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END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

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Chemical Structure and Kinetics at Liquid/Solid Interfaces

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Part I.

a. Papers Submitted to Refereed Journals.

1. "Raman Spectroscopy of the Liquid-Solid Interface: Monolayer and Bilayer Adsorption of Pyridine on Silica", S. F. Simpson and J. M. Harris, J. Phys. Chem. 94, (in press, 1990).
2. "Measurements of Energy Dispersion at Liquid-Solid Interfaces: Fluorescence Quenching of Pyrene Bound to Fumed Silica", A. L. Wong, J. M. Harris, and D. B. Marshall, Can. J. Phys. (in press, 1990).
3. "Imaging of Fluorescent and Chemiluminescent DNA Hybrids using a 2-D CCD Camera", A. Karger, J. T. Ives, R. B. Weiss, J. M. Harris, and R. F. Gesteland, SPIE Proceedings, 1206, (in press, 1990).
3. "Modification of Quartz Surfaces via Thiol-Disulfide Interchange", J. K. Lee, D. B. Parry, K. D. Caldwell, and J. M. Harris, Langmuir (revised and resubmitted).
4. "Temperature-Induced Changes in Reversed-Phase Chromatographic Surfaces: C7 and C8 Monomeric Ligands", J. W. Carr, A. J. Rauckhorst, and J. M. Harris, J. Chromatogr. (submitted).
5. "Identification of Tetragonal and Cubic Structures of Zirconia", R. Srinivasan, R. J. DeAngelis, G. Ice, S. F. Simpson, J. M. Harris, B. H. Davis, J. Mat. Res. (submitted).

b. Papers Published in Refereed Journals.

1. "In-Situ Fluorescence Studies of Aluminum Ion Complexation by 8-Hydroxyquinoline Covalently Bound to Silica", M. R. Weaver and J. M. Harris, Anal. Chem. 61, 1001 (1989).
2. "Quantitative Estimation of Component Amplitudes in Multiexponential Data: Application to Time-Resolved Fluorescence Spectroscopy", A. L. Wong and J. M. Harris, Anal. Chem. 61, 2310 (1989).
3. "Multiple Internal Reflection Fourier Transform Infrared Spectroscopy Studies of Thiocyanate Adsorption on Silver and Gold", D. B. Parry, J. M. Harris, and K. Ashley, Langmuir 6, 209 (1990).
4. "Temperature-Induced Changes in Reversed-Phase Chromatographic Surfaces: C8 and C9 Polymeric Ligands", J. W. Carr and J. M. Harris, J. Chromatogr. 481, 135 (1989).



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Part I. Continued

d. Book Chapters Published

1. "Advances in Regression: Use of Models in Spectroscopic Data Analysis", J. M. Harris, S. D. Frans, P. E. Poston, A. L. Wong, Chapter 1 in Computer-Enhanced Analytical Spectroscopy, edited by H. Meuzelaar, (Plenum, New York), 1990.
2. "Attenuated Total Reflection FTIR for Measuring Interfacial Reaction Kinetics at Silica Surfaces", D. B. Parry and J. M. Harris, in Chemically Modified Oxide Surfaces, edited by D. E. Leyden, W. T. Collins, and C. H. Lochmüller, (Gordon and Breach, New York), 1990.

e. ONR Technical Reports Published

1. "In-Situ Fluorescence Studies of Aluminum Ion Complexation by 8-Hydroxyquinoline Covalently Bound to Silica", M. R. Weaver and J. M. Harris, ONR Technical Report No. 11, July 1, 1989.
2. "Multiple Internal Reflection Fourier Transform Infrared Spectroscopy Studies of Thiocyanate Adsorption on Silver and Gold", D. B. Parry, J. M. Harris, and K. Ashley, ONR Technical Report No. 12, July 1, 1989.
3. "Advances in Regression: Use of Models in Spectroscopic Data Analysis", J. M. Harris, S. D. Frans, P. E. Poston, A. L. Wong, ONR Technical Report No. 13, July 1, 1989.
4. "Modification of Quartz Surfaces via Thiol-Disulfide Interchange", J. K. Lee, D. B. Parry, K. D. Caldwell, and J. M. Harris, ONR Technical Report No. 14, July 1, 1989.
5. "Quantitative Estimation of Component Amplitudes in Multiexponential Data: Application to Time-Resolved Fluorescence Spectroscopy", A. L. Wong and J. M. Harris, ONR Technical Report No. 15, July 1, 1989.
6. "Attenuated Total Reflection FTIR for Measuring Interfacial Reaction Kinetics at Silica Surfaces", D. B. Parry and J. M. Harris, ONR Technical Report No. 16, July 1, 1989.
7. "Raman Spectroscopy of the Liquid-Solid Interface: Monolayer and Bilayer Adsorption of Pyridine on Silica", S. F. Simpson and J. M. Harris, ONR Technical Report No. 17, January 30, 1990.
8. "Measurements of Energy Dispersion at Liquid-Solid Interfaces: Fluorescence Quenching of Pyrene Bound to Fumed Silica", A. L. Wong, J. M. Harris, and D. B. Marshall, ONR Technical Report No. 18, May 29, 1990.

