has established Working Groups in areas such as photovoltaic solar energy, food technology, advanced robotics, biotechnology, high speed trains, remote sensing from space, and advanced materials and standards. A summary of developments resulting from the Versailles Agreement was published as a News and Comment article recently in Science 228, 827 (1985).

The Versailles Project on Advanced Materials and Standards (VAMAS) consists of a Steering Committee with respresentatives from the seven nations above and the CEC. The overall aim of the project is to encourage international trade. This objective will result from international agreement on codes of practice and performance standards and from multilateral research aimed at providing the scientific and technological base necessary to achieve agreement on standards. The project is essentially a scheme for stimulating the introduction of advanced materials into high technology products and engineering structures. The ubiquity of surface analysis through all sectors of high-technology industry has been demonstrated in recent surveys, and a proposal to establish a Surface Chemical Analysis (SCA) Working Party won early approval from the VAMAS Steering Committee. This SCA Working Party is now one of nine such groups that have been approved.

The main objective of the SCA working party is to produce, by coordinated effort, the reference procedures, data, and materials necessary to establish standards for surface chemical analysis. This effort is expected to lead to the international coordination of standards-related activities before national standards are adopted and to the development of standards on an international level.

National representatives to the SCA Working Party have been appointed with C. J. Powell as Chairman for a three-year period. The most urgent needs for surface analysis pertain to the use of Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS), and sputter-depth profiling (SDP). As projects in these areas become established and as other techniques come into greater use, it is expected that the project will broaden.

Qualitative and quantitative surface analyses require consideration of the following three items:

(i) the physical principles of the measurement method;
(ii) the behavior of the measuring instrument; and
(iii) the interpretation and expression of the final result.

The basic principles of the physics of the various techniques and the selected analytical methods are vital since they lead to the working formulae which are used for quantitative analysis. Agreement must be obtained on these formulae and their regimes of applicability when working to certain accuracies for particular types of specimens and for particular techniques and methods. These formulae involve the measurement of intensities by the instrument which are then related to the composition at the surface by functions of the specimen material and the particular measurement process and by functions of the measuring instrument. Tabulations are needed of particular materials properties relevant to the various techniques and information is needed on instrument properties. Additionally, surface analyses can give chemical-state information, the interpretation of which requires a similar hierarchy of understanding, data, and reference procedures. The analyst therefore requires:

(1) an agreed base of principles, definitions of terms, and equations to relate the techniques and procedures to the measurement;

(2) reference procedures specifying how to measure intensities and spectral features;

(3) reference procedures, reference data, and reference materials for calibrating instruments, determining instrument functions, and inter-relating instruments of different designs;

(4) reference data of elemental sensitivity factors, matrix terms, information depths, libraries of chemical-state spectra, information on ion-sputtering rates, radiation damage, etc.; and

(5) standard methods of specifying an analysis.

Details of specific needs for AES, XPS, SIMS, and SDP have been identified.

Suitable infrastructures have been developed in most VAMAS states for the SCA project. In the U.S., the ASTM Committee E-42 on Surface Analysis has agreed to participate and cooperate in VAMAS SCA projects. Standards already developed by the E-42 Committee will be disseminated to the other VAMAS states; standards developed later in the other states will be considered for adoption by the E-42 Committee. Suitable projects at NBS and other U.S. laboratories also contribute to the VAMAS SCA activity.

Since January, 1985, a large number of technical projects have been started in the VAMAS states, many largely as a result of the VAMAS initiative. These projects are largely national activities, as is to be expected since it is necessary that national needs, opportunities, and priorities be established prior to the development of more extensive bi-national or multi-national projects. The first meeting of the national representatives to the VAMAS SCA Working Party took place in October, 1985 during a conference in The Netherlands. A number of cooperative projects were discussed and it was agreed that the following should be implemented.

(a) Development of thin oxide films as reference materials. It is planned to produce thin films of transition-metal oxides (Fe_2O_3, NiO, and Cr_2O_3) with thicknesses of about 25 nm on metal substrates in Canada. Films of similar thickness of SiO_2 on silicon will be produced in Italy. These films will be characterized by sputter-depth profiling at a number of laboratories in Canada and Italy. The ion sputtering yields of these oxide films under common conditions of sputter-depth profiling will be compared with similar measurements on existing Ta_2O_5 and Ni/Cr reference materials at NPL and NBS.

(b) Development of calibration data for the energy scales of Auger-electron spectrometers. Current projects exist at both NBS and NPL for the independent measurement of the kinetic energies of the principal Auger-electron transitions of copper, silver, and gold to be used as calibration data in the energy range 50-2000 eV. After intercomparison, the calibration data will be utilized in an interlaboratory comparison of Auger-electron measurements to be organized by NPL.

(c) Procedures for quantitative x-ray photoelectron spectroscopy (XPS). It is planned to investigate at NBS the suitability of recently fabricated Ta_2O_5 films on silicon and, if necessary, the oxide films prepared in project (a) as test materials for an interlaboratory comparison of angle-dependent XPS measurements. If these films can be cleaned adequately with minimal ion sputtering, NBS will organize the comparison of XPS measurements to give information on film thickness and film stoichiometry.

Two additional cooperative projects were discussed and it is likely that these will be initiated following the preparation of more definite plans. The first such project is the development of alumina reference materials with known concentrations of oxygen vacancies. These materials will be used as reference materials for problems in materials science such as wetting, adhesion, and electrical breakdown as well as for determining conditions for radiation damage. The second project is the development of reference procedures for high-resolution scanning Auger-electron microscopy so that the effects of topography, specimen crystallinity, and angle of emission can be minimized.

Plans are being developed for two workshops on surface chemical analysis for which VAMAS will be a co-sponsor. The first workshop is planned for October 24, 1986 at NBS and will precede the Tenth International Vacuum Congress and Sixth International Conference on Solid Surfaces to be held in Baltimore, October 27-31, 1986. The second workshop is planned for November 17, 1986 at NPL and will precede the fourth Conference on Quantitative Surface Analysis at NPL on November 18-20, 1986. These workshops will publicize VAMAS activities, disseminate results of recent work on quantitative surface analysis, and promote the development of new cooperative VAMAS projects. Specific attention will be given at both workshops to needs for reference data, needs for reference materials, methods of instrument calibration, and analytical methodology.

The VAMAS Surface Chemical Analysis Working Party has aroused a considerable amount of interest and enthusiasm in many of the VAMAS states. Many scientists believe that VAMAS has already provided and will continue to provide a considerable stimulus to the development of standards for surface chemical analysis in each state. Furthermore, through cooperation via VAMAS, national standards will be developed more efficiently and, it is hoped, without conflicts. The specific areas where international cooperation through VAMAS will be most effective are believed to be: (1) the development of data banks and preferred data formats; (2) the development of reference materials; (3) the development of documentary standards for instrument operation and calibration; and (4) the development of recommended procedures for data acquisition, data reduction, and expression of final results.

3. ASTM Committee D-32 on Catalysts
(R. A. Haines and R. D. Kelley)

The activities of the ASTM Committee D-32 on Catalysts are concerned with the physical and chemical properties of commercial catalysts and with developing suitable procedures for catalytic activity measurements. The membership of the Committee numbers approximately 130. Semi-annual meetings are attended by between 60-90 percent of the membership which includes a significant international component. In the past year, the expansion of Committee activities has continued. These activities involve four sub-committees: Physical/Chemical Properties - 6 task groups; Physical/Mechanical Properties - 6 task groups; Chemical Analysis - 2 task groups; Catalytic Properties - 5 task groups. In general, this expansion has moved into areas that involve complex and often controversial measurements. Examples of these are the measurement of catalyst acidity, of the sensitivity of cracking catalysts to metallic impurities, and of multi-element chemical analysis by atomic absorption.

The Subcommittee on Chemical Analysis is chaired by R. D. Kelley. This Sub-Committee is involved in finishing the test method for analysis of platinum in fresh reforming catalysts. A "final" round robin is presently under way. The effort to analyze palladium in catalysts has progressed to the round robin stage. Standardization of x-ray fluorescence analytical procedures and of procedures for the chemical analysis of spent catalysts are being discussed. In the base-metals task group, the primary emphasis is on the development of a satisfactory test method for determining several base metals by optical atomic spectroscopy.

The NBS Office of Standard Reference Materials (OSRM) will soon distribute special reference materials for catalysts. As a member of D-32, Dr. Ruth Haines, Deputy Director of the Center for Chemical Physics, is preparing the documentation required for NBS acceptance of materials used by D-32 in various round robin tests. Five years ago the Committee recognized the need to preserve the catalysts, catalyst carriers and feed stock used in their round robins. D-32 sought a private sector distributor but none was found. The OSRM can distribute the materials at cost but NBS will not certify them. Initially, samples will be available for physical properties such as surface area and particle size distribution; mechanical properties such as crush strength; chemical analysis of supported metals; and reactivity via gas oil conversion microactivity tests. A series of zeolites will also be available for which diffraction intensity, unit cell dimensions and zeolite areas have been determined. All the materials should be available within the next six months. We can then judge the desirability of producing more standards based on the extent to which these samples are requested.

3. SURFACE MEASUREMENTS PROGRAM

C. Benndorf, D. R. Burgess, Jr., R. R. Cavanagh, A. Flodstrom,
J. W. Gadzuk, S. M. Girvin, T. J. Jach, R. D. Kelley, R. L. Kurtz,
T. E. Madey, D. E. Ramaker, N. D. Shinn, R. Stockbauer, P. D. Szuromi,
T J. Udovic, M. J. Wax

The Division undertakes a number of projects directed to the improved physical and chemical characterization of surfaces and surface processes. These projects meet Division objectives through the development of new measurement techniques, improvement of existing techniques, development of theories of the measurement process, applications to important scientific and national problems, development of measurement procedures, tests of the measurement system, development of new concepts, and provision of needed data.

A. Reaction Kinetics at High Pressures over Single Crystal Catalysts (P. D. Szuromi, M. J. Wax, T. J. Udovic, R. D. Kelley, T. E. Madey)

The overall objective of this research is to provide a molecular understanding of heterogeneous catalytic chemistry on well-characterized single-crystal surfaces. Among the areas studied are the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen on metal surfaces, the mechanism of catalytic poisoning and promotion, and the reforming of alkanes over model supported Pt catalysts. The apparatus employed for these studies contains high pressure reactors contiguous to ultrahigh vacuum surface analysis chambers. The work is supported, in part, by the Division of Basic Energy Science of the Department of Energy.

Progress during the last year included studies of the hydrogenation activity of single-crystal W catalysts, as well as the poisoning effect of adsorbed S and the promoter effect of Pt thin films on the W substrates.

1. Ethane Hydrogenolysis Catalyzed by W(100)

Although W is not ordinarily considered a good catalyst, we have found that the W(100) surface is very effective in catalyzing ethane hydrogenolysis ($p \sim 100$ Torr, $550 < T < 620$ K). A carbidic overlayer forms rapidly in the early stages of reaction; this surface carbide is the "true" catalyst for the hydrogenolysis which proceeds with an activation energy of 27 kcal/mole. This is different from the activation energy for catalytic methanation over W(100), 14 kcal/mole, suggesting that methanation and hydrogenation do <u>not</u> share a rate-limiting step.

2. Thin Pt Films as Model Alkane Hydrogenolysis Catalysts

Vapor deposition of Pt onto a W(100) substrate in ultrahigh vacuum has been used to prepare model supported Pt catalysts which are free of extraneous promoters and poisons. Various Pt loadings (from fractional monolayer to multilayer) have been achieved reproducibly.

Although pure Pt is less active than W for ethane hydrogenolysis, the fractional monolayer Pt films catalyze hydrogenolysis at a rate significantly greater than the initially-clean W(100) surface.

3. Effect of S on Catalytic Methanation

The effect of adsorbed sulfur on the rate of catalytic methanation over a W(110) crystal has been studied as a function of sulfur coverage and crystal temperature. As in the case of the initially clean, non-sulfur-covered surface, carbidic carbon is formed during the course of the reaction. In Figure 3, the relative rate of reaction as a function of sulfur coverage (as determined by Auger-electron spectroscopy) is plotted for several reaction temperatures (together with similar data for Ni(100). The Arrhenius energy of reaction, 56 kcal/mole, does not change substantially with sulfur coverage, as can be inferred from the similar inhibition of the rate of reaction for each temperature at a given coverage. Although the inhibition at low sulfur coverages is not as

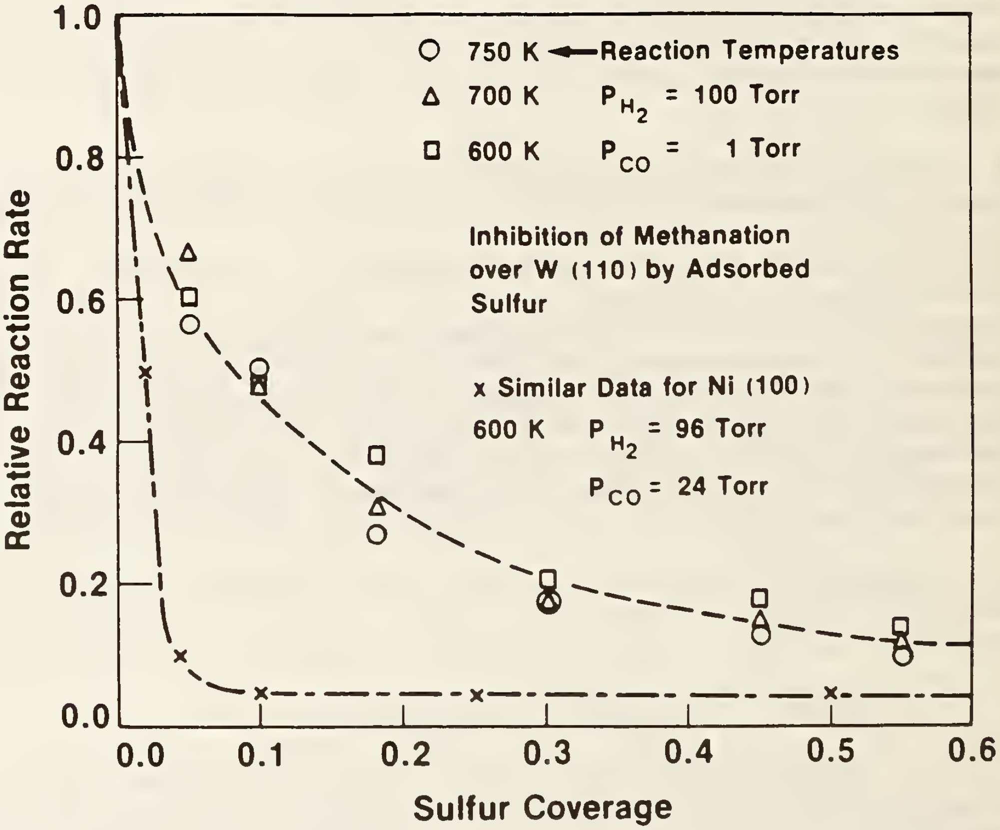
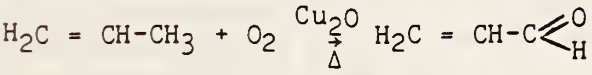


Fig. 3. Relative Reaction Rate for Catalytic Methanation over W(110) as a function of sulfur coverage (in fractions of a monolayer). Similar data for a Ni(100) are shown for comparison.

dramatic as that seen previously for this reaction over nickel surfaces, the overall rate of reaction does drop about an order of magnitude at high coverages of sulfur.

We plan next year to complete both the methanation studies of W(110) and the effect of Pt films on hydrogenolysis. The role of Pt films in the thickness range 1-2 monolayers on W(100) will be characterized for the hydrogenolysis reaction.

We plan also to initiate a new project to study partial oxidation catalysts. This important class of reactions has received little attention from surface scientists, and we propose to probe the mechanism of the catalytic oxidation of propylene to acrolein over Cu_2O:



$$\mathrm{H_2C = CH{-}CH_3 + O_2 \xrightarrow[\Delta]{Cu_2O} H_2C = CH{-}C}\begin{smallmatrix} \nearrow\!\!\!\!\nearrow \mathrm{O} \\ \searrow \mathrm{H} \end{smallmatrix}$$

Initially, the dehydrogenation of alcohols will be examined on a pure copper crystal. These reactions will be examined using apparatus which combines both a high-pressure reactor (2 atmospheres) with an ultrahigh vacuum surface analysis chamber; the surface over which the catalytic reactions occur will be probed both before and after reaction. Several aspects of the oxidation reaction are not well understood: the effect of the surface geometry of the oxide; the electronic state of the catalyst, both the oxidation state of copper and the surface valence band structure; the influence of electronegative species (S, Se, halogens) as promoters; and the Arrhenius parameters for the overall rate of reaction. These questions can be addressed by employing: single-crystal oxide surfaces to control geometric effects; post-reaction analysis by electron spectroscopies (AES, XPS and UPS); preparation of clean surfaces in ultrahigh vacuum and of promoted samples of known surface concentration; and measurement of rate data over a wide range of temperatures, pressures and reactant ratios.

B. Molecular Structure and Reactivity on Surfaces as Studied Using ESDIAD and HREELS

(T. E. Madey, N. D. Shinn, and C. Benndorf)

A major challenge in surface science continues to be the determination of the structures of molecules on surfaces, particularly in the absence of long-range order. The goals of this project are to provide a direct determination of the structures of adsorbed molecules using the electron stimulated desorption ion angular distribution (ESDIAD) method, and to characterize the structures and reactivity of surface species using high resolution electron energy loss spectroscopy (HREELS). These techniques, both singly and in combination, are powerful tools for surface structural characterization.

The present thrusts of this project are (a) to determine the influence of surface additives (e.g., catalyst promoters and poisons) on the local structure and reactivity of small molecules (CO, NH_3, H_2O) on surfaces, and (b) to determine the structures of those molecules on initially-clean surfaces, particularly in controversial cases. The work has been supported in part by the Division of Basic Energy Sciences of the Department of Energy.

During the last year, progress has been made in the following areas.

1. Evidence for Reorientation of CO when co-adsorbed with K on Ru(001)

We have used ESDIAD to address a current controversy concerning the influence of K on the structure of adsorbed CO: does CO "stand up" or "lie down" adjacent to K on Ru(001)? In the absence of K, CO is bonded with its molecular axis perpendicular to Ru(001) at all coverages. Upon coadsorption with low coverages of K, ESDIAD measurements provide evidence for a strong local interaction between CO and K, which appears to result in a reorientation of the CO to an "inclined" or lying-down bonding configuration. Moreover, complementary thermal desorption and low-energy electron diffraction measurements suggest the formation of ordered surface species having $K_x (CO)_{2x}$ stoichiometry. The question of CO bonding geometry is a major area of current interest in the surface science community, and the present measurements and models provide new insights into the CO + K surface chemistry.

2. Structure and Reactivity of NH_3 on Clean and Modified Fe(100)

Iron is an excellent catalyst in NH_3 synthesis, and adsorbed K is known to "promote" the reaction by increasing the rate. In an attempt to understand at the molecular level how K influences the bonding geometry of NH_3 to Fe, we used ESDIAD to examine the structure and reactivity of NH_3 on clean Fe(100), and on K-dosed Fe(100). On clean Fe(100), adsorption of NH_3 occurs at step sites up to $\theta(NH_3) \sim 0.02$. For higher coverages, up to saturation of the first layer ($\theta(NH_3) \sim 0.34$), ESDIAD is dominated by a "halo" H^+ pattern indicating that NH_3 is bonded via the N atom and the H atoms (with no azimuthal ordering) are pointed away from the surface. The ESDIAD data correlate well with thermal desorption data, where different binding states due to fractional monolayer, second layer, and multilayer adsorption are observed. Only a small fraction ($\theta < 0.02$) of NH_3 dissociates upon heating. When NH_3 is coadsorbed with K, the ESDIAD and thermal desorption data indicate an interaction in which the NH_3 molecular axis is tilted and the binding energy to the substrate is decreased. In contrast, the interaction between NH_3 and O does not lead to structural changes or azimuthal ordering of NH_3 as reported previously on Ru(0001) and Ni(111) surfaces. This indicates that the NH_3 - O distance is not optimal for attractive hydrogen bonding.

3. Structure of the Surface Hydration Shell of Bromide on Ag(110)

Surface science has been a valuable source of inspiration to electrochemists in recent years, particularly in studies of the interaction of water and other electrolytes with clean, well-characterized electrode surfaces. In one such study, we have attempted to synthesize an electrochemical double layer in vacuum by examining the interaction of H_2O and bromine on an Ag(110) surface using ESDIAD, LEED (low-energy electron diffraction) and TDS (thermal desorption spectroscopy). Water adsorbed on clean Ag(110) formed a disordered, hydrogen-bonded overlayer. In the presence of adsorbed bromine, the adsorbed water was characterized by a higher binding energy and pronounced orientational order. The mixed adlayers resulting from this surface hydration of bromide also exhibited long range order. The surface hydration number ($n_{H_2O}/_{Br}$) was two for $\Theta_{Br} < 0.25$, and decreased to a few tenths at the Br saturation coverage, $\Theta_{Br} \approx 0.75$. The present results have important implications for experiments in which investigators attempt to transfer electrodes from solution to a vacuum environment: neither water on the clean surface nor the hydration water remain adsorbed in vacuum at room temperature, and would be lost in a transfer experiment.

