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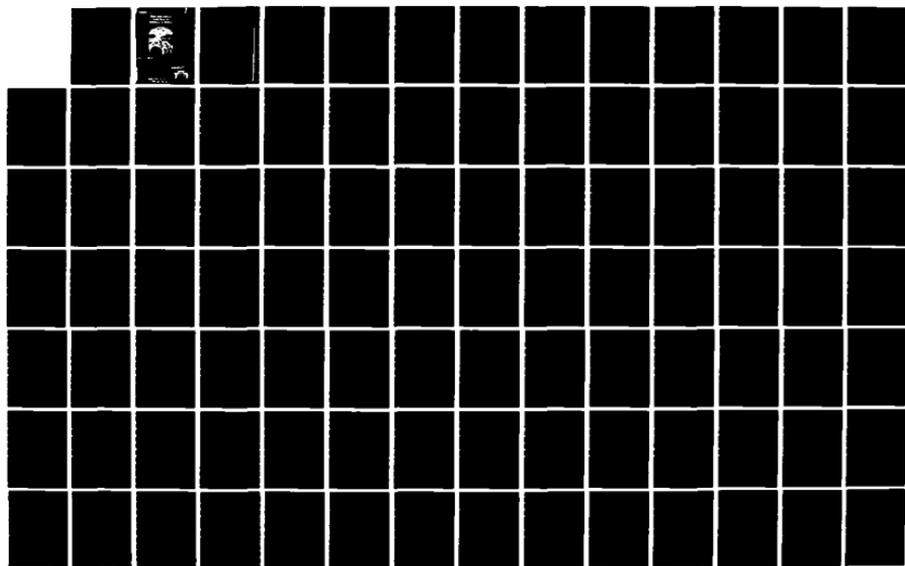
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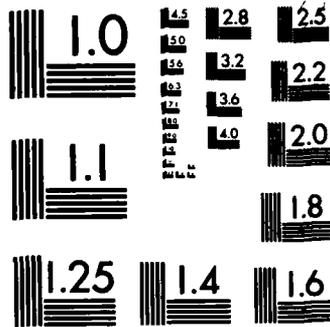
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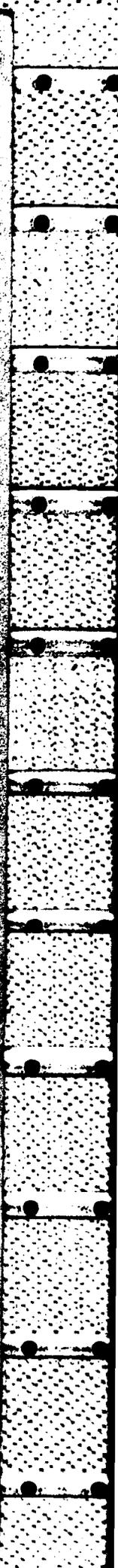
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**THIRD INTERNATIONAL CONFERENCE ON
VIBRATIONS AT SURFACES.**

September 1-4, 1982

**Asilomar Conference Grounds
Pacific Grove, California, USA**

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PRELIMINARY PROGRAM

Wednesday Afternoon, September 1, 1982

- 1:00 p.m. *H. Morawitz*, Welcome and Opening Remarks
- 1:10 p.m. *C. Duke*, Xerox Research Laboratory, Webster, New York, "Hot Atoms and Cold Facts: Mysteries and Opportunities in Vibration-Assisted Chemistry".

Session I: *Vibrational Frequency Shifts and Widths;
Lateral Interactions*
Chairman: *E. Burstein*

- 1:45 p.m. *D. King (Invited)*, University of Liverpool, England, "Phase-Transitions in Chemisorbed Layers Studied by Vibrational Frequency Shifts".
- 2:15 p.m. *R. Madix (Invited)*, Stanford University, Stanford, California, "Combined Vibrational/Programmed Reaction Intermediates on Metal Surfaces".
- 2:45 p.m. *Y. D. Chabal*, E. E. Chaban and S. B. Christman, Bell Laboratories, Murray Hill, New Jersey, "High Resolution Infrared Study of Hydrogen Chemisorbed on Si(100)".
- 3:01 p.m. *R. E. Dietz*, E. G. McRae and D. A. Kapilow, Bell Laboratories, Murray Hill, New Jersey, "Thermal Scattering of Slow Electrons During Elastic Specular Reflection from a Cu (001) Surface".
- 3:17 p.m. *Coffee Break*
- 3:40 p.m. *B. Persson (Invited)*, KFA, Julich, West Germany, "Lateral Interactions and Vibrational Lifetimes".
- 4:10 p.m. *R. Ryberg*, Chalmers University of Technology, Sweden, "The Oxidation of Methanol on Cu(100) Studied by Infrared Spectroscopy".
- 4:26 p.m. *G. Allan*, Bell Laboratories, Murray Hill, New Jersey, and J. Lopez, Universite Claude Bernard, France, "Chemisorbed Oxygen Vibrations on Nickel (110) Surfaces".
- 4:42 p.m. *Z. Schlesinger*, Bell Laboratories, Murray Hill, New Jersey, and A. J. Sievers, Cornell University, New York, "Dipole-Dipole Coupling in Adsorbate Vibrational Mode Spectra".
- 4:56 p.m. N. D. S. Channing and *M. A. Chatters*, University of East Anglia, Norwich, England, "The Reflection-Absorption Infrared Spectrum of the Dioxygen Species Adsorbed on Platinum".

Wednesday Evening, September 1, 1982

Session II: *Dynamical Processes at Surfaces*

Chairman: *W. Gadzuk*

- 7:30 p.m. *K. Schönhammer (Invited)*, and *O. Gunnarson, Universität Hamburg, West Germany, and *Max-Planck-Institut für Festkörperforschung, Stuttgart, West Germany, "Energy Dissipation at Metal Surfaces: Electronic Versus Vibrational Excitations".
- 8:00 p.m. Joachim Heidberg, *Ingo Hussle*, and Zoltan Szilagy, Universität Hannover, West Germany, "CO₂ Laser-Driven Separation of Binary Co-Adsorbates on Sodium Chloride Surfaces Under Ultra-High Vacuum".
- 8:16 p.m. *R. Viswanathan*, D. R. Burgess, Jr., P. C. Stair and E. Weitz, Northwestern University, Evanston, Illinois, "Laser-Induced Thermal Desorption of CO from Clean Polycrystalline Copper: Time-of-Flight and Surface Diffusion Measurements".
- 8:32 p.m. *S. Chiang*, R. G. Tobin and P. L. Richards, Lawrence Laboratory, Berkeley, California, "Infrared Emission Spectroscopy of CO on Ni".
- 8:48 p.m. *M. Persson*, E. Hellsing and B. I. Lundqvist, Chalmers University of Technology, "Electronic Damping Mechanism for Vibrations, Rotations and Translations of Adsorbates on Metal Surfaces".
- 9:04 p.m. *Coffee Break*
- 9:20 p.m. *T. Chuang (Invited)*, IBM Research Laboratory, San Jose, California, "Infrared Laser Stimulated Surface Processes".
- 9:50 p.m. *G. D. Kubiak*, G. Sitz, J. E. Hurst Jr., and R. N. Zare, Stanford University, Stanford, California, "The Exposure Dependence and Emission Spectrum of Chemiluminescence Produced During the Oxidation of Si(111) by O₂".
- 10:06 p.m. *N. Garcia*, J. A. Barker, and Inder P. Batra, IBM Research Laboratory, San Jose, California, "Crystallographic Determination of Metal Surfaces with Helium Scattering".

Thursday Morning, September 2, 1982

Session III: *Electron Loss Spectroscopy*
Chairman: *M. Nishijima*

- 8:15 a.m. *J. Demuth*, D. Schmeisser and P. Avouris (*Invited*), IBM Research Center, Yorktown Heights, New York, "Vibrational Spectroscopy of Adsorbates Utilizing Resonance and Impact Electron Scattering".
- 8:45 a.m. *L. H. Dubois*, and G. P. Schwartz, Bell Laboratories, Murray Hill, New Jersey, "High Resolution EELS Studies of Clean and Adsorbate Covered Semiconductor Surfaces".
- 9:01 a.m. *A. B. Anton*, N. R. Avery, B. H. Toby and W. H. Weinberg, California Institute of Technology, Pasadena, California, "The Chemisorption of Nitrogen on the (001) Surface of Ruthenium".
- 9:17 a.m. R. L. Strong, B. Firey, F. W. DeWette and *J. L. Erskine*, University of Texas, Austin, Texas, "Adsorbate Structure Modelling Based on EELS and Lattice Dynamical Calculations: Application to O/Al(111)".
- 9:33 a.m. *C. Nyberg* and C. G. Tengstal, Chalmers University of Technology, Sweden, "Vibrational Excitations of Hydrogen and Oxygen on Pd(100)".
- 9:49 a.m. *P. A. Thiry*, J. Ghijsen, J. J. Pireaux, and R. Caudano, Universitaires Notre-Dame de la Paix, Belgium, "High Resolution Electron Energy Loss Spectroscopic Study of the Interaction of Oxygen with Magnesium Single Crystal Surfaces".
- 10:05 a.m. *Coffee Break*
- 10:20 a.m. T. S. Rahman, *D. L. Mills*, and J. E. Black (*Invited*), University of California, Irvine, California, "Low Frequency Surface Resonance Modes in Electron Loss Spectroscopy".
- 10:50 a.m. *Michael R. McClellan*, F. Read McFeely, Massachusetts Institute of Technology, and John L. Gland, General Motors Research, Warren, Michigan, "Molecular and Atomic Oxygen Adsorption on the Kinked Pt(321) Surface".
- 11:06 a.m. V. Bortolani, A. Franchini, *F. Nizzoli*, and G. Santoro, Università di Modena, Italy, "Calculations of EELS Spectra of Ni(111) and Ni(100) with Adsorbed Oxygen".
- 11:22 a.m. *Paul S. Bagus*, *Inder P. Batra*, C. W. Bauschlicher Jr.* and R. Broer, IBM San Jose Research Laboratory, California, and *NASA Ames Research Center, Moffett Field, California, "Theoretical Calculation of Vibrations of Adsorbed Species".

Free Afternoon

Thursday Evening, September 2, 1982

Poster Session

5:00 - 7:00 p.m.

- P1** *N. R. Avery*, * B. H. Toby, A. B. Anton and W. H. Weinberg, *CSIRO, University of Melbourne, Australia and California Institute of Technology, Pasadena, California, "Electron Energy Loss Spectroscopic Studies of the Chemisorption of Acetone on the Ru(001) and Pt(111) Surfaces".
- P2** *Hans-Ottmar Beckmann*, State University of New York, "Ab Initio CI Investigation of the Interaction of a Hydrogen Atom with Li Clusters".
- P3** H. Y. Chin and *R. C. Benson*, The Johns Hopkins University, Laurel, Maryland, "Laser-Induced Decomposition of Sodium Azide".
- P4** S. L. Miles and *S. L. Bernasek*, Princeton University, Princeton, New Jersey and General Motors Technical Center, Warren, Michigan, "The Methoxy Intermediate on Mo(100) -- Effects of Surface Oxidation".
- P5** *Chi-Cong Chou*, C. B. Reed, John C. Hemminger and S. Ushioda, University of California, Irvine, California, "Raman Spectra of Pyridine Adsorbed on Ni(111)".
- P6** *P. A. Cox*, R. G. Egdell and P. D. Naylor, Inorganic Chemistry Laboratory, Oxford, England, "HREELS Studies of Adsorbates on Polar Solids: Water on Strontium Titanate".
- P7** A. Regis, *P. Dumas*, J. Corset, Laboratoire de Spectrochimie IR et Raman, Thiais, France, "SERS Study of Pyridine Vapor Exposed to Silver Substrates Electrochemically Prepared".
- P8** *O. Hardouin Duparc** and A. Maradudin, *Laboratoire d'Etude de Surface et Interface, Isen, France, and University of California, Irvine, "Roughness-Trapped Shear Horizontal Surface Acoustic Waves".
- P9** *Gary L. Esley*, General Motors Research Laboratories, Warren, Michigan, "Surface Raman Ellipsometry".
- P10** *Galen P. Fisher* and Gary E. Mitchell, General Motors Research Laboratories, Warren, Michigan, "A Vibrational Study of Ammonia Adsorbed on Ni(111) and Ni(110): Whither Goest the Metal-Nitrogen Stretch on FCC(111) Surfaces?"
- P11** *S. Gauthier*, J. Klein, A. Leger, S. De Cheveigne, C. Guinet, Universite Paris VII, France, "Experimental Study of Relative Intensities in Inelastic Electron Tunnelling Spectra."
- P12** *N. E. Glass* and A. A. Maradudin, University of California, Irvine, California, "Leaky Surface-Elastic Waves on Flat and Strongly Corrugated Surfaces for Isotropic Nondissipative Media".
- P13** *William G. Golden* and David D. Saperstein, IBM Instruments, Inc., San Jose, California, "Fourier Transform Infrared Reflection-Absorption Spectroscopy of Surface Species".

- P14** *B. E. Hayden* and A. M. Bradshaw, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, West Germany, "The Adsorption of CO on Pt(111) Studied by Infrared-Reflection-Absorption Spectroscopy".
- P15** W. Stenzel, H. Conrad, *B. Hayden*, K. Kretzschmar and A. M. Bradshaw, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, West Germany, "The Adsorption of NO on Ru(001) and Its Co-Adsorption with Oxygen Studied by Vibrational Spectroscopy".
- P16** *Friedrich M. Hoffmann* and Robert A DePaola, Exxon Corporate Research, Linden, New Jersey, "The Adsorption and Dehydrogenation of Cyclopentane on Ru(001) Characterized by High Resolution Electron Energy Loss Spectroscopy".
- P17** Joachim Heidberg, *Ingo Hussla* and Zoltan Szilagy, Universität Hanover, West Germany, "Infrared-Spectroscopic Investigation of the Adsorption of Methylfluoride on Sodium Chloride Surfaces under Ultra High Vacuum".
- P18** *L. L. Kesmodel* and J. A. Gates, Indiana University, Bloomington, Indiana, "Thermal Evolution of C₂H₂ and C₂H₄ on Pd(111) Studied by High-Resolution Electron Energy Loss Spectroscopy".
- P19** *K. Kunimatsu*, Hokkaido University, Sapporo, Japan, "Study of Adsorption of the Electrode/Solution Interface by In-Situ Infrared Reflectance Spectroscopy".
- P20** *David K. Lambert*, General Motors Research Laboratories, Warren, Michigan, "Electroreflectance Vibrational Spectroscopy: a New Surface Analysis Technique Using Diode Lasers".
- P21** *Harry J. Levinson*, R. G. Tobin and P. L. Richards, University of California, Berkeley, California, "Infrared Spectra of CO Adsorbed at Low Temperatures on Ni".
- P22** *B. H. Lee*, SRI International, Menlo Park, California, "Surface Enhanced Raman Spectroscopy of Palladium".
- P23** *L. Lynds* and B. A. Woody, United Technologies Research Center, East Hartford, Connecticut, "Non-Equilibrium Behavior on Pulsed Laser Evaporated Surfaces".
- P24** Michael Cates and *David R. Miller*, University of California, San Diego, California, "Measurement of Au(111) Surface Phonons by Low Energy Helium Scattering".
- P25** D. M. Lubman and *R. Naaman*, The Weizman Institute of Science, Rehovot, Israel, "Surface Enhanced Ionization".
- P26** *I. Pockrand*, C. Pettenkofer and A. Otto, Universität Düsseldorf, West Germany, "Oxygen, Water and Hydrocarbon Adsorption on Silver Films: A Raman Vibrational Study".
- P27** *Dieter Schmeisser** and J. E. Demuth, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, West Germany, and IBM Research Center, Yorktown Heights, New York, "Electronic Transitions of Ar, Xe, N₂, CO Physisorbed on Ag(111) and Al(111)".
- P28** *H. Suhl*, IBM Research Laboratory, San Jose, California, "Surface Enhanced Raman Scattering Phenomenon in Light of Recent Excitation Profile Measurements".

- P29** Brian J. Bandy, Michael A. Chesters, Bernard Keiller, Ian A. Oxton, C. E. Anson and *Norman Sheppard*, University of East Anglia, Norwich, England, "Vibrational Spectra of Ethylene and Acetylene on Metal Surfaces -- an Electron Energy Loss Study of Ethylene Adsorbed on Ni(111) and Its Carbided Surface and the Use of Metal-Cluster Analogies".
- P30** *Edward Siegel*, San Francisco, California, "Surface Vibration Correlation with d-Electron(Hole) Per Atom Ratio (d-Bandfilling) in CO Chemisorption on Supported Transition Metal Particles: Dominance of Hund's Rule and d-Electron Degeneracy in Real Supported Catalysts".
- P31** M. Oshawa and *W. Swětaka*, Tohoku University, Sendai, Japan, "Intensity Enhancement and Spectral Change in Raman Scattering of Mercaptobenzothiazole Adsorbed on Silver Electrode".
- P32** *B. H. Toby*, N. R. Avery*, A. B. Anton and W. H. Weinberg, California Institute of Technology, Pasadena, California, and *CSIRO, University of Melbourne, Australia, "An Electron Energy Loss Study of the Decomposition of Formic Acide on the (001) Surface of Ru".
- P33** *H. Ueba*, Toyama University, Takaoka, Toyama, Japan, "Vibrational State of Chemisorbed Molecules on Metal Surfaces".
- P34** *B. M. Davies* and J. L. Erskine, University of Texas, Austin, Texas, "Azimuthal Dependence of Impact Scattering in Electron Energy Loss Spectroscopy".
- P35** *N. Garcia*, IBM Research Laboratory, San Jose, California, and Universidad Autonoma de Madrid, Spain, "Exact Calculations of Scattered and Enhanced Fields of Electromagnetic Waves on Grating Surfaces".
- P36** *M. R. Philpott*, F. Barz*, J. G. Gordon II, and M. J. Weaver**, IBM Research Laboratory, San Jose, California, *Universität Bonn, West Germany, and **Michigan State University, East Lansing, Michigan, "Time Dependence of Surface Enhanced Raman Scattering During and After Oxidation-Reduction Cycles".
- P37** *Inder P. Batra*, IBM Research Laboratory, San Jose, California, "Investigation of Lateral Interactions in Chemisorption".

7:00 p.m. *Conference Banquet*

Session IV: *Electron Energy Loss Spectroscopy II*

Chairman: *W. Göpel*

- 8:30 p.m. *W. Erley*, and H. Ibach, KFA Julich, West Germany, "The Adsorption of Ammonia on a Fe(110) Single Crystal Surface Studied by High Resolution Electron Energy Loss Spectroscopy (EELS)".
- 8:45 p.m. *Simon R. Bare*, Peter Hofmann, Mark Surman and David A. King, University of Liverpool, England, "Spatial Intensity Distributions from Electron Impact Scattering Modes: W(100)p(1×1)H".
- 9:02 p.m. *M. Nishijima*, S. Masuda and M. Onchi, Kyoto University, Japan, "Hydrogen Chemisorption of Ni(110) by High-Resolution Electron Energy-Loss Spectroscopy".
- 9:18 p.m. *J. A. Schaefer*, and W. Göpel, Montana State University, "Identification of Surface Vibrations on Clean and Oxygen Covered Pt(111) Surfaces with High Resolution Electron Energy Loss Spectroscopy (EELS)".
- 9:34 p.m. *B. E. Koel*, and G. A. Somorjai, University of California, Berkeley, California, "Vibrational Spectroscopy Using HREELS of Benzene Adsorbed on the Rh(111) Crystal Surface".
- 9:50 p.m. M. Chtaib, P. A. Thiry, J. P. Deirue, *J. J. Pireaux*, and R. Caudano, Universitaires Notre-Dame de la Paix, Belgium, "HREELS Study of Formic Acid Adsorption on Gold (110) and (111) Surfaces".

Friday Morning, September 3, 1982

Session V: *Raman and Surface Enhanced Raman Scattering*
Chairman: *M. R. Philpott*

- 8:30 a.m. *A. Otto (Invited)*, Universität Düsseldorf, West Germany, "On the Contribution of Charge Transfer Excitations to SERS".
- 9:00 a.m. J. C. Tsang, *Ph. Avouris* and J. R. Kirtley, IBM Research Center, New York, "Multichannel Raman Spectroscopy of Unroughened Noble Metal and Non-Noble Metal Tunnel Junctions".
- 9:16 a.m. *Frank J. Adrian*, The Johns Hopkins University, Laurel, Maryland, "Charge Transfer Effects in Surface Enhanced Raman Scattering".
- 9:32 a.m. *George C. Schatz* and P. K. K. Pandey, Northwestern University, Evanston, Illinois, "Ab Initio Studies of Molecules Adsorbed onto Metal Clusters: Application to Surface Enhanced Raman Spectroscopy (SERS)".
- 9:48 a.m. *I. Pockrand*, Universität Düsseldorf, West Germany, "Surface Enhanced Raman Scattering (SERS) from Silver, Copper, and Gold Films in UHV: Excitation Spectra".
- 10:04 a.m. D. A. Weitz and S. Garoff, Exxon Research and Engineering, Linden, New Jersey, J. Gersten, City University of New York, and *A. Nitzan*, Northwestern University, Evanston, Illinois, "Resonance Raman Scattering and Fluorescence of Molecules Adsorbed on Silver Island Films".
- 10:20 a.m. *Coffee Break*
- 10:40 a.m. *C. Murray (Invited)*, Bell Laboratories, Murray Hill, New Jersey, "Using Surface Enhanced Raman Scattering to Study Adsorbate Vibrations".
- 11:10 a.m. *B. Pettinger (Invited)*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, West Germany, "Influence of Foreign Metal Atoms on Local and Non-Local Processes in Surface Enhanced Raman Scattering".
- 11:40 a.m. *Alan Champion*, University of Texas, Austin, Texas, "Surface Raman Spectroscopy without Enhancement".