Part I. Continued

e. ONR Technical Reports Published (continued)

9. "Temperature-Induced Changes in Reversed-Phase Chromatographic Surfaces: C7 and C8 Monomeric Ligands", J. W. Carr, A. J. Rauckhorst, and J. M. Harris, ONR Technical Report No. 19, May 29, 1990.
10. "'Identification of Tetragonal and Cubic Structures of Zirconia", R. Srinivasan, R. J. DeAngelis, G. Ice, S. F. Simpson, J. M. Harris, B. H. Davis, ONR Technical Report No. 20, May 29, 1990.

h. Invited Presentations at Meetings of Scientific Societies

1. "Kinetics of Binding Silane Reagents to Silica Surfaces", J. M. Harris, D. B. Parry, and K. R. Wallace, Chemically Modified Oxide Surfaces Symposium, Midland, MI, June 28, 1989.
2. "Time-Resolved Fluorescence Studies of Molecular Transport at Liquid/Solid Interfaces", A. L. Wong and J. M. Harris, Symposium on Solid-State Fluorescence Spectroscopy, 198th National ACS Meeting, Miami, September 14, 1989.
3. "Chemical Reaction Kinetics at Liquid/Solid Interfaces", J. M. Harris, D. B. Parry, M. R. Weaver, and A. L. Wong, 3rd International Symposium on Kinetics in Analytical Chemistry, Dubrovnik, Yugoslavia, September 26, 1989.
4. "Kinetics of Binding Silane Reagents to Silica Surfaces", Symposium on Materials for Sensors and Separations, J. M. Harris, D. B. Parry, and K. R. Wallace, Materials Research Society Meeting, San Francisco, April 16, 1990.

i. Contributed Presentations at Scientific Conferences

1. "Imaging of Fluorescent and Chemiluminescent DNA Hybrids Using a 2-D CCD Camera", A. Karger, J. T. Ives, R. B. Weiss, J. M. Harris, and R. F. Gesteland, Society of Photooptical, Instrumentation, and Electronic Engineering, Los Angeles, January 16, 1990.
2. "Raman and Infrared Spectroscopy of Diphenylchlorosilane Adsorption on Silica Surfaces", D. A. Parry, K. R. Wallace, M. R. Weaver, G. R. Phillips, and J. M. Harris, 37th Annual Meeting of the Western Spectroscopy Assoc., Asilomar, CA, January 24, 1990.

Part I. Continued

j. Honors/Awards/Prizes

Andy L. Wong, Dow Chemical Graduate Research Prize, Department of Chemistry, University of Utah, May 22, 1990.

Andy L. Wong, ACS Analytical Division Summer Fellowship, 1990.

k. Number of Graduate Students Receiving Support on ONR Contract.

Total: 4 Minorities: 1 Asian: 1

l. Number of Postdoctoral Fellows Receiving Support on ONR Contract.

Total: 3 Minorities: 0 Asian: 0

m. Other Funding.

Joel M. Harris, University of Utah

1. Supporting Agency: National Science Foundation.
Project Title: Photothermal Methods for Analytical Laser Spectroscopy.
Award Amount: \$100,000
Period: June 15, 1989--June 14, 1990.
2. Supporting Agency: National Science Foundation (Approved for funding).
Project Title: Analytical Methods for Condensed-phase Photoinitiated Processes
Proposed Award Amount: \$201,437
Proposed Period: June 15, 1990--June 14, 1991.
3. Supporting Agency: Dow Chemical U.S.A.
Project Title: High Sensitivity Spectroscopy and Photocalorimetry
Award Amount: \$12,500.
Period: January 1, 1990--December 31, 1990.

Part II.

- a. Principal Investigator -- Joel M. Harris
- c. Current Telephone Number of P.I. -- (801) 581-3585
- c. Cognizant ONR Scientific Officer -- Robert J. Nowak
- d. Description of Project

This program of research is to develop spectroscopic methods for exploring chemical structure and molecular dynamics at interfaces between dielectric solids and liquids. The research is carried out using fluorescence and vibrational spectroscopy from probe molecules where spectral and temporal differences in emission, absorption, or scattering provide information about the surface onto which they are adsorbed or bound. Studies focus on the interfacial chemistry of oxide surfaces (mostly silica) and derivatized silica in contact with liquids. The spectral and temporal response of probe molecules is used to observe differences in the chemical environment at the liquid-solid interface due to the presence of bound or adsorbed molecules. Time-resolution is also valuable in sorting out heterogeneous surface environments from differences in emission rate constants, adsorption rates, and reaction kinetics of probe molecules. The dynamics of transport, adsorption, desorption, and binding of molecules to solid surfaces are being measured using perturbation methods. Fluorescence, infrared, and Raman spectroscopy are being adapted to observe perturbations of interfacial equilibria by concentration changes on time-scales of milliseconds, by temperature-jump perturbations on time-scales of microseconds, and by photoexcitation on time-scales of nanoseconds.