4. CO Chemisorption on Cr(110): Evidence for a Precursor to Dissociation

HREELS and ESDIAD studies of the chemisorption of CO on Cr(110) have provided fascinating insights into the structure and kinetics of molecular dissociation on a metal surface. At 120 K, two molecular binding modes of CO are sequentially populated. The first, α_1CO, is a novel binding mode for a clean metal surface in which the molecules are bound with the C-O axis nearly parallel to the Cr(110) surface. Annealing experiments demonstrate that the α_1 binding mode is the precursor to dissociation on Cr(110). At higher CO coverages, $0.25<\Theta_{CO}<0.35$, the a_1CO overlayer is disordered by the addition of the second binding mode, α_2CO. The α_2CO species are terminally bound molecules adsorbed at a-top and bridge sites and aligned approximately perpendicular to the surface. Annealing studies of CO or O/CO adlayers provide evidence for a surface reaction in addition to direct dissociation at about 170 K. In contrast, adsorption at 300 K leads to direct dissociative chemisorption with no detectable intermediate molecular adsorbate. The implications of these results to catalytic reactions of CO have been considered and comparisons to CO adsorption on clean and "promoted" transition metal been made.

We plan next year to extend the ESDIAD method to the detection of negative ions; all ESDIAD measurements to date have involved positive ions. We believe that these challenging measurements will provide new insights into the structure and surface chemistry of a class of molecules (particularly those containing halogens and other electronegative groups) for which studies have not been possible previously. A new digital video system will be constructed for these measurements. This system will be used to acquire and process data for ion current versus emission angle. We expect that the digital system will be more sensitive and give more accurate information than the currently used analog system. A later phase of this work will involve characterization of similar molecules using

HREELS and synchrotron methods. The new measurements will be an exciting complement to our present studies of the influence of surface additives on the structure and chemistry of adsorbed species.

We will use ESDIAD and HREELS to address a fundamental question in hyrocarbon surface chemistry, namely, the structure of C_2H_2 on a Cu(110) surface. Different models have been proposed involving rehybridized carbon species with the C-C bond vector either parallel or perpendicular to the Cu atom rows. ESDIAD may be able to provide a unique insight into the local bonding geometry of this site.

Despite the extensive interest in the chemistry of H_2O on transition metal surfaces, there are no definitive spectroscopic studies of the adsorption and decomposition of H_2O in the temperature range 77-300K on any metal having a high heat of M-O bond formation where dissociation is likely to occur. We propose to study in detail the structure and kinetics of H_2O adsorption and decomposition on Cr(110) using ESDIAD and HREELS; the goal will be to identify the fundamental steps in this important surface reaction.

We will continue to probe the role of both electropositive and electronegative additives on the structure and chemistry of small adsorbed molecules. Of particular interest are the major differences in the "activity" of oxygen in promoting hydrogen abstraction on different surfaces.

C. Inelastic Neutron Scattering Studies of Adsorption and Reaction on Catalysts

(R. D. Kelley, R. R. Cavanagh, M. J. Wax, T. J. Udovic)

Inelastic incoherent neutron scattering (IINS) studies of adsorbates on catalyst surfaces are providing new insights into the vibrational spectroscopy of hydrogen and hydrogen-containing species adsorbed at the surfaces of high-area catalysts. NBS is ideally suited for these studies, having a unique combination of neutron physicists and surface chemists with an interest in catalysis. During the last year, advances have been made in characterization of both metal and zeolite catalysts using IINS at the NBS Reactor in collaboration with Dr. J. J. Rush of the Reactor Radiation Division. The work has been supported in part by the Division of Basic Energy Sciences of the Department of Energy.

1. Interaction of Vibrating H atoms on Pt particles

The dynamical interactions between vibrating hydrogen atoms on the surface of small Pt particles (Pt black) have been studied using IINS together with isotopic dilution (comparing pure H_{ads} with $H_{ads} + D_{ads}$). The data revealed direct information on the bonding state and dynamical non-bonded (as opposed to chemical) interactions of these species. Shifts and broadening of hydrogen vibrational features were accounted for in terms of mode dispersion due to strong H-H coupling.

2. Hydrogen Adsorption and Interaction with Oxygen on Pt

IINS was utilized to probe the nature of adsorbed hydrogen and its interaction with oxygen on platinum black. The vibrational spectra of adsorbed hydrogen at 80 K were found to be in agreement with the results of other reported IINS studies. The interaction of oxygen with adsorbed hydrogen provided vibrational spectra corroborating the existence of at least two distinct hydrogen-adsorption sites. In addition, hydrogen and oxygen adsorption on the platinum black blank both yielded spectral information concerning the chemical state of the platinum surface. Comparison of the present IINS data to published electron energy-loss spectroscopy results suggests that oxygen reacted with hydrogen over platinum black to product adsorbed hydroxyl (OH) species.

3. Neutron Scattering Study of Zeolite Rho

Incoherent inelastic neutron scattering has been used to examine the bonding of framework hydrogen to the faujasite zeolite rho in collaboration with Drs. G. D. Stucky, L. Abrams, and D. R. Corbin of Dupont. Vibrational spectra obtained from 160 to 1600 cm^{-1} are consistent with the existence of planar, symmetric AlO(H)Si units in the acid form of rho at room temperature. As the zeolite undergoes a slight change in structure on heating, an accompanying transfer of hydrogen atoms occurs to some new bonding site of unknown nature which is characterized by an unusually large-amplitude, low-energy vibration. Quasielastic neutron scattering data have allowed an upper limit (4×10^{-6} cm^2 s^{-1} at 673 K) to be set for the rate of diffusion of hydrogen on the framework of partially dehydroxylated rho, a result consistent with diffusion measurements by macroscopic methods.

We plan next year to extend the applications of IINS to the characterization of adsorbates on the internal and external surfaces of zeolite catalysts. The new measurements will build upon our recent studies of the bonding and of diffusion rates of framework hydrogen of zeolite rho, and will include both adsorbate structures and diffusive motion of adsorbates in various zeolites. One example will be the dynamics of NH_3 interactions in zeolite rho. Quasielastic neutron scattering will complement the IINS measurements, and will be used to derive the rates and nature of diffusional motion.

We will use IINS to probe the interactions of hydrogen on and in Pd black. The main effort will be devoted to cleaning and characterizing the sample before hydrogen adsorption, followed by a study of both surface and bulk hydrogen in Pd. This effort is expected to answer long-standing questions regarding the communication between surface and bulk species.

There have been few studies of adsorption and reactions on supported catalysts using IINS. Our studies to date have involved the adsorption of H_2 and small hydrocarbons on unsupported metals (Ni,Pt). We plan to extend these studies to supported metal catalysts for which there is a vast literature concerning preparation, cleaning, adsorption and reaction. In collaboration with workers experienced in noble-metal catalyst preparation, we will choose, prepare and initiate neutron-scattering studies on prototype catalysts.

D. Surface Characterization Using Synchrotron Radiation

(R. Stockbauer, R. L. Kurtz, N. D. Shinn, D. E. Ramaker, A. Flodstrom, and T. E. Madey)

Major goals of this effort are (a) to determine the electronic structure of surfaces and adsorbates using variable-wavelength synchrotron radiation and ultraviolet photoelectron spectroscopy (UPS), and (b) to identify the electronic excitations which result in the photon-stimulated desorption (PSD) of ions from molecules adsorbed on surfaces as well as from condensed molecular films. When possible, PSD ion yields are correlated with UPS of both valence states and core-electronic states of the surface species. These measurements provide tests of recent theoretical models of electron- and photon-stimulated desorption, and provide new insights into the bond-breaking processes induced by ionizing radiation incident on surfaces. The work has been supported in part by the Office of Naval Research.

Accomplishments during the past year were in six areas: (1) electronic structure of molecules adsorbed on surfaces; (2) electron-stimulated desorption (ESD) and PSD of oxide surfaces; (3) instrumentation of a new beamline at the NBS synchrotron radiation facility SURF-II; (4) construction of a new display analyzer; (5) progress at the Brookhaven National Synchrotron Light Source (NSLS); and (6) theory of stimulated desorption.

1. Electronic Structure of Molecules Adsorbed on Surfaces: Relation to Geometric Structure

Synchrotron photoemission studies of the bonding of CO to the Cr(110) surface at low temperatures have identified differences in the electronic structure of the molecularly adsorbed CO that are correlated to the molecular binding configuration. At low coverages ($\theta < 0.25$), only the α_1CO binding state is populated; in this binding state the molecules are "lying down" on the metal surface. Ultraviolet photoemission measurements reveal a unique Cr:CO 4σ bonding interaction; this result is evidence for Cr:CO bonding substantially different from the conventional Blyholder model of synergistic CO $5\sigma \rightarrow$ metal charge donation and metal → CO 1π backdonation. In contrast, the terminally-bonded α_2CO binding mode, seen at high surface coverage ($\Theta > 0.25$), is well described by this conventional model.

Figure 4 illustrates typical UPS data obtained at 40 eV photon energy in an experimental configuration which is most sensitive to photoelectron detection along the [110] surface normal direction. A spectrum for the clean Cr(110) surface, Figure 4(a), can be compared to those with only α_1CO adsorbed, Figure 4(b), and with both α_1CO and α_2CO adsorbed at high coverage, Figure 4(c). The spectral differences associated with the two

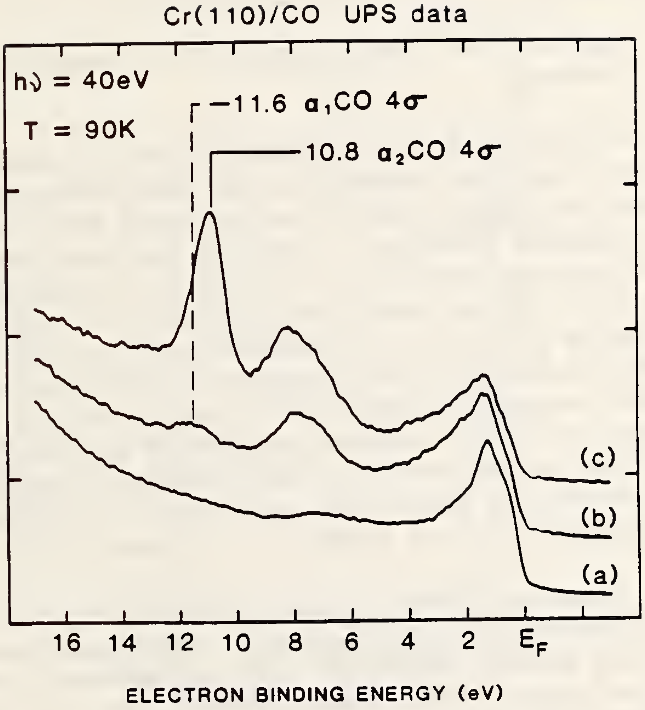


Fig. 4. Ultraviolet photoemission spectroscopy (UPS) data for CO on a Cr(110) surface; evidence for two different bonding configurations are presented. Curve (a) is the clean surface spectrum and curve (b) corresponds to the α_1 state of CO (the "lying-down" mode). Curve (c) is the spectrum which includes the α_2 state of CO (the "standing-up" mode).

binding modes are unmistakable; a weak α_1CO 4σ peak at 11.6 eV binding energy is seen in Figure 4(b) whereas an intense α_2CO 4σ peak at 10.8 eV is observed in Figure 4(c). Both the binding energy and intensity differences are strong evidence for the radically different CO binding geometries and resulting bonding variations.

Angular and photon-energy dependent data provide additional support for the CO-binding mode models developed from our previous HREELS/ESDIAD studies (Section 3.B.4). Further studies probing the dissociation of adsorbed CO and CO:O_2 interactions on Cr(110) have been performed. As first seen in the earlier vibrational studies, adsorbate interactions between co-adsorbed CO and oxygen result in the reorientation of the lying-down carbon monoxide to a terminally-bonded configuration; this mode conversion is manifested in the UPS data by the expected changes in the CO 4σ region of the spectra.

Preliminary data have been obtained for molecular nitrogen, an isoelectronic non-polar analog to CO, adsorbed on the Cr(110) surface. These results will be combined with subsequent vibrational data to determine whether a molecular "lying down" N_2(ads) species, analogous to α_1CO, is present.

2. Electron and Photon-Stimulated Desorption of Ions from Oxide Surfaces

As part of our continuing effort to understand the mechanisms involved in stimulated desorption of ions from surfaces, we have made measurements on single-crystal oxides that have forced a re-evaluation of currently accepted theories. Much of the previous work in stimulated desorption involves correlation of photon energies for producing desorption with photon spectroscopic data for atomic excitations. Such work originally gave rise to fundamentally new ideas about the types of atomic transitions that could produce desorbing ions. These mechanisms, however, are incomplete in several aspects and in particular they neglect the influence of local bonding geometries and surface structure. The experimental program presently underway is aimed at studying the influence of surface structure and is giving rise to a broader understanding of the mechanisms underlying the desorption process.

The surfaces studied to date include the (001) and (110) surfaces of TiO_2. This material is particularly important since it is the model system for the Knotek-Feibelman (KF) mechanism of desorption. This model describes the inter-atomic Auger process that can occur in a maximal-valent material such as TiO_2 when a core hole is produced in the cation by electron or photon impact. This hole is unstable and can decay by an inter-atomic Auger process involving charge transfer from the O^{2-} ligands. This results in a positively charged O-ligand which then desorbs due to the strongly repulsive Madelung potential. This model predicts that excitation of the Ti 3p level should produce desorption. It also predicts that any population of Ti 3d-electron states (i.e. no longer a maximal-valent surface) should strongly reduce the probability of the inter-atomic decay, favoring an intra-atomic decay. This would result in a much reduced ion yield.

Figure 5(b) shows the oxygen ion yield versus incident photon energy from a 700°C annealed TiO_2(001) surface; this is a maximal-valent surface. At the excitation energy of the Ti 3p level, 38 eV, there is an onset in the ion yield. It peaks at 47 eV and decays rapidly, following the decay of the excitation probability of the Ti 3p level. In Figure 5(a), we show the 0 eV constant-final-state spectrum, essentially the photoabsorption spectrum of this surface. By comparison of this and other electron-excitation spectra with the ion emission spectra, we hope to unravel the specifics of the electronic excitations that product desorption. Thus, in agreement with the predictions of the KF mechanism, we observe desorption due to the excitation of the Ti 3p level. This agreement ends, however, when we compare the magnitudes of these yield curves for the different surfaces studied.

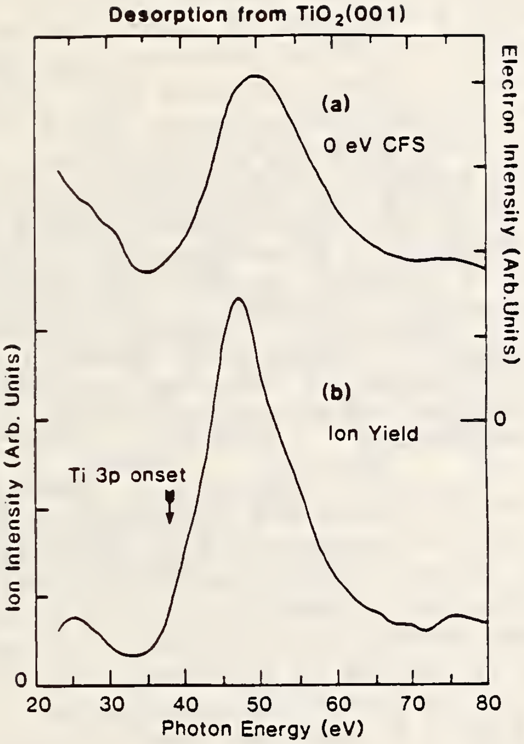


Fig. 5. Photon-stimulated desorption (PSD) of oxygen ions from an annealed TiO_2 (001) surface showing the role of core-hole excitations. (a) 0 eV constant-final-state intensity (proportional to photoabsorption cross section) versus photon energy. (b) ion yield versus photon energy.

The unexpected behavior that we have observed occurs when surface species are intentionally made non-maximal-valent (Ti 3d-electron states now populated) by the introduction of defects (by 500 eV Ar^+-ion bombardment); the magnitude of the ion yield does not always decrease as the KF mechanism would predict. It has been observed that the ion yield can even increase with such treatment, the opposite of the behavior that would be predicted by the KF mechanism. The source of this conflict can be resolved, however, when one considers the influence of surface structure and the local site geometries on the process.

It is known that surface geometric structure is drastically modified by Ar^+-ion bombardment; however, the details of the atomic rearrangements that the bombardment produces are not known. In order to compare the ion emission from surfaces with different geometries, we have resorted to studying two different surfaces of TiO_2, namely the (001) and the (110). The (001) surface is known to facet on annealing to (011) planes while the (110) surface is flat. The electron stimulated desorption ion angular distributions (ESDIAD) that we observe from the (001) surface are consistent with such a faceting; we observe emission from the faces and the edges of facets. The ESDIAD patterns from the (110) surface, on the other hand, give only a normal emission spot. Comparison of the magnitudes of the ion yields from these surfaces, however, indicates that increased ligand coordination of the Ti cations (such as is expected to be the case for a flat surface) produces decreased probability of ion desorption. The origin of this decreased probability could be an enhanced reneutralization probability or a decrease in the probability of initial excitation. There is also the possibility that surface dynamics may strongly influence the ion escape by lattice polarization and recapture. Our interest in the relative influences of these additional processes in desorption is to understand not only the initial excitation but also the decay of this excitation and the subsequent surface dynamics that lead to ion and neutral desorption.

In order to better understand the structure of complicated surfaces such as those of TiO_2, a graphics package has been written in FORTRAN that allows the display of ball-model crystal surfaces. This routine allows one to define a basis for a lattice, create a bulk crystal of specified size, and cut planes through this crystal to expose arbitrary surfaces. These surfaces can be rotated to be viewed from any perspective and surface vacancies can be introduced interactively. One such crystal ball model is shown in Figure 6 where the facet believed to be formed on TiO_2(001) after annealing to 700°C is shown. This modeling of surface structures will be associated with planned molecular dynamics calculations to be done in conjunction with our experimental efforts; we hope to better understand the variety of processes that influence desorption. Such calculations could allow us to predict site-specific desorption probabilities and to model desorption trajectories (perhaps even predict ESDIAD patterns). It is expected that such a feedback between calculation and experiment will also result in a better understanding of the structure of both perfect and defective surfaces.

During the next year, we plan to continue to study the mechanisms of ion desorption from solid oxide surfaces with both experimental studies and model calculations. Oxides have been shown to be unique systems that allow investigation of the relation between desorption mechanisms and the electronic and geometric structure. We will investigate further desorption from various surfaces of TiO_2. The recent studies of desorption from the (001) and the (110) surfaces of TiO_2 have promoted interest in the comparative study of TiO_2(011) and Ti_2O_3 (1012). Their similar surface geometric structures should permit isolation of the influence of their different electronic structures on the core-hole decay processes that lead to desorption. In addition, we intend to investigate the influence of the local-site environment in ion desorption from other surface such as MgO(100) and faceted MgO.

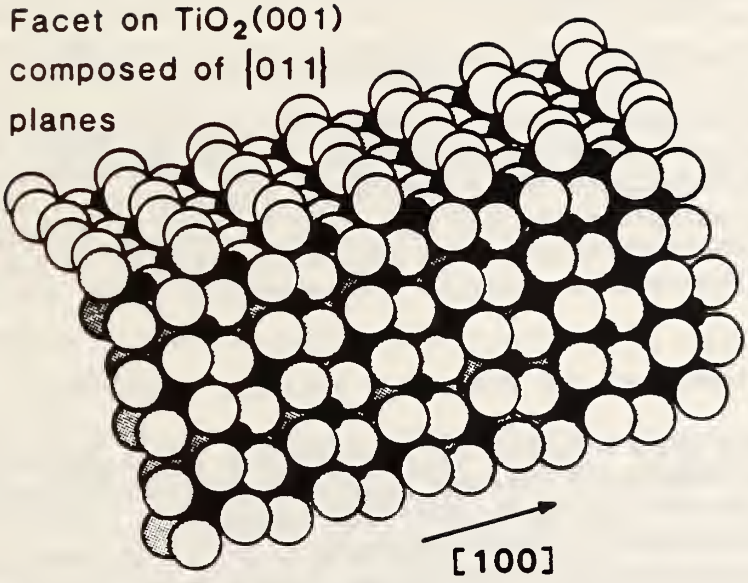


Fig. 6. Computer-generated model of faceted $TiO_2(001)$ surface.

