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6. AUTHOR(S)
Scott S. Perry

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Research Division
4800 Calhoun Blvd.
University of Houston
Houston, TX 77204-2163

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13. ABSTRACT *(Maximum 200 Words)*

The initial objective of the equipment proposal was the adaptation of polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS) to probe samples in an ultrahigh vacuum environment where samples could be prepared and characterized under well-defined conditions. The UHV surface analysis system has been completed and the infrared spectrometer has been adapted to probe samples housed in the vacuum chamber. Experiments are underway probing the adsorption, reaction, and retention of triethylphosphate on VC(100).

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Final Technical Report

Spectroscopic Studies of Perfluorinated Lubricants and Additive Interfacial Reactivity at Metal Carbide and Nitride Surfaces

Air Force Contract Number
F49620-99-1-0117

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Principle Investigator

Dr. Scott S. Perry
Department of Chemistry
University of Houston
Houston, TX 77204-5641

Cognizant Program Officer

Lt.Col. Paul C. Trulove, Ph. D.
Program Manager, Surface and Interfacial Science
AFOSR/NL
801 North Randolph Street, Room 732
Arlington, VA 22203-1977

Statement of Objectives

The original proposal requested surface analytical equipment capable of specific molecular characterization of the interfacial composition, structure, and thermodynamic stability of polymeric lubricants and lubricant additives. The proposed equipment would include (i) polarization modulation fourier transform infrared spectroscopy for characterization of molecular structure and bonding, (ii) thermal desorption spectroscopy for the measurement of lubricant/additive heats of adsorption and surface reactivity, and (iii) the associated vacuum hardware needed to interface these instruments to an existing surface analytical system. This suite of characterization tools is capable of providing submonolayer sensitivity to the molecular details of the lubricant-substrate interface in terms of the vibrational structure, molecular orientation, and reaction profiles of lubricants and additives.

The equipment was requested in order to expand the capabilities of an ongoing program in which we are studying the fundamental issues of surface chemistry and friction of carbide and nitride hard coating materials. The aim of the present research program is to further the basic understanding of these materials thus enabling their use to solve tribological needs for USAF spacecraft. The **objective** of the equipment is to extend the range of present studies to include the characterization of real lubricants and additives on these transition metal carbide and nitride surfaces. Specifically in terms of USAF applications, the ***lubrication*** of carbide and nitride interfaces is a critical topic that must be addressed before such coating materials can be employed. The implementation of such coatings is desirable for purposes of enhancing the durability and longevity of tribological interfaces found throughout current spacecraft mechanisms. The **goal** of these studies will be to establish the chemical and physical stability of classes of potential lubricants and additives for use in the conjunction with carbide and nitride coating materials and to provide critical insight into the selection and specification of mission critical tribological interfaces of USAF spacecraft.

Status of Effort

The initial objective of the equipment proposal was the adaptation of polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS) to probe samples in an ultrahigh vacuum environment where samples could be prepared and characterized under well-defined conditions. The schematic layout of the PM-IRRAS experiments is shown below. Typically ambient samples are placed in the path of the infrared beam such at grazing angles of incidence. A significant challenge to the proposed work was the design of a system capable of analyzing samples in a restrictive UHV environment.

