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

CONTINUED FROM PG 3 Infrared

A tunable diode laser spectrometer has been constructed for the study of thin protective films and inhibitors on metals and oxides. Infrared spectra can be measured over the mid-IR range on films and adsorbates under a wide variety of environments--ranging from in situ electrochemical cell to ultrahigh vacuum environments. The spectrometer uses a photoelastic modulator and commercially available diode lasers to make single-beam single-pass measurements of molecular vibrations attributable to monolayer concentrations of molecules chemisorbed or physisorbed on metal surfaces. (continued on reverse)

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(continued from Block 19)

It also measures bulk spectra of liquids from a single reflection in an attenuated total reflection (ATR) mode. With suitable sample cells it would be possible to investigate liquids or gases at wide ranges of temperature, pressure, pH, etc. The spectrometer, operating in the infrared reflection absorption spectroscopy (IRRAS) mode, was used to measure in situ molecular vibrational spectra of a variety of molecular species absorbed as monolayer films on a variety of metallic substrates. Extensive studies were made for pure and diluted liquid pyridine (C_5H_5N) in the presence of an oxidized aluminum surface in an electrochemical cell environment. Comparisons were made with results for ex situ measurements of the same system. The pyridine is found to adsorb at exposed aluminum cations (Lewis acid sites) on the oxidized aluminum surface. Results have also been obtained on thin anodic protective layers on aluminum. Preliminary studies, which will be continued, have been made for monolayer coverages of CO on Pt (111).



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"IN SITU INFRARED STUDY OF INHIBITORS AND THE
SOLID-ELECTROLYTE INTERFACE"

--FINAL TECHNICAL REPORT--

BY
HENRY W. WHITE
PRINCIPAL INVESTIGATOR

1988 AUGUST 4

U.S. ARMY RESEARCH OFFICE

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UNIVERSITY OF MISSOURI
COLUMBIA, MO 65211

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I. Overview and Summary

The primary objective of this study was to obtain information on processes of corrosion and inhibition on aluminum, to develop models for corrosion and inhibition, and to suggest means to improve performance. The project had two main goals.

The first goal was the development of a new experimental capability for study of corrosion and inhibitor systems under both ex situ and in situ electrochemical conditions. A tunable diode laser infrared spectrometer was constructed during the first two years of the project. It is a unique spectrometer that operates in the Infrared Absorption Reflection Spectroscopy (IRRAS) mode. It combines high spectral brightness of the laser sources with double modulation techniques to obtain the requisite signal-to-noise ratio, resolution, and surface sensitivity to measure thin films down to monolayer coverages located at the metal or metal oxide interface under both ex situ and in situ environments. For the purpose of measuring monolayer coverages, its spectral range extends into the infrared further than any other known infrared spectrometer, FT-IR or grating type. This extended range permits observation of metal-carbon stretch modes for monolayers that are not otherwise possible using infrared techniques. The vibrational spectra that can be obtained over the mid-IR region are critically important for a wide range of studies requiring identification of corrosion films and inhibitor species on metals and oxides with environmental conditions ranging from in situ electrochemical to UHV.

The second goal was to utilize the spectrometer for several individual projects to determine its capabilities and to study corrosion and inhibition of aluminum. Following a broad survey during which IRRAS vibrational spectra were obtained for several organic films on a number of evaporated metal substrates (e.g., Al, Cu, Pb), three projects were chosen for detailed study. These three projects had the general characteristics of problems that could be associated with the study of, 1) in situ inhibitor absorption on aluminum oxide, 2) in situ anodic film formation on aluminum oxide, and 3) ex situ studies of monolayer coverages of inhibitors on clean surfaces.

The first two projects were completed and the results published. The third was in progress when the contract ended--it is continuing and will be completed to a stage of publication with support from the University of Missouri-Columbia.

As expected, the further developments of the spectrometer system were made as projects were carried out. These included improved design of spectroelectrochemical cells,

better facilities for sample preparation, environmental control for the sample (pressure, exposure, cleaning, and temperature regulation), higher signal-to-noise ratios, and improved data acquisition.