Friday Afternoon, September 3, 1982

Session VI: *Infrared Absorption and Reflection Spectroscopy*

Chairman: *D. L. Allara*

- 1:30 p.m. *J. Overend (Invited)*, University of Minnesota, Minneapolis, Minnesota, "Infrared Spectroscopy of Adsorbates on Low-Area Surfaces: the Advantage of a Photons-in, Photons-out Technique".
- 2:00 p.m. *D. L. Allara* and R. G. Nuzzo, Bell Laboratories, Murray Hill, New Jersey, "The Application of Reflection Infrared and Surface Enhanced Raman Spectroscopy to the Characterization of Chemisorbed Organic Disulfides on Au".
- 2:18 p.m. *H. Yamada*, N. Tani and Y. Yamamoto, Kwansai Gakuin University, Japan, "Infrared Specular Reflection and SERS Spectra of Molecules Adsorbed on Smooth Surfaces".
- 2:34 p.m. *F. Träger*, T. J. Chuang and H. Coufal, IBM Research Laboratory, San Jose, California, "Surface Photoacoustic Spectroscopy - a New Technique for the Study of Surface Vibrations".
- 2:50 p.m. *Gary L. Esley*, General Motors Research Laboratory, Warren, Michigan, "Enhanced Adsorbate Raman Scattering and Surface Plasmon Radiation".
- 3:06 p.m. *Coffee Break*
- 3:25 p.m. John J. Low IV and *W. A. Godard III (Invited)*, California Institute of Technology, Pasadena, California, "Theoretical Vibrational Frequencies for NH_x and CH_x Reactive Intermediates on Nickel(100) and Nickel(111) Surfaces".
- 3:55 p.m. *J. F. Rabolt*, F. C. Burns, N. E. Schlotter and *J. D. Swalen*, IBM Research Laboratory, San Jose, California, "Molecular Orientation in Thin Monolayer Films by Infrared Spectroscopy".
- 4:11 p.m. *G. N. Zhizhin*, E. A. Vinogradov, M. A. Moskalova and V. A. Yakovlev, USSR Academy of Sciences, "Applications of Vibrational Spectroscopy to Surface Analysis of Thin Films".

Friday Evening, September 3, 1982

Session VII: *Beam-Surface Scattering; Surface Phonons*

Chairman: *D. R. Miller*

- 8:00 p.m. *G. Benedek (Invited)*, University of Milan, Italy, "The Spectroscopy of Surface Vibrations by Atom Scattering".
- 7:30 p.m. *D. Auerbach (Invited)*, IBM Research Laboratory, San Jose, California, "Internal State Distributions of Molecules Scattering and Desorbing from Surfaces".
- 8:30 p.m. Chin-fan Yu, Charles S. Hogg, and *Steven J. Sibener*, The University of Chicago, Illinois, "Hydrogen Interaction with Ag(111): Scattering Resonances, Vibrational Levels, and Interaction Potential Determination".
- 8:46 p.m. *J. W. Gadzuk*, Uzi Landman, E. J. Kuster, C. L. Cleveland and R. N. Barnett, National Bureau of Standards, Washington, D.C., "Ro-Vibrational Excitation within the Infinite Cone Well: Desorption".
- 9:02 p.m. *Coffee Break*
- 9:20 p.m. *M. Nielsen*, J. Bohr and K. Kjaer (*Invited*), Research Establishment Riso, Denmark, "Physisorbed Monolayer on Graphite Studied by Neutron and X-Ray Diffraction".
- 9:50 p.m. D. Djafari-Rouhani, L. Dobrzynski and *O. Hardouin Duparc*, Laboratoire des Surfaces et Interfaces ISEN, France, "Surface Phonons in Superlattices".
- 10:06 p.m. *A. G. Equiluz* and A. A. Maradudin, University of California, Irvine, California, "Bound States of Two Surface Phonons at a Crystal Surface".
- 10:22 p.m. *G. J. Pinas* and A. Maradudin, University of California, Irvine, California, "High Frequency Localized Vibration Modes at a Stepped Surface".

Saturday Morning, September 4, 1982

Session VIII: *Electron Tunnelling Spectroscopy;
Surface Enhanced Raman Studies in Electrochemistry*
Chairman: *H. Weinberg*

- 8:00 a.m. *P. Hansma (Invited)*, University of California, Santa Barbara, California, "Tunnelling Spectroscopy as a Probe of Adsorbate-Surface Interactions".
- 8:30 a.m. *K. Hipp (Invited)*, Washington State University, Pullman, Washington, "The Interaction of Ions and Easily Ionized Species with Oxide Surfaces as Studied by Tunnelling Spectroscopy".
- 9:00 a.m. *J. F. Owen*, T. T. Chen and R. K. Chang and B. L. Laube, Yale University, New Haven, Connecticut, "Surface Enhanced Raman Scattering of Water on a Ag Electrode".
- 9:16 a.m. *Joel W. Russell*, Oakland University, Rochester, Minnesota, and Alan Bewick, Southampton University, England, "The Bonding of Species in the Electrode Solution Interfacial Region".
- 9:32 a.m. *Rolf Dornhaus*, Physikalisches Institut der RWTH Aachen, West Germany, "Spectral Properties of Molecules Adsorbed on Metal Surfaces from Surface Enhanced Raman Scattering (SERS)".
- 9:48 a.m. *Coffee Break*

Session IX: *Conference Summary and Outlook*
Chairman: *H. Morawitz*

- 10:10 a.m. *T. B. Grimley*, Conference Overview: Theory
- 10:55 a.m. *H. Ibach*, Conference Overview: Experiment
- 11:40 a.m. *Conference Conclusion*

Charge Transfer Effects in Surface Enhanced Raman Scattering*

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ABSTRACT

Surface enhanced Raman scattering (SERS) due to charge-transfer interactions between the adsorbed molecule and the metal surface is analyzed using the semiempirical Wolfsberg-Helmholz method¹ to relate the molecule-surface interactions and the resulting charge-transfer states to the overlap integrals between the metal conduction-band orbitals and an acceptor or donor molecular orbital of the molecule. Calculations for the model system of ethylene adsorbed on silver, with charge-transfer excitation of an electron from the metal to the antibonding ethylene π^* orbital, show that charge-transfer Raman enhancements of the order of 10 to 1000 are possible if the charge-transfer band is partially resonant with the exciting radiation. The net enhancement is the product of the charge-transfer gain and the electrodynamic enhancement due to plasmon resonances at surface roughness elements. Symmetric vibrations usually will be enhanced substantially more than nonsymmetric ones by charge-transfer because, in contrast to nonresonant Raman scattering, the vibrational coupling is primarily Franck-Condon (due to differences in the equilibrium nuclear configurations of the ground and excited charge-transfer states and the resulting nonorthogonality of different vibrational sublevels of these states) rather than Herzberg-Teller (due to vibrationally induced changes in the electronic wave functions). The charge-transfer mechanism is selective with the most enhanced vibrations involving those atoms which experience the greatest change in electron density between the ground and excited charge-transfer state. A recent report of SERS for benzene on platinum,² strongly suggests charge-transfer enhancement because the electromagnetic-field-enhancing plasmon resonances are strongly damped in this metal.

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¹ M. Wolfsberg and L. Helmholz, J. Chem. Phys. 20, 837 (1952).

² W. Krasser and A. J. Renouprez, Solid State Comm. 41, 231 (1982).

CHEMISORBED OXYGEN VIBRATIONS
ON NICKEL (110) SURFACES

- by -

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ABSTRACT

Using a simple tight-binding scheme to describe the nickel d states and the oxygen p states, we calculate the positions and the vibration frequencies of chemisorbed oxygen atoms on a nickel (110) surface. This model has been successfully used to study the influence of chemisorbed oxygen atoms on nickel (100) and (111) surface vibrations.¹

We have considered three adatom positions:

- a. the short bridge site (along dense $[1\bar{1}0]$ rows),
- b. the two-fold hollow site,
- c. the long-bridge site (along non-dense $[001]$ rows).

And two superstructures to evaluate the vibration frequencies at low and high oxygen coverages:

- a. the observed (2x1),
- b. a hypothetical (2x2).

The comparison between our results and the high resolution electron energy loss measurements² suggest a long-bridge chemisorption site at low and high coverages. Such a site agrees with the Rutherford backscattering measurements.³

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2. S. Masuda, M. Nishijima, Y. Sakisaka, M. Onchi, Phys. Rev. B25, 863 (1982); A. M. Baro, L. Olle (to be published).
3. J. A. Van Den Berg, L. K. Verheij, D. G. Armour, Surf. Sci. 91, 278 (1980); R. G. Smeenk, R. M. Tromp, J. F. Van Der Veen, F. W. Saris, Surf. Sci. 95, 156 (1980); M. Schuster, C. Varelas (to be published).

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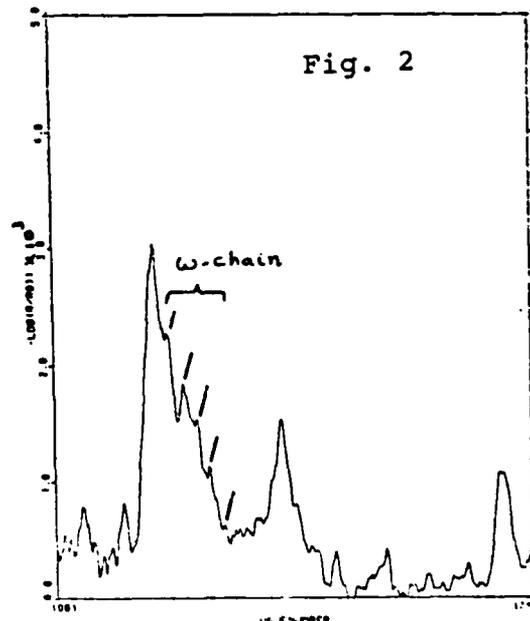
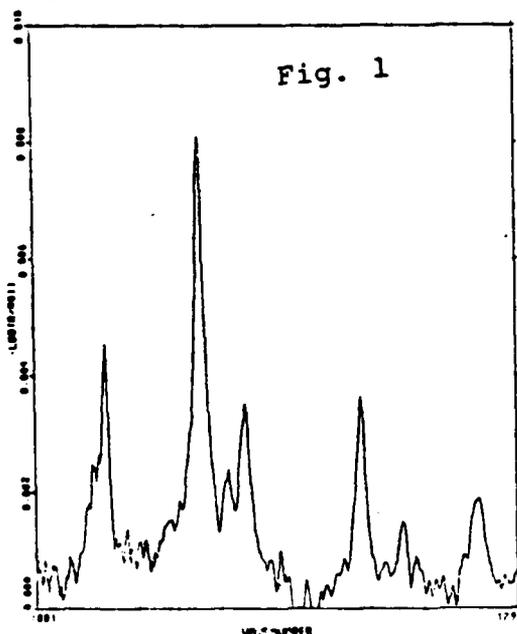
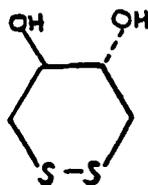
D. L. Allara and R. G. Nuzzo

We have found that a variety of organic molecules containing the S-S linkage strongly adsorb on freshly evaporated or electrochemically cleaned gold surfaces. Adsorption stops at monolayer coverage and the packing density of the molecules can be close to the limit set by the size of the molecules. Reflection infrared spectra show that the films are strongly oriented and in the case of long alkyl-chain-substituted disulfides the films have structures similar to those of Langmuir-Blodgett type films.

Most of the films were prepared by freshly evaporating gold onto polished single crystal silicon substrates. Immediately after the deposition the films were removed from the vacuum system (under N_2) and placed in solutions of the disulfides. After rinsing the films were examined by ellipsometry at 6328Å and 4420Å and in general, the results are consistent with monolayer structures with close packing similar to bulk crystallites. Infrared spectra were obtained using a Digilab 15B Fourier transform infrared spectrometer with a high f/number optical system and small beam spot size for glancing reflection. Spectra were obtained between 800 and 3200 cm^{-1} using a mercury cadmium telluride detector. The spectrum of a monolayer of the di-p-nitrobenzoate ester of trans-o-Dithiane-4,5-diol is shown in Figure 1. The structure of the diol is given below.

The spectrum of the monolayer of the di-ester of the C_{16} acid ($n-C_{15}H_{31}CO_2H$) is given in Figure 2. Notice the alkyl chain mode band series in the monolayer spectrum which indicates crystalline packing of the chains. The infrared spectra are consistent with oriented structures which maximize packing densities. No direct evidence is yet available for defining a Au-S bond. However, a sample in which the monolayer of the p-nitrobenzoate derivative has been covered with 400Å average thickness of CaF_2 and 200Å of smooth silver has yielded an enhanced Raman spectrum ($\lambda(\text{excite})=4880\text{Å}$, ~ 50 mW power) in which the normally strong S-S stretching mode observed at 504 cm^{-1} in bulk samples is absent in the monolayer.

These studies demonstrate an application of surface vibrational spectroscopy to defining molecular structures at surfaces. Work is presently underway to quantitatively calculate molecular orientation from the infrared spectra and to more carefully determine the extent of any ordering in appropriate monolayers.



"The Chemisorption of Nitrogen on the (001) Surface of Ruthenium"^{†*}

by

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Abstract

High resolution electron energy loss spectroscopy, thermal desorption mass spectrometry, and low-energy electron diffraction have been used to investigate the molecular chemisorption of N₂ on Ru(001) at 75 K and 95 K. Adsorption at 95 K produces a single first order thermal desorption feature with a desorption rate maximum shifting from 128 K to 120 K with increasing surface coverage. Saturation at 95 K occurs for exposures greater than 4 L and produces a ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern. Electron energy loss spectra recorded under these conditions show two dipolar modes—the frustrated translation of the N₂ molecule with respect to the surface [$\nu(\text{Ru-N}_2)$] at 300 cm⁻¹ and the N-N stretch [$\nu(\text{N-N})$] at 2220 cm⁻¹—indicating adsorption at on-top sites with the axis of the molecule standing perpendicular to the surface. Quantitative coverage estimates for saturation at 95 K yield $\theta = 0.35 \pm 0.07$, implying formation of a complete ($\sqrt{3} \times \sqrt{3}$)R30° ($\theta = 0.33$) ordered overlayer. Adsorption at 75 K produces a second thermal desorption feature, appearing initially at 100 K for an exposure of 1 L and shifting with increasing coverage to 88 K for a saturation exposure of 3 L. Thermal desorption measurements performed after sequential exposure to ¹⁴N₂ and ¹⁵N₂ verify the existence of two distinct binding states on the surface [and rule out the possibility of a compression structure as observed for the adsorption of CO on Ru(001).¹] The probability of adsorption increases by a factor of two from its zero-coverage value when the low temperature state begins to populate. Thermal desorption spectra obtained after saturation coverage at 75 K show decreased population of the high temperature state relative to spectra corresponding to saturation coverage at 95 K, indicating nonequilibrium adsorption at 75 K with population of the low temperature state occurring at the expense of population in the high temperature state. Coverage estimates for saturation at 75 K give $\theta = 0.50 \pm 0.10$ and indicate that the surface density of N₂ in the low temperature state is approximately twice that in the high temperature state. Electron energy loss spectra recorded for adsorption at 75 K show only two dipolar modes: $\nu(\text{Ru-N}_2)$, appearing initially at 280 cm⁻¹; and shifting with increasing coverage to 300 cm⁻¹ at saturation, and $\nu(\text{N-N})$, appearing initially at 2240 cm⁻¹ and shifting with increasing coverage to 2195 cm⁻¹ at saturation. The intensities of these loss features increase monotonically with total surface coverage of both states observed in the thermal desorption spectra.

¹ E. D. Williams and W. H. Weinberg, *Surface Sci.* **82**, 93 (1979).

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INTERNAL STATE DISTRIBUTIONS OF MOLECULES SCATTERING AND DESORBING FROM SURFACES

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ABSTRACT:

Recently there has been considerable interest in the application of state specific detection techniques to molecules interacting with surfaces. Laser induced fluorescence, multiphoton ionization, and IR excitation of molecules have all been used to study rotational and vibrational distributions of molecules which scatter or desorb from a surface. In direct inelastic scattering of NO from Ag(111), coupling of translational to rotational motion is found to be a dominant channel. Vibrational excitation, although observable, has a very small probability. Measured rotational state distributions exhibit several interesting features including rotational rainbows and rotational alignment. Such measurements give quite sensitive information about the angular variation of the molecule surface interaction potential. For molecules bound on the surface this aspect of the potential is connected to low frequency librational modes. The transition from the bound to free molecule can be studied by making measurements of internal state distributions for desorbing molecules. Contrasting results are found on different systems. Cavanagh and King, using temperature programmed desorption of NO from Ru(001), measured a rotational temperature of 235 K while the surface temperature was 455 K at the desorption maximum. We have studied NO desorption from Ag(111) in a scattering experiment by studying molecules which trap on the surface and then desorb. This method has the advantage that a far wider range of temperatures can be studied than using temperature programmed desorption. The trapping desorption channel can be distinguished from direct inelastic scattering on the basis of the incident energy dependence and angular and velocity distributions. For temperatures less than 300 K, NO desorbs from Ag(111) with a $T_R \approx T_S$ while for higher surface temperatures, T_R is less than T_S with increasing deviations at larger T_S .

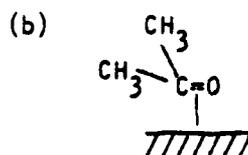
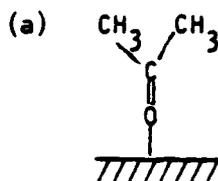
"Electron Energy Loss Spectroscopic Studies of the Chemisorption of Acetone on the Ru(001) and Pt(111) Surfaces"*

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Abstract

Vibrational spectra of acetone chemisorbed on the close-packed (001) surface of Ru and (111) surface of Pt have been recorded as a function of annealing temperature using high resolution electron energy loss spectroscopy. The energy loss spectrometers and ultrahigh vacuum systems used for these studies have been described previously (1,2).

Spectra corresponding to multilayers of acetone were assigned by comparison to the IR and Raman spectra of gas and liquid phase acetone (3). At all temperatures on Pt(111) and at 80 K on Ru(001), spectra measured at submonolayer coverage were similar to the multilayer spectra. This is interpreted as an "end-on bonded" form of acetone on both Ru(001) and Pt(111), (a) below. An increase in the intensity of the $\nu(\text{C}=\text{O})$ mode relative to the intensity of the other modes with increasing coverage is observed on Pt(111). This may well be due to a change in the C-O-Pt bond angle (toward 180°).



Acetone desorbs without significant decomposition from Pt(111) upon heating. Furthermore, there are no additional stable surface intermediates observed in EELS other than end-on bonded acetone, although this is not surprising since the temperature of desorption of the end-on bonded acetone (200 K) is coincident with the temperature at which slight decomposition occurs. On Ru(001), however, annealing to approximately 150 K induces the occurrence of a different stable intermediate on the surface, the electron energy loss spectrum of which is consistent with a "side-on bonded" form of acetone, (b) above. Annealing the surface on which this intermediate is present to 250 K results in partial decomposition to adsorbed carbon monoxide and methyl groups. Subsequent annealing to 290 K results in further decomposition to adsorbed carbon monoxide, CH_x fragments ($x < 3$), and hydrogen. Final annealing to 350 K leaves only chemisorbed carbon monoxide and carbon with some hydrogen that has not yet desorbed. These results indicate that decomposition proceeds initially by C-C bond cleavage, followed rapidly by C-H bond cleavage with hydrogen desorption, a reaction path which is consistent with the initial presence of a side-on bonded species. Thermal desorption results indicate that hydrogen desorbs over a broad temperature regime between 300 and 420 K, carbon monoxide desorbs in a single desorption limited step with a peak temperature of 480 K, and carbon remains adsorbed irreversibly.

¹G. E. Thomas and W. H. Weinberg, Rev. Sci. Instrum. 50, 497 (1979).

²N. R. Avery, Appl. Surface Sci. (in press).

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*Supported by the National Science Foundation under Grant No. CHE77-16314.

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Multichannel Raman Spectroscopy of Unroughened Noble Metal and Non-Noble Metal Tunnel Junctions

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The use of surface enhanced Raman spectroscopy (SERS) as a tool for interfacial analysis is limited by the small number of substrates which support the necessary conduction electron resonances in the visible. Recently, however, it has been shown that multichannel optical detectors have sufficient sensitivity to allow the observation of Raman scattering from adsorbates on arbitrary substrates.

We have used a multichannel detection system to study the Raman scattering from smooth noble metal tunnel junctions, e.g. Al/AlO_x/Ag, and non-noble metal junctions, e.g. Al/AlO_x/Sn doped with p-nitrobenzoic acid (PNBA) and p-aminobenzoic acid (PABA). These systems have previously been inaccessible to Raman scattering.

The Raman scattering from the smooth Ag junctions is enhanced by over 10². This enhancement is much smaller than those observed on the deliberately roughened systems previously studied. This enhancement is due to either the presence of microscopic roughness due to the evaporated films or the direct interaction of the molecules and the metals of the tunnel junctions. The observation of significant changes in the Raman spectrum of PNBA in the junction as compared to PNBA in the doping solution, supports the latter possibility.