We plan to make a molecular-dynamics calculation of the lattice response to a desorption process. An investigation will first be made of the often complicated geometric structure of oxide surfaces using software that can produce ball-model drawings of idealized surfaces. This software will be combined with the molecular-dynamics calculation in which the initial excitation and decay are assumed to occur rapidly; the subsequent charge reversal of a ligand then results in the motion of both the ligand and the rest of the lattice. The calculation should reveal information about the specifics of the sites that result in desorption and their angular distributions.

3. New Beam Line at SURF-II

The Surface Science Division has established a new beam line at the NBS synchrotron light source SURF-II. This will replace the existing beam line which we have used for the past 5 years. The heart of the new beam line is a toroidal grating monochromator designed by us to deliver high photon flux to investigate ion emission from surfaces with low ion yield. The monochromator has been calibrated and characterized and delivers 1×10^{10} photons per second per milliamp of ring current at a wavelength resolution of 4 A. With SURF-II routinely operating in the

100 mA range, we will have ~10^{12} photons per second on the sample at the same resolution. The useful energy range is from 17 to 90 eV. A new laminar grating is being manufactured which will decrease the amount of second order light being transmitted, and a second new grating will extend the range of the monochromator to 180 eV.

4. Construction of Angle-Resolving Display Analyzer

A new ellipsoidal-mirror angle-resolving electron- and ion-energy analyzer is nearing completion. This outstanding instrument was designed at NBS (based on an instrument constructed at IBM by D. Eastman) and is being constructed here. It is ideally suited for angle-resolved PSD, and will be the only such analyzer in North America used for the measurements. Details and scientific plans are given in Section 4.B.3.

5. Experiments at the Brookhaven National Synchrotron Light Source

A major effort during the last several years has been the initiation of an NBS-Naval Research Laboratory collaboration to establish four beamlines at the Brookhaven National Synchrotron Light Source (NSLS). We are providing surface science instrumentation to be used on one of the beamlines at the x-ray ring. The planned experiments have been delayed due to machine problems but these now appear to be largely overcome.

Our planned research will be an extension of the experiments performed at the NBS SURF-II facility (see above) to the higher-photon energies and more intense light available at the NSLS. Light from a unique, extended-range monochromator (5-5000 eV) will be used to study surface electronic structure and surface bonding of molecules. Experimental probes will include photoemission spectroscopy, surface extended x-ray absorption fine structure, and photon-stimulated desorption.

The main experimental chamber has been installed at NSLS and a sample preparation chamber has been acquired. The first experiments using the limited range of the monochromator presently available (20-200 eV) will involve measurements of electron attenuation lengths as a function of electron kinetic energy for condensed thin films of molecular solids. The synchrotron-based method for these measurements was developed and tested at SURF-II. These measurements will provide benchmark data for electron transport through organic materials in an energy range near the minimum value of the attenuation length. When the monochromator energy range is extended to ~1000 eV, we will undertake detailed studies of the roles of both core-level and valence excitation in the photon-stimulated desorption of ions from covalently bonded molecules on surface.

6. Theory of Stimulated Desorption

Work continued on the elucidation of the mechanisms that can give rise to electron- and photon-stimulated desorption of ions from adsorbates on surfaces as well as from single crystals. During this year, attention was given to the role of secondary electrons in photon-stimulated desorption and the extent to which these effects distort the ion yield spectra. Our studies suggest that these effects are not as dramatic as indicated in the literature. Work was also begun on understanding the mechanisms for negative-ion desorption from surfaces under electron bombardment and the role these mechanisms may play in negative-ion ESDIAD. Our understanding of the role of secondary electrons and the mechanisms for negative-ion desorption are important for planned future experiments (Section 3.B).

E. Dynamical Effects Associated with Core-Level Ionization

(T. J. Jach)

The NBS Quantum Metrology Group under the direction of Dr. R. D. Deslattes is developing an experiment to study electronic effects associated with core-level ionization in atoms, molecules, and at surfaces. Specific effects to be studied include dynamical effects in inner-shell vacancy production, relaxation of the extra-atomic environment, and production of multiple vacancies with or without ionization. One member of the Surface Science Division staff has been assigned to work half-time on this project.

During the past year, experimental work involving synchrotron radiation was pursued with two particular goals in mind. First, the long-awaited routine operation of the x-ray ring of the Brookhaven National Synchrotron Light Source (NSLS) became a reality. We aligned and corrected problems in our tunable focussed soft x-ray beamline (X-24A) to the point where it is the most intense source of photons in the 2-7 keV photons available in the world ($\sim 10^{11}$ photons/sec at 3 keV with <0.4 eV resolution). Second, we initiated experiments to study multi-electron core-level excitations in atoms and at surfaces.

1. NSLS X-24A Soft X-Ray Beamline (800 eV-7 keV)

The development of the NSLS X-24A beamline at Brookhaven officially came to fruition in September with the production of a stable, focussed, tunable x-ray beam in the energy range 2-7 keV. Using a nickel-coated aluminum collecting mirror (which also acts as a low-pass filter), a double-crystal monochromator, and a nickel-coated focussing mirror, we obtained a focussed spot 2 mm high by 1 mm wide with the flux mentioned above. The entire system is in ultra-high vacuum (uhv) with no windows whatsoever (it is contiguous with the main ring vacuum) and operates stably and comfortably at the highest intensity conditions reached by the x-ray ring so far (125 mA stored current at 2.5 GeV). The system is entirely computer controlled. The flux at this time exceeds all other tuned sources including the LBL/Exxon 54-pole wiggler at the Stanford

Synchrotron Research Laboratory over the energy range described above. Although an active program of experiments has already begun, we are actively soliciting other potential users.

2. Photon-Excited Multi-Electron Core-Level Excitations Using Synchrotron Radiation

We have begun a series of experiments aimed at the better understanding of multi-electron excitations which are photoexcited. Such effects as the threshold behavior of x-ray resonant Raman fluorescence, the energy shift due to post-collisional interactions, and the couplings between different decay channels from multi-electron excited states are all topics of importance in a number of surface spectroscopies. In collaboration with the NBS Quantum Metrology Group, we have initiated a three-step program: first, to observe x-ray fluorescence and Auger-electron decay in monatomic gases; second, to observe these decays in multi-atom gases; and finally, to observe the decays from solid surfaces of transition metals. All of these measurements are to be made as a function of photon energy in the vicinity of the threshold energies for core-level ionization. Data such as line widths, energy shifts, and threshold behavior will be used to understand multi-electron excited states and the dynamics of the decay process.

During the past year we have taken preliminary data on two systems. We observed K-shell x-ray fluorescence from argon gas using a windowed gas cell and a uhv bent-crystal (Si) x-ray spectrometer. This work was the first experiment on the x-24A beamline at NSLS described above. The incorporation of ion chambers into the gas cell allowed us to tune precisely the incident beam energy anywhere in the vicinity of the argon K-edge (including the 4p "white line") and permitted precise tuning of both the input and output photons.

The second system used an argon gas jet in vacuum and a cylindrical-mirror electron energy analyzer to observe K-shell photoemission and KVV Auger-electron decay. This system was put into operation on the 54-pole wiggler beam line at the Stanford Synchrotron Research Laboratory. The wiggler was operated as an indulator for the first time and once again ion chambers monitoring absorption of the photons in argon gas were used to tune the incident beam.

Both experimental systems yielded spectra with count rates lower than expected. The coming year will be devoted to system modifications which are intended to give higher count rates and eliminate other problems which showed up in the first runs. The same systems will, of course, be used to take data on monatomic and more complex gases.

A surface-science chamber which has been designed to perform uhv studies on the x-24A beamline or elsewhere is presently being constructed. It will permit us to perform the second phase of the multi-electron excitation work using thin films and single crystals of transition metals. The lower energy limit of this beamline (~800 eV) was intentionally chosen to allow study of the L-shell excitations in nickel and copper. We have previously studied the Auger-electron spectra of these metals with near-threshold electron excitation and believe that experiments with near-threshold photon excitation will help resolve uncertainties in interpretation. We expect to measure x-ray fluorescence, photoemission, and Auger-electron spectra in the new experiments. Our new chamber will incorporate a precision goniometer, allowing added surface sensitivity to be obtained by orienting the sample at glancing incidence.

F. Production and Characterization of Ultrasmooth Surfaces
(T. J. Jach)

Previous surface science experiments have indicated a need for surfaces which are extremely flat and smooth on an atomic scale. An example of this need is the desire to study photoemission from a metallic thin film at grazing incidence to obtain maximum surface sensitivity. There are also obvious reasons for wanting to make smooth defect-free substrates and thin films such as in the semiconductor industry where device widths of 100Å are being approached. We have initiated an effort to (a) characterize substrates and thin films for roughness down to a scale of 3Å; and (b) push the limit of surface smoothness attainable to 10Å or better for a variety of materials.

Reflection electron microscopy (REM) has been used to measure the roughness of metal surfaces. In collaboration with Drs. G. Hembree of the NBS Mechanical Production Metrology Division and L. B. Holdeman of Comsat, a series of thin gold films were deposited on float glass substrates at a range of temperatures between 30°C to 430°C. We have been able to photograph structure on the film surfaces with a resolution of about 10Å. The study indicated that gold films deposited at room temperature are far rougher (100Å rms or greater) than previously thought; other standard techniques such as stylus or scanning electron microscopy photos failed to reveal this roughness. REM should be capable of directly detecting step dislocations or other such features on gold films down to a height of one atom; such a resolution is almost as good as scanning tunneling microscopy. The methods are complementary, however, since REM is better at looking at large areas rather than small ones. We have also determined that the roughness is due to initial surface nucleation and whisker growth which varies in a complex way with temperature.

During the following year, we will be extending the reflection electron microscopy technique to examine GaAs substrates as well as continuing work on the gold films. We hope that the success we have had in characterizing gold films can be used to determine the polishing and etching methods that produce the smoothest GaAs substrates.

G. Laser Diagnostics of Surface Dynamics

(D. R. Burgess, Jr. and R. R. Cavanagh)

The pathways and rates of energy transfer at surfaces remain the key unresolved issues for understanding chemical reactions at interfaces. Such information has eluded experiments which rely on conventional surface-characterization techniques. A variety of laser-based techniques, however, have recently demonstrated their utility in probing such molecular dynamics in both the gaseous and liquid states. In this program, the focus is on exploiting similar laser-based techniques for addressing the issues of energy transfer at surfaces. The program utilizes both the temporal and spectral characteristics available in state-of-the-art lasers. Strong collaborations with Drs. M. P. Casassa, E. J. Heilweil, D. S. King, D. A. Mantell and J. C. Stephenson of the NBS Molecular Spectroscopy Division play a vital role in these efforts.

1. Laser-Excited Fluorescence as a Probe of the Dynamics of Thermal Desorption

Thermally activated desorption remains a key step in a wide variety of reactions at surfaces. While it is frequently assumed that the desorbed species can be accurately viewed as being in equilibrium with the surface, there have been no direct tests of this assumption. For instance, the potential for developing surface chemistries which exploit non-equilibrium reactions of excited-state species will depend on the efficiency of the accommodation process.

We have studied the thermal desorption of NO from Pt(111) using laser-excited fluorescence. The rotational-state distribution have been examined as a function of NO coverage ($\theta = 0.1$ to 1.0 of saturation) and we have found that the internal energy of the desorbed NO can be described by a Boltzmann distribution with $T_{int} = (0.95 \pm 0.05)\ T_{surf}$ (see Figure 7). We have also examined the influence of coadsorbed CO. While the adsorption sequence can change the desorption rate of the NO, resulting in temperatures for the maximum desorption rate being lowered by 25%, the internal energy is still found to be distributed in a Boltzmann manner, with $T_{int} \approx T_{surf}$. Additional experiments to probe the extent of rotational alignment of the desorbed NO have indicated that there is no preferred spatial orientation of the rotational angular momentum. Experiments to measure the kinetic energy in individual rotational states are presently in progress. It is anticipated that the degree of accommodation found for the NO/Pt(111) system will make it an excellent "benchmark" in future studies of rapid desorption processes (see Sections 2 and 4 below). Future plans include the extension of the NO/Pt(111) measurements to the NO/Pt(110) system in order to probe the influence of competition from step-induced NO dissociation with the molecular NO desorption channel. This work is supported in part by the Department of Energy.

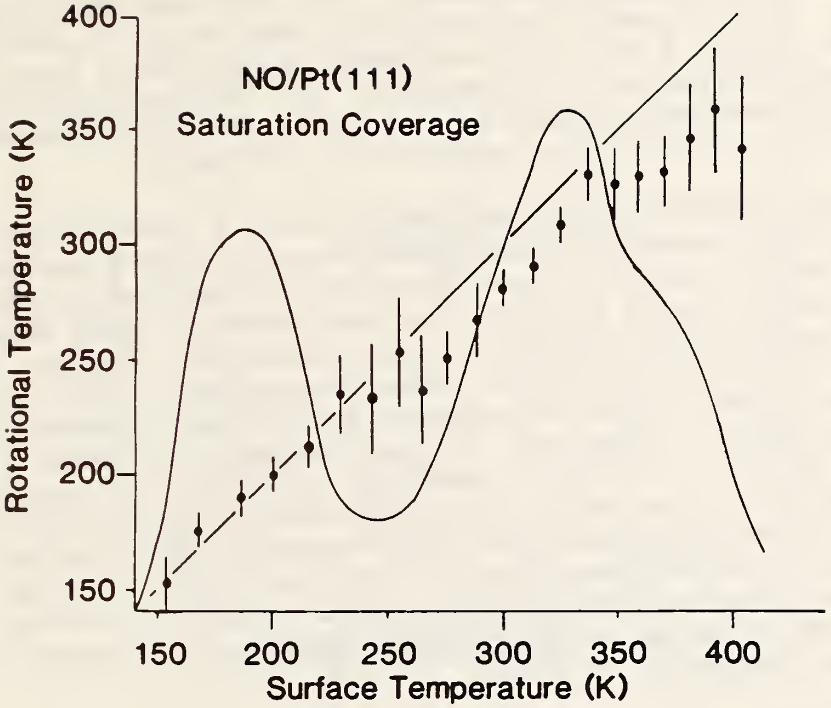


Fig. 7. Rotational temperature of NO thermally desorbed from Pt(111), determined by laser-excited fluorescence, as a function of surface temperature.

2. Laser-Induced Desorption

Lasers have recently become popular tools for inducing desorption from surfaces. The majority of the work in this area has focused on the removal of near-monolayer quantities of adsorbed species within the region illuminated by the laser. From the gas-phase species which are generated, one can identify and measure concentration gradients of adsorbates and probe adsorbate diffusion by monitoring the relaxation of the laser-induced concentration gradient. We have recently begun a series of experiments aimed at using laser-excited fluorescence to measure the internal-energy distribution as a result of desorption induced by a laser pulse.

In the past year we have been able to assemble a vacuum system for these studies. It is anticipated that this system will permit us to use laser-excited fluorescence and multi-photon ionization as state-specific probes of the laser-induced desorption process. We have already successfully used a quadrupole mass spectrometer to probe the desorption of H_2, CO, and NO from a polycrystalline platinum foil upon irradiation with the second harmonic from a frequency-doubled NdYAG laser. The laser-desorption yield has been monitored both as a function of the surface-temperature rise (laser pulse energy) and as a function of surface coverage. In all cases, the desorption yield was non-linear in laser intensity and there was a minimum energy density below which no detectable desorption was observed. Furthermore, this threshold decreased with increasing coverage, consistent with the shift to lower temperatures observed in standard thermal desorption experiments.

A major concern in all experiments where a laser is used to heat a surface is the accurate determination of the surface temperature. Classical heat conduction equations have been employed to establish the surface temperature in the past, and are currently being used to analyze the desorption yields obtained in this laboratory. However, experimental efforts to validate the surface temperature actually achieved due to laser heating are sparse. A direct measure of the laser perturbation of the surface properties would offer the most satisfactory probe of the heating effects. At this time we are examining the utility of blackbody radiation as a signature of the extent and the reproducibility of laser-surface heating. It is anticipated that state-specific detection will be incorporated into this experiment in the coming year in order to determine the degree to which laser heating is manifest in the internal and translational energies of the desorbed molecules. This work is supported in part by the Department of Energy.

3. Time resolved measurements of vibrational energy transfer

Direct characterization of the time scales and mechanisms for relaxation and dephasing of vibrational excitation in adsorbed layers is the aim of this work. Such measurements can provide a quantitative understanding of a substrate's ability to quench the energy released upon chemisorption, reaction, or irradiation.

Following our report last year of the first measurements of vibrational relaxation on surfaces (OH on colloidal SiO_2), the technique has been extended to self-supporting pressed discs of the same material. A longer T_1 time for population decay was observed (220 ± 20 ps) than in any of the measurements where a solvent was also present. Chemical treatment of the SiO_2 surfaces has generated BOH, NH_2, and OCH_3 adsorbates which have been probed. The temperature dependence of the vibrational relaxation rate for both OH and OD on SiO_2 has been measured and each is found to fit a multiphonon model for the thermally-enhanced relaxation (see Figure 8). These experiments provide a first test of the pathways involved in vibrational relaxation at surfaces. They also demonstrate that over the temperature range employed by most industrial reactors, the relaxation mechanisms on this model catalytic support can be generally accounted for by a simple multiphonon model of the relaxation process. Additional work has extended the technique to relaxation measurements of the OH groups on the zeolite ZSM-5 and of both OH groups and free carriers on ZnO.

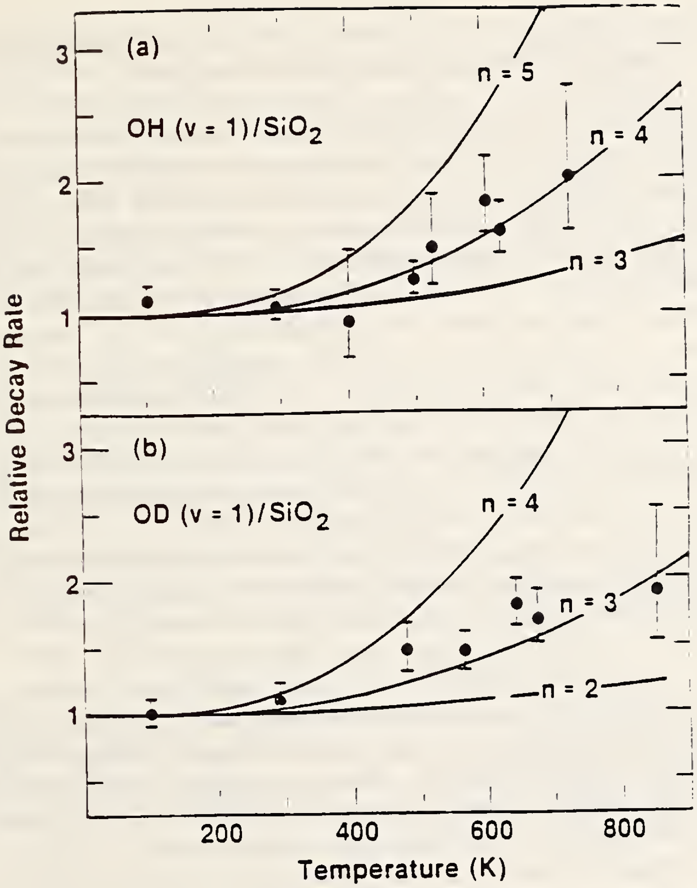


Fig. 8. Vibrational relaxation rates ($1/T_1$) for OH and OD as a function of temperature. For each isotope, the rates have been normalized to the rates observed at room temperature. The solid curves represent the temperature dependence of the relaxation rate predicted by a multiphonon relaxation model, where n is the number of phonons involved in the relaxation process.

Future work is planned on a range of zeolites in an effort to measure the differences between the vibrational relaxation rates for OH groups bound at silica sites as compared to alumina sites. It has long been postulated that these two sites have distinctly different catalytic activity and thus it is reasonable to expect that they will have distinctly different vibrational relaxation rates. By comparing a range of samples with known catalytic activity, it will be possible to ascertain the degree of correlation between the observed relaxation rates and the catalytic activity. We also anticipate that the existing laser system can be extended into the absorption range of the adsorbed carbon monoxide fundamental. With this advance in picosecond laser technology, we will be able to explore the T_1 times for CO bound to small supported transition-metal particles. This project is supported in part by the Air Force Office of Scientific Research.

4. High-Resolution Infrared Reflection-Absorption Spectroscopy and Picosecond/Femtosecond Measurements

To date, we have been able to contribute to a more detailed picture of the relevant steps in energy transfer at surfaces. While there remains a great deal still to be done with the techniques which we have developed, it is becoming clear that several major advances will be required before direct measurements of vibrational relaxation at well-characterized single-crystal surfaces will be possible. The four major technical issues which must be addressed are: i) Extension of the tuning range down to 5 μm in order to probe oscillators with large absorption cross sections such as CO and NO. ii) Increased time resolution to the range of $\leq$ 2 ps in order to follow the faster relaxation rates anticipated for systems which can couple to electron-hole pairs. iii) A high-resolution ($\approx$0.1 cm^{-1}) reflection-absorption spectrometer to measure the shape, cross section, and spectral position of the infrared absorption feature. iv) An optical detection scheme with increased dynamic range in order to measure changes on the order of 1 part in 10^5 in the two polarization components in an individual laser shot.