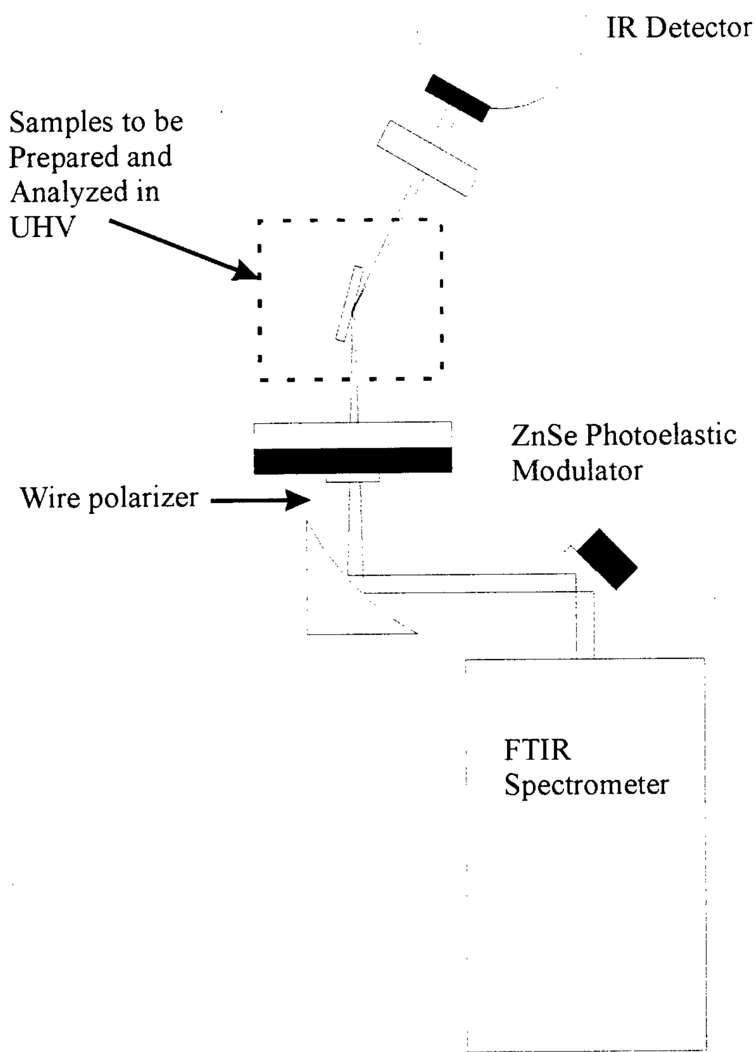

Figure 1. PM-IRRAS makes use of the surface selection rule in surface IR spectroscopy and a photoelastic modulator to simultaneously collect sample and background signals. This approach has demonstrated superior sensitivity to monolayers quantities of adsorbates.

The status of the effort is that the UHV surface analysis system has now been completed and the Infrared Spectrometer has been adapted to probe samples housed in the vacuum chamber. The system is described in the following paragraph and pictures. Work is currently under way in analyzing the first carbide samples and their interactions with model lubricant additives. The surface chemistry triethylphosphate has been initially probed with thermal desorption spectroscopy and X-ray photoelectron spectroscopy in a separate chamber. The results of these initial measurements will provide the basis of experiments designed to elucidate the molecular pathways of reaction and retention on the carbide materials using surface vibrational spectroscopy.

The custom stainless steel UHV chamber (Huntington Laboratories) is pumped by a 240 L/sec ion pump (Physical Electronics), a titanium sublimation pump (Physical Electronics) and a 345 L/sec Turbovac-361 turbomolecular pump (Leybold). An Omicron ISE 5 electron gun is utilized for sputtering of sample surfaces. Further sample preparation is carried out with a Kepco HV power supply, which allows for annealing by electron bombardment. Sample positioning is acquired by a RNN series differentially pumped rotary seal manipulator (Thermionics). The chamber is equipped with Spectraleed optics and a control unit (Omicron) capable of both LEED and Auger analysis for sample characterization. The chamber is also outfitted with a Fisions Instruments Mass Spectrometer for use in temperature programmed desorption experiments. Infrared reflection experiments are conducted with a dual channel Nicolet Nexus 670 FT-IR. The spectrometer contains a mid-IR source, a KBr beam splitter, and a liquid nitrogen cooled MCT detector. Polarization modulation takes place with a PEM-90, 47 KHz photoelastic modulator (Hinds Instruments).