Although the use of smooth Al/AlO_x and rough Sn films on glass substrates does not produce a significant (>5 x) enhancement of the Raman spectrum of PABA, a significant enhancement is observed in the Sn tunnel junctions. The enhancement increases with increasing Sn film thickness, saturates at a maximum value of 500-1000 and begins to decrease as the Sn film becomes continuous and smooth as seen both in electron microscopy and the film resistivity. This enhancement is connected with the discontinuous nature of the Sn overlayer. The magnitude of our enhancement and its dependence on the Sn thickness suggest that it results from the interaction of the optical fields with the discontinuous Sn particles and the excitation of the evanescent fields of the Al surface plasmons by the local fields of the Sn particles. This is a new configuration for surface Raman scattering since the coupler is non-resonant and distinct from the surface supporting the conduction electron resonances.

Spatial Intensity Distributions from Electron Impact Scattering Modes:
W{100}p(1 x 1)H

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For the W{100}p(1 x 1)H system calculations of the loss intensities for the inelastic scattering of low energy electrons with one-quantum energy loss to the adsorbate vibrations have been performed by Aers et al.¹, using LEED wavefunctions and a muffin tin potential model. These angular dependencies show a wealth of structure in the loss currents, in particular if the detector is moved out of the plane of incidence. Previously only in-plane "off specular" experimental data had been reported.²

We have now recorded a large data base of high resolution inelastic electron loss spectra for saturation coverage of atomic H adsorbed on W{100} at 300 K. In agreement with earlier work² we find only a single electron loss (130 meV) in the specular direction, while away from the specular direction additional losses at 80 meV and 160 meV appear. These losses correspond to the symmetric stretching, the wagging and asymmetric stretching modes respectively of hydrogen atoms occupying a C_{2v} bridge site. In general agreement with the theoretical predictions,¹ we also find large intensity variations for all these modes particularly in backscattering directions and out of the plane of incidence. We find for example that the wagging mode is ~5 times more intense than the other modes for certain angles.

The origin of these spatial intensity variations, and their usefulness in adsorbate structure determination, will be discussed. It is pointed out that in some cases the signal enhancement with electron collection in the plane orthogonal to the incidence plane may allow the observation of otherwise weak impact modes.

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2. W. Ho, R.F. Willis and E.W. Plummer, Phys. Rev. Letters 40 (1978) 1463.

THEORETICAL CALCULATION OF VIBRATIONS OF ADSORBED SPECIES**P. S. BAGUS, I. P. BATRA, C. W. Bauschlicher, Jr* and R. Broer****IBM Research Laboratory
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The chemisorption of oxygen on Lithium, Aluminum, and Copper surfaces has been investigated using the ab initio Hartree-Fock cluster model. These substrates have the possibility for different bonding in that Li is a simple s metal, Al an s, p, and Cu an s, p, d metal. In all cases we have calculated binding energy curves as a function of the oxygen-metal distance. Using these curves, we have derived oxygen-metal normal vibrational frequency, the equilibrium bond distance, and the chemisorption bond strength. We have compared the calculated vibrational energy with electron energy loss spectroscopic (EELS) data for Al and find a satisfactory agreement.

Theoretical results are also presented for O adsorbed on Ni(100) and compared with the EELS data. The results for both O/Al and O/Ni provide a basis for evaluating the reliability of the cluster model calculations.

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INVESTIGATION OF LATERAL INTERACTIONS IN CHEMISORPTION

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It is believed that lateral interactions play an important role in chemisorption site selection. With the advent of angular resolved and polarization dependent photoemission spectroscopies, one is able to compare computed band structure with angular resolved photoemission (ARP) data. This advance coupled with theoretical calculations provides an excellent opportunity for investigating direct (adsorbate-adsorbate) and indirect (adsorbate-substrate-adsorbate) *lateral* interactions at surfaces.

We have investigated the chemisorption of atomic and molecular oxygen on aluminum using Linear Combination of Atomic Orbital techniques. Electronic structures of isolated monolayers of O and O₂, in configurations appropriate to the surface under consideration, have also been calculated. By comparing the calculated results with the ARP data we find that for O/Al(111) chemisorption system, monolayer calculations (direct lateral interactions only) provide a good framework for interpreting the data. For O₂ monolayer the direct lateral interactions are also appreciable and lead to significant dispersion in the calculated energy bands. We therefore believe that it is also important to include direct lateral interactions in calculating normal vibrational modes of adsorbed species.

We also examined the chemisorption of CO on Pd(100). For this molecular chemisorption case dispersions of 4 σ , 5 σ + 1 π bands have been measured.¹ We computed the electronic structure for two dimensional isolated layers of CO in ordered configurations observed on a Pd(100) surface. The calculations were performed as a function of coverage. We satisfactorily accounted for the shape and width of the 4 σ - derived band with this direct lateral interaction only model. The calculated dispersion for 5 σ - and 1 π - derived bands did not agree with the observations.¹ This demonstrated the need for including indirect lateral interactions among adsorbates. From these studies we conclude that direct lateral interactions have prominent effects in geometrical arrangements of adsorbed layers. Observed and calculated energy band dispersions also establish the need for incorporating direct lateral interactions in normal vibrational modes calculations.

1. I. P. Batra, K. Hermann, A. M. Bradshaw, and K. Horn, *Phys. Rev. B* **20**, 801 (1979).

Ab Initio CI Investigation of the Interaction
of a Hydrogen Atom with Li Clusters

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Correlation effects are important for the proper description of the electronic structure of the clusters which can serve as models for the interaction between an H-atom and the (100) or/and (110) bcc-Li-surfaces. A majority of the clusters investigated exhibits lowest singlet and lowest triplet states with almost degenerate energies. The models used to describe the interaction of hydrogen with lithium surface show that a dissolution of hydrogen atoms inside the Li lattice in interstationary positions is very probable when the less "compact" (100) bcc surface is exposed to hydrogen. The more "compact" (110) surface should also allow the entry of an H-atom inside the Li-lattice, although under energetically less favorable conditions. These consequences of the study with rigid Li-cluster models would certainly be even more pronounced if the relaxation effects were taken into account. It is generally observed that a smaller number of nearest neighbors in the plane perpendicular to the line of approach of the H-atom favors stronger bonds to the hydrogen atom. This fact can cause higher surface activity if irregularities in the form of "peaks", "ridges" or "hills" are present in the surface. The higher surface activity is indicated by an increase in the H concentration inside the region of the irregularities. This effect is enhanced when the surface irregularities have a high degree of biradicaloid character.

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THE SPECTROSCOPY OF SURFACE VIBRATIONS BY ATOM SCATTERING

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Abstract

The recent progress in the production of highly monochromatic atomic beams is opening new perspectives in surface physics, having made way to a full determination of the surface vibrational structure. A short review is presented on the direct measurement of surface phonon dispersion curves, first achieved by Brusdeylins, Doak and Toennies in alkali halides, from time-of-flight (TOF) spectra of scattered He atoms. A comparison is made with the existing theories of surface phonons in ionic crystals. The state-of-the-art in the theory of inelastic scattering processes is briefly illustrated in order to discuss the theoretical interpretation of TOF spectra. The one-phonon energy-loss spectra of He scattered from LiF(001) calculated for a hard corrugated surface model are found to be in general good agreement with the experimental TOF spectra. From such a comparison evidence is obtained i) that one-phonon processes are predominant, and ii) that in addition to Rayleigh waves important contributions to the inelastic scattering come from the surface-projected density of bulk phonons.

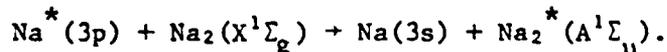
Important effects due to inelastic resonances with surface bound states are put in evidence and explained by simple kinematical considerations. The possible determination of Rayleigh wave dispersion curves from angular distributions exploiting the kinematical focussing effect is finally discussed.

LASER-INDUCED DECOMPOSITION OF SODIUM AZIDE

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The decomposition of sodium azide, NaN_3 , has been studied using a pulsed CO_2 laser. The mode of thermal decomposition is thought to involve the dissociation of the azide ion into the azide radical and free electron¹. The electrons recombine with the cations (or more readily with a cation that is associated with a cluster of free metal atoms), and the azide radicals recombine in the gas phase (and possibly on the surface) to form free nitrogen. With such large amounts of energy (203 kcal/mole) liberated in the recombination of the azide radicals, it is not surprising that emission has been observed from excited species. In flow-tube experiments of NaN_3 decomposition at low pressure, emission has been observed from sodium atoms, nitrogen molecules, and as yet unidentified species¹. The objective of the present experiments is to use the laser-induced decomposition technique we have developed so that the chemiluminescence can be measured with the solid in the detector field of view rather than downstream in a flow-tube. The technique is advantageous for observing transient excited species since effects caused by processes occurring on the sample cell walls are minimized. Because the solid is in the field of view, chemiluminescence from surface reactions can also be detected.

A pulsed CO_2 laser was used as the radiant heat source to decompose the NaN_3 . The visible chemiluminescence spectrum was measured with an optical multichannel analyzer that was equipped with various gratings to obtain a range of spectral dispersions across the detector array. Near the threshold energy, the emission spectrum consisted of the $\text{Na } 3p \rightarrow 3s$ transition at 589 nm (Na D-line) and a series of partially resolved bands near the Na D-line. This broadband emission has not been observed in other experiments¹. The emission was most prominent after the azide pellet had been irradiated several times, and dark spots were visible in the pellet. For incident laser energies below 70 mJ, ablation did not appear to occur (the pellet surface remained smooth), although measurable pressure rises indicated that decomposition was occurring. Raman spectra have been obtained for the irradiated material. It appeared that decomposition was occurring below the pellet surface to form sodium, which remained in the crystal lattice; the nitrogen was evolved, which resulted in a pressure rise. For laser energies below 70 mJ, the emission appeared to originate from the azide surface. The broadband emission is not characteristic of any excited N_2 emission nor is it characteristic of the bound-free emission from plasmas. The broadband emission was not observed in the laser-induced decomposition of potassium azide and rubidium azide, which suggests that the emitting species contains sodium. Although the emission band is not consistent with thermally excited Na_2 , it is consistent with Na_2^* that is formed by an atom-molecule exchange process:



This excitation mechanism populates high vibrational levels close to the dissociation limit and results in emission bands near the atomic line, which is in agreement with the experiments.

¹L. G. Piper, R. H. Krech, and R. L. Taylor, *J. Chem. Phys.*, 71, 2099, (1979) and references therein.

The Methoxy Intermediate on Mo(100)
Effects of Surface Oxidation

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and

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Methanol absorption and decomposition was characterized on clean and two distinct molybdenum (100) surfaces using high resolution electron energy loss spectroscopy and temperature programmed reaction spectroscopy. A methoxy intermediate was found on both the clean and partially oxidized surfaces but not on the completely oxidized surface. The adsorbed methoxy was bound more tightly on the clean surface than on the partially oxidized surface. No dissociative methanol adsorption was observed on the completely oxidized surface. Surface passivation correlated directly with the degree of surface oxidation.

Surface Raman Spectroscopy

Without Enhancement

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Using multichannel optical detection to improve efficiency, we have observed Raman scattering from submonolayer concentrations of molecules adsorbed on well-characterized single crystal surfaces. Since our method does not require enhanced cross sections, it is more widely applicable than SERS. We will compare our technique with other surface vibrational spectroscopies, addressing such areas as selection rules, detection limits, and applications such as heterogeneous catalysis and electrochemistry.

The Reflection-Absorption Infrared Spectrum of the Dioxygen Species
Adsorbed on Platinum

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The reflection-absorption infrared spectrum of oxygen adsorbed at 80K on a (111) recrystallized platinum foil, recorded using a Digilab FTS 14 Fourier transform spectrometer, is described. A single band at 875 cm^{-1} is observed at saturation coverage in agreement with earlier electron energy loss (EEL) studies. The band is inherently quite broad (half width $\sim 20\text{ cm}^{-1}$) and shifts from $845 \pm 5\text{ cm}^{-1}$ to 875 cm^{-1} with increasing surface coverage. Experiments using $^{16}\text{O}_2$, $^{18}\text{O}_2$ and an equilibrated mixture of these isotopes ($^{16}\text{O}_2$ 25%, $^{18}\text{O}_2$ 25%, $^{18}\text{O}^{16}\text{O}$ 50%) confirm that the band is due to a dioxygen species.

The results are discussed in terms of a model in which the oxygen-oxygen bond of the adsorbate is parallel to the metal surface and the high intensity of the reflection-absorption band results entirely from dynamic metal-adsorbate charge transfer. This model also accounts for the large inherent width of the reflection-absorption band.

The effective charge, e^* , calculated from the intensity of the reflection-absorption band is in good agreement with that calculated from the EEL spectrum assuming a dipole scattering mechanism.

INFRARED EMISSION SPECTROSCOPY OF CO ON Ni*

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We report the first observation of thermally emitted infrared radiation from vibrational modes of molecules adsorbed on clean, single-crystal metal surfaces. The observation of emission from CO adsorbed on Ni demonstrates the surface sensitivity of a novel apparatus for infrared vibrational spectroscopy, with a resolution of 1 to 15 cm^{-1} over the frequency range from 330 to 3000 cm^{-1} . These capabilities should make possible detailed frequency and linewidth measurements at the frequencies characteristic of both adsorbate-substrate and molecular vibrations. The single crystal sample is mounted in an ultra-high vacuum system equipped with surface preparation and characterization facilities, such as LEED, Auger, and thermal desorption spectroscopies. Thermal radiation from the room temperature sample is focused onto the entrance slit of a liquid helium-cooled grating spectrometer. Results of measurements of frequencies and linewidths of CO on single-crystal Ni surfaces, as a function of coverage, will be discussed.

The sensitivity of emission spectroscopy to molecular surface signals on metallic substrates is expected to be greater than that of reflection-absorption spectroscopy, since substrate emission is much smaller than substrate reflection. The use of a low-noise photoconductive detector in the liquid helium-cooled grating spectrometer makes possible the detection of the weak infrared emission from a sample at 300 K. The instrument routinely detects ~ 1 monolayer of CO, with a surface signal to noise ratio of ~ 10 in a one-minute spectrum, without benefit of modulation.

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Raman Spectra of Pyridine Adsorbed on Ni(111)

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We have measured the intensities of the 992 cm^{-1} (ν_1) and 1032 cm^{-1} (ν_{12}) lines in the Raman spectra of pyridine multilayers adsorbed on a Ni(111) surface, as a function of multilayer thickness. These experiments have been carried out in a standard ultra high vacuum chamber with Auger electron spectroscopy and mass spectroscopy capabilities. We find that the intensity of the 992 cm^{-1} line decreases linearly with multilayer thickness down to ~ 5 layers. From these data we predict an observable intensity for unenhanced spectra for monolayer amounts of pyridine on Ni(111). Initial attempts at monolayer spectra have yielded spectra which are sample preparation dependent, possibly indicating chemical effects for the first pyridine monolayer. We will report on additional monolayer experiments with pyridine and other adsorbate systems on Ni(111).

INFRARED LASER STIMULATED SURFACE PROCESSES

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ABSTRACT: Gas-surface interactions generally include the process of chemisorption, the reaction involving the adsorbates and the adsorbent, the formation of reaction products and the desorption of adsorbed species. An infrared photon beam can directly excite the gaseous molecules, the chemical species adsorbed on the surface and the solid atoms and thereby affect surface reactions. In this report, a brief review of current studies on ir laser induced surface processes will be given. Examples to illustrate the basic processes, in particular, the interactions of SF₆ with silicon and pyridine with KCl and silver surfaces influenced by a CO₂ laser will be discussed.

HREELS STUDIES OF ADSORBATES ON POLAR SOLIDS: WATER ON
STRONTIUM TITANATE

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As part of a wider study of the surface chemistry and electronic structure of metal oxides, we have used high-resolution electron energy loss spectroscopy (HREELS) to study the vibrations of some adsorbates on insulating surfaces. We report here results for water on strontium titanate (100).

Heats of adsorption on well-annealed oxide surfaces are quite low, but the creation of defects by argon ion etching leads immediately to strong adsorption. We have obtained spectra from surfaces with coverages ranging from sub-monolayer to multilayer thicknesses. In the former case the O-H stretch and bending vibrations are observed at frequencies very close to those of free water, showing that water does not chemisorb dissociatively on SrTiO_3 (100). Spectra from multilayer coverages (corresponding effectively to a layer of ice on the sample) are similar to those reported for water on metal surfaces, and show both free and hydrogen-bonded O-H stretching frequencies.

Since polar insulators have strong intrinsic loss spectra, resulting from excitation of optical phonons in the substrate¹, HREELS is a less sensitive technique for studying adsorbates on these materials than on metals. Nevertheless the intensities of O-H stretching vibrations make it a suitable method for detecting water on oxide surfaces. We are comparing the intensities of our adsorbate spectra, and the attenuation of substrate vibrations with increasing overlayer thickness, with calculations based on the dipole scattering mechanism.

1. A D Baden, P A Cox, R G Egdell, A F Orchard and R J D Willmer, J Phys C: Solid State Phys, 14, L1081 (1981).

Azimuthal Dependence of Impact
Scattering in Electron Energy Loss
Spectroscopy

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High-resolution electron energy loss spectra for a saturation coverage of H adsorbed on W(110) exhibit loss peaks due to impact scattering from adsorbate vibrational modes. The intensity of this scattering has been measured as a function of the azimuthal angle between the scattering plane and a mirror plane of the surface. The angular dependence has strong maxima oriented perpendicular to the $\langle 111 \rangle$ rows of atoms on the surface, and retains the C_{2v} symmetry of the surface. This dependence contrasts with that of dipole scattering from O adsorbed on W(110), which exhibits uniform angular dependence, within instrumental error.

High Resolution Electron Energy Loss Studies of Adsorbates Utilizing
Impact and Resonance Scattering⁺

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We discuss the nondipolar scattering processes of impact and resonance electron scattering from adsorbed molecules and their ability to provide new physical insight to adsorption and surface reactions. Although these scattering processes become essential in understanding EELS from nonspecular surfaces, we demonstrate their importance and utility on single crystal surfaces. The examples considered here will include the physical adsorption of oxygen and hydrogen on Ag(111) as well as the weak chemical adsorption of benzene, pyridine and cyclohexane on Ag(111). We demonstrate the ability of resonance electron scattering to probe the adsorbate potential energy surface as well as of impact scattering to probe the local vibrational modes of complex adsorbates thru their overtones. The general applicability of these phenomena to other systems will also be discussed.

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- 1 -

THERMAL SCATTERING OF SLOW ELECTRONS DURING ELASTIC SPECULAR
REFLECTION FROM A Cu (001) SURFACE.

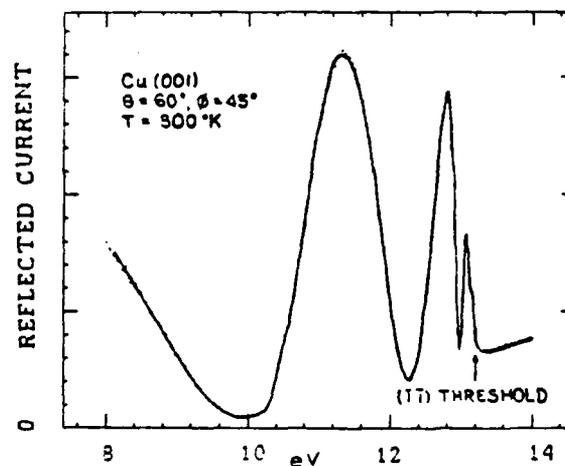
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We have studied the effects of thermal scattering of slow electrons ($E < 20$ eV) specularly and elastically reflected from a Cu(001) surface at temperatures up to 1000 K. These effects are important in surface spectroscopies that depend on conservation of momentum parallel to the surface. The structure in the reflected electron current as a function of electron energy near diffracted beam emergence thresholds, as shown in fig 1, are found to be sensitive to temperature. The overall specular current decreases sharply with increasing T , and the current in the peaks close to threshold diminishes relative to the current in the lowest energy peak with increasing T and with decreasing polar angle of incidence.

We have fitted the observed lineshapes in I vs E plots as in fig 1 with a calculation which takes account of (a) multiple scattering between the substrate and the surface potential barrier (SPB) modelled by a saturated image potential(1); (b) thermal diffuse scattering (TDS) at the substrate; and (c) electron energy loss due to electron-electron interactions as represented by a short-range imaginary potential. The TDS is taken to zeroth order for direct (Bragg) reflection, and to second order in the transferred momentum for indirect reflection wherein the electron is momentarily trapped by the SPB. The mean-square amplitudes of vibration perpendicular and parallel to the surface are taken as parameters, and values slightly larger than bulk values are found to satisfy the data.

Scattering due to phonon modulation of the long range SPB as proposed recently by Rahman and Mills (2) would lead to a relative attenuation of the peaks farthest from threshold. This is not observed, and we conclude that the long-range interaction is swamped by the contact interaction at the substrate.

- (1) R. E. Dietz, E. G. McRae, and R. L. Campbell, Phys Rev Lett 45, 1280 (1980)
(2) T. S. Rahman and D. L. Mills, Phys. Rev. B, 21, 1432 (1980).



Abstract:

SPECTRAL PROPERTIES OF MOLECULES ADSORBED ON METAL SURFACES
FROM SURFACE ENHANCED RAMAN SCATTERING (SERS)

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The observation of enormously enhanced Raman spectra of molecules adsorbed on metal surfaces such as silver, copper and gold promises to make available an instrumental method which gives highly resolved spectral data from these molecular adsorbates. We have made a comparative study of SERS and normal Raman spectra for several series of adsorbates (2-,3-,4-aminobenzoic acid; 2-,3-,4-aminopyridine; pyridine-2, 3, 4-carbonic acid; SO_2 ; sodium-azide; ect.) on electrode surfaces, metal-air-interfaces and colloidal metal particles. A detailed analysis of the vibrational spectra, their relative intensities, shifts and linewidths and their changes with time and ambient conditions gives information about orientation and bonding of the adsorbates to the metal surface. An especially interesting point is the breakdown of Raman selection rules for several nonpolar molecules. Possible mechanisms for this breakdown will be discussed. Time-resolved spectra of certain adsorbates on electrode surfaces indicate the importance of special adsorption sites, with might be connected to special active sites in catalytic processes.