Each of the four technical issues mentioned above would have a substantial impact on the existing program, i.e. new adsorbates could be studied, faster processes could be followed, damage which accompanies laser-induced heating could be characterized, and smaller population changes could be seen. However, if all four objectives can be achieved, it will then be possible to measure vibrational relaxation rates at the surfaces of single-crystal metal surfaces. Our efforts to date in the four areas can be summarized as follows: i) We are currently exploring several methods for extending the tuning range available to the present laser system. We have generated $\approx$ 10% of the required tunable infrared energy in the 5μm region by mixing the output of the existing optical parametric amplifier. A dye laser based on the Nd^{+3} YAG is being constructed to permit difference-frequency generation in $LiIO_3$. ii) A shorter duration ($\approx$ 2 ps FWHM) synchronously-pumped tunable dye laser is being amplified in order to generate sufficiently intense pulses for mixing in nonlinear crystals. iii) The feasibility of a high-resolution ($\approx$ 0.1 cm^{-1} resolution) infrared reflection-absorption spectrometer based on a 20 ns Nd^{+3}YAG pumped difference-frequency generator is being explored. iv) In collaboration with Dr. A. Luntz of IBM, optical detection techniques with improved dynamic range (yet suitable for use in pulsed-laser experiments) are being explored.

H. Spin Polarization in Secondary-Electron Cascades in Ferromagnets
(S. M. Girvin)

Recent experimental progress in the production and detection of spin-polarized, low-energy electrons is opening up new avenues of research in the study of both bulk and surface magnetism. One of the key requirements for a proper interpretation of many experimental measurements is an understanding of inelastic scattering and the production of secondary electrons. In collaboration with Drs. D. R. Penn and S. P. Apell of the NBS Electron Physics Group, a theory has been developed of spin polarization in secondary-electron cascades in ferromagnets. We have found that measurement of the secondary polarization versus kinetic energy provides useful information about the inelastic scattering which cannot be obtained from traditional measurements of secondary intensity versus kinetic energy. In particular, we have found that the ratio of majority- to minority-spin inelastic lifetimes at an energy E is well approximated by the simple relation

$$\tau_{\uparrow}(E)/\tau_{\downarrow}(E) = \frac{1-p_B}{1+p_B}\;\frac{1+P(E)}{1-P(E)}$$

where P(E) is the measured secondary-electron polarization at energy E and p_B is the bulk polarization.

The lifetime ratios deduced from experimental measurements on Ni and Fe are shown in Figure 9. The rise in the ratio at low energies is due to the ability of minority electrons to scatter into the empty minority d-band states which arise form the bulk magnetization.

These results will prove useful in interpretation of photoemission and inverse-photoemission spectra and of polarized low-energy electron diffraction data. They also provide a testing ground for microscopic theories of inelastic and exchange scattering in ferromagnets.

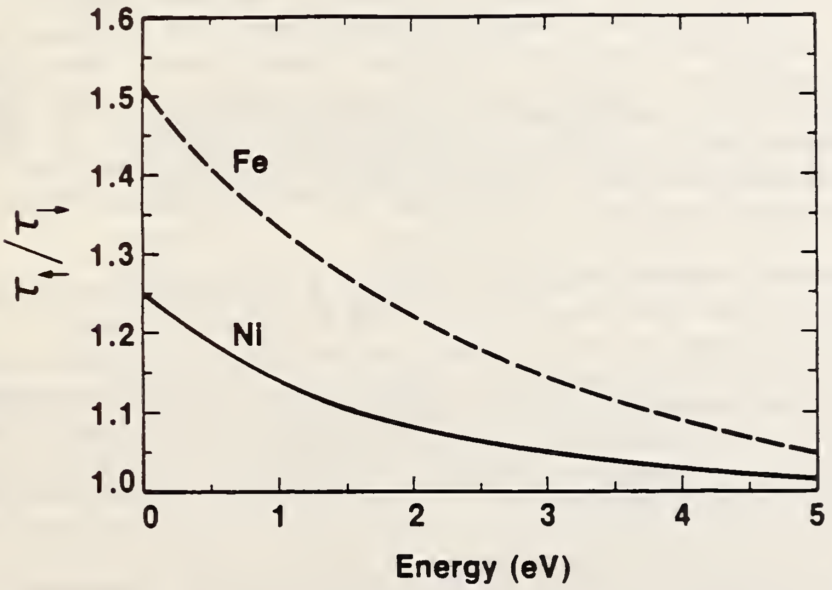


Fig. 9. Ratio of spin-up to spin-down lifetimes as a function of energy for Ni and Fe.

I. Theory of Dynamical Molecular Processes at Surfaces

(J. W. Gadzuk)

This project is part of a continuing effort directed to understanding both the static and dynamic behavior of atoms, molecules, solids, surfaces, radiation and their mutual interactions. This understanding comes from consideration of the microscope atomic-scale properties of individual entities as well as from larger-scale statistical properties of ensembles. Based upon our studies, phenomenological model theories are constructed which relate to the chemical physics and statistical mechanical behavior and to the intrinsic properties of relevant physico-chemical systems. In addition, a significant effort is invested in the study of the role of an actual measurement process in determining observed quantities in different surface spectroscopies. Ways in which measurement-process-specific quantities such as line shapes, satellite structures, etc. provide additional information on system dynamics are of considerable interest.

A large-scale theoretical effort has been underway aimed at the modeling of reaction dynamics at metallic surfaces and at interfaces of electro-chemical signficance. Major focus in the past has been on the role of internal degrees of freedom (vibrational, rotational, and electronic) of molecules in determining energy flow and redistribution occurring in elementary molecular processes at surfaces.

Work has remained focused on the role of intra-molecular vibrational degrees of freedom in reactive surface dynamics. In these situations, energy must be directed in order to break bonds or be extracted to stabilize highly vibrationally excited species formed for instance at curve crossings where electronic rearrangement takes place. There has been significant progress in several different directions in the application of an analytic model (developed in collaboration with Dr. S. Holloway of Liverpool University) for obtaining classical trajectories of a diatomic molecular beam incident upon a surface and in which charge-transfer/curve-crossing events take place.

In collaboration with Dr. Holloway and Ms. M. Karikorpi of Liverpool University, calculations have been made of the multi-dimensional Landau-Zener probabilities for a two-state molecule/surface scattering event. We have obtained the correct branching ratios between scattered vibrationally-hot neutral molecules and negative-molecular ions. This is believed to be the first molecular-scattering calculation involving a physical surface which properly includes non-adiabatic coupling between electronic states of the molecule.

Computer codes have been constructed to calculate the classical trajectories of molecules over arbitrary potential-energy surfaces (PES) with emphasis again on those PES which include a curve crossing/seam. The example shown in Figure 10 represents a vibrationally cold I_2 molecule, with its molecular axis ρ in an orientation parallel to the physical surface, normally incident upon the surface with center-of-mass translational energy ≈ 1eV. Near the surface, I_2^- can form and this is characterized by an intra-molecular potential with large equilibrium separation and also by stronger bonding to the surface. The grill work structure at the top of Figure 10 is the PES. Contours of constant potential have been projected onto the (ρ,z) plane (bottom of Figure 10) where the trajectory is also shown. Note that the incident molecule becomes trapped for several oscillations as a negative-molecular ion before scattering, in this case with ~ 0.7 eV translational energy. Amongst other things, we have calculated the probability for dissociative scattering as a function of incident kinetic energy, treating parametrically the well depth of the I_2^-/surface bond (the depth of the far left potential vs. z curve in Figure 10). Results are shown in Figure 11 together with experimental observations of Kolodney and Amirav. The significant point here is that, in both our theory and in the experiments, the dissociative scattering probability

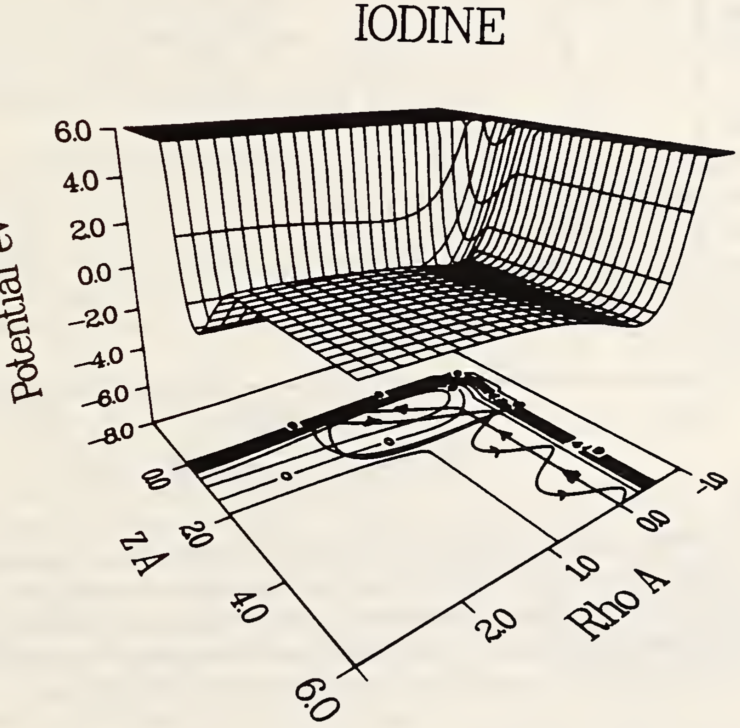


Fig. 10. A proposed potential energy surface (top) for an iodine molecule incident upon a physical surface in which dissociative adsorption is possible in the potential well at the surface for the molecule-surface separation z ≈ 1Å along the intra-molecular coordinate ρ. Contour plot (bottom) of the PES in the (ρ,z) plane and a trajectory for a scattering event in which translational-to-vibrational energy redistribution occurs.

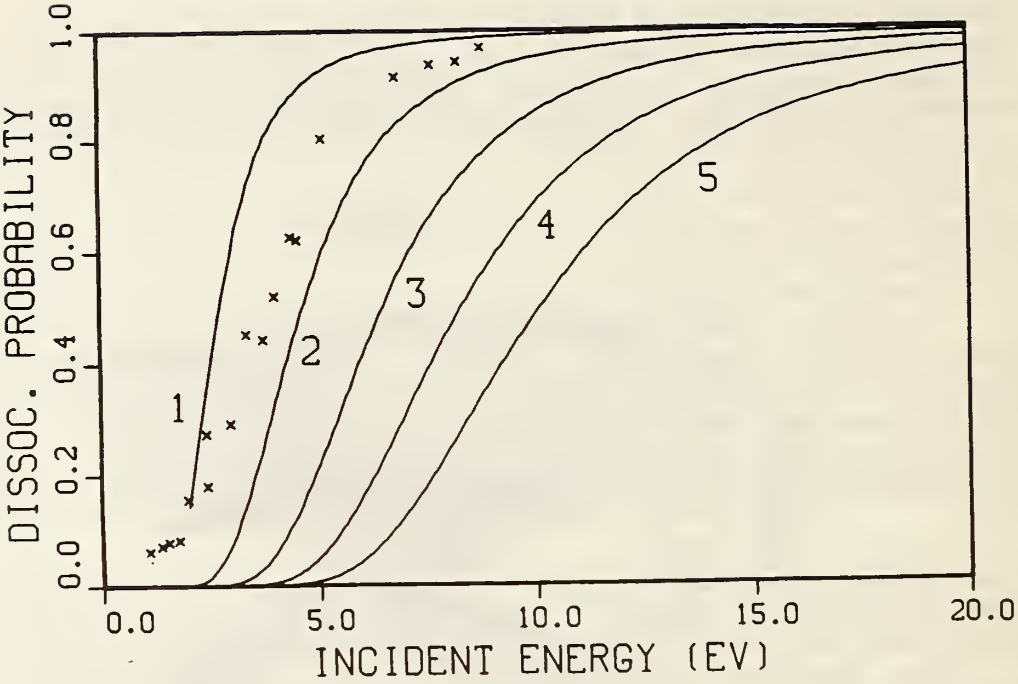


Fig. 11. Normalized probability for dissociative scattering of I_2 from a surface as a function of the kinetic energy of the incident I_2 molecular beam, treating the adsorption energy of I_2^- (in eV) parametrically. The points are reported results of Kolodney and Amiray for I_2 scattering from a MgO surface.

rises from zero at threshold to a saturation value over a kinetic energy range of ~ 4-6 eV. On the basis of the similarity between experiment and theory, it is believed that the charge-transfer mechanism is important in molecule-surface interactions.

We have developed further the "trajectorized wave-packet theory" reported last year to a point where it now satisfies microscopic reversibility and energy conservation (significant and ubiquitous flaws in most previous "imposed-trajectory" theories). At the request of the editor of "Comments on Atomic and Molecular Physics", a review article on "Surface Harpooning" was written. The principles of charge-transfer/curve-crossing collisions were sequentially developed for atom-atom, atom-molecule, atom-surface, and finally molecule-surface collisions. By working up in order of complexity, it was easy to see how one could use and adapt the results obtained in less complex collisional events.

Considerable progress has been made in the area of surface vibrational spectroscopy, at least in part because of the intimate connection between atom trajectories and vibrational spectra. A major review article was written on "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces" in which the physics of the excitation process involved in the five most prevalent experimental techniques was developed from a single, unified point of view.

Further work on shape-resonances in electron scattering from molecules demonstrated how a shape-resonance/temporary-negative-molecular ion, created in an electron energy-loss experiment, not only leads to overtone enhancement in the intra-molecular excitations but also for any modes which have a component normal to the surface.

Finally, vibrational lineshapes and spectra of adsorbed molecules have been studied in terms of the quasi-periodic trajectories over multi-dimensional PES. This is a particularly prudent way to include the anharmonic effects which lead to dynamically interesting lineshapes because one can "see" what the oscillator is doing to acquire the lineshape. The lineshape or vibrational spectrum of an excited oscillator is

$$I(\omega) = \frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{2T} \left\langle \left| \int_0^{2T} Y(t)\, e^{i\omega t}\, dt \right|^2 \right\rangle$$

where $y(t)$ is the oscillator displacement as a function of time after initial excitation. As an example, the trajectory of an initially excited "harmonic" oscillator in the y direction ($Y_{in} = 0.1$, $X_{in} = 0.01$), which is anharmonically coupled to an x-oscillator with half the frequency is shown in the top of Figure 12. A number of well-defined y oscillations occur prior to a swing into the large-amplitude low-frequency oscillator and then return to y. This is a characteristic Fermi resonance and the vibrational spectrum shown in the bottom left of Figure 12 is a typical slightly-split doublet ($\Delta\omega/\omega \sim 0.1$ here). Increasing the initial displacement, hence anharmonicity, leads to a breakdown of quasiperiodicity. Thus chaotic motion prevails, as indicated in the spectrum shown in the bottom right of Figure 12 ($Y_{in} = 0.13$, $X_{in} = 0.01$). The main peak is very much reduced in height, broadened, and an erratic background appears. We are applying this methodology for determining vibrational spectra to current problems of active interest in the surface vibrational-spectroscopy community.

We plan to continue work in the area of surface reaction dynamics with near-term emphasis on the determination of self-consistent reaction trajectories, realistic electron-hole pair coupling constants, determination of energy-redistribution patterns amongst translational, vibrational, rotational, and electronic degrees of freedom of "reactant" molecules and electron and phonon modes of surfaces. Analyses are made for controllable dynamic and reactive conditions with synthesis of the various components of the elementary reaction theories into theories of experimentally realizable processes. Special emphasis will be placed on the phenomenon of dissociative surface processes and on the role of non-linear dynamics.

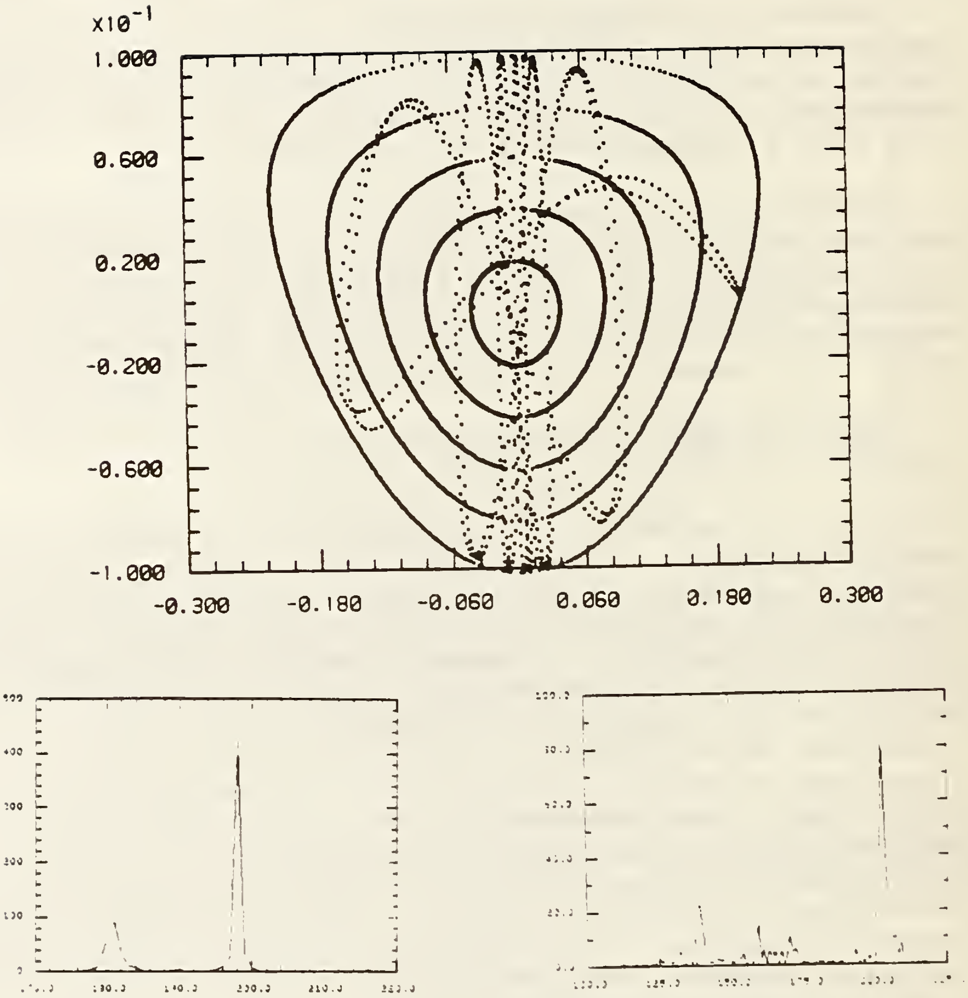


Fig. 12. Initial trajectory (top) for an excited oscillator oriented along the Y axis but anharmonically coupled to an X-oriented oscillator with half the frequency. Also shown are constant potential-energy contours. Vibrational spectra (bottom), I(ω) vs ω (arbitrary units), accompanying such an excitation for initial excitation below (left) and above (right) the chaotic threshold. Note the scale change between the two spectra.

In addition, analysis will be made, whenever possible, of novel experimental results. Current interest includes laser-assisted surface processes and state-to-state analysis, high-resolution surface vibrational spectroscopy, neutron spectroscopy of metal hydrides, and other experimental probes of non-adiabatic effects.

4. SURFACE COMPETENCE PROGRAM

W. F. Egelhoff, Jr., J. Fine, S. M. Girvin, T. J. Jach
R. Klein, T. E. Madey, A. J. Melmed, R. Stockbauer

The Surface Competence Program is a part of the NBS "Competence Program." The NBS program was introduced to provide long-term support of the establishment and maintenance of areas of excellence in science and technology contributing to the NBS mission and the projected needs of the NBS clientele.

The Surface Competence Program (NBS Task 26117) was established October, 1984 with two principal components, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". The initiation of this program represents a new focus on these topics. Each program component consists of several technical projects; some of these projects are extensions of activities in the Division that had existed prior to the start of this Competence Program while others have been launched this year. The principal objectives of each program component are described in the following two main Sections together with reports of the individual projects.

A. Novel Two-Dimensional Materials

In recent years an increasing awareness has developed of the important modifications in physical properties which occur in materials as they approach the ultra-thin two-dimensional limit. Some examples of unusual behavior discovered in such systems include the enhanced catalytic properties of a gold surface with two monolayers of platinum compared to bulk platinum, superconductivity of a silver monolayer on germanium, the quantum Hall effect, the enhanced magnetism in alternating monolayers of iron and cobalt, the electrical properties of metal-semiconductor junctions (Schottky barriers), and multiple quantum-well systems for optical logic devices. These examples suggest a whole new range of scientifically and technically important chemical and physical properties waiting to be explored in the two-dimensional regime. Concepts and methods developed in surface and interface science have been particularly valuable in many areas of application, and it is believed that these concepts and methods can be further developed and extended to two-dimensional systems with component thicknesses from one to one hundred atomic layers.