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- e. Significant Results during the Past Funding Year

The structure of pyridine monolayers at silica surfaces has been studied by Raman spectroscopy, where the proton transfer to the adsorbate was observed to vary with adsorbate coverage under the control of the surface potential. The spectral methods were adapted in a collaborative study to the structural forms of zirconia, and may be extended to surface site identification. The investigation of the rates of siloxane reactions at oxide surfaces was completed using ATR-FTIR and Raman. Solid-surface disorder in pyrogenic silicas was found to be a source of inhomogeneous kinetics in the fluorescence decay of surface-bound excited states. Fluorescence thermometry was used to prove feasibility of conductive temperature-jump perturbations of porous silica samples.

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Part II. Continued

f. Brief Summary of Plans for the Next Funding Year

The role of the surface in the rates of diffusion-controlled reactions at interfaces will be more thoroughly investigated. Preliminary results from nanosecond fluorescence quenching measurements indicate that two-fold enhanced reaction rates can be observed when the one of the reaction partners diffuses on the surface. The influence of the structure of a porous solid on these rates will also be considered. A stopped-flow mixer will be delivered within the month, and will be used to study faster rates of siloxane binding to silica slurries. This methodology will also be extended to measure the conformation kinetics of proteins adsorbed to oxide surfaces. Temperature-jump relaxation techniques have been adapted by our group to porous solid samples; these methods will be applied to study desorption kinetics of inhomogeneous surface environments. The relationship between the reaction kinetics and surface energetics will be identified by changes in the vibrational frequencies of the adsorbate obtained from time-resolved Raman spectra.

g. Graduate Students and Postdoctoral Fellows Currently Working on Project

Postdocs:

Dr. Kathy Rowlen, Ph.D. University of Colorado

Graduate Students:

Mr. Andy Wong, B.S. from University of Idaho
Mr. Scott Waite, B.S. from University of Arizona
Mr. Haibo Wang, B.S. from University of Peking
Mr. Eric Ellison, B.S. from University of Idaho

Part III. Research Highlight

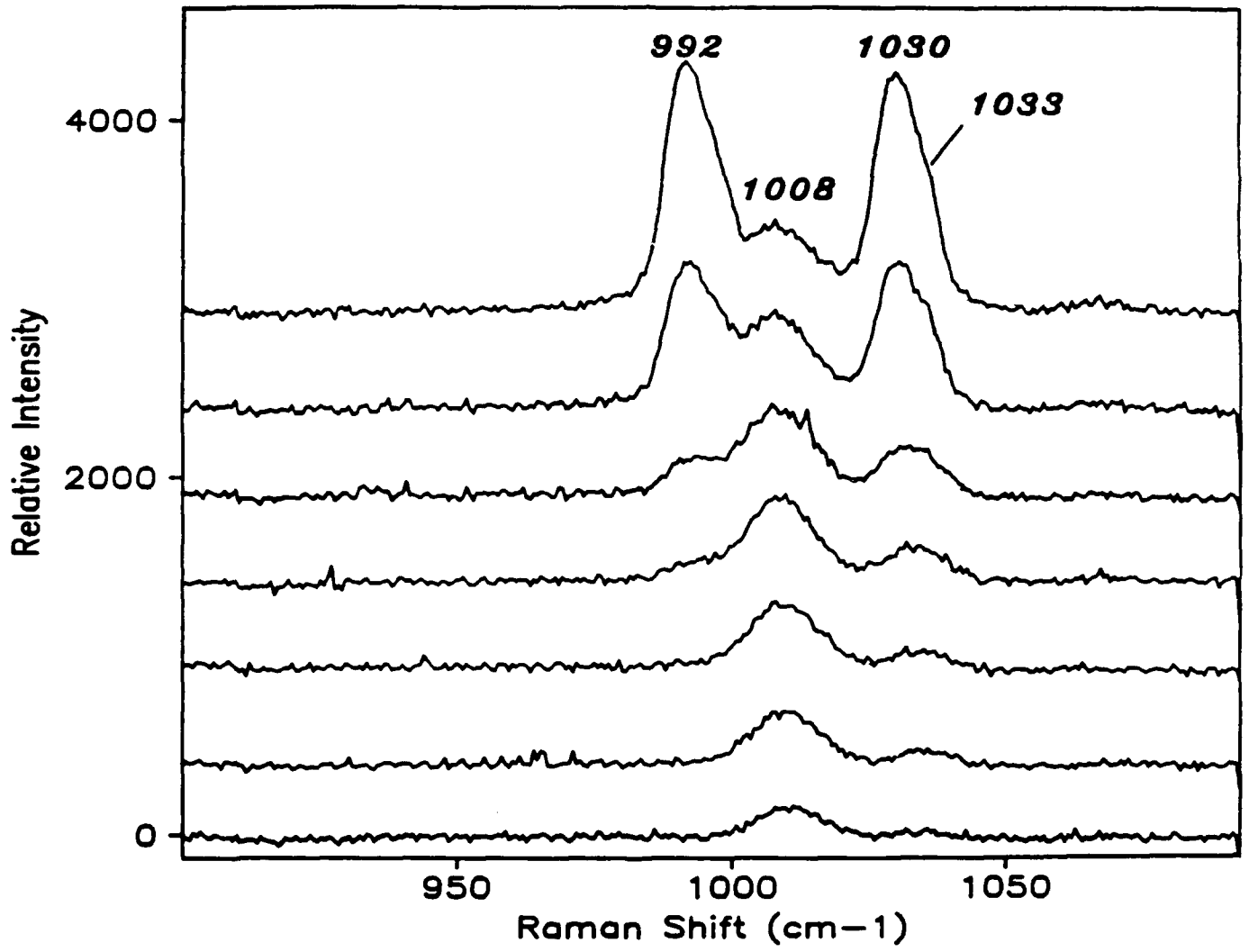
- a. Introduction (attached)
- b. Figure (attached)
- c. Conclusions (attached)
- d. Explanatory Text