High Resolution EELS Studies of Clean and Adsorbate Covered Semiconductor Surfaces

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The advent of high resolution electron energy loss spectroscopy (EELS) has provided a valuable tool for the study of "near surface" phonons on compound semiconductor surfaces. The inelastic scattering process results from the interaction of the Coulomb field of the incoming electron with the electrostatic potential set up in the vacuum by oscillating surface and near surface atoms. This scattering mechanism can potentially provide detailed information on surface optical (SO) phonons associated with clean semiconductor surfaces as well as phonon frequencies related to thin oxide overlayers whose growth goes beyond the chemisorption regime. The technique also provides an additional tool for examining surface effects such as residual disorder and doping.

High resolution EELS data for surface optical phonons on clean, sputter/annealed surfaces are presented for the polar (100) and non-polar (110) faces of GaAs, InP, GaP and CdTe. The observed vibrational frequencies are in excellent agreement with theoretical predictions (within 5 cm^{-1}) and are independent of crystal orientation, method of sample preparation and bulk doping level. The latter observation provides a unique determination of dopant depletion in the near surface region on heavily doped substrates. These findings can be rationalized by comparing the effective sampling depth of the incident electron beam with depths characteristic of surface disorder, reconstruction and dopant depletion. This probe depth is characterized by $|Q_{||}|^{-1}$, the electron momentum transfer parallel to the surface, which is of order 200 \AA .

Previous experiments have shown that disordered insulating films on metal surfaces can be studied by high resolution EELS. We have now extended these studies to compound semiconductor surfaces. Experiments on CdTe and GaP have been undertaken in order to delineate both the potential and the limitations of this technique for characterizing thin oxide films. Those two systems are prototypes insofar as TeO_2 forms an epitaxial overlayer on CdTe(110) whereas GaPO_4 grows as a single phase polycrystalline film.

HOT ATOMS AND COLD FACTS: MYSTERIES AND OPPORTUNITIES IN VIBRATION-ASSISTED SURFACE CHEMISTRY

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ABSTRACT

The exploitation of motions of surface atoms is central to modern industrial economies. The decomposition and reforming of molecules at surfaces is the fundamental atomic process which underlies the energy and chemical industries. Reactions of radiation and excited molecules with surfaces to form new volatile species constitute the foundation of device fabrication technologies in the microelectronics and communications industries. All agriculture ultimately derives from the induction of chemical reactions by the absorption of solar radiation. Thus, the control of hot atoms is a central modern technological theme.

The science of hot atoms at surfaces can be divided into three broad areas: spectroscopy, theory, and process dynamics. A brief overview of each area is given in which the main mysteries which have emerged during the past decade are noted. The resolution of such mysteries provides the traditional type of opportunity for scientific discovery. We argue that most of the currently visible frontiers lie, however, in the development of applications of the techniques of vibrational spectroscopy, so that these scientific opportunities tend to be different in kind than they were a decade ago.

Another type of opportunity is the development of technologies for hot atom control. Several such opportunities are indicated. Inspection of current activity in these areas reveals, however, that a gap exists between the development of the techniques of vibrational spectroscopy as applied to well-defined model systems and the systematic application of these techniques to develop new hot-atom process technologies. LASER-induced surface chemistry is examined as an example of an area in which such a gap currently exists and which affords a unique opportunity for surface vibrational spectroscopy and theoretical chemistry to play a significant role in the development of fabrication technologies for electronic devices. Our discussion concludes with an assessment of the importance of this type of opportunity in the climate set by current federal science policy in the USA.

SURFACE PHONONS IN SUPERLATTICES

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We report the existence of surface localized phonons for a superlattice consisting of alternating layers (parallel to the surface) of two different crystals. The superlattice has a larger periodicity in the direction perpendicular to the layers and therefore many phonon branches in the folded Brillouin zone. In the gaps existing between these phonon branches appear the surface localized modes.

The superlattice under study here is build up from respectively L_1 and L_2 (001) atomic planes of two different simple cubic lattices having the same lattice parameter and characterized by their force constants (γ_1 and γ_2) and their masses (M_1 and M_2). The force constant which binds at the interfaces the two different media is taken to be $\tilde{\gamma}$. This simple model enables to obtain in closed form the bulk and surface Green's function for the superlattice. The analytic knowledge of these functions enables to study easily all the bulk and surface vibrational properties of a superlattice, which otherwise would require huge numerical calculations. Here we concentrate on the study of the surface localized phonons as a function of the physical parameters defined just above. These surface phonons depend also on the kind of layer (1 or 2) being near the (001) surface.

The extension of this model to study the electronic properties of superlattices is also mentioned.

Roughness-Trapped Shear Horizontal Surface Acoustic Waves

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Abstract

Shear horizontal surface acoustic waves do not exist on the flat surface of a semi-infinite elastic (i.e. non-piezoelectric) medium. It has been shown by several authors recently that such waves can exist on a periodically corrugated, planar surface. In the present paper we show on the basis of the Rayleigh method that shear horizontal surface acoustic waves exist on a randomly rough planar surface of an isotropic elastic medium. The dispersion relation for these waves has the form $\omega_{SH}(k_{\parallel}) = c_t k_{\parallel} - (\delta/a)^2 (f_1(k_{\parallel}) + i f_2(k_{\parallel}))$, where c_t is the speed of transverse waves in the medium, k_{\parallel} is the magnitude of the wave vector of the wave parallel to the surface, δ is the root mean square departure of the surface from flatness, and a is the transverse correlation length of the roughness. These waves are only weakly localized to the surface, i.e. they penetrate deeply into the medium. They have a finite lifetime, that is long, due to their roughness-induced scattering into other surface acoustic waves and into bulk waves.

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Giant enhancement of the Raman signal of pyridine adsorbed on silver substrates is connected to the presence of surface roughness. The role and the scale of this roughness has been widely discussed(1). Such a phenomenon has been observed either on activated electrodes, at room temperature, or on a metal prepared in a UHV environment, at lower temperatures.

Is pyridine adsorbed at room temperature, by exposing a silver substrate to the gas phase? To answer this question, silver electrodes were prepared electrochemically, by successive oxydo-reduction cycles in KCl, KBr, and KNO_3 electrolytes. After withdrawn from the solution, washed with double distilled water, and dried under N_2 flows, the electrodes were exposed to a saturated vapor of pyridine in a previously evacuated cell.

When cycled in presence of KCl and KBr, the Raman spectrum observed on electrodes withdrawn at a potential of -0.6 V/SCE , shows intense peaks at $1010, 1025,$ and 1036 cm^{-1} in the $1000-1100 \text{ cm}^{-1}$ region. An intense peak at lower frequency for silver prepared in a KCl electrolyte: 240 cm^{-1} , and in a KBr electrolyte: 130 cm^{-1} , is observed.

When silver electrodes are withdrawn after oxidation in KCl and KBr electrolytes (coated with various thicknesses of AgCl or AgBr), the same bands are observed. Nevertheless, at high halide coverage, the 1036 cm^{-1} band disappears -see fig.1-

Our experiments allows the attribution of the 1010 and 1036 cm^{-1} bands to pyridine adsorbed on silver aggregates, and the bands at 1010 and 1025 cm^{-1} to a silver halide-pyridine complex. This is confirmed by the Raman spectrum of a silver electrode prepared in a KNO_3 electrolyte, exposed to pyridine vapor: only two bands at 1010 and 1036 cm^{-1} are detected. It can be noticed that the intensity of the 1010 cm^{-1} decreases by an order of 10 when the gas pressure is pumped out from the cell, while the 1036 cm^{-1} one tends to become more weaker.

The origin of the low frequency band is probably related to a $\nu(\text{Ag-X}^-)$ or a $\nu(\text{X-X})$ stretching vibration. To check such an hypothesis, silver electrode coated with a AgCl layer was submitted to a laser beam ($\lambda=4880 \text{ \AA}$), without pyridine. The peak at 240 cm^{-1} was then detected.

Our experiments demonstrate that pyridine is chemically adsorbed at room temperature on these silver substrates

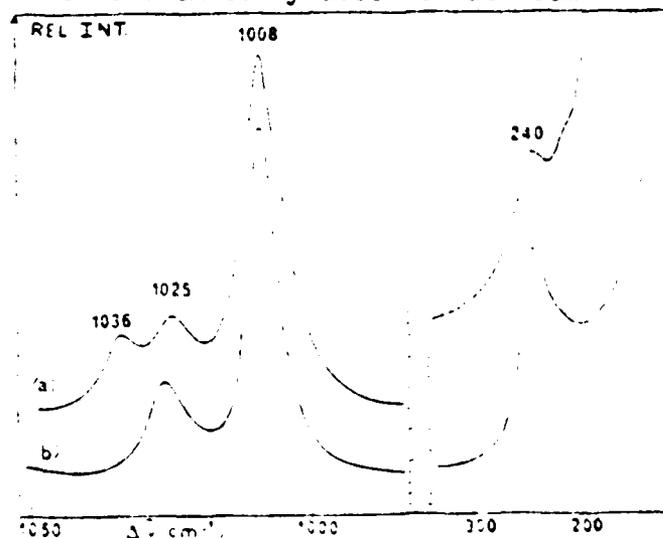


Fig.1 :Raman spectrum of pyridine adsorbed on Ag, coated with low AgBr coverage (a) and high AgBr coverage (b)

Surface Raman Ellipsometry

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Presentation: Third International Conference on Vibrations at Surfaces, Pacific Grove, California, 1 September 1982

Publication: Conference Proceedings

ABSTRACT

A method for achieving the ultrahigh sensitivity required for surface Raman spectroscopy is described. Polarization selective heterodyne detection permits shot-noise limited submonolayer detection with classically noisy picosecond laser sources. Preliminary experimental results show that the polarization selectivity can be used to reduce the overwhelming thermally induced changes in metal surface reflectivity.

Enhanced Adsorbate Raman Scattering and Surface Plasmon Radiation

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Presentation: Third International Conference on Vibrations at Surfaces, Pacific Grove, California, 1 September 1982

Publication: Conference Proceedings

ABSTRACT

We present the first experimental results which demonstrate a quadratic relationship between the enhanced Raman scattering from molecules on Ag surfaces and roughness-coupled surface-plasmon radiation. These results are interpreted by a model which includes both roughness assisted surface-plasmon scattering and radiative coupling.

Bound States of Two Surface Phonons at a Crystal Surface*

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Abstract

The theoretical and experimental study (the latter via, e.g., Raman scattering) of the bound states of two surface phonons can provide useful information about the vibrational properties of crystal surfaces, both clean and in the presence of adsorbates.

There are in the literature several examples of bound states of two elementary excitations in a solid, where the binding occurs due to nonlinearities in the properties of the solid. However, virtually all studies of such bound states have referred to bulk excitations, e.g. bulk phonons and bulk magnons. To our knowledge only one study of bound states of two surface excitations has been carried out, viz. a variational calculation of the bound states of two surface spin waves by Chiu-Tsao (Phys. Rev. B11, 4525 (1975)).

Assuming that the Hamiltonian of the system is the lattice Hamiltonian in the presence of both cubic and quartic anharmonic terms, we have derived a Bethe-Salpeter equation for an appropriate two-phonon Green's function. To lowest order in the anharmonic coupling constants, that equation can be expressed as a closed equation for the two-surface phonon Green's function, that is for the Green's function describing the propagation of two surface phonons. Because of their interaction (we note that the cubic anharmonic terms give rise to an indirect interaction mediated by the bulk phonons), the possibility of the existence of a two surface phonon bound state arises. Formally such a state manifests itself as an isolated pole (outside the continuum of two-phonon states) of the two surface phonon Green's function.

We numerically obtain the poles of the two surface phonon Green's function for a simple cubic crystal with nearest neighbor, central and non-central force interactions between atoms. As shown by Cunningham (Surf. Sci. 33, 139 (1972)), this simple model supports surface acoustic waves at a stress free (110) surface. Given the fact that the mean square displacement of an atom at the surface is enhanced relative to that for an atom in the crystal interior (thus enhancing the relative importance of anharmonic effects at the surface) we expect that the bound states of two surface phonons be more easily realized in practice than their bulk counterparts.

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The Adsorption of Ammonia on a Fe(110) Single Crystal Surface Studied by
High Resolution Electron Energy Loss Spectroscopy (EELS)

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EELS spectra of ammonia adsorbed on a Fe(110) single crystal surface at 120 K reveal four different molecular adsorption states:

1. At very low exposures (0.05 L) three vibrational losses at 345 cm^{-1} , 1170 cm^{-1} and 3310 cm^{-1} are observed which are attributed to the symmetric Fe-N stretching-, N-H₃ deformation and N-H₃ stretching modes of chemisorbed molecular ammonia, respectively. The observation of only three vibrational losses indicates an adsorption complex of high symmetry (C_{3v}).
2. Further exposures up to 0.5 L cause the appearance of additional losses at 1450 cm^{-1} , 1640 cm^{-1} and 3370 cm^{-1} . The latter two are interpreted as the degenerate NH₃ deformation and - stretching modes of molecularly adsorbed NH₃. The 1450 cm^{-1} loss is a combination of the losses at 345 cm^{-1} and 1105 cm^{-1} . The observation of 5 vibrational losses is consistent with an adsorption complex of C_s symmetry.
3. In the exposure range from 0.5 to 2 L adsorption of molecular ammonia in a second layer is observed. This phase is characterized by a symmetric deformation mode at 1190 cm^{-1} and by two additional very intense modes at 160 cm^{-1} and 350 cm^{-1} which are due to rotational and translational modes.
4. Exposures above 2 L cause multilayer condensation of ammonia characterized by translational and rotational bands at 190 cm^{-1} , 415 cm^{-1} and 520 cm^{-1} , and a symmetric deformation mode at 1090 cm^{-1} . A broad loss feature around 3300 cm^{-1} is attributed to hydrogen bonding in the condensed layer.

Thermal processing of a Fe(110) surface ammonia covered at 120 K leads to decomposition of the ammonia into hydrogen and nitrogen above 260 K. No vibrational modes due to adsorbed NH or HN₂ species were detected.

Thermal desorption spectra of hydrogen after the adsorption of ammonia at 120 K reveal two maxima at 220 K and 420 K. The first one may be correlated with the desorption of molecular ammonia and the second one is identical with the hydrogen desorption peak from a clean Fe(110) surface.

Adsorbate Structure Modeling Based on EELS
and Lattice Dynamical Calculations:
Application to O/Al(111)[†]

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We show that a lattice dynamical model based on pair interactions is able to account for the primary features of high resolution electron energy loss spectra (EELS) for the O/Al(111) system. This particular system is complicated by the simultaneous formation of an oxygen overlayer and underlayer at low gas doses. Both overlayer and underlayer oxygen produce (1X1) LEED patterns, however, various LEED IV studies and SEXAFS studies arrive at different bond lengths and positions for oxygen atoms. Recent experimental results for O/Al(111) shows overlayer and underlayer oxygen can be studied using EELS.¹ This system exhibits two major loss peaks attributed to surface oxygen (80 MeV) and subsurface oxygen (105 MeV), and a third smaller peak at about 40 MeV which is associated with coupling of first and second layer Al planes through the subsurface oxygen. We have analyzed seven high symmetry overlayer/underlayer configurations which yield (1X1) LEED 2-dimensional order using a lattice dynamical model.² The configurations involve two inequivalent 3-fold surface sites, two inequivalent tetrahedral subsurface sites, a subsurface octahedral site and a modified octahedral site. Of these configurations, it is possible to eliminate all but one based on unrealistic O-O and O-Al interaction constants required to obtain a fit to experimental results from the model. The favored configuration is one with surface oxygen atoms at the 3-fold site with no second layer Al atom directly below, and subsurface oxygen in the tetrahedral site above a second layer Al atom. This underlayer site is predicted by SEXAFS studies. We find the model discriminates between several possible (1X1) oxygen configurations on Al(111), accurately models the frequencies, and in addition yields eigenvectors which provide insight into the atomic motion and relative scattering cross sections for the 2 displacement modes.

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[†]Research supported by AFOSR-80-0154 and NSF DMR-81-21916.

EXACT CALCULATIONS OF SCATTERING AND ENHANCED
FIELDS OF ELECTROMAGNETIC WAVES ON GRATING SURFACES

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and

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We present scattered intensities and values of the electromagnetic field for p-polarized light on Ag grating surfaces using the theory of Toigo, Marvin, Celli and Hill(1). The theory is based on the application of the extinction theorem to Green's theorem. The program for calculations is set for any shape of the grating profile. Calculations are performed when the incident light is in resonance with the surface plasmon polariton. The shape of the scattered intensities are calculated for different grating amplitudes and it is shown that, for example, the reflectivity can present a minimum or a maximum depending on the amplitude and shape of the grating. It is shown that the enhanced field (the ratio between the modulus squared of the scattered field to the modulus squared of the incident field)(e) has a maximum when the reflectivity is a minimum as a function of the incident angle. The maximum of e is larger when the minimum in the reflectivity is smaller as a function of the grating amplitude. The value of e is calculated in a fine grid near to the grating and the values of the maxima are of the order of 300. The width of the resonances as well as the plasmon dispersion relation will be also presented.

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CRYSTALLOGRAPHIC DETERMINATION OF METAL SURFACES WITH HELIUM SCATTERING

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Helium-surface diffraction data has been used to construct the interaction potential between a Helium atom and a metal surface. The constructed potential fits experimental data for all beam energies and angles of incidence and more importantly is independent of beam energy. Such a potential essentially consists of two parts: a short range repulsive corrugated potential due to electronic overlap, and a long range attractive potential due to dispersion forces. We have generated potentials for He scattering for Ni, Cu and Au and in all cases found excellent agreement with experiments.

The repulsive part of the He scattering potential has been generated using the Ejsberg-Norskov¹ relation and an atomic superposition model for surface charge density. This procedure enabled us to calculate the potential from a first principles calculations without invoking any adjustable parameters. The calculated corrugations and the softness parameter were then fed into the coupled channel programs to calculate scattered intensities. We found the agreement to be excellent for He/Cu(110) when the outermost layer for Cu(110) was relaxed inwards by 10% of the interlayer spacing. LEED experiments and calculations predict that the last layer of Cu(110) is in fact relaxed by this amount. This implies that for those metals for which a charge density-potential relation can be found, one can determine surface crystallography from first principles without adjustable parameters.

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Leaky Surface-Elastic-Waves on Flat and Strongly
Corrugated Surfaces for Isotropic Nondissipative Media

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Abstract

The dispersion relation for Rayleigh waves propagating across a grating, on the surface of a semi-infinite, nondissipative, isotropic, elastic medium was recently calculated by Rayleigh's method and equivalently by a formally exact method based on Green's theorem. Using a complex wave vector k or complex frequency ω in the present work, we continue the solutions of the dispersion relation into the radiative region of the $k\omega$ -plane (i.e. above the bulk transverse sound-line) and into the first frequency-gap on the boundary of the Brillouin zone caused by the grating periodicity. Here the surface waves have components that radiate outwardly into the bulk. The acoustic attenuation for the Rayleigh waves, calculated from the imaginary part of k , agrees very well with experiment: all the observed peaks, including those missed by previous perturbation scattering theories, are found. Moreover, a branch is found in the dispersion relation, to which a corresponding complex-solution is also found for the flat surface, between the bulk transverse and longitudinal sound lines, that represents an intrinsically leaky flat-surface-wave or surface resonance. The principal peak in the Rayleigh wave attenuation can be associated with an interaction between the Rayleigh wave and this new leaky wave.

RO-VIBRATIONAL EXCITATION WITHIN THE INFINITE CONE WELL: DESCRIPTION

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Several recent experimental studies including laser induced fluorescence determination of the rotational state distribution of NO molecules scattered and desorbed from metal surfaces, as well as N₂ sputtered from Si have reported highly non-equilibrium rotational distributions suggesting that energy transfer into or out of the possibly-hindered rotational modes of the molecule in interaction with the surface is a significant factor governing the dynamics of the particular ejection process. Theoretical modeling has also supported this view. Thus to properly understand the dynamics of molecular processes at surfaces, one must have an adequate understanding of the ro-vibrational modes of the hindered molecule involved.

We have recently presented an analytic model, called the "Infinite Cone Well", in which upon sudden removal of a hindering potential, the zero point rotational energy of the rotor is effectively converted into excess apparent rotational energy in the free rotor final state distribution. Calculated state distributions, in terms of rotational Franck-Condon factors, have been presented for processes involving only hindered to free rotational energy transfer. For actual processes in which a diatomic molecule is ejected from a surface, the role of hindered rotational to center-of-mass translational transfer must also be included. We have now extended the original model to also include the vibrational modes associated with the bond between the molecule and the surface and thus, in a natural way, deal with the inter-conversion between ro-vibrational energy of the initial state and free rotation/center-of-mass translation in the final state. Calculated rotational distributions of photo-desorbed molecules, which include the translational degrees of freedom, display intriguing departures from naive expectations, as a function of energy above the desorption threshold. Analogies with very related phenomena in photodissociation of gas phase polyatomic molecules will be drawn and discussion, in terms of currently existing desorption data, given.