There exist major gaps in current understanding of the fundamental principles which govern the chemical and physical properties of layered structures in the two-dimensional limit. In this component of the program, it is planned to synthesize and determine the fundamental chemical and physical properties of ultrathin layered materials with layers so thin (a few atoms thickness) that they exhibit two-dimensional behavior. Knowledge of the factors influencing the growth and properties of ultrathin layered systems is expected to allow optimization of desired chemical and physical characteristics and will thus benefit a number of scientific fields ranging from catalysis to novel semiconductor devices.

We are performing work in four project areas. First, we are planning to develop the techniques needed to synthesize, by alternating monolayer deposition, a new class of materials: non-equilibrium ordered alloys. The structural properties of these materials as grown and during thermal processing will be investigated by x-ray and electron diffraction. The chemical reactivity, catalytic activities, and magnetic properties of these materials will also be investigated. Second, we plan to determine the microstructure and microcomposition of candidate layered structures by atom-probe and field-ion microscopy methods with emphasis on the interface region. These techniques provide composition and structure data with near-atomic spatial resolution. Third, we will apply modern many-body theoretical techniques to the study of the quantum Hall effect, magnetism, and other electronic properties of layered structures. Finally, we are planning to develop techniques for the study of the growth and morphology of modulated structures using glancing-incidence diffraction of x-rays from a synchrotron source and other extensions of modern surface methods.

1. Surface and Interface Chemical Physics of Ultrathin Films
(W. F. Egelhoff, Jr.)

Interest in ultrathin metal films (down to the two-dimensional limit of one atomic layer) on the part of the surface-science community has greatly increased in the past several years as it has become clear that an understanding of such structures will contribute to solving a wide range of problems in surface science. Among these are an understanding of the differences between surface and bulk electronic structure, the changes of surface electronic structure associated with chemisorption, the basis of surface magnetism, the modification of surface-layer properties by the substrate, the relationship between electronic structure and epitaxial growth, and the surface properties of alloys. The experimental program presently underway is using an integrated approach to study single-crystal surfaces, alloys and ultrathin films to contribute to an understanding of all of the above problems.

We reported last year on the discovery of a new aspect of x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) and have termed it the "searchlight effect". The searchlight effect is manifested in single-crystal samples by enhanced XPS and AES peak intensities along nearest-neighbor and next-nearest-neighbor directions in the lattice.

The searchlight effect is a powerful, new probe of short-range order and is ideally suited for studying a variety of problems associated with ultrathin films, surfaces, and interfaces. We now have the opportunity to perform real-time studies of surface morphological and compositional dynamics such as clustering of overlayers, surface segregation, and surface alloying or interdiffusion at interfaces. Although these phenomena are interesting in their own right, we are planning to investigate them in association with our current primary objective of synthesizing a new class of materials, non-equilibrium ordered alloys, by epitaxial growth of alternating metal monolayers. This work has the potential for opening up a whole new area of materials science. The XPS searchlight effect is a near-perfect tool for diagnosing, in real time, any growth processes that interfere with the desired synthesis and should thus aid greatly in recognizing and overcoming barriers. We anticipate the capability of producing novel material properties by tailor-making the lattice structure. Later, we expect to characterize the materials with x-ray diffraction and electron microscopy and to study their chemical reactivity, catalytic activity, and magnetic properties.

We are in the process of improving our XPS instrument to carry out the work just described. Changes in electron optics and detection will provide substantially better operating characteristics. These changes will, in part, permit application of the XPS searchlight effect to higher electron energies than the conventional XPS range where it should have increased diagnostic power. We are also designing a system of ultrahigh-vacuum ovens to provide the sources with constant metal vapor flux that are needed to grow high-quality films with alternating monolayers by molecular-beam epitaxy.

The source of the angular anisotropies of electron emission in XPS and AES that give rise to the searchlight effect have been investigated using single-scattering calculations. These calculations, performed for copper films as a function of thickness, demonstrate that the enhancements are associated with forward scattering by nearest-neighbor and next-nearest-neighbor atoms in the lattice. The searchlight effect can thus be used with confidence as a structural probe. The effect, however, is a serious complication in the conventional method of measuring (and using) electron attenuation lengths with single-crystal specimens. Further details of this analysis are given in Section 2.A.4.

Work has continued on the development of the equivalent-core approximation (ECA) as an interpretative tool for analyzing core-level binding-energy shifts. Figure 13(a) shows how the Ni $2p_{3/2}$ core-level shift induced by the adsorption of CO is governed by total-energy considerations that can readily be understood with the ECA. In the final state, a fully-screened core hole on Ni becomes (by the ECA) the chemical equivalent of Cu. We consider the difference between final states with clean or CO-covered Cu, as in Figure 13(a). Since there is a choice in the final state between CO on a Ni atom and CO on the Cu atom, we can immediately use the greater Ni-CO bond strength to predict that the final state leaving Cu clean will have the lower total energy. The Ni $2p_{3/2}$ core-level binding energy is just the energy to get from the initial state to the indicated final states. We therefore deduce that the clean Ni must exhibit the smaller binding energy and the CO-induced shift must be to larger binding energy. Figure 13(b) shows the use of the ECA in

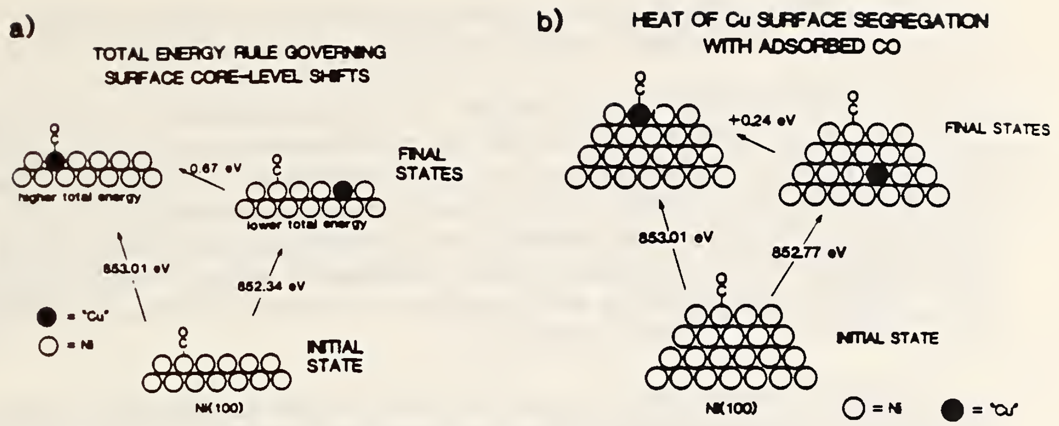


Fig. 13. (a) Illustration of how total energy considerations govern the CO^-induced surface core-level shift in Ni(100). (b) Illustration of how the bulk-to-surface core-level shift can predict the heat of CU surface segregation to a surface site with adsorbed CO.

determining from the bulk-to-surface Ni $2p_{3/2}$ core-level shift that Cu segregation to a CO-covered surface site is an endothermic process by 0.24 eV (5.5 kcal/mole). This result is in sharp contrast to the case of Cu segregation to a clean Ni surface which is 0.43 eV (10 kcal/mole) exothermic. The adsorption of CO will therefore drive Cu into bulk Ni.

Finally, a major invited article titled "Core-Level Binding-Energy Shifts at Surfaces and in Solids" has been completed for Surface Science Reports. This review article will, as it appears, be approximately 200 pages long and contain over a thousand references. The article consists of a review of the theoretical principles of core-level shifts and a selection of the most illustrative, experimental case studies. The theoretical principles section is written with the experimentalist in mind and explains the essential concepts such as core eigenvalues, initial-state contributions, total energy differences, charge-transfer screening, and polarization and dielectric screening without resorting to the usual, opaque mathematics. Particular attention is paid to the principles of the reference-level problem since many important fine points have often been glossed over in previous descriptions. The section on experimental case studies contains selected results which illustrate, in the most clear-cut manner possible, the basic mechanisms governing core-level shifts. The topics include atomic coordination number, charge transfer, Madelung potentials, cluster size, surface work function, image-charge and charge-transfer screening, band bending, and sample charging. In this section, particular attention is paid to the relative merits of the two basic conceptual frameworks for interpreting core-level shifts, the equivalent-core-energy-cycle framework and the initial-state--final-state framework.

2. Microcomposition and Microstructure of Thin Films

(A. J. Melmed and R. Klein)

This effort is directed to the measurement of microcomposition in relation to microstructure of thin layers on well-characterized solid substrates and the determination of interfacial diffusion. The methods of investigation for these purposes are field-ion microscopy (FIM), capable of qualitative atomic structural determination, and atom-probe analysis for compositional depth-probing on an atomic scale. Both in situ and ex situ specimen preparation will be used in order to vary widely the layer-formation process parameters.

During this reporting period, the unique capability of FIM to characterize the microstructure of novel materials was demonstrated. One of the recently discovered class of rapidly solidifed aluminum-based alloys, which appeared by electron diffraction in the transmission electron microscope (TEM) to have icosahedral long-range order and no translational symmetry, was made available to us. A considerable amount of theoretical work has been done to explain and predict the relevant atomic structure. Thus far, several theoretical models have predicted correctly most of the observed diffraction features, but no complete description of atomic positions has been given. The alloy, approximately Al_6Mn, was provided to us in the form of pieces of very brittle ribbon, a few millimeters on a side and some 0.040-0.050 mm thick, and presented some complications in specimen preparation. However, we succeeded in obtaining reproducible FIM images which clearly showed that the material has a phase in real space with structure consistent with icosohedral long-range order; that is, appropriate two-,three- and five-fold symmetries are present, over a lateral distance of about 200 nm, and no translational symmetry is evident. Also, we found no evidence for multiple twinning, the major counter-viewpoint to the acceptance of real icosohedral symmetry. In those regards, the FIM results clearly agree with the TEM results. Additionally, the FIM images showed that the microstructure is replete with micro-defects. Atomic disSection of the material by field evaporation clearly showed that these features prevailed through a depth of at least 300 nm. Further microscopy remains to be done in an effort to determine the details of atomic packing in this complex material.

The construction of our energy-corrected atom-probe (ECAP), which will be used for determining composition profiles through thin layers and layer/substrate interfaces, has been recently completed. All features of the ECAP have been tested and found to function qualitatively as expected. Initial quantitative evaluation has indicated that the mass resolution is better than anticipated in the lower-resolution Section of the ECAP; that is, $M/\Delta M$ appears to be at least ~ 250 and possibly is as high as 500 (compared to an expected value of about 150). Quantitative evaluation of the high-resolution Section has been thwarted so far by a mechanical misalignment introduced during the ECAP fabrication.

We have found it increasingly useful to combine our atom-probe analyses with the imaging capability of TEM (in collaboration with colleagues in the NBS Metallurgy Division). The atom-probe-FIM--TEM combination is extremely powerful in providing microscopy with a wider range of contrast and magnification than available to the separate techniques. For this purpose, we have developed a specimen holder which allows us to shuttle specimens between the atom-probe FIM and the TEM. Using this extended capability, we have begun microcomposition and microstructure analyses of nickel-based superalloys (of interest as turbine-blade materials) and of a newly developed class of Al-Li-Cu alloys.

During the next year, it is planned to complete the quantitative evaluation of the ECAP and to bring the associated electronics to a convenient working arrangement. Presently, the ECAP is operated using the timing electronics of the general-purpose atom-probe FIM developed earlier which is awkward for the user. A more appropriate system is partially developed.

Further microscopy and possibly atom-probe analysis of the icosohedral-symmetry alloys and related materials are planned. Atom-probe analyses of nickel-based and aluminum-based alloys will also be done. It is hoped that an ultra-high-vacuum FIM can be assembled specifically for in situ thin-layer deposition and microstructure characterization.

After full evaluation of the ECAP performance, a program of depth-probe analyses of thin-layer/substrate combinations will be undertaken. Metal/metal systems prepared by alternate-layer vapor deposition will be investigated in order to characterize the interfacial composition and to determine the extent of intermixing. Appropriate choices of elemental metals and preparation parameters will be made in concert with other related experiments (e.g., Section 4.A.1 above).

3. Theory of the Quantum Hall Effect
(S. M. Girvin)

Artificial semiconductor superlattices (heterostructures or multi-quantum wells) consisting of alternating atomically smooth layers of GaAs and GaAlAs are among the most novel and successful two-dimensional materials. By suitable doping one can create at the GaAs-GaAlAs interface a two-dimensional electron gas which exhibits many interesting effects.

One of the most remarkable phenomena which has been observed in the GaAs-GaAlAs system is the quantum Hall effect. At very high magnetic fields (~10 T) and low temperature (< 4 K), the Hall resistance of the two-dimensional electron gas takes on universal quantized values of the form h/e^2i where h is Planck's constant and e is the elementary charge. The quantum number i is an integer or simple rational fraction. Associated with this quantization is the existence of persistent nearly dissipationless currents similar to those occurring in superconductors and superfluids. These unexpected findings have stimulated considerable experimental and theoretical work at many laboratories.

In collaboration with Drs. A. H. MacDonald (National Research Council, Ottawa) and P. M. Platzman (AT&T, Bell Laboratories, Murray Hill) a "magneto-roton" theory has been developed of the collective excitations in these fractional quantum-number states. This theory is closely analogous to the Feynman theory of superfluid helium and provides new insight into the physics underlying the persistence of currents.

The collective modes at long wavelength are predicted to be phonons (density waves) and magneto-rotons analogous to the roton excitations in superfluid helium. The predicted mode spectrum is shown in Figure 14. Independent numerical calculations on model systems by Dr. F. D. M. Haldane of AT&T Bell Laboratories have shown that this magneto-roton theory is remarkably accurate. Figure 14 illustrates the good agreement between the predicted mode energy and Haldane's numerical results. One of the advantages of our theory is its analytic simplicity which allows one for the first time to compute quite easily experimentally relevant and

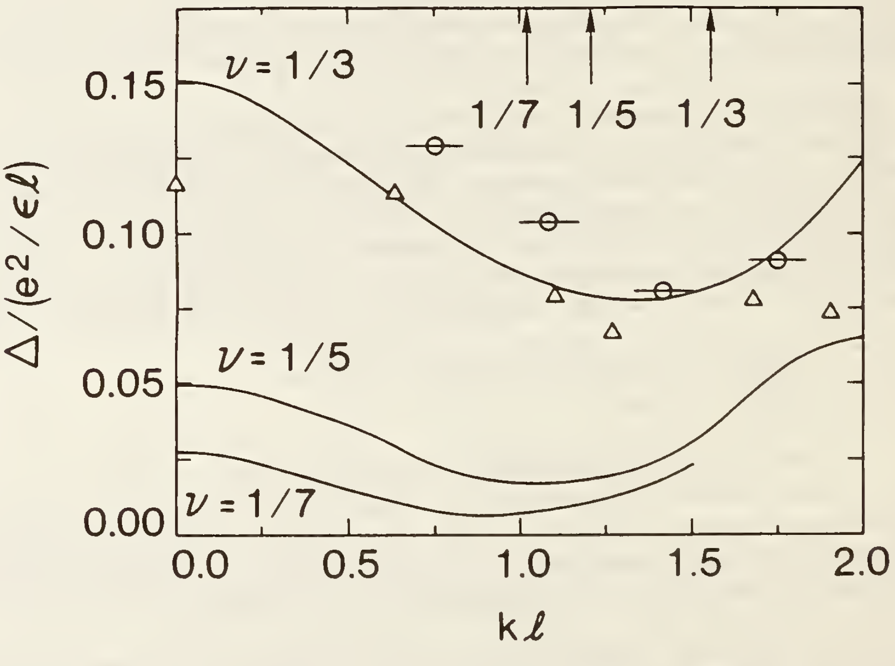


Fig. 14. Collective excitation energy Δ versus wave vector for $\nu = 1/3$, 1/5, and 1/7. The solid lines are analytic results of the magneto-roton theory. The circles and triangles are from numerical calculations for $\nu = 1/3$ on small spherical and hexagonal systems by Haldane and Rezayi. Arrows indicate position of reciprocal lattice vectors of the Wigner crystal at the appropriate densities.

previously inaccessible quantities such as the dielectric response. Experimental attempts to observe the predicted magneto-roton excitations via the dielectric response are currently under way in two separate groups at AT&T Bell Laboratories.

This magneto-roton theory nicely complements earlier work we have done on the Wigner crystallization transition. As the magnetic field is increased, the magneto-roton mode goes "soft" at the wave vector corresponding to the Wigner-crystal reciprocal-lattice vector. The critical field at which the magneto-roton softening makes the liquid state unstable agrees quite well with our previous predictions for the field at which the Wigner crystal becomes stable. Hence the combination of these two theories gives us a much deeper and more complete understanding of the liquid-solid transition in this system.

Future work in this area will address questions of the finite-temperature statistical mechanics of the quantum Hall effect and the effects of disorder. Another project which will take place in the coming year is the organization of a quantum Hall effect lecture series at the University of Maryland. In collaboration with Professor R. E. Prange, plans are being made to edit and publish the lecture notes of the invited speakers as a Springer-Verlag book. This book is intended to be a tutorial introduction to this rapidly expanding field for both experimentalists and theorists.

Another area of planned future work concerns the field of metallic superlattices. Dr. Michael DeWeert will be joining the Division as an NRC postdoctoral fellow. His area of expertise is superconductivity, proximity effects, and related phenomena in metallic superlattices. Close interaction is expected with the superlattice experiments in the Division and with the proximity effect work in the NBS Temperature and Pressure Division.

4. Dynamical Diffraction of X-Rays from Crystal Surfaces at Glancing Incidence

(T. J. Jach)

The structure and registry of adsorbed atoms with respect to the underlying crystal lattice remains one of the major concerns of surface science. Diffraction techniques such as low-energy electron diffraction provide some of this information, but some foreknowledge of potential sites of the atom and extensive calculation are usually required. We have developed a new technique using the dynamical diffraction of x-rays in a glancing-incidence geometry to provide the same type of information. The technique is surface sensitive but could be employed at interfaces as well.

Although the theory for dynamical x-ray diffraction has been developed previously, it had not been tested experimentally since the necessary experiments require an intense source of monochromatized x-rays (e.g., from a synchrotron source), a well-collimated beam, and a specimen crystal with a smooth, defect-free surface. In collaboration with Drs. P. Cowan and S. Brennan of the NBS Quantum Metrology Group and Drs. M. Bedzyk and G. Materlik of the Deutsches Elektronen Synchrotron (DESY) at Hamburg, an experiment was conducted last fall at DESY to test the theory. We observed surface diffraction from Ge(220) planes normal to the (111) surface at 8 keV with angles of incidence as low as 1 milliradian. X-ray beam collimation at the Bragg angle was about 5 microradians (Figure 15). This extreme collimation, possible only on a synchrotron light source, allowed us to obtain data which turned out to fit the theory very well.

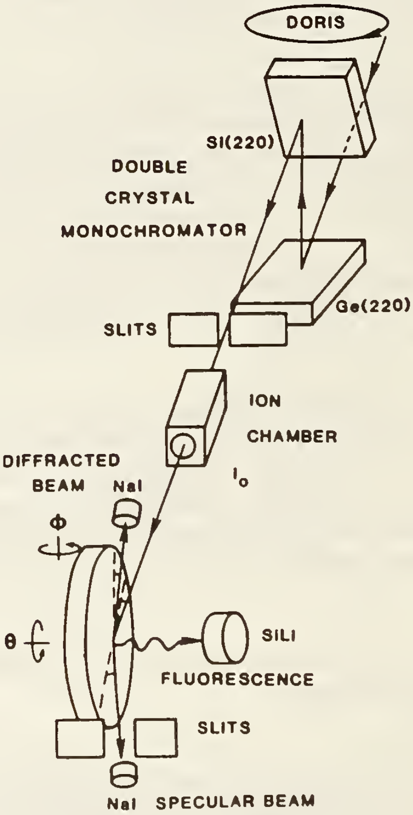


Fig. 15. Experimental set-up for grazing-incidence x-ray diffraction.

During the past year we have done considerable data analysis which gave us a great deal of insight into surface dynamical diffraction theory. Because we are able to diffract an x-ray beam from a crystal at incidence angles less than the critical angle for total reflection (~ 4 milliradians), the x-rays inside the crystal are only evanescent (exponentially-decaying) waves. There are two waves, however, and their linear combination at the crystal surface forms an x-ray standing wave.

Slight changes in the angle of incidence or deviations from the Bragg angle translate this standing wave back and forth on the surface, selectively exciting surface atoms whose fluorescence was observed. The interference process which makes this possible is illustrated in Fig. 16(a) where the specularly reflected beam is shown to have either a strong absorption or a maximum at the Bragg condition depending on the angle of incidence.