There was one major disappointment. The mass spectrometer purchased from VSW, Inc. (Manchester, England) proved to be of limited use. It was delivered one year late, was not reliable, and the service from the factory and the factory representative (Microscience, Inc., Braintree, MA) was extremely poor. Because of poor performance of the mass spectrometer unit, we have been unable to develop TDS (Thermal Desorption Spectroscopy) as an auxiliary tool for the ex situ monolayer absorption studies on metals and oxides. It is used for individual partial pressures, however.

II. Project Efforts

A. Development of Tunable Diode Laser Spectrometer

We started with a model SP 5150 spectrometer purchased earlier from Laser Analytics, Inc., (New Bedford, MA) now a division of Spectra Physics, Inc. It was designed for high resolution, low pressure gas studies. The optics were reconfigured for reflection-absorption grazing incidence studies of metal and oxide surfaces. A new data acquisition and control system was added and software developed for laser scan control, signal processing and data storage. The scan range was increased from about 1 cm^{-1} to the full range of each diode laser, typically about 100 cm^{-1} , by adding a precision temperature control unit.

A double-modulation scheme first described by Golden, Dunn, and Overend¹ was adapted for signal detection. The incident beam is chopped at $f_c = 1\text{ kHz}$ then the relative phases of the two polarizations are modulated at $f_m = 40\text{ kHz}$. Polarizers are used to balance the in-plane and out-of-plane intensities at the sample surface, which are labeled as I_p and I_s , respectively. The I_s component is not absorbed by surface species; I_p is absorbed by dipoles oriented with a component perpendicular to the surface. Using appropriate filtering, the difference $I_p - I_s$ is obtained by successive demodulation of the signal at $2f_m$ and f_c respectively. The sum $I_p + I_s$ is obtained by demodulation at f_c only. The difference is ΔR , the sum is proportional to R , which is the reflectivity with no absorption at the surface. The ratio $\Delta R/R$, the differential reflectance, is measured as a

function of incident wavenumber. The spectra are a measure of the vibrational modes of absorbed surface species and surface oxide modes. Since the effective sample region in grazing incidence geometry extends out from the surface approximately one wavelength, the beam will also sample the electrolyte in the immediate vicinity of the metal-electrolyte interface.

There are two other important useful attributes associated with the double modulation scheme: the ratio $\Delta R/R$ is insensitive to absorptions in the beam away from the sample or to fluctuations in power of the source; and 2) the ratio is not affected by thermal emission from the sample when at elevated temperature (e.g., 1000 °C). The spectrometer design has been published.² A schematic of the spectrometer is shown in Fig. 1.

B. Specific Investigations

1. Pyridine on Aluminum

The major application of the spectrometer was the study of the pyridine-aluminum oxide interface. This study clearly demonstrated that tunable diode laser IRRAS was a valuable tool for studying the metal or metal oxide electrolyte interface. Such information is typically needed in many corrosion and inhibitor studies. In this study, less than one monolayer of pyridine absorbed at Lewis Acid sites on the aluminum oxide could be detected with an overlayer of 10 microns of pyridine. The sample cell held a thin layer of pyridine between the sample surface and a ZnS hemispherical window. Spectra of $\Delta R/R$ versus frequency were taken in the mid-IR range using a series of diode lasers. Spectra of the bulk and the surface were obtained successively by changing the incident angle of the beam. Locations of absorption peaks in the bulk were in good agreement with those obtained by transmission FT-IR using a variable path length cell. The surface spectra on both polished aluminum and evaporated aluminum films showed an additional peak at 1455 cm^{-1} which was identified as a ring breathing mode of pyridine absorbed at exposed aluminum cation sites. This work has been published.³ Bulk and surface spectra are shown in Fig. 2.