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EXPERIMENTAL STUDY OF RELATIVE INTENSITIES IN
INELASTIC ELECTRON TUNNELING SPECTRA

(S. Gauthier, J. Klein, A. Léger, S. de Cheveigne, C. Guinet) *

ABSTRACT :

We present here an experimental study of the relative intensities in inelastic tunneling spectra of formic and acetic acid chemisorbed on alumina. The theoretical framework is given by the simplest theory of tunneling intensities, the theory of Scalapino and Marcus. The comparison between our experimental results and the predictions of this theory provides evidence of an important discrepancy in the relative intensities in the spectrum of a given molecule. This disagreement is only partially resolved by considering the influence of the counter-electrode of the junction on the tunneling intensities. So, on the basis on an alternative derivation of the results of the theory of Scalapino and Marcus, we discuss to what extent it can be applied to the interpretation of tunneling spectra.

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THEORETICAL VIBRATIONAL FREQUENCIES FOR NH_x AND CH_x REACTIVE INTERMEDIATES ON NICKEL(100) AND NICKEL(111) SURFACES

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Theoretical studies have been performed on CH_x and NH_x species chemisorbed on threefold and fourfold sites of nickel clusters. From this work we have obtained geometries and vibrational frequencies that can be compared with experimental data concerning these species chemisorbed on Ni(100) and Ni(111) surfaces. These results can be used to help assign the observed losses in EELS spectra for CH on the Ni(111) surface.

FOURIER TRANSFORM INFRARED REFLECTION-ABSORPTION SPECTROSCOPY OF SURFACE SPECIES. William G. Golden and David D. Saperstein, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, CA 95110

Dispersion spectrometers have been shown very capable of obtaining infrared spectra of adsorbed monolayers [1]. The technique, known as infrared reflection-absorption spectroscopy (IRRAS) uses polarization modulation to utilize the well known surface selection rules of grazing incidence reflection to produce infrared spectra of species adsorbed on low area metal surfaces. Recently, Dowry and Marcott [2] have adapted the polarization modulation approach to FTIR and shown that FT-IRRAS, like VCD [3], is compatible with FTIR equipment. The ability to discriminate against gas-phase species has not yet been shown to be as effective as dispersion IRRAS.

We have been able to demonstrate progress in FT-IRRAS by incorporating an additional switching circuit into the data acquisition electronics of an air-equilibrated IBM IR/98 FTIR spectrometer such that it is possible to obtain simultaneously both the reference and polarization modulated spectrum. These spectra ratio to produce good discrimination against gas-phase species. The operating principles of this approach to FT-IRRAS and sample spectra of monolayer assemblies of cadmium arachidate adsorbed on silver will be discussed.

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Tunneling Spectroscopy as a Probe of
Adsorbate-Surface Interactions

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ABSTRACT

Tunneling spectroscopy is a sensitive probe of two classes of adsorbate-surface interactions: interactions of the adsorbate with the substrate on which it is adsorbed and adsorbate interactions with the top metal electrode that is evaporated on top of it. The talk by Professor Hipps focuses on the first of these classes. This talk focuses on the second. In general, the interaction of the adsorbed molecules with the top metal electrode produces a down-shift in the vibrational mode position ranging in size from $\leq 0.1\%$ to $\leq 10\%$ depending on the dipole derivative of the mode and the type of top metal electrode.

The Adsorption of NO on Ru(001) and its Co-Adsorption
with Oxygen Studied by Vibrational Spectroscopy

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The adsorption of NO on Ru(001), and its co-adsorption with oxygen, has been studied by LEED, TPD, EELS and IRAS (with particular emphasis on the vibrational spectroscopies) over a wide range of temperatures. It has been well established /1, 2/ that the adsorption of NO on Ru(001) at room temperature is initially dissociative with molecular adsorption taking place only after a dissociative layer is formed. It therefore seemed appropriate to study the effect of oxygen co-adsorption on the adsorption of NO under well-defined conditions. The dissociation layer is characterised by a (2x2) LEED structure and is found to influence the subsequent molecular adsorption of NO in exactly the same way as a saturated, pre-chemisorbed layer of oxygen. One effect of oxygen co-adsorption is to suppress the ν_1 intensity in the desorption spectra /1/ (the ν_2 peak remains essentially unchanged), while simultaneously producing a new TPD peak of NO ($\nu_1(0)$) with lower binding energy. In the corresponding EELS spectra these two species (ν_1 and $\nu_1(0)$) are clearly distinguished.

Our inability to observe anything other than an absorption band at $\sim 1800 \text{ cm}^{-1}$ in the IRAS experiments led us to repeat the EELS experiments /2/ together with TPD to elucidate more clearly the nature of the ν_1 molecular species /1/. The results indicate that the adsorption of NO at low temperatures ($\sim 95\text{K}$) initially produces a species of NO with an N-O stretch frequency of 1400 cm^{-1} . This is the only species observed up to an exposure of 0.5 Langmuirs, and on warming to room temperature it dissociates completely to produce the (2x2) pattern described above. Pre-adsorption of oxygen prevents the formation of this species of NO. Only subsequent to the saturation of this species during adsorption at low temperature do two bands at $\sim 1490 \text{ cm}^{-1}$ and $\sim 1810 \text{ cm}^{-1}$, associated with the ν_1 and ν_2 molecular species /1/, appear. We suggest that the low temperature, low coverage species is lying down, and the molecular species ν_1 and ν_2 are both adsorbed on "on top" sites but corresponding to the bent and linear forms of the NO molecule, respectively.

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The Adsorption of CO on Pt(111) Studied by Infrared-
Reflection-Absorption Spectroscopy

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The adsorption of CO on Pt(111) between 85 K and 300 K has been studied by infrared-reflection-absorption spectroscopy together with TPD and LEED. The intensity of the absorption band due to the CO stretch of the linear species shows a maximum at the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern followed by a minimum at the $c(4 \times 2)$ structure during the adsorption of CO at low temperatures (≤ 150 K). The absorption band due to the C-O stretch of the bridging species appears only after the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern and reaches maximum intensity at the $c(4 \times 2)$ structure. Adsorption of CO to higher coverages (corresponding to the compression structures) broadens and shifts this absorption band. At higher temperatures (≥ 150 K) a third peak is observed at $\sim 40 \text{ cm}^{-1}$ below the peak due to the bridging species and is attributed to adsorption in three-fold sites. At 300 K both peaks in this region are very broad. The intensity data differs from that measured with EELS /1/ and favours a "fault-line" structure of the type proposed by Avery /2/. Together with the additional information from band widths it is possible to distinguish between the various structural models. The results obtained here may also be important in explaining data from other systems such as CO/Cu.

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Invited Paper

Title: The Interaction of Ions and Easily Ionized Species with Oxide Surfaces as Studied by Tunneling Spectroscopy.

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Abstract

The physical and chemical properties of thin film alumina and magnesia, the most frequently used substrates, are reviewed. The composite barriers, $\text{AlO}_x/\text{SiO}_y\text{H}_z$ and AlO_x/SO_y , are also discussed. Tunneling studies of anionic transition metal complexes adsorbed on alumina are shown to provide significantly more information about the nature of the surface species than corresponding infrared studies. A short review of the redox chemistry of alumina, as demonstrated by tunneling spectroscopy, is presented. The adsorption of TCNE on alumina from fluid solution is used to exemplify how tunneling spectroscopy may be integrated into a manifold of conventional techniques (IR, ESR, and elution studies in this case).

The Adsorption and Dehydrogenation of Cyclopentane
on Ru(001) Characterized by High Resolution Electron
Energy Loss Spectroscopy

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The adsorption of cyclopentane on Ru(001) has been investigated with EELS, Thermal Desorption Mass Spectrometry and work function measurements. At 90K cyclopentane adsorbs associatively in a chemisorbed first layer followed by multilayer formation. The vibrational spectrum of the chemisorbed layer is characterized by a frequency shift of the C-H stretching mode to 2600 cm^{-1} . Heating of the surface above 200K results in desorption of the multilayer and dehydrogenation of the first chemisorbed layer to cyclopentene. The latter is characterized by C-H stretching modes at 3020 cm^{-1} (=C-H) and 2820 cm^{-1} (-C-H) and a strong ring deformation mode at 750 cm^{-1} . The results are compared with the adsorption behavior of cyclopropane[1] and cyclohexane[2] on this surface. It is concluded that the dehydrogenation of cycloparaffins C_nH_{2n} occurs for larger molecules ($n \geq 5$) via a C-H-metal interaction, as evidenced by the C-H soft mode[3]. The observation of a C-H soft mode for cyclopentane demonstrates the general nature of this C-H-metal interaction, which apparently does not require necessarily a geometrical fit between the molecule and the metal surface as has been previously assumed for cyclohexane.

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CO₂ LASER DRIVEN SEPARATION OF BINARY co-ADSORBATES ON SODIUMCHLORIDE
SURFACES UNDER ULTRA HIGH VACUUM

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The problem of laser-induced separation of molecules, having very similar chemical properties was tried to solve in selective vibrationally excitation of one compound which is co-adsorbed with another component. On solid surfaces, where fast relaxation may compete with non-equilibrium energy accumulation in specified modes, induction of processes by selective excitation of adsorbate vibrational modes with resonant infrared laser radiation has been realized recently. Efficient desorption of molecules has been detected with a quadrupole mass analyzer in time-of-flight mode after absorption of resonant CO₂ laser radiation in e.g. the adsorption systems CH₃F-NaCl ¹⁾ and pyridine-KCl ²⁾. Preliminary results of infrared laser stimulated processes in binary co-adsorbates on solid surfaces were published very recently in the binary co-adsorbates CH₃F-NaCl and C₂H₆-NaCl ³⁾. Here further results of processes stimulated by selective excitation of internal vibrational adsorbate modes in binary co-adsorbates on sodiumchloride crystal surfaces will be reported. The infrared absorption spectra of the binary absorption systems under ultra high vacuum will be presented.

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INFRARED-SPECTROSCOPIC INVESTIGATION OF THE ADSORPTION OF METHYLFLUORIDE
ON SODIUMCHLORIDE SURFACES UNDER ULTRA HIGH VACUUM

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Methylfluoride, one of the best investigated molecules in the gas and in low temperature matrices with respect to its vibrational dynamics, has attracted interest by desorption of methylfluoride after vibrational excitation of $\text{CH}_3\text{F-NaCl}$ adsorbate by laser infrared under ultra high vacuum. The results of a systematic infrared-spectroscopic investigation of the adsorption of CH_3F on sodiumchloride surfaces under ultra high vacuum in a broad temperature and pressure range are presented. Three different sorption phases were detected by their ir-spectra. All normal modes of the adsorbates $\text{CH}_3\text{F-NaCl}$ were observed and could be assigned. The frequencies are shifted to higher or lower values with respect to the gaseous or solid state. The largest shift was observed for the most intense mode, the ν_3 , with a value of 102 wavenumbers for $\alpha\text{-CH}_3\text{F-NaCl}$. From these ir-measurements adsorption isotherms were obtained and the isosteric heats of adsorption were determined. A model for the adsorption sites will be discussed and evidence for the model will be presented by calculations of the frequency of the ν_3 mode using the theory of dynamic coupled oscillators.

Thermal Evolution of C_2H_2 and C_2H_4 on Pd(111) Studied by
High-Resolution Electron Energy Loss Spectroscopy

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The chemisorption and thermal evolution of the hydrocarbons acetylene (C_2H_2) and ethylene (C_2H_4) on a palladium (111) surface have been characterized for the first time by high-resolution electron energy loss spectroscopy (EELS) at a resolution of 9-10 meV. An extensive set of vibrational spectra for C_2H_2 and C_2H_4 and their deuterated counterparts has been obtained in the temperature range 150K-500K under conditions of both specular and off-specular scattering. EELS data on the thermal evolution of C_2H_2 is presented both for the clean Pd(111) surface and in the presence of preadsorbed hydrogen since hydrogen plays a major role in these surface reactions.

Several conclusions emerge from this study with regard to both the thermal behavior of the hydrocarbons as well as the EELS scattering mechanism. The low temperature (150K) phase of C_2H_2 is shown to be a strongly rehybridized ($\sim sp^{2.5}$) species. Detailed specular and off-specular analysis permits classification of the vibrational modes in terms of long-range dipole and short-range impact scattering mechanisms for this species. Impact scattering is found to be relatively strong for some modes even in specular scattering. The low temperature phase of C_2H_4 is characterized by carbon-carbon and carbon-hydrogen stretching frequencies which are not markedly shifted from the gas phase. However, there is strong evidence of hydrogen-bond like interactions between the molecule and the metal surface.

The thermal evolution of both C_2H_2 and C_2H_4 on Pd(111) is characterized at various temperatures by relatively complex EELS spectra which show mixed phases of reacted and unreacted molecules and intermediate species. However, it has been possible to conclude that both C_2H_2 and C_2H_4 evolve at 300K to mainly ethylidyne ($\geq C-CH_3$). Spectra of C_2H_2 from 150K-300K both with and without preadsorbed hydrogen indicate that a $\geq C=CH_2$ type of surface species is a reaction intermediate in the formation of ethylidyne. Finally, it is found that the molecules dehydrogenate at higher temperatures (400-500K) to a surface CH species which is characterized by a relatively simple vibrational spectrum. These results will be discussed in the context of earlier work on platinum, nickel, and rhodium.

PHASE-TRANSITIONS IN CHEMISORBED LAYERS
STUDIED BY VIBRATIONAL FREQUENCY SHIFTS

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For a number of chemisorption systems, adsorbate vibrational frequencies have been found to shift considerably with increasing coverage, usually towards higher frequencies for CO adsorption. Unward shifts of about 35 cm^{-1} have been found for CO on P(111) and (110), and the largest shift, for CO on Pd(100), is about 100 cm^{-1} . There are two cases, however, where small downward shifts have been observed. These are for CO on Cu(111) and on polycrystalline Au. A method for obtaining the vibrational frequency for an isolated molecule, using isotopic mixtures, has now been applied to a number of these systems, providing an accurate means of determining the extent of the frequency shift which can be attributed to dipole coupling interactions. The remaining observed shift can then be attributed to chemical (or bonding) effects or to island growth of the adsorbate. The use of such data to provide information on adsorbate phase transitions and bonding characteristics, and for the determination of island dimensions, will be discussed in detail.

Vibrational Spectroscopy Using HREELS of Benzene
Adsorbed on the Rh(111) Crystal Surface

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ABSTRACT

High resolution electron energy loss spectroscopy (HREELS) has been used to study the structure of adsorbed benzene (C_6H_6 and C_6D_6) monolayers on the Rh(111) surface at temperatures above 300K. There are two ordered phases: one exists below 75°C and the other forms after annealing at 125°C. Heating the crystal to 140°C causes disordering and partial dehydrogenation, and the adsorbed species can be completely dehydrogenated by heating to 400°C. The ordered and disordered layers of adsorbed benzene are characterized by HREELS and the vibrational data is analyzed. Structural models are proposed and compared to experimental results obtained in other laboratories for benzene adsorption on Ni(111) and Pt(111).

Acknowledgment: This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

The Exposure Dependence and
Emission Spectrum of Chemiluminescence Produced
During the Oxidation of Si(111) by O₂.

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Chemiluminescence produced during the low pressure oxidation of a Si(111) surface by O₂ has been investigated. Carefully cleaned and annealed samples yield chemiluminescence at pressures as low as 6×10^{-7} torr, corresponding to a peak chemiluminescence yield of 2.2×10^{-7} photons per incident molecule and comparing favorably with the value of 1×10^{-7} measured by Bruce and Comas.¹ The evolution of the emission shows a hyperbolic decrease in time at pressures above 1×10^{-4} torr but becomes more complex at the lowest exposures studied. The spectrally broad chemiluminescence was dispersed at medium resolution and recorded with an Optical Multichannel Analyzer in an attempt to identify and characterize the energy content of the emitting species.

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It has been already shown¹⁾ that the in-situ infrared reflectance spectroscopy assisted by the potential modulation method can now be applied for studying the nature of adsorbed species at the electrode/solution interphase. One of the important applications was the study of methanol adsorption on a platinum electrode.²⁾ The study showed clearly that adsorbed species produced by chemisorption of methanol molecules was not COH , which has been widely accepted on the basis of electrochemical measurements, but CO (both linear and bridge types) species. The potential modulation method employed in earlier studies was particularly useful in assisting detection of spectra of adsorbed species. The spectra observed, however, were difference spectra between two electrode potentials, which has made it rather difficult to study the behaviour of the adsorbed species in detail. A new method is proposed in the present report to determine a spectrum of adsorbed species at a fixed electrode potential without the help of potential modulation method. It is essentially a linear sweep optical voltammetry at fixed wave lengths. It will be reported in this study that dependence on potential of band intensity and wave number of maximum absorption ν_m of CO(a) species can now be studied in detail on a platinum electrode. It is shown that there is a close relation between the shift of ν_m and change of surface charge density on the platinum electrode. Oxidation of CO(a) species at around 1.2 V (NHE) has been observed also by the linear sweep optical voltammetry and mechanism of oxidation of methanol molecules will be discussed on the basis of these new data.

Application to other systems will be reported too.

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ELECTROREFLECTANCE VIBRATIONAL SPECTROSCOPY:
A NEW SURFACE ANALYSIS TECHNIQUE USING DIODE LASERS

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ABSTRACT

Electroreflectance Vibrational Spectroscopy (EVS) is proposed as a new, sensitive technique for the study of adsorbed molecules on surfaces. The vibrational frequencies of adsorbed molecules are modulated by an applied alternating electric field. This in turn causes a modulation of infrared adsorption that can be measured using a diode laser. Our calculations indicate that EVS can be used to measure submonolayer coverages of specific adsorbed molecules on flat metal or insulator surfaces under realistic atmospheric pressure conditions. The EVS technique also makes it possible to study adsorbates on metal and insulator surfaces in an ultra high vacuum environment with resolution and sensitivity unmatched by other techniques. It is a derivative technique and is consequently relatively more sensitive to sharp structure in the vibrational spectra. We also report some measurements of diode laser intensity noise, a limit to the sensitivity of the EVS technique.

INFRARED SPECTRA OF CO ADSORBED AT LOW TEMPERATURES ON Ni^{*}

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The infrared absorption of CO adsorbed on Ni films at 1.5 K has been measured for exposures between 0.05 L and 4.0 L. For the first langmuir the CO is almost entirely chemisorbed, a physisorption spectral line appearing only at the highest coverages. Two principal chemisorption infrared absorption peaks appear in the spectra, corresponding to top- and bridge-bonded configurations. A third peak of low intensity, corresponding to a three-fold site is seen at certain exposures. The line width is narrow at low exposures (22 cm^{-1} FWHM for the top site), broadening at intermediate coverages (90 cm^{-1} FWHM for the top site at 0.7 L exposure) and narrowing again at the highest exposures (40 cm^{-1} FWHM at 1.0 L exposure). This behavior as a function of coverage is markedly different from that seen in other systems. The peak position for the top site shifts from 2018 cm^{-1} at 0.1 L to 2090 cm^{-1} at 1.0 L, while the bridge site peak shifts from 1864 cm^{-1} to 1944 cm^{-1} . Significant changes in the distribution of chemisorption sites can be seen after heating the sample to temperatures as low as 50 K. Physisorbed CO on top of the chemisorbed layer has negligible effect on the infrared peak positions and widths, indicating that the electronic polarizability plays a small role in influencing these quantities.

* Work supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

Third International Conference on Vibrations at Surfaces

Surface Enhanced Raman Spectroscopy of Palladium

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Large enhancements in the Raman scattering signals have been observed from molecules and ions adsorbed on a palladium surface. The largest enhancement factor is in the order of 10^5 . Results will be discussed in terms of theoretical models on the surface enhanced Raman scattering process.

NON-EQUILIBRIUM BEHAVIOR ON PULSED LASER EVAPORATED SURFACES

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Absorption of intense laser optical fields by metallic surfaces generates dense neutral atomic beams with high average translational energies (Ref. 1). Mechanisms explaining this behavior are based on an equilibrium model invoking high temperature and pressures (Refs. 1, 2). We have made experimental observations on yttrium and uranium atomic beams produced from laser evaporated targets which suggest an alternative mechanism. Pulsed Nd:YAG 1.06 μ m laser radiation having an intensity of 1-10 MW/cm² was used to excite the metal surfaces. The resulting fast neutral beams had average energies in the range of 3-12 eV. They were interrogated with high resolution single mode dye lasers to determine the distribution of population in the low-lying metastable electronic states: U(⁵L₇^o), U(⁵H₃^o), U(⁵K₆^o) and Y(⁴F_J). Distribution of population in these states carries a partial history of dynamical processes occurring on the surface during dissociation in the presence of large optical fields. In dramatic contrast to thermal equilibrium oven sources, metastable states were not observed in the laser-generated atomic beams. Ground state densities were in the range of 10¹³ to 10¹⁵ atoms cm⁻³ depending on optical parameters. Dimers were also observed but were not electronically excited. These results suggest fast, adiabatic multiphoton excitation of the surface vibrational modes as a possible mechanism. Experimental and qualitative theoretical results will be discussed.

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COMBINED VIBRATIONAL/PROGRAMMED REACTION INTERMEDIATES ON METAL SURFACES

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In many cases temperature programmed reaction spectroscopy (TPRS) and surface vibrational spectroscopy can be effectively combined to yield the details about the mechanism of surface reactions. When reaction products are evolved from the surface in reaction-limited steps, TPRS is often sufficient to identify the stable reaction intermediates. On the other hand, if product evolution is desorption-limited, vibrational spectroscopy, as well as XPS or UPS, is indispensable for identification of reaction intermediates. In some cases, the two methods complement one another, and both the identity of the intermediates and its orientation can be defined. In this talk examples of the combined use of these techniques will be given. Specifically, reactions of formaldehyde and CO_2 with oxygen preadsorbed on $\text{Ag}(110)$ will be shown to lead to the formation of H_2CO_2 and CO_3 moieties, which decompose with further heating. Also, acetylene is successively dehydrogenated to $\text{C}_2\text{H}_{(a)}$ and $\text{C}_{2(a)}$ by adsorbed oxygen, these species lying nearly parallel to the surface. As a further example, the dehydration of formic acid on $\text{Ni}(110)$ will be shown to proceed via the formation of coadsorbed CO and formate intermediates.