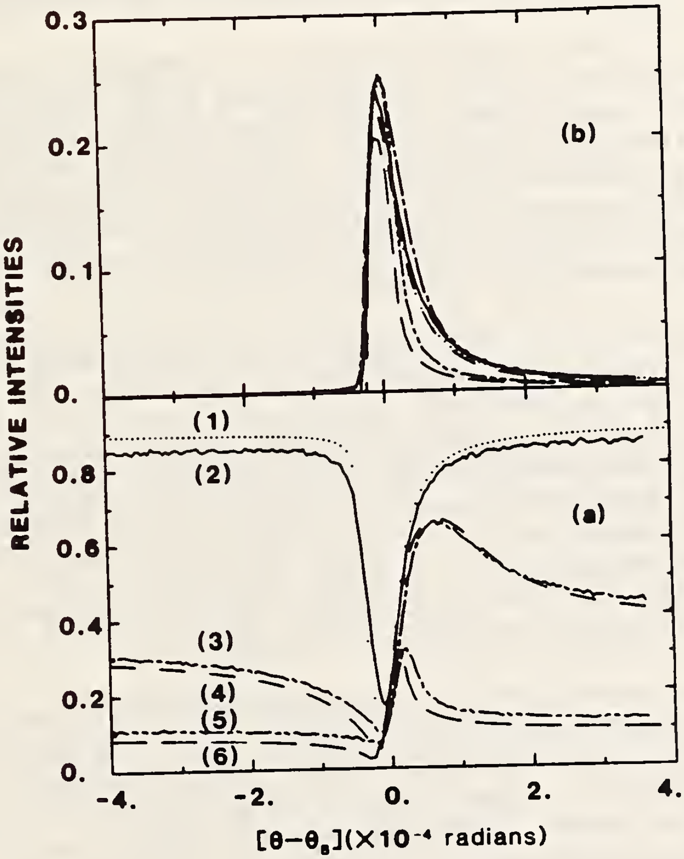


Fig. 16 Intensities of (a) specular beam and (b) diffracted beam as a function of deviation from the ideal Bragg angle Θ_B for various fixed angles of incidence ϕ. Curves 2, 3, and 5 are experimental results and curves 1, 4, and 6 are results from dynamical diffraction theory. The measurements and calculations are for three angles of incidence: ϕ = 4.74 milliradians, less than the critical angle for total reflection (curves 1 and 2); ϕ = 5.55 milliradians, at the critical angle (curves 3 and 4); and ϕ = 6.35 milliradians, greater than the critical angle (curves 5 and 6).

These initial experiments were carried out in helium at atmospheric pressure and we are building a chamber to continue the work in ultra-high vacuum. We intend to measure position-dependent fluorescence, photoemission, and Auger-electron decay from surface atoms. To this end, we have already built a new bent-crystal ultrahigh vacuum (uhv) x-ray spectrometer. The principal task during the coming year will be to design and build a uhv crystal goniometer which will be accurate to a few seconds of arc. The equipment is designed to be used on our new focussed x-ray beam line, X-24A, at the Brookhaven National Synchrotron Light Source.

B. State Characterization of Energetic Species Ejected from Surfaces

Specific state characterization of desorbed and ejected species from surfaces, whether induced by sputtering or by electron and photon bombardment, is still rare. It is now possible to address such dynamical surface interactions using laser techniques to determine the energy state, velocity, and angular distributions of all the ejected species--especially the neutrals which are the most abundant. Such studies can provide detailed microscopic information concerning energy transfer in these excitation/interaction processes.

The objective in this component of the program is to understand the excitation dynamics by which atoms and molecules are desorbed from surfaces in ion-sputtering processes as well as in electron- and photon-stimulated processes. Detailed characterization of the internal energy, kinetic energy, and desorption thresholds of desorbed species will provide a microscopic understanding of the nature of the electronic excitations leading to desorption due to collisions with electrons, photons, and ions. Angular distributions will provide direct structural information concerning the surface geometry, as well as information concerning energy transfer during the collisonal interaction.

We are combining ultrahigh-vacuum surface-science techniques with state-of-the-art laser spectroscopy in several experiments involving electron-stimulated desorption (ESD), photon-stimulated desorption (PSD), and ion sputtering. Specifically, we propose to use multiphoton ionization and other laser-spectroscopic techniques to detect and analyze neutral species released from crystalline surfaces by electron, photon, and ion bombardment. These measurements will provide unique insights into the mechanisms of desorption induced by both electronic transitions and by direct momentum transfer. Measurements of neutral angular distributions will be compared directly with ion angular distributions using a new two-dimensional display analyzer, thus providing a detailed description of competing desorption pathways.

We are performing work in three project areas. First, we are designing an experiment in which laser-spectroscopic techniques will be used to determine the energy states of neutral atoms and molecules sputtered from surfaces by ion bombardment. Second, we are collaborating with scientists at Vanderbilt University on a similar experiment in which neutral species desorbed from surfaces by electron or photon excitation will be detected and characterized. This experiment may lead later to similar work at NBS. Finally, we are constructing a new type of display analyzer to measure angular and energy distributions of neutral species desorbed from surfaces by electrons or photons to obtain surface-geometry information and to test theories of ejection mechanisms. Close contact is made with the related experimental and theoretical projects in the Division described in Sections 3.B, 3.D, 3.G and 3.I.

1. Energy States of Neutral Species Sputtered from Surfaces
(J. Fine)

Energetic ion-surface collisions generate extensive near-surface collision cascades in a solid. The energy transfer and atomic excitations that take place as a result of such collisions are not well understood in part because, until rather recently, the primary method for monitoring these collision phenomena was to measure macroscopic effects such as the total sputtering yield. The collision cascade causes the ejection of atoms, ions, electrons, and photons from the surface but it has only been in the past few years that measurements of the ejected particles or radiation have been utilized to obtain detailed information of specific atomic collisions that take place in condensed materials.

In recent experiments in which aluminum or silicon targets were bombarded by argon ions, we have shown that the Auger decay of collisonally excited Al or Si atoms can take place outside the solid depending on the distance from the surface (within the material) at which the excitation occurred, the atom's velocity, and the lifetime of the atomic excitation. As a result of our Monte-Carlo calculation to analyze these experiments, we expect that such sputtered atoms will have rather high kinetic energies - extending up to hundreds of electron volts. Collisions capable of transferring this much energy and creating inner-shell (2p) excitation can generate sputtered atoms (ions) which are in highly excited states. Such energy-transfer and excitation mechanisms are basic to our enhanced understanding of collisional processes in condensed materials. Information is required of those atomic processes which lead to electron promotion, excitation and ionization, and particle ejection. It is now possible to obtain this type of information by: (1) probing specific ejected (sputtered) atoms via resonant, multiphoton laser techniques; (2) monitoring the Auger-electron de-excitation of ejected atoms as well as those which decay inside the solid; (3) analyzing the emitted secondary-electron energy distributions. Progress made during the first year of this project in each of these areas is described below.

(a) Laser Spectroscopy of Sputtered Atoms and Ions

In collaboration with Drs. L. J. Moore (NBS Inorganic Analytical Research Division) and T. B. Lucatorto (NBS Radiation Physics Division), a new series of experiments has been planned and designed to determine the kinetic energy distributions of specific sputtered atoms (ions) and their states of excitation. Resonance multiphoton laser-ionization schemes have been developed to detect sputtered atoms in specific excited states and time-of-flight techniques will be used to measure their kinetic energy distributions. Pulse timing and gating sequences have been designed and estimates made of signal intensity indicate that such measurements are feasible. A new apparatus has been designed for this experiment and consists of an ultrahigh vacuum chamber (that allows ion-beam-angle-dependent measurements to be made) connected to a time-of-flight analyzer. This chamber, which is under construction, will be coupled to two ultraviolet pulsed-laser systems. We plan to investigate atoms (ions) sputtered from surfaces of magnesium, aluminum, and silicon and to determine their charge state, excitation state, and kinetic energy distributions.

(b) Auger-Electron De-Excitation of Sputtered Atoms

In collaboration with Drs. C. Le Gressus and J. P. Durand (Centre d'etudes Nucleaires de Saclay, France), a new series of measurements were begun to investigate the Auger-electron emission from ion-bombarded single-crystal aluminum surfaces. Aluminum (100) and (111) surfaces were bombarded with argon ions and the dependence of atomic-like and band-like Auger-electron emission was monitored as the crystals were rotated about an axis normal to the surface. Preliminary results indicate a very marked change in Auger-electron emission intensity as a function of rotation angle. Intensity minima correspond to geometrical conditions where the incident ion beam is aligned with a string of atoms (i.e., there is a shadowing of underlying atoms by the outermost surface atom of a given string). Measurements of this phenomena are still in progress in Saclay; we anticipate extending this investigation of collisional excitation processes in single-crystal solids at NBS.

(c) Secondary-Electron Energy Distributions Due to Ion Bombardment

In collaboration with Dr. I. Terzic (Boris Kidric Institute, Belgrade, Yugoslavia), an experiment has been designed to study the secondary-electron energy distributions that result from Ga^+-Ga collision at ion energies from 20 to 60 keV. Previous measurements at NBS indicate that collisional excitation may account for the high energy (> 100 eV) emitted electrons observed. An apparatus is presently under construction in Belgrade which will enable us to examine inner-shell excitation thresholds in this system.

2. Electron- and Photon-Stimulated Desorption of Neutral Species Using Laser Detection Techniques

(T. E. Madey)

In a collaborative effort with Prof. N. Tolk at Vanderbilt University, we have initiated measurements to characterize the mechanisms by which neutral species are excited and desorbed from surfaces using electron- and photon-stimulated desorption (ESD/PSD).

The majority of species removed from surfaces via ESD and PSD are neutral atoms and molecules. However, virtually all measurements of the energy and angular distributions of desorbing species have been of the more-easily-detected minority ionic species; only recently have laser techniques been applied to the detection of neutral species. The few measurements made to date have concentrated on desorption from poorly characterized surfaces, or radiation-induced decomposition of bulk solids (e.g., alkali halides).

Our experiments are designed to search for and characterize the ESD of both ground-state and excited Li and Na atoms desorbed from fractional-monolayer films of Li and Na adsorbed on both clean and oxygen-covered W(100) surfaces. We will employ laser-induced fluorescence to detect the ground-state neutrals, and light emission following metastable deexcitation to detect excited neutral species. A later stage of the measurements will involve the use of synchrotron radiation to determine the threshold energies for desorption via photon-stimulated desorption. The choice of experimental systems for these first studies (Na, Li on O/W(100)) is based on previous related experiments and the theoretical interest in these conditions.

2. Angular and Energy Distributions of Desorbed Ionic Species
(R. Stockbauer and T. E. Madey)

We have designed a special analyzer to measure simultaneously the angular, energy, and mass distributions of ions desorbed from surfaces. The analyzer will in addition be used for angle-resolved photoemission.

The construction of a new angle-resolving, display-type ion and electron energy analyzer is nearing completion. This instrument is based on the IBM design of Dr. D. Eastman. After completion of the analyzer and assembly, the analyzer will undergo initial testing in the laboratory using an electron impact source. The video processing software which will display the two-dimensional data in an appropriate form will be developed during this initial testing. This same software will be used to process similar two-dimensional data from a video system to be installed for our ESDIAD project (Section 3.B).

The initial test experiments using the new analyzer will be a series of quantitative ESDIAD (Electron Stimulated Desorption-Ion Angular Distributions) studies of small molecules adsorbed on metal surfaces. The test systems will include NH_3 and H_2O on Ni(111), as well as the coadsorption of each of these molecules with electronegative (O, S, Br) and electropositive (K, Na) additives. Some of these systems have been studied previously but a number of longstanding and important fundamental questions remain for which the new analyzer can provide quantitative answers. Experiments are planned to address the following questions.

- What are the angular profiles of the ion beams?
- Is there quantitative structural information in individual ESDIAD beam shapes?
- How do the angular profiles of individual ion beams vary with adsorption coverage and the presence of co-adsorbates?
- How do the ESDIAD patterns vary as a function of electron excitation energy?
- Are the ion energy distributions a function of desorption angle?
- How do measured ion trajectories compare with theory?

In later experiments at the NBS synchrotron radiation source SURF-II, the analyzer will be used in angle-resolved photon-stimulated desorption studies of clean and adsorbate-covered oxide surfaces. Desorption thresholds and energy dependences will be correlated with angle-resolved electron spectroscopic measurements (ultraviolet photoelectron spectroscopy, constant-initial-state, constant-final-state measurements). These measurements will be the first detailed, angle-resolved mechanistic studies of photon-induced bond-breaking processes at surfaces.

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Shinn, N. D. and Madey, T. E., "CO Chemisorption on Cr(110): Evidence for a Precursor to Dissociation," J. Chem. Phys. (in press).

Shinn, N. D. and Madey, T. E., "Observation of a Metal: CO 4σ Bonding Interaction for Chemisorbed CO on Cr(110)," Phys. Rev. B (submitted).

Shinn, N. D. and Madey, T. E., "Chemisorption and Dissociation of O_2 on Cr(110): An EELS/ESDIAD Study," Nucl. Instr. & Meth. B. (in press).

Stockbauer, R., Kurtz, R. L., Usuki, N. and Madey, T. E., "The Use of Synchrotron Radiation to Measure Electron Attenuation Lengths in Condensed Molecular Solids," Nucl. Instr. & Meth. B. (submitted).

Twigg, M. E., Melmed, A. J., Klein, R., Kaufman, M. J. and Fraser, H. L., " A Microanalytical Study of Secondary Precipitation in a Nickel-Base Superalloy with use of Atom Probe Field Ion Microscopy and Analytical Electron Microscopy," Proc. Fifth Int. Symposium on Superalloys (in press).

Wang, F. W., Lowry, R. E. and Cavanagh, R. R., "Picosecond Excimer Fluorescence Spectroscopy: Applications to Local Motions of Polymers and Polymerization Monitoring," Polymer (submitted).

Wax, M. J., Cavanagh, R. R., Rush, J. R., Stucky, G. D., Abrams, L. and Corbin, D. R., "A Neutron Scattering Study of Zeolite Rho," J. Phys. Chem. (submitted).

Wax, M. J., Kelley, R. D. and Madey, T. E., "Ethane Hydrogenolysis Catalyzed by W(110)," J. Catalysis. (submitted).

Yates, Jr., J. T., Madey, T. E. and Campuszano, J. C., "The Chemisorption of Carbon Monoxide by the Transition Metals," The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, D. A. King and D. P. Woodruff, eds., Elsevier (in press).

c) Recent Publications of New Staff Members (Burgess and Szuromi)

Burgess, Jr., D. R., Hussla, I., Stair, P. C., Viswanthan, R., and Weitz, E., "Pulsed Laser-Induced Thermal Desorption from Surfaces: Instrumentation and Procuedures," Rev. Sci. Instrum. 55, 1771 (1984).

Szuromi, P. D., Engstrom, J. R. and Weinberg, W. H., "The Reaction of Saturated and Unsaturated Hydrocarbons with the (110)-(1x2) and (111) Surfaces of Iridium," J. Chem. Phys. 80, 508 (1984).

Szuromi, P. D., Engstrom, J. R. and Weinberg, W. H., "Adsorption and Reaction of N-Alkanes on the Pt(110)-(1x2) Surface," J. Phys. Chem. 89, 2497 (1985).

Szuromi, P. D. and Weinberg, W. H., "The Adsorption and Reaction of Normal Alkanes on the the Ir(110)-(1x2) Surface," Surf. Sci. 149, 226 (1985).

6. TALKS

Cavanagh, R. R., "Energy Transfer at Surfaces: Pump-Probe Measurements of Vibrational Relaxation," Department of Chemistry, California Institute of Technology, Pasadena, CA, November 26, 1984.

Cavanagh, R. R., "Energy Transfer at Surfaces: Pump-Probe Measurements of Vibrational Relaxation," Department of Chemistry, University of Irvine, Irvine, CA, November 27, 1984.

Cavanagh, R. R., "Laser Diagnostics of Gas/Surface Interactions," American Institute of Chemical Engineers, San Francisco, CA, November 28, 1984.

Cavanagh, R. R., "Energy Transfer at Surfaces: Pump-Probe Measurements of Vibrational Relaxation," Department of Chemical Physics, IBM, San Jose, CA, November 29, 1984.

Cavanagh, R. R., "Picosecond Pump-Probe Measurements of Vibrational Relaxation at Surfaces," Department of Chemistry, Rutgers University, Piscataway, NJ, April 1, 1985.

Cavanagh, R. R., "Energy Transfer at Surfaces: Laser Based Measurements," Local Section of American Vacuum Society, University of Minnesota, Minneapolis, MN, May 16, 1985.

Cavanagh, R. R., "Energy Transfer at Surfaces: Laser Based Measurements," Physical Chemistry Department, General Motors Company, Detroit, MI, May 24, 1985.

Cavanagh, R. R., "Nitric Oxide Thermally Desorbed from Pt(111): A Microscopic Test of Transition State Theory," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 17, 1985.

Cavanagh, R. R., "Hydrogen on Small Metal Particles: Structure and Dynamics from Neutron Scattering," Gordon Research Conference on Metal Hydrides, Tilton, NH, July 15, 1985.

Cavanagh, R. R., "Vibrational Relaxation at Surfaces: Time Resolved Results," Gordon Research Conference on the Dynamics of Gas-Surface Interactions, New London, NH, July 29, 1985.

Cavanagh, R. R., "Picosecond Pump Measurements of Vibrational Relaxation at Surfaces," Vibrations at Surfaces IV Conference, Bowness-on-Windermere, England, September 17, 1985.

Cavanagh, R. R., "Inelastic Incoherent Neutron Scattering: Vibrational Spectroscopy of Hydrogen on Platinum Black," Vibrations at Surfaces IV Conference, Bowness-on-Windermere, England, September 18, 1985.

Egelhoff, W. F., Jr., "X-Ray Photoelectron Forward Scattering: A New Tool for Studying Epitaxy and Interfaces," Materials Research Society Meeting, Boston, MA, November 29, 1984.

Egelhoff, W. F., Jr., "Heats of Adsorption of H and O on Cu-Ni Alloy Surfaces from XPS Data," 31st National Symposium of the American Vacuum Society, Reno, NV, December 5, 1984.

Egelhoff, W. F., Jr., "Role of Forward Scattering in Angular Dependent XPS," 31st National Symposium of the American Vacuum Society, Reno, NV, December 5, 1984.

Egelhoff, W. F., Jr., "New Applications for Angle Resolved XPS," American Vacuum Society Chapter Meeting, Tampa, FL, February 6, 1985.

Egelhoff, W. F. Jr., "The XPS Searchlight Effect: A New Analytical Tool for Layered Structure, Epitaxy and Interfaces," American Physical Society Meeting, Baltimore Convention Center, Baltimore, MD, March 25, 1985.

Egelhoff, W. F. Jr., "A Core-Level Binding-Energy Shift Analysis of CO, H, and O Adsorption on Cu-Ni Surfaces," American Physical Society Meeting, Baltimore, MD, March 28, 1985.

Egelhoff, W. F., Jr., "Forward Scattering in XPS: A Structural Tool for Surfaces, Interfaces and Epitaxy," Chemistry Department, University of California, Berkeley, CA, April 25, 1985.

Egelhoff, W. F., Jr., "Forward Scattering in XPS: A Structural Tool for Surfaces, Interfaces and Epitaxy," Applied Physics Department, Stanford University, Stanford, CA, April 26, 1985.

Erickson, N. E., "Characterization of the Imaging Properties of a Double-Pass Cylindrical-Mirror Analyzer," 6th Symposium on Applied Surface Analysis, University of Maryland, College Park, MD, May 15, 1985.

Fine, J., "Ion-Beam Mixing and Radiation-Induced Segregation During Sputter Profiling of Nickel/Silver Interfaces," Condensed Matter and Radiation Sciences Division Seminar, Naval Research Laboratory, Washington, D.C., November 1, 1984.

Fine, J., "Characterization of NBS Standard Reference Material 2135 for Sputter Depth Profile Analysis," 31st National Symposium of the American Vacuum Society, Reno, NV, December 4, 1984.

Fine, J., "A Comparison of Sputtered Ni/Cr Interface Depth Resolution as Obtained by the Quartz Crystal Microbalance Mass-Loss Method and Auger Spectroscopy," 31st National Symposium of the American Vacuum Society, Reno, NV, December 5, 1984.

Fine, J., "Interface Depth Resolution of Auger Sputter Profiled Ni/Cr Interfaces: Dependence on Ion Beam Parameters," 31st National Symposium of the American Vacuum Society, Reno, NV, December 7, 1984.

Fine, J., "Sputter Profile Shapes and Widths of Ni/Cr Interfaces: Their Dependence on Ion Bombardment Parameters," Seventh International Conference on Ion Beam Analysis, Hahn Meitner Institute, Berlin, W. Germany, July 9, 1985.

Gadzuk, J. W., "Molecular Scattering, Energy Redistribution, and Dissociative Adsorption at Surfaces," Surface Science Seminar, Imperial College, London, England, September 24, 1984.