2. Anodic Films on Aluminum

Anodic films grown on aluminum were studied by both in situ and ex situ IRRAS. The vibrational properties of various oxide film thickness were measured in the mid-IR region and analyzed. This work was presented at Corrosion/1988 and published as a paper.⁴

3. Monolayer Adsorbates on Metals

a. CO on Pt (111)

This project was started late in the program because equipment was not available on a timely basis. Our mass spectrometer, manufactured by VSW, arrived more than one year after schedule and has had chronic problems. We have also experienced subtle vacuum problems that have prevented us from obtaining pressures in the low 10^{-10} torr region. Spectra are now being obtained. Overall, this project was not given the resources or priority of the in situ work; however, it has the potential in the long term to be very exciting. The reason is that it would provide rather direct spectroscopic data on the nature of absorption of inhibitors on single and polycrystalline surfaces, including type of site and bonding energy, on monolayer coverages over the mid-IR range including the spectral region 300 to 1000 cm^{-1} . To our knowledge, no spectra for monolayer and submonolayer coverages of molecules on metal surfaces exist in the longer wavelength region below approximately 1000 cm^{-1} . This important region contains nearly all metal-carbon stretch modes that would be associated with organic inhibitors on metals and oxide films.

Ex situ studies can be made under controlled conditions. Pressures of various gases can be controlled from atmospheric to 10^{-10} torr. Sample temperature can be controlled from 80 to 1500 K. The sample surface can be cleaned by argon ion bombardment. At this time we are uncertain about the operational reliability of our mass spectrometer for TDS measurements. We strongly recommend against the purchase of mass spectrometers from VSW, Inc.

Our initial studies in this region have focussed on CO on Pt (111) since it is the "standard" by which to determine our operating conditions, resolution, and sensitivity. Studies on other organics and inhibitors can follow immediately.

The CO studies are progressing with funds from the University of Missouri-Columbia

until the project is completed so that the graduate student on the project can complete her Ph.D.

b. Organics on metal oxides

Spectra for a number of organics, including inhibitors, were studied on several evaporated metal films such as aluminum, copper and lead to help ascertain the operating capabilities of the spectrometer for measuring their films of corrosion inhibitors and other organics under ex situ conditions. We have used some of these results in the laboratory for diagnostic purposes. We chose to make a detailed study of the pyridine system, as described earlier. These spectra are unpublished and would need follow-up studies prior to publication.

References:

1. W. G. Golden, D. S. Dunn and J. Overend, J. Catal. 71, 395 (1981).
2. J.L. Wragg, H.W. White, and L.F. Sutcu, Rev. Sci. Instru. 59, 89 (1988).
3. J.L. Wragg, H.W. White, and L.F. Sutcu, Phys. Rev. B 37, 2508 (1988).
4. J.L. Wragg, H. W. White, and L.F. Sutcu, Corrosion/88, Paper No. 151.

III. Students Supported

Jeffrey Wragg. Ph.D. completed December 1987.
Dissertation title, "Experiments in Polarization Modulated Tunable Diode Laser Infrared Spectroscopy."

Leyla Sutcu. Ph.D. in progress; to be completed approximately December 1988.

IV. Subcontracts

During the first year of the contract, a subcontract was issued to The BDM Corporation, Albuquerque, NM, with Dr. Charles Crowder, PI. His responsibility was to calculate Quantum Mechanical Electrostatic Potential (QMEP) calculations on molecules of interest. He calculated the QMEP of pyridine. Dr. Crowder changed employers during the second year; a subcontract was not issued during the second and third years of the contract.

V. List of Publications

1. In Situ Infrared Spectroscopy of the Metal/Liquid Interface, H.W. White. McDonnell Douglas Res. Labs (St. Louis) July 7, 1988.
2. Tunable Diode Laser Infrared Spectroscopy of the Solid Liquid Interface: Pyridine on Aluminum Oxide, H.W. White, J.L. Wragg and L.F. Sutcu, APS meeting in New Orleans, March 21-25, 1988.
3. In Situ Infrared Spectroscopy of the Solid/Liquid Interface, J.L. Wragg and H.W. White NACE meeting in St. Louis, Mo. March 21-25 1988 (Invited).