MOLECULAR AND ATOMIC OXYGEN ADSORPTION ON THE
KINKED Pt(321) SURFACE

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ABSTRACT

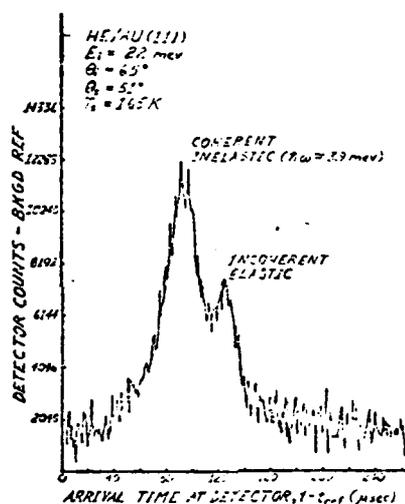
Oxygen adsorption and desorption on the Pt(321) surface has been studied using high resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS), and Auger electron spectroscopy. With the Pt(321) surface cooled to 100°K, the predominately adsorbed species is observed to be molecular oxygen. HREELS showed that the molecular oxygen is adsorbed in a peroxy-like state at all coverages studied. Other vibrational losses are also observed which are due to co-adsorbed atomic oxygen. This result indicates that the activation energy for dissociation is lower on the Pt(321) surface than on the flat Pt(111) surface. TDS results give a heat of desorption for the molecular oxygen of ~5kcal/mole. Annealing the surface to 285°K produces two states of adsorbed atomic oxygen. One of these states has a vibrational loss at 485 cm⁻¹ due to the Pt-O stretch of atomic oxygen adsorbed on the terraces and is analogous to the atomic oxygen adsorbed on the flat Pt(111) surface. The other state has a vibrational loss at 560 cm⁻¹ and has not previously been observed. It is due to the Pt-O stretch of atomic oxygen adsorbed at the kink sites. The heat of desorption of both these states is approximately equal and is found to decrease from ~70 kcal/mole to ~47 kcal/mole as the coverage increases. Atomic oxygen is also observed to adsorb in a temperature unstable state. The vibrational loss of this species is at 715 cm⁻¹ and is interpreted as atomic oxygen adsorbed in a top site.

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MEASUREMENT OF Au(111) SURFACE PHONONS BY LOW ENERGY HELIUM SCATTERING*

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Single phonon inelastic scattering of low energy helium atoms (22 meV) from low temperature Au(111) surfaces in the $\langle 11\bar{2} \rangle$ direction provides information on the surface phonon dispersion relation, $\omega(Q)$, in analogy to bulk neutron scattering. Our time-of-flight experiments utilize a high pressure, cold helium beam (speed ratio ≈ 42 , resolution $\approx 4\%$) to probe the surface phonon interactions. The figure shows an example of the raw time-of-flight data.



The inelastic peak shown is due to the annihilation of a phonon ($\hbar\omega \sim 3.9$ meV). This particular inelastic peak represents about 10^{-5} of the incident helium beam intensity. The elastic peak is due to incoherent elastic scattering and serves as a check on our timing. We have $\omega(Q)$ data to within 20% of the Brillouin zone edge along the $\langle 11\bar{2} \rangle$ direction. We will also report intensity data, surface temperature dependence, and a comparison with H_2 scattering. At glancing incidental angles ($\theta_i \approx 80^\circ$), well resolved intensity extrema occur at low $\omega(Q)$. It is not yet clear whether these are due to a peculiar low frequency mode, incoherent effects, or resonance effects involving the helium-surface scattering potential.

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Low Frequency Surface Resonance Modes in
Electron Energy Loss Spectroscopy

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Abstract

Electron energy loss spectroscopy has proved a powerful probe of vibrational modes of a wide variety of adsorbed species. Here the primary focus has been on modes with frequency well above the maximum phonon frequency of the substrate. Examples are internal vibration modes of adsorbed molecules, possibly shifted significantly in frequency from their gas phase analogues, and high frequency vibrations of an adsorbed molecule or atom against the substrate. Recent experiments explore features in the energy loss spectrum with frequency below the maximum phonon frequency of the substrate, for ordered overlayers of atoms adsorbed on low index metal surfaces. We shall summarize our theoretical studies of such spectra for several adsorbate/substrate combinations, with emphasis on the physical origin of the features which appear in the calculations. We obtain a good account of the existing data, within the framework of a rather simple lattice dynamical model, and the calculations show that the features which appear are quite sensitive to the symmetry of the adsorption sites, and other details of the surface geometry. We shall illustrate this with several specific examples.

Abstract for invited paper, Third International Conference on Vibrations at Surfaces, Asilomar, CA. September 1-4, 1982.

Using surface enhanced Raman scattering (SERS) to study
adsorbate vibrations

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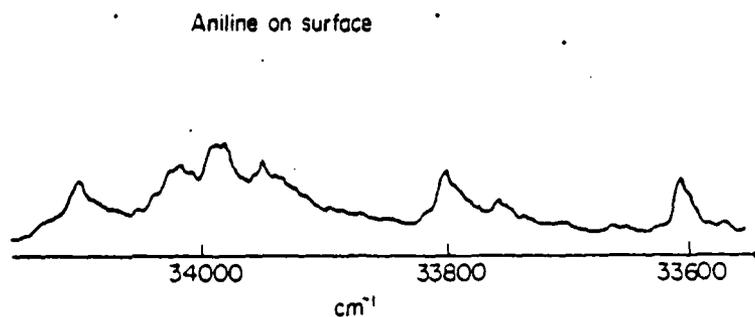
The use of a very thin metal overlayer on suitably prepared silver surfaces may allow one to achieve up to a thousand-fold enhancement of Raman scattering from adsorbates on the top metal. My investigations of these overlayer systems is directed towards determining whether use can be made of SERS for studying actual adsorption systems of interest rather than visa-versa. Certainly we can learn a great deal more about chemisorption if the vibrational spectrum of an adsorbed molecule is studied on different substrates. As a number of different metallic overlayers have been found¹ to deposit on silver without interdiffusion into the bulk at room temperature, the overlayer technique seems to be promising for generally boosting the Raman signals from adsorbates on the overlayers over a large range of excitation frequency. In particular, combined with new techniques² for generating narrow mass distributions of small metallic clusters, this overlayer method has the potential for adding additional Raman enhancement to that which may already exist due to actual resonances of the clusters with the exciting laser. Thus vibrational spectroscopy, absorption and photochemistry can be studied both on and off a natural resonance of a system small enough to compare directly with self-consistent ab-initio calculations. The SERS from CN adsorbed on gold overlayers (< 1-10 Å thick) on silver islands is consistent with a simple electromagnetic description of the broadening and shifting of the silver island film conduction electron resonance due to an absorbing overlayer. Studies of nickel overlayers on silver are in progress.

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Surface Enhanced IonizationD.M. Lubman and R. NaamanDepartment of Isotope Research, The Weizmann Institute of Science,
Rehovot, IsraelAbstract

In this work we report the first observation of the Surface Enhanced Ionization (SEI) of adsorbed molecules. A large pulse, low peak power laser ionized adsorbed molecules on various surfaces. The wavelength dependence of the process reproduced basically the single photon absorption spectra of the molecules. SEI is distinguished from gas phase multiphoton ionization in its linear dependence on laser intensity, an enhanced signal of several orders of magnitude, and a dramatic dependence on the sign of the bias voltage.



SEI spectrum of aniline adsorbed on 100Å aluminium film.

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Physisorbed monolayer on graphite studied
by neutron and X-Ray diffraction.

Abstract

Monolayers of rare gas atoms and of simple molecules physisorbed on the (002) surfaces of graphite substrates are studied primarily for the purpose of investigate phase transitions in two-dimensional systems. Recent results will be reviewed for the following transitions: Melting of incommensurate and of commensurate films, transitions from commensurate to incommensurate structures and transitions involving uniaxially deformed structures (stripe phases).

HYDROGEN CHEMISORPTION ON Ni(110) BY HIGH-RESOLUTION ELECTRON ENERGY-LOSS SPECTROSCOPY

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The interaction of hydrogen with nickel has been the object of numerous investigations because of its importance in catalytic hydrogenation, etc. In this paper is reported our study on the interaction of hydrogen with the Ni(110) surface using high-resolution electron energy-loss spectroscopy. This is a part of our investigation series on the gas-Ni(110) surface interactions (CO, O₂).

The high-resolution electron spectrometer constructed for the present study consists of a monochromator and an energy analyzer, both of 127° cylindrical deflector type. In the direct mode, an electron current at the collector entrance of 2.3×10^{-11} A is obtained with the energy spread of 60 cm⁻¹ for 5-eV electrons. Electron energy-loss spectroscopy can be combined in situ with low-energy electron diffraction and Auger electron spectroscopy.

The loss spectrum of the Ni(110) (1 X 2)-H surface at 300 K has the hydrogen-induced peaks at 641, 936 and 1121 cm⁻¹. Hydrogen exposure measurements have shown that the 936-cm⁻¹ peak intensity is increased even after the 641- and 1121-cm⁻¹ peak intensities are saturated. Angle-dependent measurements have indicated that the intensities of the three losses are peaked in the specular direction.

The experimental results are interpreted to indicate the following: (1) hydrogen is adsorbed dissociatively, (2) hydrogen is not adsorbed in the on-top site, (3) the number of the adsorbed states of hydrogen is two or three, (4) it is most probable that hydrogen atoms are adsorbed in the hollow sites of the inclined rudimentary (111) face, and (5) hydrogen may also be adsorbed in the short-bridge and/or hollow sites of the (110) face.

The low-temperature (~100 K) study is now in progress. The vibrational energy-loss study of hydrogen-covered Ni(110) surfaces both at 300 K and at ~100 K will be reported in correlation with the structural and electronic studies using low-energy electron diffraction and medium-resolution electron energy-loss spectroscopy (electronic transition), respectively.

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CALCULATIONS OF EELS SPECTRA OF Ni(111) AND Ni(100) WITH ADSORBED OXYGEN

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We present a slab calculation of the nickel surface phonons for the (111) and (100) surfaces with various overlayers of oxygen. The Ni bulk lattice dynamics is evaluated within a force constants parametrization, by taking central and angular forces into account up to second nearest neighbours, so that the bulk phonon spectrum is reproduced with high accuracy.¹ The loss function is computed in the dipole coupling approximation.

The O-Ni force constants for the Ni(111) surface are fitted to the experimental EELS peaks of isolated adsorbed oxygen atoms.² The computed spectra for the p(2x2) and the ($\sqrt{3}\times\sqrt{3}$) R30° oxygen overlayers are in good agreement with the measured spectra.² This realistic calculation allows us to discriminate between the zone boundary modes of the substrate (Rayleigh wave) and the modes induced by the oxygen atoms. In particular we have found that the peaks in the range 30-33 meV cannot be assigned to modes of the Ni(111) but are due to a oxygen-nickel stretching vibration.¹

The p(2x2) and c(2x2) oxygen overlayers on the Ni(100) surface have been object of controversy for what concerns the distance between the oxygens and the Ni surface. Recent normal photoelectron diffraction³ and atom scattering⁴ results confirm the LEED analysis⁵ indicating an equal oxygen distance in the two adsorption geometry (0.9 Å). Within this assumption we are able to reproduce the positions and the intensities of the experimental peaks in the loss spectra⁶ by taking the Ni-O central force constant of the p(2x2) 1.5 times that of the c(2x2). In particular for the p(2x2) we identify the two peaks at high frequency as due to oxygen-nickel stretching modes, while the low frequency peak is assigned to the continuum of Ni phonons in the X and M points of the surface zone.

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ADSORPTION OF HYDROGEN AND OXYGEN ON Pd(111) AND Pd(100)

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Recent results of high resolution electron energy loss spectroscopy (HEELS) and low energy electron diffraction (LEED) have been used to study the adsorption of hydrogen and oxygen on Pd(111).

Hydrogen is adsorbed in a $\sqrt{3}\times\sqrt{3}$ structure at all temperatures studied ($T > 10$ K) and nuclear magnetic resonance (NMR) shows that for the $\sqrt{3}\times\sqrt{3}$ structure a dipole excited loss is observed at 44 meV. This is consistent with adsorption in the hollow position with the hydrogen atoms located above the Pd surface.

Oxygen is dissociatively adsorbed at room-temperature and forms a $p(2\times 2)$ structure for low exposures. A dipole excited vibrational mode is observed at 44 meV implying adsorption in the hollow site. At low temperature (< 110 K) both atomic and molecular adsorption occurs. The intra-molecular stretch vibration of molecularly adsorbed oxygen appears at 90 meV and is dipole excited.

Coadsorption of oxygen and hydrogen at low temperature (~ 90 K) yields a disordered overlayer. Raising the temperature causes a successive ordering and segregation, hydrogen forming $\sqrt{3}\times\sqrt{3}$ islands and oxygen forming $p(2\times 2)$ islands. Finally, at about 200 K, hydrogen and oxygen reacts to form water, which desorbs from the surface.

Infrared Spectroscopy of Adsorbates on Low-Area Surfaces;
The Advantages of a Photons-in Photons-out Technique

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The technique of double modulation permits the simultaneous measurement of $(I_p - I_s)$ and $(I_p + I_s)$ where I_p and I_s are the intensities of radiation polarized parallel and perpendicular to the plane of incidence at the sample. I_p and I_s are attenuated in exactly the same way by a randomly oriented sample in the gas or liquid phase, and the ratio $(I_p - I_s)/(I_p + I_s)$ is unencumbered by the spectrum of a gas or liquid sample and contains only the spectrum of species which are preferentially oriented. Thus the infrared spectrum of a surface adsorbate may be measured in the presence of substantial quantities of bulk-phase adsorbant.

We have used this technique to study the infrared spectra of NO and CO adsorbates on Pt surfaces. Some of the measurements were made under uhv conditions, some were made at relatively high gas pressures (~ 1 torr) and at elevated temperatures, and some measurements of CO on a Pt electrode surface have been made in the presence of 1 M H_2SO_4 or $HClO_4$ saturated with CO.

The results of these studies shed new light on the origin of the well-established wavenumber shifts which are associated with structural changes in the adlayers formed from simple diatomic molecules. In particular, in the electro-chemical experiment, we observed a marked shift to high wavenumber as the electrode potential was made more positive so as to withdraw electrons from the surface. This provides experimental evidence that the electrons can play a significant role in determining the wavenumber shifts. Through these results we have been led to re-explore the previous explanations of the structurally related wavenumber shifts in CO adsorbates and have, we believe, shown that these shifts originate from structurally induced changes in the principal CO stretching force constant, from dipole-dipole interaction between molecules adsorbed on adjacent sites and from a second interaction force constant, the origin of which is related to the electrons in the surface.

Surface Enhanced Raman Scattering of Water on a Ag Electrode

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Surface enhanced Raman scattering of adsorbates on a Ag electrode in various electrolytes (e.g., 0.1 - 1.0 M KF, KCl, KBr, KI, K_3PO_4 , and NaN_3) has been investigated in an effort to elucidate the mechanism of the enhancement of water compared to that for other adsorbates. (It is well known, for example, that pyridine exhibits large enhancement in 0.1 M KCl while SERS from water is not detectable unless the salt concentration is raised to almost 1 M.) Use of an optical multichannel analyzer allowed rapid recording of Raman spectra, and SERS intensities of adsorbates could therefore be monitored simultaneously during a continuous oxidation-reduction cycle. Potential dependences of SERS intensities when the electrode potential is cycled in a non-faradaic potential range immediately following oxidation and reduction indicate that adatoms are partially responsible for the Raman enhancement. Furthermore, the anions in the electrolyte play an important role in stabilizing these "active sites." For this reason, the degree of enhancement is influenced by the solubility of the Ag compound formed during oxidation and the specific adsorption of the anions to the Ag surface. Preferential alignment of H_2O molecules with their oxygen ends facing the surface at positive potentials, the tendency of anions in the electrolyte to disrupt hydrogen bonding with the water network, and the weak hydrogen bonding of H_2O with the anions give rise to a SERS lineshape from adsorbed H_2O molecules which is narrower than, and thus distinguishable from, the Raman line of bulk water. Thus, the degree to which the particular anions in the electrolyte disrupt hydrogen bonding among water molecules and reform hydrogen bonding between the anions and H_2O molecules influences the SERS lineshape and the apparent enhancement of the H_2O Raman emission.

We gratefully acknowledge the partial support of this work by the Army Research Office (Grant No. DAAG29-82-K-0040), the Gas Research Institute (Basic Research Grant No. 5080-363-0319), and the National Science Foundation (Grant No. ECS-8204890).

ON THE CONTRIBUTION OF CHARGE TRANSFER EXCITATIONS TO SERS

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ABSTRACT

Resonant Raman scattering due to dynamical charge transfer from the silver metal to the lowest unoccupied orbital of pyridine and other adsorbates contributes 1 to 2 orders of magnitude to SERS. Several experimental observations indicate, that this mechanism is particularly effective at sites of atomic scale roughness.

LATERAL INTERACTIONS AND VIBRATIONAL LIFETIMES

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ABSTRACT: In this work I will consider three related topics, namely:

- (A) Lateral interactions between adsorbed molecules (§1-7);
- (B) Optical properties of two-dimensional systems of small metallic particles (§8-10);
- (C) Damping of excitations at surfaces (§11-13).

None of these topics will be treated in great detail. I hope to be able to show, however, that topics (A)-(C) are closely related and that they constitute a unified body of knowledge, which should be useful in gaining insight into such diverse fields as the optical properties of solar energy absorbers, heterogeneous catalysis and photosynthesis.

THEORETICAL STUDY OF DAMPING FOR VIBRATIONS, ROTATIONS AND TRANSLATIONS OF MOLECULES ON METAL SURFACES.

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Further theoretical evidence for the importance of the electronic mechanism for the energy exchange between an adsorbate and a metallic substrate is provided by first-principle calculations of the damping of vibrational modes of chemisorbed H and H₂ on free-electron-like metal surfaces. By varying adsorbate and substrate parameters a systematic correlation is shown between the damping rate and adsorbate-induced features in the electronic structure. The damping is enhanced when an adsorbate-induced resonance crosses the Fermi level of the substrate conduction electrons.

The calculations amount to evaluating the self-energies of the adsorbate modes under considerations to the lowest order in the screened ion-electron interaction. In the quasi-static limit the electronic system should then be considered in its ground state, which is described by performing a full chemisorption calculation within the density functional scheme using the local-density approximation for the exchange and correlation effects.

The good agreement between the calculated and measured vibrational linewidth for H on W(100)¹ shows that the electron-hole-pairs excitations of a metal substrate provide an important channel for energy dissipation from chemisorbed species on metal surfaces, at least for modes with a light effective mass.

For systems with no resonance at the Fermi level, the data indicate that the local density of electrons is a key parameter. This gives a basis for the use of a simple phase-shift-formula for rough estimates of the electronic contribution to the damping rate for several chemisorption systems.

With a resonance, however, the local electron structure has to be considered.

Estimates of the damping of translational and rotational motion will also be presented.

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INFLUENCE OF FOREIGN METAL ATOMS DEPOSITED AT ELECTRODES ON
LOCAL AND NON-LOCAL PROCESSES
IN SURFACE ENHANCED RAMAN SCATTERING.

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Surface Enhanced Raman Scattering (SERS) at electrodes exhibits a reversible potential dependence only in a limited potential range. Cathodically of that it is irreversible quenched, at Ag electrodes down to 5% of the initial SERS intensities. This holds for adsorbed pyridine molecules, for chloride, bromide, iodide, cyanide or thiocyanide ions and for water or deuteriumoxide. Since the (sub)microscopic roughness is not altered by this procedure, the quenching has to be explained with a vanishing of SERS active sites, an idea which is clearly confirmed in metal deposition experiments using SERS for pyridine as probe: In some cases, the deposition of a fraction of a monolayer ($\theta < 1\%$) of a foreign metal on Ag is sufficient to modify significantly the intensity, the Raman shift and the halfwidth of the SERS bands. In the case of Cu deposition the almost total quenching of SERS on Ag electrodes is prevented to a great extent with coverages as low as $\theta = 0.003$. In other cases the impurity metals act mainly on the SERS intensity, obviously by damping the electromagnetic resonances. These effects clearly reveals the importance and cooperation of local and non-local enhancement processes.

**TIME DEPENDENCE OF SURFACE ENHANCED RAMAN SCATTERING
DURING AND AFTER OXIDATION-REDUCTION CYCLES**

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ABSTRACT: The time-development of surface enhanced Raman scattering from silver electrodes immersed in simple electrolytes has been measured during and after oxidation-reduction cycles of the linear scan double step type. Raman spectra were recorded in times as short as 0.1 second, using a spectrograph equipped with an optical multichannel detector and analyzer. Correlations between Raman spectra and current or charge passed were found, and in mixed electrolytes the displacement of one anion by a more strongly adsorbing anion was observed. In addition, unexpectedly strong effects of laser irradiation and hydrogen evolution prior to the oxidation-reduction cycle have been observed in the intensity of SERS bands after the cycle. These last two effects are attributed to peculiar surface morphologies.