A technique for the acquisition of Raman spectra of molecules adsorbed at the liquid-solid interface has been developed. Spectra are collected using low power, red excitation in conjunction with a charge-coupled-device detector to minimize fluorescence interference from the solid support while providing adequate sensitivity for detecting scattered radiation in the near-infrared region. A flow-through cell is employed to control the illuminated surface area of the porous silica samples and to minimize background from solution phase species. The technique is applied to study the adsorption of pyridine onto a silica surface from carbon tetrachloride solution. Spectroscopic adsorption isotherms are acquired which allow monolayer and bilayer forms of adsorbed pyridine to be distinguished and quantified. The isotherm data were found to fit a Frumkin model which accounts for the dependence of the free energy of adsorption on surface coverage which governs the surface potential.

In the accompanying figure, Raman spectra are shown for a packed bed of silica gel at equilibrium with pyridine concentrations ranging from 1.9 mM to 1.9 M. For the lowest concentrations, the band center of the totally symmetric ring breathing mode appears at a frequency, $\nu_1 = 1012 \text{ cm}^{-1}$, while the frequency of the trigonal symmetry ring mode initially appears at $\nu_{12} = 1034 \text{ cm}^{-1}$. The ratio of the scattering intensity of the trigonal mode to that of the totally symmetric mode is initially 0.25. The symmetric ring frequencies of adsorbed pyridine together with the observed intensity ratio are characteristic of pyridinium ion formed by proton transfer from silica. As the concentration is increased, the pyridine surface coverage becomes more complete, as shown by the growth in intensity of the ν_1 mode. A limiting intensity is reached at about 100 mM pyridine, which signals the formation of a monolayer. At concentrations exceeding this value, additional Raman bands from pyridine begin to appear at frequencies $\nu_1 = 992 \text{ cm}^{-1}$ and $\nu_{12} = 1030 \text{ cm}^{-1}$ which are indistinguishable from pyridine in free solution. These bands correspond to solution phase molecules and a small surface excess concentration of a pyridine bilayer which stabilizes the surface potential.

Raman Spectroscopy of Dielectric Solid/Liquid Interfaces Adsorption of Pyridine on Porous Silica

- * Multichannel Raman spectrometer with
Charged-coupled device detector
- * High optical thru-put, near IR sensitivity
- * 647 nm excitation (low fluorescence)
- * Flow cell packed with porous silica gel
- * Illuminated surface area constant
- * Symmetric ring modes of pyridine are
sensitive to interactions on nitrogen



Raman Spectroscopy of Dielectric Solid/Liquid Interfaces Adsorption of Pyridine on Porous Silica

- * Proton-transfer from silica to pyridine decreases with adsorbate coverage
- * Frumkin isotherm describes surface concentration
- * Adsorbate repulsion energy is 0.48 kcal/mole due to double-layer potential
- * Adsorbed pyridine bilayer also detected
- * Significance:
 - surface potential effects on adsorption at dielectric interfaces
 - role of pyridine in alkylsilane binding rxns
 - correlations between surface energetics and changes in adsorbate structure