VI. List of Presentations and Abstracts

1. In Situ Infrared Spectroscopy of the Metal/Liquid Interface, H.W. White. McDonnell Douglas Res. Labs (St. Louis) July 7, 1988.
2. Tunable Diode Laser Infrared Spectroscopy of the Solid Liquid Interface: Pyridine on Aluminum Oxide, H.W. White, J.L. Wragg and L.F. Sutcu, APS meeting in New Orleans, March 21-25, 1988.
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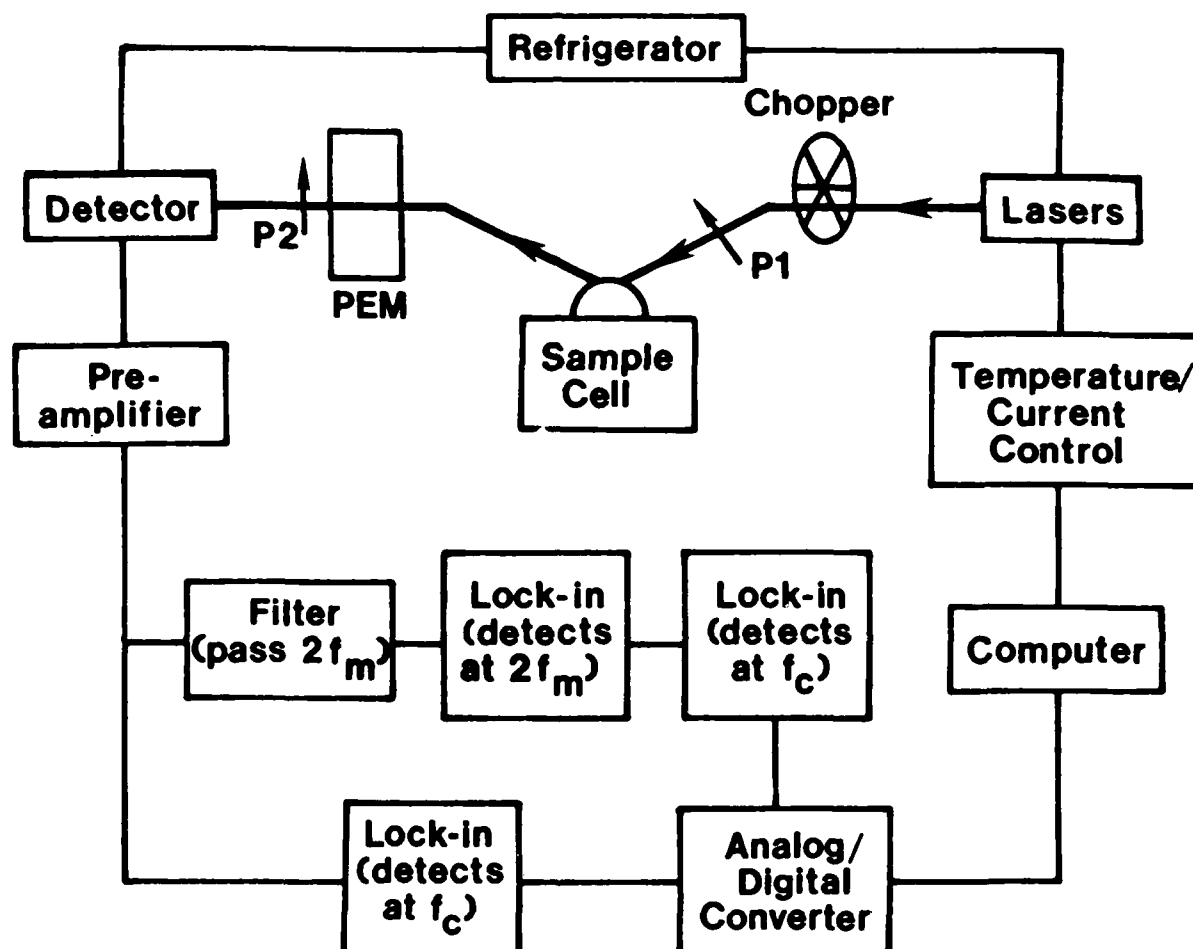


Fig. 1. Schematic diagram of the IRRAS spectrometer. P1 and P2 are polarizers. P1 is used to balance the relative proportions of the p and s polarization components of the beam. The photoelastic modulator (PEM) modulates the beam polarization at $f_m=40$ kHz. The rotating chopper interrupts the beam at $f_c=1$ kHz. From J.L. Wragg, H.W. White and L. Sutcu, Phys. Rev. B 37, 2508 (1988).