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High Frequency Localized Vibration Modes at a Stepped Surface*

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Abstract

Phonons with frequencies above the maximum frequency of the bulk crystal have been observed by Ibach and Bruchmann⁽¹⁾ in electron energy loss measurements on the (332) or $6(111) \times (1\bar{1}\bar{1})$ surface of platinum. It is assumed that these high frequency surface phonons arise due to the stiffening of the atomic force constants that accompanies the relaxation in the atomic positions in the vicinity of the steps that exist on such a high Miller index surface. Mostoller and Landman⁽²⁾ have shown that an increase of 30-40% in the largest force constants for atoms in the vicinity of a step will yield a localized mode frequency in agreement with the value measured by Ibach and Bruchmann. However, in their work no attempt was made to include relaxation to new equilibrium spacings of the atoms near the surface. It is therefore not clear whether the increases in the force constants they obtained are compatible with the relaxations in the atomic positions that occur in fact. In the present work we study a simpler stepped surface, viz. the (102) surface on a simple cubic crystal with nearest and next nearest neighbor, central force interactions, that are described by a Morse potential. The static relaxations in the positions of the atoms in the sixty atomic layers closest to the surface have been calculated by minimizing the potential energy of the crystal. The atomic force constants have then been calculated in the relaxed atomic configuration, and used in a calculation of local phonon densities of states for atoms at several points on the stepped surface by the real space continued fraction/recursion method. Conditions for the existence of a high frequency surface mode are obtained in terms of the parameters of the interface potential.

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HREELS STUDY OF FORMIC ACID ADSORPTION ON GOLD (110) AND (111) SURFACES.

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The adsorption at 100 K and the temperature decomposition of formic acid were investigated on clean and oxygen covered (110) and (111) gold single crystal surfaces by means of High Resolution Electron Energy Loss Spectroscopy (HREELS), using a RIBER-SEDRA system with the typical conditions : impact energy = 5 or 6 eV, resolution = 70 cm^{-1} counting rate \approx 100 kHz in the elastic peak.

For low exposures (below 20 L) of HCOOH on Au(110), the spectra exhibited all the characteristic bands of molecular formic acid except the $\nu(\text{O-H})$ stretching mode : that band appeared only for higher exposures at 3150 cm^{-1} , i.e. with a considerable shift to lower energy : a multilayer formation of formic acid develops with strong hydrogen bonding.

Contrasting with the Au(110) surface, the $\nu(\text{O-H})$ band is detected on Au(111) at 3150 cm^{-1} at low coverage (5L) together with a strong band at 570 cm^{-1} . This latter peak disappeared right after subsequent adsorption and the $\nu(\text{OH})$ band shifted down to 2700 cm^{-1} . Therefore molecular adsorption of HCOOH on Au(111) seems to occur from the beginning of the exposures.

After adsorption of 100 L of HCOOH at 100 K and the annealing of both gold crystals, the main vibrational modes observed revealed the presence of the formate species in the bidentate position on the surface. Subsequent heating decomposed the acid to CO_2 and H_2 . The characteristic temperatures of the two processes are 170 - 190 K range and \approx 450 K.

When oxygen is adsorbed at 550 - 600 K on the two gold surfaces, different vibrational bands are detected : therefore, different sites are occupied on the (110) and (111) crystals. This predosing induced different behaviours for subsequent doses of formic acid : on the (111) face, molecular adsorption (with very strong H bonding) is observed, whereas on the (110) plane, most of the sites are occupied by oxygen, allowing only a very slow adsorption of formate species.

Those results will be compared with data recorded for HCOOH adsorbed on Cu(100) [1], and Ag(110) [2] surfaces.

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This work was partly supported by the Belgian Fund for Joint Basic Research (FRFC).

+ Research Associate of the National Fund for Scientific Research (Belgium).

SURFACE ENHANCED RAMAN SCATTERING (SERS) FROM SILVER, COPPER, AND GOLD FILMS
IN UHV: EXCITATION SPECTRA.

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Excitation spectra are particularly useful to reveal the nature of surface enhanced Raman scattering (SERS). They provide information on the intermediate electronic states of the scattering process as well as on the surface topography of the metal via the local field strength which affects the scattered intensity. A variation of appropriate experimental parameters may allow to discriminate the contribution of different mechanisms to the excitation profile.

We have measured SER excitation spectra of different vibrational lines of various molecules (C_5H_5N , C_2H_4 , O_2 , CO) adsorbed to 'coldly' evaporated Ag-, Cu-, and Au-films in UHV. Spectra from exposed silver films exhibited in every case resonance-like excitation profiles. Independent of the adsorbed species the observed maxima shift with vibrational energy from ~ 2 eV (623 cm^{-1} line of C_5H_5N) to ~ 2.5 eV (3033 cm^{-1} line of C_5H_5N). A continuous increase of the SER intensity with increasing excitation wavelength has been observed for C_5H_5N on Cu and Au (no signals for blue excitation, only very weak signals for green excitation). The shape of the excitation curves suggests a maximum at approximately 700 - 800 nm outside the accessible wavelength range. For pyridine on Ag the influence of exposure (10^{-2} L - 10^3 L) and annealing on the excitation profile resonances has also been investigated. We observed a red-shift of the resonance with coverage, which saturates after deposition of only \sim three layers of pyridine.

Our observations can be explained by assuming an electromagnetic origin of the excitation profile resonances. We estimated a very small size of $\sim 1 - 2$ nm of the 'SERS relevant' surface roughness (bumps) and consequently a short range 'classical' enhancement restricted to mainly the first layer of adsorbed molecules. The results suggest, that the total enhancement for evaporated silver films ($\geq 10^4$) is composed of an electromagnetic part ($\leq 10^2$) and an as yet unspecified 'chemical' part ($\geq 10^2$).

OXYGEN, WATER, AND HYDROCARBON ADSORPTION ON SILVER FILMS:

A RAMAN VIBRATIONAL STUDY.

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Surface enhanced Raman vibrational spectroscopy has been used to investigate some adsorbate/silver systems, which are of interest in connection with the catalytic activity of silver in ethylene oxidation.

Oxygen exposure ($\sim 10^2 - 10^3$ L) of 'coldly' evaporated silver films leads to SER lines from a molecularly adsorbed species. Several peaks between 600 cm^{-1} and 1300 cm^{-1} are attributed to O-O stretching vibrations of different kinds of dioxygen O_2^{n-} with various values of n (the assignment to stretching vibrations is supported by $^{18}\text{O}_2$ experiments). The results differ from EELS data from oxygen exposed silver single crystal faces /1/.

Evaporated Ag films exposed to water (~ 10 L) display a characteristic SER spectrum! Line assignment is performed by comparison of H_2O and D_2O spectra. The influence of oxygen preexposure on water adsorption will be discussed.

Exposure to saturated hydrocarbons (80 L of CH_4 , 40 L of C_2H_6) does not lead to any features in the Raman spectrum which could be related to vibrations of these molecules. However, characteristic SER spectra are observed after C_2H_2 and C_2H_4 exposure (40 L). Lines are identified by isotope shifts ($\text{C}_2\text{D}_2/\text{C}_2\text{D}_4$, $^{13}\text{C}_2\text{H}_2/^{13}\text{C}_2\text{H}_4$) and by comparison to corresponding EELS results from silver single crystal faces /2/. The most intense SER peaks (C-C stretching and CH_2 scissors of C_2H_4), which are easily seen after only 10^{-3} L exposure, display a pronounced asymmetric, Fano-type line shape. The compatibility of three possible interpretations with experimental results (e.g. exposure dependence) is discussed: (a) inhomogeneous line broadening due to various adsorption sites; (b) lateral vibrational (dipole) coupling /3/; Fano-resonance in the SER process as discussed in /4/.

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MOLECULAR ORIENTATION IN THIN MONOLAYER FILMS BY INFRARED SPECTROSCOPY

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ABSTRACT: Fourier transform infrared spectroscopic measurements have been made on monolayer samples of cadmium arachidate in order to determine orientation and molecular packing on the surface. This was accomplished by using both grazing angle reflection methods, where the polarization of the infrared radiation is very close to being perpendicular to the surface, and transmission methods, where the incident optical electric field is polarized parallel to the surface. Hence these two methods are sensitive to molecular vibrations whose change in dipole moment lies along different directions. Our results showed that independent of the substrate, silver for the reflection experiments and silver bromide for the transmission experiments, the chains of the fatty acid salt (no evidence for any free acid was found) are oriented within a few degrees of the normal to the surface of the substrate. From a detailed analysis of the observed vibrational bands in the two orientations, combined with the known literature values and assignments, we were able to make a "complete assignment" of the observed bands. Our experimental results and conclusions will be presented.

THE BONDING OF SPECIES IN THE ELECTRODE SOLUTION INTERFACIAL REGION

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We have recently developed and tested a technique to obtain *in situ* infrared spectra of species adsorbed on electrodes in aqueous solution. This technique promises to provide very important data on the electrode solution interface. In addition to evidence for the identity and orientation of adsorbed species, information on interactions between electrode-adsorbates, adsorbate-adsorbate, and adsorbates-solution species may be obtained. Two different modulation schemes may be used to discriminate between oriented surface species and randomly oriented solution species. Electrochemically modulated infrared reflectance spectroscopy, EMIRS (1,2), employs square wave potential modulation to produce difference spectra. Infrared reflection adsorption spectroscopy, IRRAS (3,4), utilizes polarization modulation to obtain spectra of oriented species and permits the electrode potential to be held at selected constant values. Three specific applications of the EMIRS/IRRAS method concerning bonding of species in the interfacial region will be discussed.

The chemisorption of CO on platinum has been the subject of several spectroscopic studies which showed a significant frequency shift for the CO stretching mode as a function of coverage. (See reference 5 and the reference shown therein.) The coverage effect was first attributed to a change in the amount of platinum back bonding (6) and later considered due to dipole coupling between adsorbed molecules (7). Cross^{lev} and King (8) showed the coverage shift could be reproduced at uniform coverage using various $^{12}\text{CO}/^{13}\text{CO}$ ratios thus supporting the dipole coupling explanation. Our EMIRS/IRRAS results show that both metal back bonding and adsorbate dipole coupling are important. At constant CO coverage the frequency of the CO stretching mode shifts with changes in the electrode potential. Our direct variation of the electrode potential provides a more sensitive probe of the overlap of platinum and CO orbitals than was formerly possible. Variation of electrode potential, surface coverage, and isotopic composition permit the contributions to the bonding to be distinguished.

The structure of water at the interface with gold and silver electrodes was shown in a preliminary EMIRS study (9) to be a function of the electrode potential. The results of a much more detailed study using improved instrumentation and isotopically mixed samples will be presented. As a final example the bonding of acrylonitrile to platinum and gold will be discussed in terms of a possible violation of the surface selection rule. The observed shifts in the CN and CC stretching frequencies suggest the molecules is oriented parallel to the metal surface. The implications of this observation to the surface selection rule will be shown.

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THE OXIDATION OF METHANOL ON Cu(100) STUDIED BY
INFRARED SPECTROSCOPY

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Infrared spectroscopy has been used to study the C-O stretch vibrational mode at 1000 cm^{-1} of different coverages of CH_3O adsorbed on a Cu(100) surface. There is a large coverage dependent shift of the vibration frequency, which is caused by the dipole-dipole interaction between the molecules. CH_3O is an intermediate formed when methanol reacts with atomic surface oxygen; $2\text{CH}_3\text{OH} + \text{O} \rightarrow 2\text{CH}_3\text{O} + \text{H}_2\text{O}$. Recording of the vibration frequency was used as a measure of the CH_3O coverage, which then indicated the probability for a methanol molecule to react with a surface oxygen atom under different conditions. LEED was used for structural studies and showed that the CH_3O could form both a $c(2 \times 2)$ and a hexagonal structure. A model for the oxidation of methanol on Cu(100) is proposed, stressing the structural aspects. The model implies, that the reaction can only occur if there exist empty nearest neighbour adsorption sites adjacent to the oxygen atom and that the reaction can be prevented by presence of an excess of oxygen atoms or highly mobile CH_3O molecules on the surface. It was also found that methanol physisorbed on the surface was not able to react with the oxygen.

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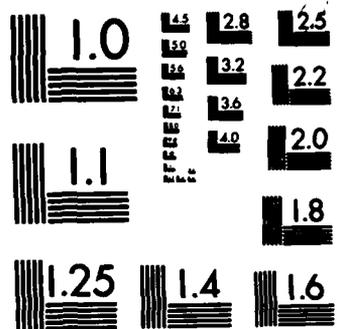


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Identification of Surface Vibrations on Clean and Oxygen Covered Pt(111) Surfaces with High Resolution Electron Energy Loss Spectroscopy (EELS)

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Stokes as well as anti-Stokes lines of surface phonons ($\hbar\omega_s = \pm 24$ meV) have been observed for the first time at a clean metal surface, i.e. Pt(111). In agreement with theory¹ their excitation probability is inverse proportional to the primary energy. Defects at {111} recrystallized Pt foils enhance surface phonon excitation significantly. In contrast to the conclusion drawn from earlier experiments², regular step arrays are not essential for this enhancement.

Extremely small exposures of gases like H₂ or O₂ lead to additional loss as well as gain features at ± 48 meV. Peak intensities and simultaneously observed intensity reductions of phonon peaks are proportional to the coverage of adsorbed particles. Reduction of phonon losses is more pronounced for O₂ than for H₂ adsorption.

At oxygen exposures $\leq 0.3L$ and $T=150$ K the fundamental vibrational E-mode of chemisorbed oxygen at 50 meV as well as its overtone at 100 meV have been identified on {111} recrystallized Pt foils whereas on ideal Pt(111) surfaces dipole selection rules rule out the observation of the fundamental E-mode³. Larger exposures $>0.6L$ lead to chemisorption of both, molecular and atomic oxygen, with pronounced characteristic losses at 107.5 meV and 60 meV, respectively. Oxide like loss features between 110...130 meV are observed after annealing of oxygen covered Pt(111) surfaces to 1000 K $< T < 1300$ K. Concentrations of different oxygen species depend on exposure, temperature, and time.

Geometric models, thermodynamics, and kinetics of Pt/O₂ interaction steps are discussed on the basis of our EELS results.

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Ab Initio Studies of Molecules Adsorbed onto Metal Clusters:
Application to Surface Enhanced Raman Spectroscopy (SERS)

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A number of studies now indicate that the enormous enhancements in Raman intensity associated with adsorption of molecules onto metal surfaces is partly but not completely due to (a relatively long ranged) enhancement in local fields which occurs because of roughness induced excitation of surface plasmons¹. There is much less certainty at present concerning the influence of short ranged interactions between molecules and metals on Raman (and other) intensities, although a number of papers² have pointed out the possible importance of such short ranged mechanisms as Raman reflectance, image effects, and resonance Raman coupling to surface or metal states.

In order to develop a better quantitative understanding of both the short and long ranged interactions between molecules and metals, we have performed time dependent Hartree-Fock calculations of frequency dependent polarizabilities and polarizability derivatives for molecules adsorbed onto metal clusters. The clusters considered to date have been of the type H_2Li_n ($n = 2, 4, 6$) with all electrons including the calculation, and the metal orbital widths modelled to make the polarization properties of the clusters similar to those of bulk metal lithium. The calculations have been done both at the optimized molecule plus cluster geometry and as a function of the molecule-metal separation.

The results of the calculations indicate that the H_2 Raman intensities are enhanced by 10^3 - 10^4 at the equilibrium adsorption geometry at frequencies close to the metal plasmon frequency. The enhancement factor decreases with increasing distance from the surface, following the predictions of the electromagnetic mechanism at long range. Near equilibrium, both the electromagnetic mechanism and short ranged mechanisms make comparable contributions, with Raman reflectance being the dominant short ranged mechanism. The enhancements are found to be only weakly dependent on cluster size, but strongly dependent on adsorbate geometry. Although the polarizability derivatives are greatly enhanced, the polarizabilities themselves and the metal and molecule energy levels are only weakly influenced by molecular adsorption.

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DIPOLE-DIPOLE COUPLING IN ADSORBATE
VIBRATIONAL MODE SPECTRA

by

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Separating chemical effects from those due to long range dipole interactions is a recurring problem in the analysis of adsorbate vibrational mode spectra^{1,2,3}. For adsorbate systems containing only one site and one type of adsorbate (homogeneous systems), agreement between theory and experiment has been obtained³. For systems containing inequivalent occupied sites or more than one adsorbate species (inhomogeneous systems), the analysis of effects due to dipole coupling can become complicated. We will show that a simple effective medium model, similar to those used for thin film coatings^{4,5}, can be used to analyze such systems. The validity of this model is tested by comparing its results to those obtained by numerically solving the exact equations of motion for arrays of coupled point dipole oscillators.

Dramatic line narrowing due to dipole coupling, as well as the more well known frequency³ and intensity² shifts are exhibited in both models. Using a simple prescription to determine the effective thickness and density for the effective medium model, we obtain results which are both qualitatively and quantitatively equivalent to those of the much less tractable point dipole model. (This equivalence can be viewed as a consequence of the long range collective nature of the long wavelength modes in a dipole coupled system). We conclude that, despite its extreme simplicity, an effective medium model can be used to accurately treat the effects of dipole coupling in inhomogeneous as well as homogeneous adsorbate systems.

Partially supported by AFOSR Grant #81-0121.

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Electronic transitions of Ar, Xe, N₂, CO physisorbed on Ag(111) and Al(111)

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High Resolution Electron Energy Loss Spectroscopy has been extended to study also the excitonic (low lying electronic) transitions of physisorbed rare gas atoms (Ar, Xe) and diatomic molecules (N₂, CO) on Ag(111) and Al(111) surfaces at ~20 K. Electron Loss Spectra were performed using a pair of hemispherical analysers mounted at a fixed scattering angle (90°). This spectrometer allowed high transmission in the range of 0-15 eV loss energies and incident beam energies up to 20 eV. AES, LEED and UV Photoemission (HeI) were also used in situ to characterize these surfaces and to identify the adsorbed gases and delineate their absolute coverage regimes.

In contrast to optical absorption experiments, we observe both, optical (dipole) forbidden and allowed electronic transitions which show vibrational fine structure for condensed multilayers. By comparison to gas phase data we find only weak perturbations in the condensed state. The observed electronic excitations show changes in intensity and FWHM depending on the coverage of the adsorbed gases.

The FWHM of the electronic excitations of CO and N₂ adsorbed in the monolayer regime is larger than in multilayers. Nitrogen, on both surfaces exhibits an increase from 60 meV to 120 meV (FWHM) whereas for CO the vibronic features are broadened out leaving peaks with FWHM of ~1 eV.

The intensities of the electronic losses for all gases are smaller in the first monolayer than in the second or in multi-layers. At submonolayer coverage the loss intensities due to electronic excitations are strongly reduced and no longer observable although vibrational bands and photoelectron spectra show the presence of physisorbed adsorbates.

Our results will be compared to optical absorption experiments¹ on similar systems and to atom-on-jellium calculations².

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ENERGY DISSIPATION AT METAL SURFACES: ELECTRONIC VERSUS VIBRATIONAL EXCITATIONS

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Abstract:

A theoretical description of the energy transfer between a surface and an atom or molecule approaching a surface is presented. In many cases the excitation of substrate phonons by the impinging adsorbate is the dominating process. In the case of metal substrates, however, it has been realized that the excitation of electron-hole (e-h) pairs can lead to sticking coefficients or vibrational damping at surfaces of the same order as found experimentally.

We focus on the description of the electronic excitations and compare our results with a very simple model of the phonon mechanism. Two special cases are treated in detail: 1) The sticking of a light chemically reactive adsorbate with an affinity level close to the Fermi energy and 2) The inelastic scattering of rare gas atoms. In case 1 the elastic scattering probability can be very small, when the affinity level crosses the Fermi energy rather far from the metal surface and the contribution of the e-h pair mechanism to the sticking probability is very important. In case 2 on the other hand the total inelastic scattering probability due to e-h pair excitations is of order 10^{-5} for thermal He atoms on a Cu surface and therefore negligible compared to the inelasticity due to phonons.

SURFACE ENHANCED RAMAN SCATTERING PHENOMENON IN LIGHT OF
RECENT EXCITATION PROFILE MEASUREMENTS

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ABSTRACT

The ultra high vacuum (UHV) surface enhanced Raman scattering (SERS) excitation profile has recently been reported for pyridine and CO on two different kinds of silver surfaces prepared in situ. The curves all show a maximum and the peak positions depend both on the adsorbed molecule and the preparation of silver surface. The optical spectra of these systems have also been measured using an oscillating beam spectrometer which compares the difference in the reflected light at two adjacent areas with and without the adsorbed molecules. The SERS phenomenon investigated in UHV is reviewed in light of these results.

Vibrational Spectra of Ethylene and Acetylene on Metal Surfaces - An Electron Energy Loss Study of Ethylene Adsorbed on Ni(110) and its Carbided Surface, and the Use of Metal-Cluster Analogies

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An analysis of on- and off-specular Electron Energy Loss Spectra (EELS) from C_2H_4 and C_2D_4 adsorbed on a clean Ni(110) and on a carbided Ni(110) surface will be reported. The carbided surface was prepared by heating the clean Ni surface in ethylene in excess of 573°C.

The spectra from ethylene at low temperatures (125K) on the clean surface is different from, but related to, those previously obtained on Ni(111) and Pt(111) at low temperatures and can reasonably be interpreted in terms of a C_2H_4 surface species with the CC bond parallel to the surface. On the carbided surface at 125K an analogous less strongly perturbed species is obtained with a spectrum closely similar to that expected for a π -bonded C_2H_4/Ni complex.

Spectral changes occur on warming C_2H_4 on clean Ni above 200K leading to a rather poorly defined spectrum at 300K which differs substantially from that associated with the CH_3CM_3 species in Pt, Rh or Pd(111) surfaces at this temperature.