Gadzuk, J. W., "Intra-Molecular Wavepacket Dynamics in Molecule-Surface Scattering," Workshop on Interactions of Molecular Beams with Solid Surfaces, St. John's College, Cambridge, England, September 27, 1984.

Gadzuk, J. W., "Vibrational Lineshapes of Adsorbed Molecules," Department of Physical Chemistry Seminar, University of Liverpool, Liverpool, England, October 1, 1984.

Gadzuk, J. W., "Dynamic Effects in Electronic Excitation and Molecular Scattering from Surfaces," Department de Medecine Nucleaire and Radiobiologie, Centre Hospitalie-Universitarire, Sherbrooke, Quebec, Canada, January 21, 1985.

Gadzuk, J. W., "Recent Advances in Vibrational Spectroscopy at Surfaces," Department de Medecine Nucleaire and Radiobiologie, Centre Hosptialie-Universitaire, Sherbrooke, Quebec, Canada, January 22, 1985.

Gadzuk, J. W., "Molecular Dynamics at Surfaces: Harpooning, Vibrational Excitation, and Dissociative Adsorption," Physics Department Colloquium, University of Waterloo, Waterloo, Ontario, Canada, January 25, 1985.

Gadzuk, J. W., "Dissociation Dynamics in Molecule-Surface Collisions," American Physical Society Meeting, Baltimore Convention Center, Baltimore, MD, March 25, 1985.

Gadzuk, J. W., "Collision Induced Dissociation of Diatomic Molecules on Surfaces," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 17, 1985.

Gadzuk, J. W., "A Classical Trajectory Surface Hopping Approach to Non-Adiabatic Processes Occurring During Diatom-Surface Scattering," 1985 Conf. on the Dynamics of Molecular Collisions, Snowbird Resort, Snowbird, UT, July 16, 1985.

Gadzuk, J. W., "A Trajectorized Quantum Model for Surface Harpooning Processes Occurring in Diatom-Surface Scattering," 1985 Conf. on the Dynamics of Molecular Collisions, Snowbird Resort, Snowbird, UT, July 17, 1985.

Gadzuk, J. W., "The Vibrational Lineshapes of Adsorbed Molecules," Vibrations at Surfaces IV Conference, Bowness-on-Windermere, England, September 17, 1985.

Girvin, S. M., "Collective Excitation Gap in the Fractional Quantum Hall Effect," AT&T Bell Laboratory, Murray Hill, NJ, October 31, 1984.

Girvin, S. M., "The Quantum Hall Effect," Solid State Theory Seminar, Oak Ridge National Laboratory, Oak Ridge, TN, November 2, 1984.

Girvin, S. M., "Rotons in Superfluid Helium and the Fractional Quantum Hall Effect," Center for Basic Standards Colloquium, National Bureau of Standards, Gaithersburg, MD, January 9, 1985.

Girvin, S. M., "Introduction to the Quantum Hall Effect," James Franck Institute Colloquium, University of Chicago, Chicago, IL, January 15, 1985.

Girvin, S. M., "Rotons in Superfluid Helium and the Fractional Quantum Hall Effect," Department of Physics, University of Chicago, Chicago, IL, January 16, 1985.

Girvin, S. M., "The Quantum Hall Effect," Department of Physics, Catholic University, Washington, D.C., February 21, 1985.

Girvin, S. M., "Rotons in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, Princeton University, Princeton, NJ, March 6, 1985.

Girvin, S. M., "Rotons and Vortices in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, March 11, 1985.

Girvin, S. M., "Collective Excitation Gap in the Fractional Quantum Hall Effect," American Physical Society Meeting, Baltimore Convention Center Baltimore, MD, March 26, 1985.

Girvin, S. M., "Rotons and Vortices in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, SUNY, Stony Brook, NY, April 26, 1985.

Girvin, S. M., "Rotons and Vortices in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, University of Minnesota, Minneapolis, MN, May 6, 1985.

Girvin, S. M., "Introduction to the Quantum Hall Effect with Applications to GaAs Heterostructures," Center for Microelectronics and Information Science, University of Minnesota, Minneapolis, MN, May 7, 1985.

Girvin, S. M., "Rotons, Vortices and Superfluidity in the Fractional Quantum Hall Effect," Institute of Theoretical Physics, University of California, Santa Barbara, CA, June 4, 1985.

Girvin, S. M., "Introduction to the Quantum Hall Effect," Department of Materials Science, Harry Diamond Laboratories, Adelphi, MD, August 12, 1985.

Girvin, S. M., "Fractional Quantum Hall Effect: Superfluidity, Magneto-Rotons and Fractionally Charged Vortices," International Conference on Magnetism and Magnetic Materials, San Francisco, CA, August 30, 1985.

Girvin, S. M., "Introduction to the Quantum Hall Effect," Physics Department, Texas A&M University, September 26, 1985.

Jach, T., "Observations of Dynamical X-Ray Diffraction from a Crystal Surface at Glancing Incidence," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 26, 1985.

Jach, T., "Dynamical X-Ray Diffraction at Glancing Incidence: A New Tool for Surface Science," Physical Electronics Conference, University of Wisconsin, Milwaukee, Wi, June 18, 1985.

Kelley, R. D., "Catalytic Activity of Single Crystal Tungsten and Tungsten Carbide Surfaces," Symposium on Advances in Catalytic Chemistry III", Hotel Utah, Salt Lake City, UT, May 22, 1985.

Kurtz, R. L., "Site Specificity in Stimulated Desorption from TiO_2," 2nd International Workshop on Desorption Induced by Electronic Transitions, Elmau, Germany, October 15, 1984.

Kurtz, R. L., "Surface Studies of the Oxides of Titanium: Electronic Structure, Chemisorption, and Desorption from Ti_2O_3 and TiO_2," IBM Thomas J. Watson Research Laboratories, Yorktown Heights, NY, November 8, 1984.

Kurtz, R. L., "Surface Studies of the Oxides of Titanium: Electronic Structure, Chemisorption and Desorption from Ti_2O_3 and TiO_2," Applied Physics Division, Harry Diamond Laboratories, Adelphi, MD, November 20, 1984.

Kurtz, R. L., "Site Specificity in Stimulated Desorption from TiO_2," 31st National Symposium of the American Vacuum Society, MGM Grand Hotel, Reno, NV, December 6, 1984.

Kurtz, R. L., "Influence of Local Environment in Stimulated Desorption from TiO_2," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 27, 1985.

Kurtz, R. L., "Application of Surface Analytical Techniques to the Characterization of Adsorption and Desorption from Solids," Physics Department Colloquium, Brandeis University, Waltham, MA, April 30, 1985.

Kurtz, R. L., "Surface Science Applications of Residual Gas Analyzers," Residual Gas Analyzer Calibration Workshop, National Bureau of Standards, Gaithersburg, MD, May 7, 1985.

Madey, T. E., "Uses and Limitations of ESDIAD for Determining the Structures of Surfaces Molecules," 2nd International Workshop on Desorption Induced by Electronic Transitions, Garmisch, W. Germany, October 16, 1984.

Madey, T. E., "Desorption Induced by Electronic Transitions," Pittsburgh Surface Science Center Symposium, University of Pittsburgh, Pittsburgh, PA, October 30, 1984.

Madey, T. E., "Use of ESDIAD in Surface Chemistry," Department of Chemistry, Iowa State University, Ames, IA, November 27, 1984.

Powell, C. J., "Energy and Material Dependence of the Inelastic Mean Free Path of Low-Energy Electrons in Solids," 31st National Symposium of the American Vacuum Society, MGM Grand Hotel, Reno, NV, December 6, 1984.

Powell, C. J., "Physics--What Physicists Do," Career Awareness Day, Walt Whitman High School, Bethesda, MD, December 10, 1984.

Powell, C. J., "Techniques for Surface Analysis," Analytical Topical Group of the New York Section of the American Chemical Society, New York, NY, April 4, 1985.

Powell, C. J., "Developments in Quantitative Surface Analysis by Electron Spectroscopy," Eastern Electron Spectroscopy Society Mtg., General Electric R&D Center, Schenectady, NY, June 7, 1985.

Powell, C. J., "Chemical Bonding Studies at the Solid/Gas Interface with Techniques Using Detected Electrons," Fifth Internat. Conf. on Surface and Colloid Science and 59th Colloid and Surface Science Symposium, Clarkson University, Potsdam, NY, June 25, 1985.

Shinn, N. D., "Oxygen-Induced CO Reorientation on Cr(110)," 31st National Symposium of the American Vacuum Society, MGM Grand Hotel, Reno, NV, December 7, 1984.

Shinn, N. D., "Chemisorption on Cr(110): Uncommon Results for O_2 and CO," Surface Physics Group, Sandia National Laboratory, Livermore, CA, December 10, 1984.

Shinn, N. D., "Recent Results and Realistic Goals of Silicon-Fluorine Chemisorption Studies," Surface Physics Group, Hughes Research Laboratory, Malibu, CA, December 12, 1984.

Shinn, N. D., "Novel O_2 and CO Chemisorption on Cr(110) as Revealed by Stimulated Desorption and Surface Spectroscopies," Los Alamos National Laboratory, Los Alamos, NM, March 12, 1985.

Shinn, N. D., "CO Chemistry on the Cr(110) Surface: Insights from Unexpected Results," Sandia National Laboratory, Albuquerque, NM, March 14, 1985.

Shinn, N. D., "A Molecular Precursor to CO Dissociation on Cr(110): The α_1CO Binding Mode," Americal Physical Society Meeting, Baltimore Convention Center, Baltimore, MD, March 27, 1985.

Shinn, N. D., "Synchrotron Photoemission Study of Chemisorbed α_1CO and α_2CO on Cr(110)," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 17, 1985.

Shinn, N. D., "CO:O_2 Interactions on Cr(110): Insights into Surface Poisoning by Electronegative Adatoms," Department of Physics, Cornell University, Ithaca, NY, August 14, 1985.

Stockbauer, R., "Photon and Electron Stimulated Desorption of Ions from Surfaces: Mechanisms and Applications," Physics Department Colloquium, University of Nebraska, Lincoln, NE, April 4, 1985.

Madey, T. E., "Mechanisms and Applications of Electron and Photon Stimulated Desorption," 1985 Symposium on Surface Science (3S'85), Bundessportschule Obertraun, Obertraun, Austria, January 29, 1985.

Madey, T. E., "Early Applications of Vacuum, From Aristotle to Langmuir," National Bureau of Standards Colloquium, Gaithersburg, MD, February 8, 1985.

Madey, T. E., "The Structures of Molecules on Surfaces as Determined Using Electron Stimulated Desorption," Department of Chemistry, University of Montreal, Montreal, Canada, February 27, 1985.

Madey, T. E., "The Structures of Molecules on Surfaces as Determined Using Electron Stimulated Desorption," Department of Chemistry, Howard University, March 8, 1985.

Madey, T. E., "Characterization of Surfaces Using Electron Stimulated Desorption," Ceremonial Symposium Honoring the Retirement of Homer Hagstrum, AT&T Bell Laboratories, Murray Hill, NJ, March 22, 1985.

Madey, T. E., "Evidence for Molecular Reorientations in Coadsorption of CO and K on Ru(001)," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 28, 1985.

Madey, T. E., "Adsorption and Orientation of NH_3 on Clean and Modified Fe(100)," 7th European Conference on Surface Science, Aix-en-Provence, France, April 3, 1985.

Madey, T. E., "Mechanisms and Applications of Electron Stimulated Desorption," Department of Physics, Vanderbilt University, Nashville, TN, April 26, 1985.

Madey, T. E., "Electron and Photon Stimulated Desorption of Adsorbed Metals: An Overview," Department of Physics, Vanderbilt University, Nashville, TN, June 21, 1985.

Madey, T. E., "The Structure and Chemistry of H_2O on Silver Surfaces," Department of Chemistry, Iowa State University, Ames, IA, June 26, 1985.

Madey, T. E., "Influence of Surface Additive Atoms on the Structure and Chemistry of H_2O on Ag(110)," American Chemical Society Meeting, Americana Congress Hotel, Chicago, IL, September 9, 1985.

Melmed, A. J., "Long-Range Orientational Order and Icosahedral Symmetry in a Metallic Phase Observed by Field Ion Microscopy," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 28, 1985.

Melmed, A. J., "Field Emission Microscopy-Trends and Perspectives," 3rd International Field Emission Symposium, Wheeling, W.Va., July 17, 1985.

Melmed, A. J., "Field Emission Microscopy-Trends and Perspectives," Seventh International Summer Institute in Surface Science, University of Wisconsin, Milwaukee, WI, July 23, 1985.

Stockbauer, R., "Photon and Electron Stimulated Desorption of Ions from Surfaces: Mechanisms and Applications," Rice University, Houston, TX, June 1985.

Stockbauer, R., "The Use of Synchrotron Radiation to Measure Electron Attenuation Lengths in Condensed Molecular Solids," Synchrotron Radiation Instrumentation Conference, Stanford University Conference Center, Stanford, CA, August 1, 1985.

Szuromi, P. D., "UHV Studies of Alkane Activation on Iridium and Platinum Surfaces," Department of Physics and Astronomy, University of Maryland, College Park, MD, February 1, 1985.

Szuromi, P. D., "Site Specificity of Dissociative Alkane Adsorption on Platinum and Iridium Surfaces," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 18, 1985.

Szuromi, P. D., "The Effect of Adsorbed Sulfur on the Hydrogenation of of CO over W(110)" American Chemical Society Meeting, Americana Congress Hotel, Chicago, IL, September 10, 1985.

Szuromi, P. D., "Comparative Studies of Alkane Activation by Low Index Surfaces of Platinum and Iridium," American Chemical Society, Americana Congress Hotel, Chicago, IL, September 10, 1985.

Twigg, M. E., "An Atom Probe Study of Superalloy Microstructure," 5th Annual Symposium on Superalloys, Seven Springs Mountain Resort, Champion, PA, October 9, 1984.

Wax, M. J., "Neutron Scattering Studies of Zeolite Rho," 189th National Meeting of the American Chemical Society, Miami Beach Convention Center, Miami, FL, April 29, 1985.

Wax, M. J., "Thin Platinum Films as Model Alkane Reforming Catalysts," 189th National Meeting of the American Chemical Society, Eden Roc Hotel, Miami, FL, May 2, 1985.

Wax, M. J., "Thin Platinum Films as Model Alkane Reforming Catalysts," Symposium on Applied Surface Analysis, University of Maryland, College Park, MD, May 16, 1985.

Wax, M. J., "Reforming Reactions of Ultrathin Film Model Catalysts," American Chemical Society, Chicago, IL, September 10, 1985.

7. SEMINARS

Bennett, J. M., Naval Weapons Center, China Lake, CA, "Optical Evaluation Techniques for Films and Surfaces," November 21, 1984.

Bishop, H. E., Materials Development Division, AERE Harwell, England, "Electron Channeling Effects in Auger Electron Spectroscopy and Secondary Electron Emission," September 26, 1985.

Cavanagh, R. R., National Bureau of Standards, Gaithersburg, MD, "Temporal and Spectral Probes of Surfaces Processes: New Opportunities with Laser Diagnostics," May 21, 1985.

Egelhoff, W. F., Jr., National Bureau of Standards, Gaithersburg, MD, "The XPS Searchlight Effect: A New Analytical Tool for Layered Structures, Epitaxy, and Interfaces," February 11, 1985.

Einstein, T., University of Maryland, College Park, MD, "How and Why to Study Critical Properties of Surfaces and Adsorbates," October 11, 1984.

Ekardt, W., Fritz Haber Institute, Berlin, W. Germany, "Size Dependent Photoabsorption and Photoemission From Small Metal Particles," April 18, 1985.

Flodström, A., Lund University, Lund, Sweden, "Angle Resolved Photoemission Studies of Semiconductor Surfaces: Mostly Silicon and Germanium," June 13, 1985.

Freeman, R., AT&T Bell Laboratories, Murray Hill, NJ, "Picosecond Time Resolved Photoemission from Surfaces of Semiconductors," (cosponsored with NBS Radiation Physics Division) January 31, 1985.

Gurney, B. A., Cornell University, Ithaca, NY, "Adsorption and Desorption of CO on Ni(110)," December 17, 1985.

Heiland, W., Vanderbilt University, Nashville, TN, "Polarized Light Emission from Grazing Incidence He + Ni(111) Interactions," September 18, 1985.

Hicks, R., WR Grace & Company, Columbia, MD, "The Effects of Metal-Support Interactions on Palladium: Methanol Synthesis Catalysts," April 25, 1985.

Israelachvili, J. N., Australian National University, Canberra, Australia, "Forces Between Surfaces," (cosponsored with NBS Inorganic Materials and Thermophysics Divisions) July 1, 1985.

Johnson, A. L., University of California, Berkeley, CA, "Orientation of Molecules by NEXAFS (Near Edge X-Ray Absorption Fine Structure)," April 12, 1985.

Karikorpi, M., University of Liverpool, Liverpool, England, "Interaction of H_2 with Metal Surfaces: Dynamics," July 10, 1985.

Klein, R., National Bureau of Standards, Gaithersburg, MD, "Weighty Considerations on the Micro-Mass-Analysis of Alloys with the Atom Probe," April 19, 1985.

Kurtz, R. L., National Bureau of Standards, Gaithersburg, MD, "Implications of Recent Results on Photon-Stimulated Desorption," November 15, 1984.

McKay, J. M., Yale University, New Haven, CT, "Electronic Structure of NiO-CO, O_2, and H_2O Surface Interactions," June 12, 1985.

Myers, H. P., Chambers University of Technology, Goteborg, Sweden, "Mixed Valence in Sm Overlayers on Al(001) and Cu(001) Surfaces," January 14, 1985.

Paal, Z., Hungarian Academy of Sciences, Budapest, Hungary, "Activity, Surface Structure and Composition of Pt-Black," September 19, 1984.

Pearlstine, K., Harvard University, Cambridge, MA, "Hydrocarbon Chemistry on Modified Tungsten Surfaces: C-H and C-C Bond Activation," March 4, 1985.

Renouprez, A., Institut de Recherches sur la Catalyse, Villeurbanne Cedex, France, "EXAFS Study of the Structure of Pd Microaggregates. A Combined EXAFS and Neutron Study of Hydride Formation," July 23, 1985.

Rys, F., Fritz Haber Institute, Berlin, W. Germany, "Surface Roughening and Small-Particle Faceting-With Epitaxial Overtones," April 2, 1985.

Sass, J., Fritz Haber Institute, Berlin, W. Germany, "Surface Science Model Studies of the Electrochemical Interface," January 17, 1985.

Sawatzky, G., University of Groningen, Groningen, The Netherlands, "The Electronic Structure, Bandgap, and Spectroscopic Properties of Transition Metal Compounds," (cosponsored with Electron Physics Group) August 20, 1985.

Schwalke, U., California Institute of Technology, Pasadena, CA, "Vibrational Spectra of Chemisorbed NO_2 and Condensed N_2O_4 on the Ru(001) Surface," July 26, 1985.

Seah, M., National Physical Laboratory, Teddington, Middlesex, England, "Electron Spectrometer Intensity Transmission Functions for ESCA," November 29, 1984.

Steigerwald, D., Carnegie-Mellon University, Pittsburgh, PA, "Surface Segregation in NiAu Alloys," March 20, 1985.

Stockbauer, R., National Bureau of Standards, Gaithersburg, MD, "Studies of Electron Transport and Radiation Damage in Condensed Molecular Films Using Synchrotron Radiation," February 14, 1985.

Strasser, G., University of Maine, Orono, ME, "Nitrogen Adsorption on Fe(111) from the Extrinic Precursor to Atomic Nitrogen," September 16, 1985.

Szuromi, P. D., National Bureau of Standards, Gaithersburg, MD, "Alkane Activation of Low Index Surfaces of Iridium and Platinum: Comparative Studies," March 13, 1985.

Szymonski, M., Jagellonian University, Krakow, Poland, "Electron Stimulated Desorption of Neutrals from Alkali Halide Surfaces," January 16, 1985.

Tomanek, D., Free University of Berlin, Berlin, Germany, "Calculation of Potential Energy Surfaces for CO and N_2 Dissociation on Transition Metals," May 28, 1985.

Trenary, M., University of Illinois, Chicago, IL, "Infrared Reflection-Absorption Spectroscopy of CO on Clean and Sulfided Ni(111)," November 28, 1984.

Yarmoff, J., University of California, Los Angeles, CA, "Low Energy Ion Backscattering Spectroscopies Applied to the Determination of Surface Structure," March 20, 1985.

8. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Cavanagh, R. R.

Surface Science Division Safety Officer

Treasurer, General Committee of the Physical Electronics Conference (from 7/85)

Erickson, N. E.

Member, ASTM Committee E-42 on Surface Analysis

Fine, J.

Chairman, Subcommittee E-42.09 on Standard Reference Materials of ASTM Committee E-42 on Surface Analysis

Member, Program Committee, 11th Conference on Atomic Collisions in Solids, Washington, D.C., August, 1985.