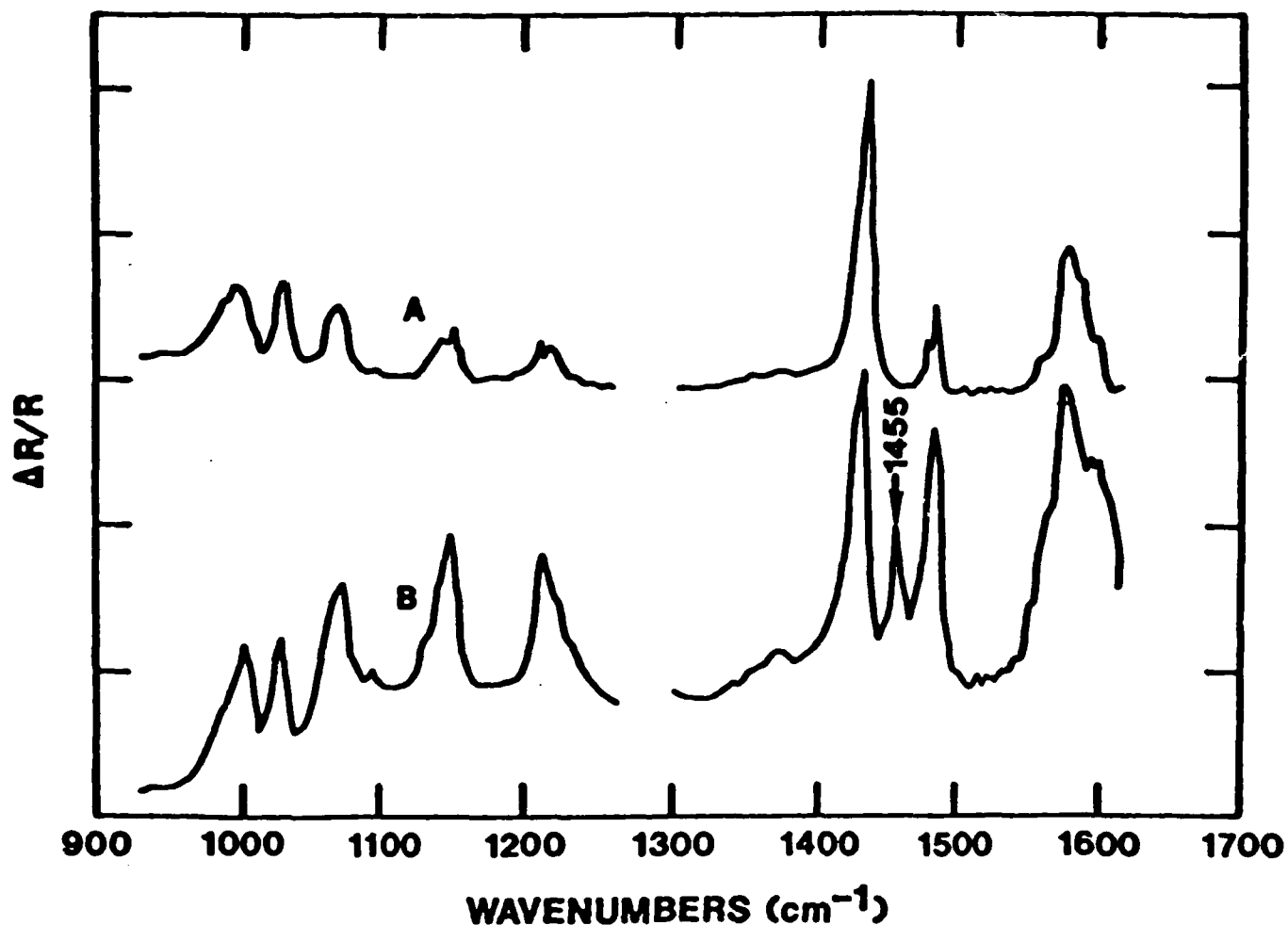


Fig. 2. IRRAS spectrum for pure pyridine, for both the bulk (curve a) and in the presence of an aluminum oxide surface (curve b). The appearance of the peak near 1455 cm^{-1} is interpreted as being due to the adsorption of pyridine at exposed aluminum cations (Lewis acid sites). From J.L. Wragg, H.W. White and L. Sutcu, *Rev. Sci. Instr.* 59 89 (1988).