The interpretation of vibrational spectra from acetylene and ethylene on metal surfaces will be briefly reviewed in the light of evidence from metal-cluster compounds, and with particular reference to recent studies of clusters with acetylene-related ligands.

Hydrogen Interactions with Ag(111): Scattering Resonances,
Vibrational Levels, and Interaction Potential Determination*

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The elastic and rotationally resolved inelastic scattering of H_2 , D_2 , and HD supersonic molecular beams from Ag(111) has been examined.² These studies have been undertaken primarily for two reasons: to determine the laterally averaged isotropic and anisotropic components of the hydrogen/Ag(111) interaction potential, and to test the accuracy of different levels of quantum gas-surface scattering calculations.

Very weak minima in specularly reflected H_2 and D_2 beams have been detected as a function of incident angle and azimuthal crystal orientation for several beam energies. These minima have been found to be predominantly due to diffractive selective adsorption scattering resonances. However, a few of the scattering resonances precess in the K_x - K_y plane about the (00) reciprocal lattice vector - indicating that rotationally mediated selective adsorption is also occurring. These resonances have been used to determine the bound vibrational levels for the various hydrogen isotopes on Ag(111). Model potentials are currently being fit to the data. These measurements are, to our knowledge, the first diffractive selective adsorption studies ever reported for a metallic close-packed fcc surface, and have shown that this technique can be used even on extremely smooth (low-corrugation) surfaces. Preliminary results on the rotational state dependence of the vibrational levels for hydrogen physisorbed on Ag(111) will also be presented. The interaction potentials derived in these experiments are being used as input for quantum calculations of rotationally inelastic scattering events.

*This work was supported in part by grants from the Office of Naval Research, the NSF-MRL, at the University of Chicago, and the Camille and Henry Dreyfus Foundation.

Surface Vibration Correlation With d-Electron(Hole) Per Atom Ratio (d-Bandfilling) in CO Chemisorption on Supported Transition Metal Particles: Dominance of Hurd's Rule and d-Electron Degeneracy in Real Supported Catalysts

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The findings of Guerra and Schulman¹ of a correlation between force constant of metal-CO chemisorbed species (admoecules) with the number of d-holes per atom (1-number of d-electrons per atom, or d-bandfilling) of the transition metal particle (supported) surface is treated using the ten-fold degenerate Hubbard² (TDHM) and Anderson (TDAM)³ models developed for magnetic and Mott metal-insulator transition problems in transition metals, alloys and compounds. Their experimental finding that, via infra-red spectroscopy on the CO adsorbed species (admoecule) bond, the infra-red surface vibrational frequency, CO bond order and CO bond force constant were nearly linear versus the number of d-holes per transition metal surface atom is easily explained via the TDHM and TDAM via their inherent d-bandfilling dependent (alloy specific) Coulomb and exchange enhanced coupling strength between d-electrons or d-holes.⁴ Even the Fulde⁵ correction to the number of d-electrons(holes) per surface atom as a function of transition metal particle size does not change the excellent agreement, but merely renormalizes the measured functional properties versus d-hole per atom ratio for a suite of equally fine sized transition metal particles. So it seems that in admoecule chemisorption (at least for CO) the degenerate electronic properties of the surface dominate the vibrational and bonding properties of the admoecular species rather completely!

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**most important*

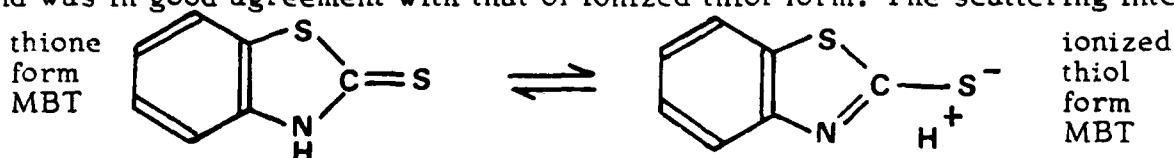
Intensity Enhancement and Spectral Change in Raman Scattering of
Mercaptobenzothiazole Adsorbed on Silver Electrode

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The discovery of surface-enhanced Raman scattering has furnished us a powerful tool for in situ observation of species present on an electrode surface. In the present paper, we have investigated the major cause of intensity enhancement in Raman spectrum of mercaptobenzothiazole (MBT) present on a silver electrode as well as changes in spectrum arisen from the changes in pH of solution and anion species. MBT was chosen in the investigation, because it is an effective corrosion inhibitor for various metals and the strong surface-enhancement of Raman intensity in this compound enables us to obtain information from trace species on electrode.

Mechanically polished silver electrode was activated by a single oxidation-reduction cycle. Charge passed the electrode in the oxidation process was limited to 10 mC/cm^2 so as to prevent excessive surface roughness. The 514.5 nm laser beam from an Ar^+ ion laser was used for the excitation.

When sulfate salt was used as electrolyte, the spectrum of MBT was almost invariant regardless of pH of solution unless solution pH was less than 2, and was in good agreement with that of ionized thiol form. The scattering intensity



from the thiol species increased proportionally to the logarithm of MBT concentration in solution in the range of $1 \times 10^{-8} \text{ mol/l} \sim 5 \times 10^{-7} \text{ mol/l}$. Adsorbed quantity of MBT in the most concentrated solution was estimated from the intensity of an absorption band at 310 nm of MBT remaining in solution, and a value of $5 \times 10^{14} \text{ molecules/cm}^2$ was obtained, assuming a roughness factor of 2 for the electrode surface. The surface concentration thus estimated corresponds to the completion of monolayer of MBT oriented normal to the metal surface. After the monolayer completion, Raman intensity decreased upon addition of MBT in solution. From these facts it can be deduced that the enhancement in scattering intensity takes place in chemisorbed species. The deduction is supported by the absorption spectrum of dissolved MBT, showing the thiol species is present in equilibrium with the thione one in neutral solutions and the former is absent in acidic solutions.

When the MBT concentration decreased passing a critical value of $1 \times 10^{-8} \text{ mol/l}$, Raman intensity of adsorbed species decreased abruptly. At the critical concentration, the electrode surface can accommodate all the MBT molecules present in the solution in a flat orientation. The species at the flat orientation may have a scattering cross section smaller than that in the normal orientation. The sudden decrease in intensity is, therefore, probably arisen from the change in orientation of adsorbed molecule.

Because halide ions are believed to play an important role in electrode reaction, in situ observation of their behavior on electrode is very interesting. Addition of bromide or chloride ion in an acidic solution of pH 2 resulted in the change of adsorbed species. The conversion to the thione species of a part of adsorbed thiol was detected on an electrode at the presence of Cl^- ion of 0.1 mol/l in concentration, and the complete conversion was obtained in a solution containing bromide ion of the same concentration. Considerable difference was noted between the spectrum of free thione species and that of the surface species. These facts may be elucidated by assuming the formation of a surface complex.

HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPIC STUDY OF THE INTERACTION OF OXYGEN
WITH MAGNESIUM SINGLE CRYSTAL SURFACES.

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For the first time, High Resolution Electron Energy Loss Spectroscopy (HREELS) has been used to study the interaction at room temperature of oxygen with the (0001) and (1100) magnesium single crystal surfaces. Owing to the high sensitivity of the method, the clean surfaces were observed to react rapidly with the residual oxygen in the UHV environment ($5 \cdot 10^{-11}$ Torr), leaving only minutes to gain data for the very low pressures.

From the very beginning of the adsorption on both the (0001) and (1100) surfaces, two bands were simultaneously observed around 500 cm^{-1} and 640 cm^{-1} , typical of metal-atomic oxygen stretching vibrations. There was no evidence of molecular oxygen adsorption even at low temperature (100 K). The first band is attributed to the vibration of atomic surface oxygen. The second band is characteristic of embedded oxygen, precursor to the oxide formation. For the basal plane, this is consistent with the following model⁽¹⁾: the oxygen is incorporated in the six-fold symmetry site, under a magnesium atom, which is raised above the surface, offering a preferential site of adsorption for the surface oxygen. The "oxide" character of the 640 cm^{-1} band is confirmed by the observation of overtones excitations as well as energy gain for the same vibration.

The relative intensities of both vibrational bands and their evolution with oxygen coverage appeared to be dependent on the crystal orientation: on the (1100) surface, these intensities are increasing more rapidly with exposure and at low exposure (below 5 L) the relative intensity of the first band (500 cm^{-1}) is greater than the relative intensity of the second band, indicating that there is more adsorbed oxygen on the surface than incorporated oxygen in the surface. This is not the case for the (0001) surface where the relative intensity of the first band always remains lower than that of the second one.

The widths (FWHM) of the two peaks were measured to be two or three times the width of the elastic peak ($\sim 65 \text{ cm}^{-1}$). This broadening is interpreted as a coupling to the electron-hole pairs of the metal. Off specular measurements did not bring significant information.

These results will be compared with data obtained with XPS, LEED, AES and $\Delta\phi$ techniques on the same crystals.

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^{*} Research Associate of the National Fund for Scientific Research (Belgium).

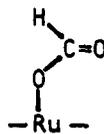
"An Electron Energy Loss Study of the Decomposition
of Formic Acid on the (001) Surface of Ru"^{**}

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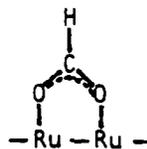
Abstract

The decomposition of formic acid on Ru(001) has been studied using high resolution electron energy loss spectroscopy (EELS) and thermal desorption mass spectrometry (TDMS). The EEL spectrometer and ultrahigh vacuum system used for this study have been described previously (1).

EEL spectra recorded for exposures of formic acid greater than 4 L at 80 K show bands characteristic of the molecular species, indicating multilayer condensation. EEL spectra recorded for exposures at 80 K corresponding to submonolayer coverages, however, show bands consistent with a mixture of monodentate (a) and bidentate bridging (b) forms of adsorbed formate, demonstrating total conversion of chemisorbed formic acid to formate and adsorbed hydrogen. In the monodentate species, a hydrogen-surface interaction is indicated by a "softening" of the $\nu(\text{C-H})$ mode, lowering its



(a)



(b)

frequency from approximately 2950 to 2375 cm^{-1} . Annealing the surface on which these formate species are present to 200 K causes bands corresponding to the bidentate bridging species to increase in intensity and bands corresponding to the monodentate species to disappear, demonstrating irreversible conversion of monodentate to bidentate bridging formate.

TDMS results indicate that formate decomposes via two competing mechanisms. One proceeds via C-O bond cleavage, yielding chemisorbed carbon monoxide, hydrogen, and oxygen; and the other proceeds via C-H bond cleavage, evolving carbon dioxide and leaving chemisorbed hydrogen. Some recombination of chemisorbed hydrogen and formate occurs, yielding small amounts of molecular formic acid. The chemisorbed oxygen and hydrogen combine to evolve water and molecular hydrogen, and EELS results show trace amounts of chemisorbed oxygen remaining after all other products desorb.

The products of formic acid decomposition evolved from Ru(001) are the same as those reported for Ni(110), Ni(111), and Ru(100) (2). On these surfaces, however, the presence of a surface-stabilized formic anhydride intermediate was inferred from the distribution of the gaseous decomposition products. EELS results show no evidence for a formic anhydride intermediate on Ru(001).

¹G.E. Thomas and W.H. Weinberg, Rev. Sci. Instrum. 50, 497 (1979).

²R.J. Madix, Advances in Catalysis (Academic Press) 29, 1 (1980), and references therein.

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**Surface Photoacoustic Spectroscopy -
A New Technique for the Study of Surface Vibrations**

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In photoacoustic spectroscopy (PAS) the sample under study is excited with a modulated or pulsed light source. Subsequent radiationless decay causes local heating. Due to thermal expansion this results in sound waves that can be detected. Thus, the PA signal reflects the optical properties of the sample. Any change of the absorption of a solid material, e.g. by species adsorbed on its surface, can then result in changes of the PA signal. PAS can be quite surface sensitive, in particular if the absorption of the substrate is not too high. Indeed, PAS has been applied recently to study phonon spectra of a few monolayers of Al_2O_3 on aluminum (1).

In order to explore the feasibility of surface photoacoustic spectroscopy at submonolayer coverage, we have studied SF_6 and $\text{C}_5\text{H}_5\text{N}$ adsorption on silver surfaces by means of a tunable cw CO_2 laser. A piezoceramic disc metalized on both sides serves as a transducer. One of its electrodes is polished and coated with silver, i.e. the silver surface is in direct mechanical contact with the detector. Additional silver deposition in situ is possible as well as cleaning of the surface with Ar^+ -ion bombardment. The sample is cooled to 90 K for gas exposure in a UHV chamber. The surface coverage can be determined by XPS and a quartz crystal microbalance. The laser is intensity modulated with a chopper and the PA signal is detected with a lock-in amplifier.

The results obtained so far show that for SF_6 adsorbed on a silver surface, the laser energy absorbed by the ν_3 vibrational mode is near $\nu\text{-}940\text{ cm}^{-1}$. For pyridien the asymmetric ring mode vibration (ν_8) centers around 1032 cm^{-1} , very similar to that observed with surface-enhanced Raman scattering. So far, PA signals have been detected with surface coverage as small as $\theta \leq 0.5$ monolayer. An even higher sensitivity is envisaged by further increasing the stability of the IR laser. In addition, the technique of surface photoacoustic spectroscopy provides high spectral resolution ($<0.1\text{ cm}^{-1}$) and should be applicable to a wide variety of adsorbates and substrates.

(1) S. O. Kanstad, P. E. Nordal, *Appl. Surf. Sci.* **5**, 286 (1980)

Vibrational State of Chemisorbed Molecule on Metal Surface*

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Sophisticated experimental works using infrared absorption-reflection, electron energy loss and Raman scattering spectroscopies have provided a variety of informations on the vibrational properties of chemisorbed molecules on metal surfaces. Extensive studies have been done for CO molecule on transition metal surfaces. Common features involved therein are the large red shift in the frequency and the short life time of the order of 10^{-12} sec for the C-O stretching mode upon chemisorption. The back donations of metal electrons into the antibonding orbitals of CO¹⁾ and the electron-hole pair excitations due to the charge fluctuation between molecule and metal²⁾ have been claimed for the explanations of the frequency shift and life time, respectively.

A purpose of this paper is to study the vibrational properties of chemisorbed molecule by focusing an interest on the dynamical interaction between localized vibrational state and the continuum of electron-hole pair excitations of the coupled molecule-metal system, where the electronic properties of chemisorbed molecule are taken into account within the Newns-Anderson model supplemented with a local displacement Q associated with molecular vibration²⁾.

The Hamiltonian describing the present model is then given by

$$H = (\epsilon_a^0 + Un_a) c_a^+ c_a + \sum_k \epsilon_k c_k^+ c_k + \Omega b^+ b + V \sum_k (c_k^+ c_a + c_a^+ c_k) + \lambda c_a^+ c_a (b + b^+),$$

where the notations have the usual meaning except the electron-localized vibration coupling strength evaluated as $\lambda = Q_0 (\epsilon_a' + U'n_a + Un_a')$, the prime denotes a derivative with respect to Q . Within the second order perturbation expansion, the shift and broadening of vibrational states are calculated as

$$\begin{aligned} \Pi_R(\omega) &= |\lambda|^2 \int_{-\infty}^{\epsilon_f} \rho_a(\epsilon_\alpha) d\epsilon_\alpha \int_{\epsilon_f}^{\infty} \rho_a(\epsilon_\beta) d\epsilon_\beta \left[\frac{1}{\omega + \epsilon_\alpha - \epsilon_\beta} - \frac{1}{\omega - \epsilon_\alpha + \epsilon_\beta} \right], \\ \Pi_I(\omega) &= \pi |\lambda|^2 \int_{\epsilon_f - \omega}^{\epsilon_f} \rho_a(\epsilon_\alpha) \rho_a(\epsilon_\alpha + \omega) d\epsilon_\alpha, \end{aligned}$$

where ϵ_f is the Fermi energy of metal and $\rho_a(\epsilon)$ is the density of states of adsorbed molecule, which is calculated in a self-consistent manner.

The vibrational line shapes thus calculated are characterized by both large red shift in the frequency and large width, where the charge fluctuation in the molecular electronic states and also $\rho_a(\epsilon)$ are found to play an important role in understanding the change of the vibrational properties of molecule upon chemisorption.

1) G. Blyholder, J. Chem. Phys. 79, 756 (1975).

2) B.N.J. Persson and M. Persson, Solid State Commun. 36, 175 (1980).

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Laser-Induced Thermal Desorption of CO from Clean Polycrystalline Copper:
Time-of-Flight and Surface Diffusion Measurements.

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Pulsed laser-induced thermal desorption was utilized as a technique to study the dynamics of desorption and surface diffusion of CO on clean polycrystalline copper at 85 K in UHV. Single pulses of a focused KrF excimer laser (248 nm, 15 ns FWHM) were used to desorb the CO molecules, which were subsequently detected by a quadrupole mass spectrometer (effective time constant = 4.4 μ s). The time-of-flight (TOF) flux distribution was recorded using a fast transient recorder (Biomation 610B/8100). The surface diffusion measurements were made using a versatile technique¹ recently developed in our laboratory, which can be used on any system where the adsorbate can be desorbed thermally. In this technique, a small area on the surface is initially depleted of adsorbate with a laser pulse. Measurements of the time dependence of the growth of the integrated desorption flux from subsequent pulses yield a diffusion coefficient.

The TOF desorption spectra could be fit to Boltzmann distributions, and effective translational temperatures of the desorbed CO molecules were obtained from these fits. The desorption process was studied as a function of laser power density, and a desorption threshold corresponding to an absorbed power density of 10 MW cm⁻² was observed. Near threshold, both the desorption flux and velocity distribution varied rapidly with laser power density. At power densities much larger than the threshold (30-75 MW cm⁻²), the peak desorption flux varied approximately linearly with power density. In the range of power densities studied, the most probable velocity of the CO molecules varied between 350 and 500 M s⁻¹, corresponding to Boltzmann temperatures between 200 and 400 K. The applicability of the classical desorption rate equation for laser induced desorption will be discussed. A preliminary analysis of the diffusion data for CO adsorbed on polycrystalline copper at 110 K yielded a value for the diffusion coefficient $D = 5 \times 10^{-7}$ cm² s⁻¹ ($\pm 2 \times 10^{-7}$ cm² s⁻¹).¹ The temperature dependence of the diffusion coefficient is currently being investigated in detail in order to accurately determine the activation energy for the diffusion process.

1. R. Viswanathan, D. R. Burgess, Jr., P. C. Stair and E. Weitz, *Journal of Vacuum Science and Technology*, 20, 605 (1982).

Resonance Raman Scattering and Fluorescence of Molecules Adsorbed on Silver Island Films

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The enhancement of regular Raman scattering (RS), resonance Raman scattering (RRS) and fluorescence from molecules adsorbed on identical well characterized silver island films are reported. A hierarchy of enhancement ratios is found with typical values of $\sim 10^5$ for RS, 10^3 for RRS and 0.1-3 for fluorescence, the latter depending on the quantum yield associated with the fluorescence of the free molecule. These experimental results are discussed within the framework of the electromagnetic theory of SERS generalized to treat molecular resonance phenomena. The relative intensities associated with the observed RS, RRS and fluorescence processes lead to a determination of the role played by the surface plasmon resonances and by the surface induced damping of the molecular excitation, in these various types of light scattering processes. The observed hierarchy of enhancements is shown to have important spectroscopic consequences.

Infrared Specular Reflection and SERS Spectra of Molecules Adsorbed on Smooth Surfaces

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Polarized infrared specular reflection spectra of carbon monoxide, benzoic acid and its derivatives adsorbed on vacuum evaporated Ag and Ni metals were measured. A peak of CO adsorbed on Ag was observed at 1940 cm^{-1} , shifted by 200 cm^{-1} , indicating the existence of a chemisorbed species on Ag as was known on Ni. Benzoic acid and its derivatives adsorbed on the metals showed the peaks to be assigned to the ionized species, $-\text{CO}_2^-$ ions. The spectra of inorganic ions adsorbed on Ag and Ni also showed the bands which were assigned to the chemisorbed species.

Surface enhanced Raman scattering (SERS) spectra of pyridine adsorbed on metal oxides, TiO_2 (optically flat surface) and NiO (cleaved surface of single crystal), were obtained and were compared with those of pyridine adsorbed on various kinds of metals (Ag, Au, Ni, Pd, Pt and Ti). The peak frequencies and the ν_0 dependence were clarified.

In order to elucidate the influence of carbon on SERS, Raman spectra of pyridine directly adsorbed on carbon were examined. It was found that the enhancement factor of adsorbed pyridine was not so large as those for the pyridine adsorbed on the metals.

The experimental facts here obtained strongly support a resonance Raman mechanism, involving a charge-transfer, of the chemisorbed species for such marked SERS.

Applications of surface polaritons for detection and vibrational spectral analysis of thin films on metals and dielectrics.

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The vibrational spectra (infrared absorption) of monomolecular films are detected by surface electromagnetic wave (SEW)-surface plasmon-polaritons propagating along the metallic support. The comparison of reflection-absorption method with SEW broad-band ($650\text{-}2500\text{cm}^{-1}$) FT-IR method of thin films detection is made. The better (5+7times) sensitivity of last one is shown. The Laser SEW excitation provides better photometric sensitivity in comparison with ordinary IR thermal radiation sources, but much shorter IR-range of available tunable lasers, limits their applications for IR vibrational spectroscopy problems of adsorbates. The prism, grating and edge methods of SEW excitations in IR are discussed.

Phonon-polaritons interaction with molecular vibrations of thin films is used for detection of oscillator spectral position, the gap in polariton branch is proportional to Vd , d -thickness of the film on dielectric support.

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