Gadzuk, J. W.

Treasurer, General Committee of the Physical Electronics Conference (through 6/85)

Member, Editorial Advisory Board, "Progress in Surface Science"

Kelley, R. D.

Chairman, Subcommittee D-32.03 on Chemical Analysis of ASTM Committee D-32 on Catalysts

Madey, T. E.

Member, Executive Committee of the Governing Board of the American Institute of Physics (through 3/85); member of AIP Committee on Corporate Associates, and member of AIP Subcommittee on Electronic Publishing

U.S. Representative to Surface Science Division of the International Union of Vacuum Science, Technique and Applications (IUVSTA) and Secretary of Committee

Member, International Advisory Committee, Second International Conference on the Structure of Surfaces, Amsterdam, The Netherlands, June, 1987

Program Chairman, International Vacuum Congress and International Conference on Solid Surfaces, Baltimore, MD, October, 1986

Member, Organizing Committee, 11th Conference on Atomic Collisions in Solids, Washington, D.C., August, 1985

Member, International Advisory Committee, Second Workshop on Desorption Induced by Electronic Transitions, Garmisch, W. Germany, October, 1984

Member, Program Advisory Commitee for the Synchrotron Radiation Center of the University of Wisconsin, Madison, Wisconsin

Member, Advisory Committee for Laboratory of Surface Science and Technology at the University of Maine, Orono, ME

Member, Davisson-Germer Prize Committee of the American Physical Society

Chairman, Committee for Foreign Interactions, American Vacuum Society

Co-Editor, "History of Vacuum Science and Technology", a monograph to commemorate the 30th Anniversary of the American Vacuum Society (published 11/84)

Member, ASTM Committee E-42 on Surface Analysis

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of two volumes in series

Member, Editorial Board, "Journal of Vacuum Science and Technology"

Melmed, A. J.
Secretary, Steering Committee, International Field Emission Symposium

Powell, C. J.
Chairman, ASTM Committee E-42 on Surface Analysis

Chairman, Surface Chemical Analysis Working Party, Versailles Project on Advanced Materials and Sandards

Member, Board of Trustees, Gordon Research Conferences; Vice-Chairman of Board and Chairman of Selection and Scheduling Committee

Chairman, American Vacuum Society Surface Science Division (through 11/84)

Trustee, American Vacuum Society Scholarships and Awards Committee

Instructor, American Vacuum Society Short Course: "Surface Analysis by Electron Spectroscopy"

Chairman, Study Group to Examine AVS-ASTM E-42 Interactions

Chairman, Local Committee, Meeting of American Physical Society, Baltimore, MD, March 1985

Member, Editorial Board, "Applications of Surface Science"

Member, Editorial Board, "Surface and Interface Analysis"

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of one volume in series

Stockbauer, R.
Assistant Program Chairman, International Vacuum Congress and International Conference on Solid Surface, Baltimore, MD, October, 1986.

9. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Cavanagh, R.R.

Collaborating with Dr. D. S. King of the NBS Molecular Spectroscopy Division on state-specific diagnostics of molecular desorption processes

Collaborating with Drs. M. P. Casassa, E. J. Heilweil and J. C. Stephenson of the NBS Molecular Spectroscopy Division on real time measurements of vibrational relaxation processes at surfaces

Collaborating (with R. D. Kelley and M. J. Wax) with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbates on high-surface-area transition metals

Collaborating with Dr. J. J. Rush of the NBS Reactor Radiation Division, Dr. G. D. Stucky of du Pont, and Dr. M. J. Wax on vibration and diffusion properties of hydrogen and ammonia in zeolite H-rho

Collaborating with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division and Dr. B. J. Tatarchuk of Auburn University on neutron inelastic scattering measurements from adsorbates on dispersed ruthenium catalysts

Egelhoff, Jr., W. F.

Collaborating with Dr. R. A. Armstrong of the National Research Council, Ottawa on a theoretical analysis of the basic physics of the XPS searchlight effect for the purpose of defining and extending its range of applicability as an analytical tool for surfaces and interfaces.

Fine, J.

Collaborating with Prof. B. Navinsek of the J. Stefan Institute, Ljubljana, Yugoslavia on the effect of surface topography on measurements of sputtering yields, on depth resolution at interfaces, and on the fabrication and characterization of standard reference materials for surface analysis. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. I. Terzic of the Boris Kidric Institute, Belgrade, Yugoslavia on electronic excitation and electron emission for ion-bombarded surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Drs. L. and N. Tanovic of the University of Sarajevo, Yugoslavia on characterizing surface topography changes that result from ion bombardment. This collaboration is conducted under the auspices of the U.S-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. T. Nevadovic of the Boris Kidric Institute, Belgrade, Yugoslavia on the surface-topography effect of both particle and laser-beam interactions with thin solid films. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. L. J. Moore of the NBS Inorganic Analytical Research Division and Dr. T. Lucatorto of the NBS Radiation Physics Division on the use of laser multiphoton ionization techniques to identify sputtered atoms and to determine their kinetic energies.

Collaborating with Dr. W. Kirchhoff of the NBS Chemical Thermodynamics Division on a data analysis procedure for sputter-depth-profile interface characterization.

Collaborating with Dr. R. F. Fleming of the NBS Inorganic Analytical Research Division on thin-film thickness measurements of standard reference materials for surface analysis.

Collaborating with Dr. P. A. Lindfors of the Physical Electronics Division of Perkin-Elmer Corp. on the interface depth resolution of sputter-profiled Ni/Cr interfaces.

Collaborating with Drs. C. Le Gressus and J. P. Duraud of the Centre d'Etudes Nucleaires de Saclay, France on the collisional excitation and electron decay of atoms at single-crystal surfaces.

Gadzuk, J. W.

Collaborating with Prof. M. Sunjic of the Rudnor Boskovic Institute and the University of Zagreb, Yugoslavia on theories of electron spectroscopies and dynamics of molecular processes at surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Prof. U. Landman of the Georgia Institute of Technology on theoretical modeling of non-linear and stochastic molecular processes at surfaces.

Collaborating with Dr. S. Holloway and Ms. M. Karikorpi, University of Liverpool, England on classical trajectory theories of molecular processes at surfaces. This collaboration is assisted by a grant from the NATO Scientific Affairs Division.

Collaborating with Dr. E. Hood, California Institute of Technology, on a theory of polarized-metastable-helium de-excitation spectroscopy at magnetic surfaces and on electron-transfer probabilities.

Invited lecturer and participant at the Fourth Electrochemistry Study Group, Fritz-Haber-Institute, Berlin, September 22-27, 1985.

Girvin, S. M.

Collaborating with Drs. A. H. McDonald of the National Research Council of Canada, Ottawa and P. M. Platzman of AT&T Bell Laboratories, Murray Hill on developing a new theory of collective excitations in the fractional quantum Hall effect.

Collaborating with Dr. M. Jonson of Chalmers University of Technology, Gothenburg, Sweden on the theory of the thermoelectric effect in disordered quantum Hall systems.

Collaborating with Drs. D. R. Penn and S. P. Apell of the NBS Radiation Physics Division on a theory of spin polarization in secondary cascades in ferromagnets.

Collaborating with Prof. R. E. Prange of the University of Maryland in the organization of a lecture series on the quantum Hall effect during fall, 1985. It is planned to publish the lectures as a book.

Visited the Institute of Theoretical Physics at Santa Barbara during June 3-8, 1985 at the invitation of Prof. J. R. Schrieffer.

Visited AT&T Bell Laboratories, Murray Hill during July 2-12, 1985 at the invitation of Dr. D. S. Fisher.

Jach, T. J.

Collaborating with Drs. P. Cowan and S. Brennan of the NBS Quantum Metrology Group on the development of a beamline at the National Synchrotron Light Source, Brookhaven and on experiments to study electronic effects associated with core-level ionization in atoms, molecules, and solids.

Collaborating with Drs. P. Cowan and S. Brennan of the NBS Quantum Metrology Group and with Drs. G. Materlik and M. Bedzik of the German Electron Synchrotron Laboratory DESY, Hamburg on surface and interface x-ray diffraction experiments at DESY using glancing incidence.

Collaborating with Drs. G. G. Hembree of the NBS Mechanical Production Metrology Division and L. B. Holdeman of COMSAT on the fabrication and characterization of ultra-smooth surfaces and thin films.

Collaborating with Dr. P. Cowan of the NBS Quantum Metrology Group on glancing incidence x-ray excitation of surface atoms to measure surface core-level binding-energy shifts.

Collaborating with Dr. R. Perera of Lawrence Berkeley Laboratory on an experiment to measure Auger-electron spectra of argon for near-threshold excitation at the Stanford Synchrotron Radiation Laboratory.

Collaborated with Dr. H. Winick of the Stanford Synchrotron Radiation Laboratory to improve undulator efficiency.

Kelley, R. D.

Collaborating (with R. R. Cavanagh and M. J. Wax) with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Division on neutron inelastic scattering measurements of adsorbates on optically opaque high-surface-area transition metals.

Working on detail as a Program Manager with the Department of Energy Office of Energy Research, Division of Chemical Sciences. This detail is on a 70% part-time basis for a two-year period beginning May, 1985.

Kurtz, R. L.

Collaborating with Prof. V. E. Henrich of Yale University on studies of the chemisorption of molecules of catalytic interest on transition-metal oxide surfaces.

Collaborating (with R. Stockbauer) with Drs. C. Kunz and J. Schmidt-May of the German Synchrotron Laboratory DESY, Hamburg and Dr. A. Flodström of Lund University, Sweden in studies of the mechanisms of the photon-stimulated desorption of ions from surfaces.

Collaborating (with R. Stockbauer) with Dr. A. Flodström of Lund University, Sweden on experiments at the NBS synchrotron radiation facility of SURF-II to investigate (1) mechanisms of photon-stimulated desorption of ions from a non-maximal-valent oxide and (2) angular distributions (ESDIAD) of ions desorbing from adsorbates on semiconductors.

Collaborating (with R. Stockbauer) with Dr. V. Bermudez of the Naval Research Laboratory on studies at the NBS SURF-II facility of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with T. E. Madey and R. Stockbauer) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest College on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating (with R. Stockbauer) with Mr. J. Jimenez of Yale University, Prof. D. Caldwell of the University of Florida, and Dr. D. L. Ederer of the NBS Radiation Physics Division on measurements of the angular distribution of fluorescence from molecules excited by synchrotron radiation from the NBS SURF-II facility.

Collaborating with Dr. J. Pena of the University of Mexico, Mexico City on the preparation of TiO_2 samples suitable both for photon-stimulated desorption experiments at NBS and for secondary-ion mass spectroscopy experiments in Mexico.

Madey, T. E.

Collaborating with Drs. I. Terzić, J. Vukanić and Z. Mišković of the Boris Kidrić Institute, Belgrade, under the auspices of the U.S.-Yugoslav Agreement for Cooperation in Science and Technology, on theoretical and experimental studies of electron-stimulated desorption and scattering of alkali ions from surfaces.

Collaborating (with R. L. Kurtz and R. Stockbauer) with Drs. W. R. Hunter, J. Rife and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest College on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating with Drs. J. Sass and K. Bange of the Fritz-Haber-Institute, Berlin, and with Dr. E. Stuve of the University of Washington on fundamental studies of electrochemical phenomena with emphasis on the interaction between water and surfaces.

Collaborating with Dr. N. Tolk of Vanderbilt University on studies of electron-stimulated desorption of excited-alkali neutral atoms from surfaces.

Collaborating with Dr. C. Benndorf of the University of Hamburg, under the auspices of a NATO grant, on studies of the influence of surface additives on local molecular structure.

Collaborating with Prof. P. A. Thiel of the Dept. of Chemistry, Iowa State University in writing a comprehensive review article on the interaction of water with solid surfaces.

Melmed, A. J.

Collaborating as a co-principal investigator with Prof. W. R. Graham of the University of Pennsylvania on studies of atomic reconstruction of metal and semiconductor surfaces.

Collaborating with Dr. W. A. Schmidt and Prof. J. H. Block of the Fritz-Haber-Institute, Berlin on properties of semiconductors in electric fields and effects due to metallic overlayers.

Collaborating with Dr. B. Rioja of the Aluminum Corporation of America to determine feasibility of atom-probe analysis of a newly developed class of Al-Li-Cu alloys.

Collaborating with Dr. R.D. Arollia of the General Electric Company and Prof. H. Fraser of the University of Illinois to investigate atomic structure and chemical microcomposition for a series of nickel-based superalloys.

Collaborating with Mr. J. Smith and Prof. H. Fraser of the University of Illinois on studies of three related nickel-based superalloys using field ion microscopy, transmission electron microscopy, and atom probe analysis.

Collaborating with Dr. M. J. Kaufman of the NBS Metallurgy Division on comparative studies with atom-probe field-ion microscopy and transmission electron microscopy of nickel-based superalloys and a series of Al-Li-Cu alloys.

Collaborating with Dr. J. W. Cahn of the NBS Institute for Materials Science and Engineering on investigations of the atomic structure in rapidly solidified Al-Mn alloy ribbons exhibiting icosahedral long-range order by electron diffraction.

Consulted with Dr. R. D. Young of the NBS Mechanical Production Metrology Division and Mr. S. R. Mielczarek of the NBS Radiation Physics Division on probe preparation techniques for scanning tunneling microscopy.

Powell, C. J.

Member of Solid State Physics Review Panel for Office of Naval Research.

Collaborating with Dr. M. P. Seah of the National Physical Laboratory, London on the development of plans and programs for the Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards.

Stockbauer, R.

Collaborating (with R. L. Kurtz) with Drs. C. Kunz and J. Schmidt-May of the German Synchrotron Laboratory DESY, Hamburg and Dr. A. Flodström of Lund University, Sweden in studies of the mechanisms of the photon-stimulated desorption of ions from surfaces.

Collaborating (with R. L. Kurtz) with Dr. A. Flodström of Lund University, Sweden on experiments at the NBS synchrotron radiation facility SURF-II to investigate (1) mechanisms of photon-stimulated desorption of ions from a non-maximal-valent oxide and (2) angular distributions (ESDIAD) of ions desorbing from adsorbates on semiconductors.

Collaborating (with R. L. Kurtz) with Dr. V. Bermudez of the Naval Research Laboratory on studies at the NBS SURF-II facility of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with R. L. Kurtz and T. E. Madey) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest College on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating (with R. L. Kurtz) with Mr. J. Jimemez of Yale University, Prof. D. Caldwell of the University of Florida, and Dr. D. L. Ederer of the NBS Radiation Physics Division on measurements of the angular distribution of fluorescence from molecules excited by synchrotron radiation from the NBS SURF-II facility.

Collaborating with Dr. A. C. Parr of the NBS Radiation Physics Division and with Dr. D. Holland of Daresbury Laboratory, England on measurements of the fragmentation of molecules using photoelectron-photoion coincidence techniques.

Interacting with Drs. A. C. Parr, H. Hardis, and D. L. Ederer of the NBS Radiation Physics Division, Dr. J. L. Dehmer of Argonne National Laboratory, and Drs. J. B. West and D. Holland of Daresbury Laboratory, England on measurements of photoelectron angular distributions as a function of photon energy in gas-phase molecules.

Szuromi, P.

Collaborating with Drs. S. Semancik and D. F. Cox of the NBS Chemical Process Metrology Division in an investigation of the surface properties of semiconducting oxide surfaces used in gas sensing applications using ultraviolet photoemission spectroscopy. The interaction of H_2O with tin oxide (a widely used sensor material) has been studied.

Udovic, T. J.

Collaborating (with R. R. Cavanagh, R. D. Kelley, and M. J. Wax) with Dr. J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbed molecules on catalyst materials.

Collaborating (with R. R. Cavanagh) with Dr. J. J. Rush of the NBS Reactor Radiation Division and with Dr. B. J. Tatarchuk of Auburn University on neutron inelastic scattering measurements of the adsorptive behavior of hydrodesulferization catalysts.

Wax, M. J.

Collaborated (with R. R. Cavanagh) with Dr. J. J. Rush of the NBS Reactor Radiation Division and Dr. G. D. Stucky of du Pont on the application of inelastic incoherent neutron scattering to study diffusional motion of hydrogen in zeolite rho.

Collaborated (with R. R. Cavanagh, R. D. Kelley, and T. J. Udovic) with Dr. J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbed molecules on catalyst materials.

10. VISITING SCIENTISTS

The Surface Science Division has been host during the past year to a number of scientists who have worked with the Division staff on problems of mutual interest.

Barak, D., Head of the Electronic Design Department of the Israeli Nuclear Research Center-Negev, is working at NBS for one year beginning August, 1985. He is helping to design, construct and test improvements in the angle-resolved x-ray photoelectron spectrometer (XPS) consisting of a new electron lens system and a position-sensitive electron detection system.

Benndorf, C., of the University of Hamburg, W. Germany spent two months at NBS in early autumn 1984 initiating measurements of the structure and chemistry of ammonia on both clean and alkali-promoted Fe(100).

Chambers, G. P., a graduate student at the University of Maryland, has worked at NBS this past year under a cooperative agreement. He has been involved in the development of a data base system for the compilation of evaluated sputtering yield data.

Clinton, W. L., of the Department of Physics of Georgetown University is spending five months at NBS beginning September, 1985 to perform theoretical studies relating to electron- and photon-stimulated desorption of ions and neutral species from surfaces.

Flodström, A., of Lund University, Sweden worked at NBS between May and August, 1985. He initiated a study of adsorbate structures on semiconductor surfaces using ESDIAD, participated in photon-stimulated desorption measurements from non-maximal-valent oxides, and cooperated in the set up and calibration of a new toroidal grating monochromator at SURF-II.

Hashiguchi, Y., of the Nippon Steel Corporation, Japan has worked at NBS since March, 1985 on a one-year assignment. He is studying the interface-width dependence on ion bombardment parameters as well as collisional excitation and laser ionization of sputtered atoms.

Holloway, S., of the University of Liverpool visited NBS for two weeks during the summer of 1985 to work on theoretical modeling of reactive molecular processes at surfaces.

Jansen, W. R., a graduate student of the Twente University of Enschede, The Netherlands worked at NBS for three months in the fall of 1985. He extended the existing computer software for automated XPS measurements to permit operation in a timesharing mode, completed the interfacing of the computer to the XPS sweep supply, and extended the data reduction software.

Jimenez, J., a graduate student of Yale University, used the surface science beam line at SURF-II for three months during the fall of 1985 to study the angular distributions of fluorescence from gas-phase molecules.

Karikorpi, M., a graduate student of the University of Liverpool visited NBS for two weeks during the summer of 1985 to work on theoretical modeling of reactive molecular processes at surfaces.

Roovers, A. D., a graduate student of the Twente University of Technology, Enschede, The Netherlands, worked at NBS for three months in the fall of 1984. He wrote the basis system software to automate the angle-resolved XPS instrument with a minicomputer as well as basic software for data reduction.

Shinn, N. D., of Sandia National Laboratory, Albuquerque, NM, is spending four months at NBS during the fall of 1985 studying adsorbed molecules on metal surfaces using high-resolution electron energy-loss spectroscopy.

Tanuma, S., of the Nippon Mining Company is working at NBS on a two-year assignment beginning August, 1985. He will be participating in measurements of core-level binding energies by different electron-spectroscopic methods and in calculations of electron inelastic mean free paths in solids.

11. Surface Science Division Staff

As of September 30, 1985 the Surface Science Division was staffed as follows:

C. J. Powell, Chief
L. M. Johnson, Secretary
D. R. F. Burgess, Jr.[*]
R. R. Cavanagh
W. F. Egelhoff, Jr.
N. E. Erickson
J. Fine
J. W. Gadzuk
S. M. Girvin
T. J. Jach[**]
U. Landman[@]
A. J. Melmed

Surface Structure and Kinetics Group

T. E. Madey, Group Leader
G. Reyna, Secretary
P. M. Connelly[#]
R. D. Kelley
R. L. King[+]
R. L. Kurtz
E. O. Neitzel[#]
A. Pararas[++]
D. E. Ramaker[@]
R. L. Stockbauer
P. D. Szuromi[*]

[*] NBS-NRC Postdoctoral Research Associate
[@] Expert, Part-Time
[#] Engineering Technician
[+] Electronics Technician
[++] Contractor
[**] Half time with Quantum Metrology Group

NBS-114A (REV. 2-8C)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 86-3304	2. Performing Organ. Report No.	3. Publication Date FEBRUARY 1986

4. TITLE AND SUBTITLE
Technical Activities 1985
Surface Science Division

5. AUTHOR(S)
C. J. Powell

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report summarizes technical activities of the NBS Surface Science Division during Fiscal Year 1985. These activities include surface-standards work, experimental and theoretical research in surface science, the development of improved measurement methods, and applications to important scientific and national problems. A listing is given of publications, talks, professional committee participation, and professional interactions by the Division staff.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*
surface chemistry; surface physics; surface science; surface standards

13. AVAILABILITY

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☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES
122

15. Price
$16.95