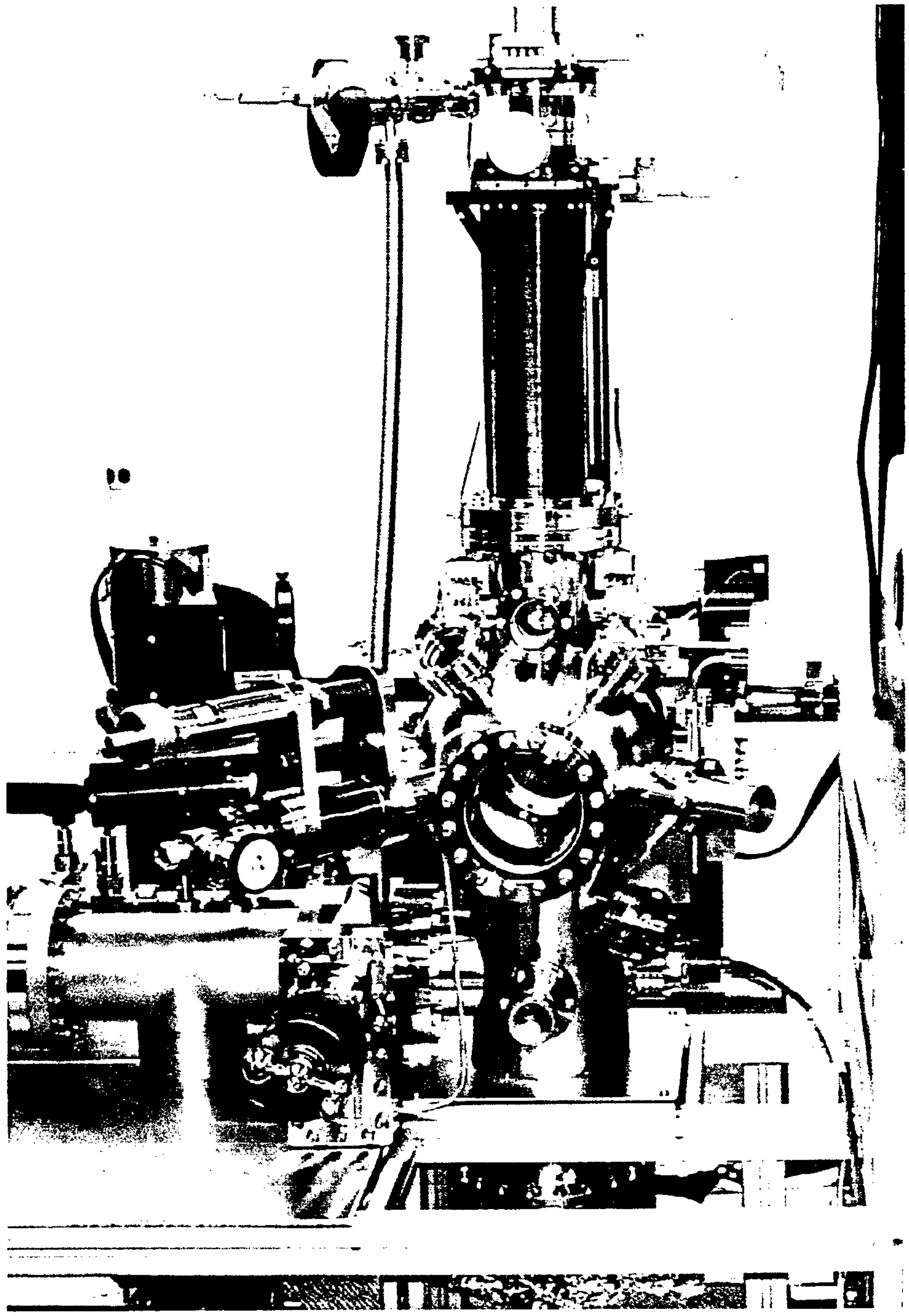

Figure 2. The custom UHV chamber has two stages for sample preparation and analysis. The lower position (centered in the front window) allows substrate sputtering, adsorbate dosing, TPD, LEED, and Auger. The upper position provides the optical path for interrogating the prepared sample with the IR beam exiting the adjacent FTIR bench. The tall bellows manipulator allows *in-situ* translation between the two positions.

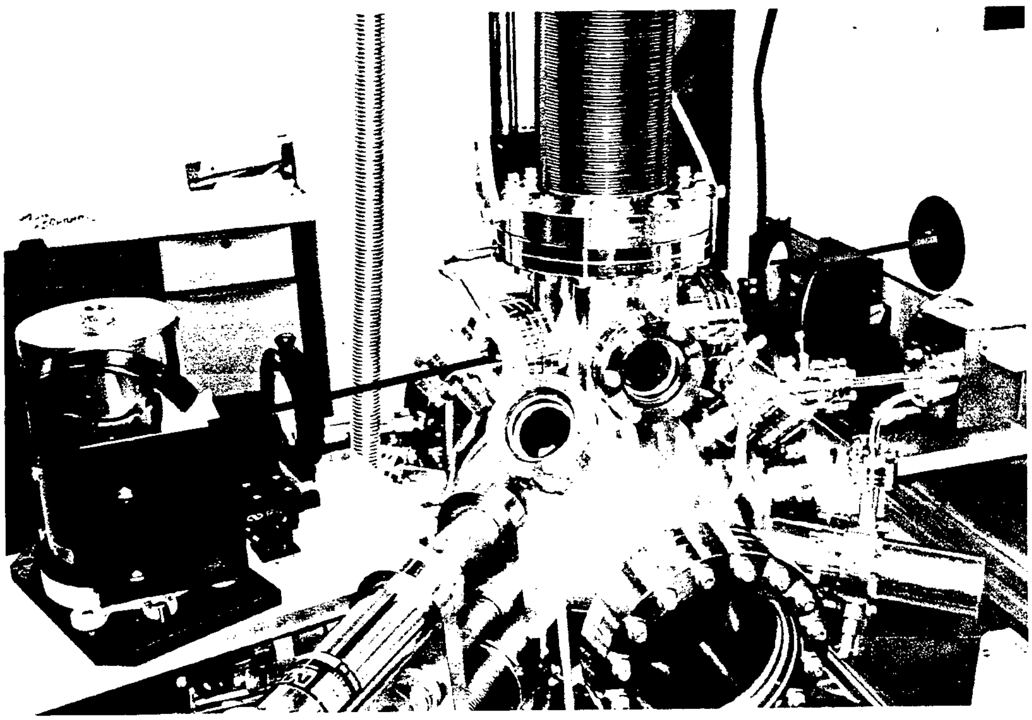

Figure 3. The path of the IR beam is artificially represented by the red line. The sample sits at the focal point of an off-axis parabolic mirror. Diverging light is collected by a BaF_2 lens and refocused onto an externally mounted MCT IR detector.

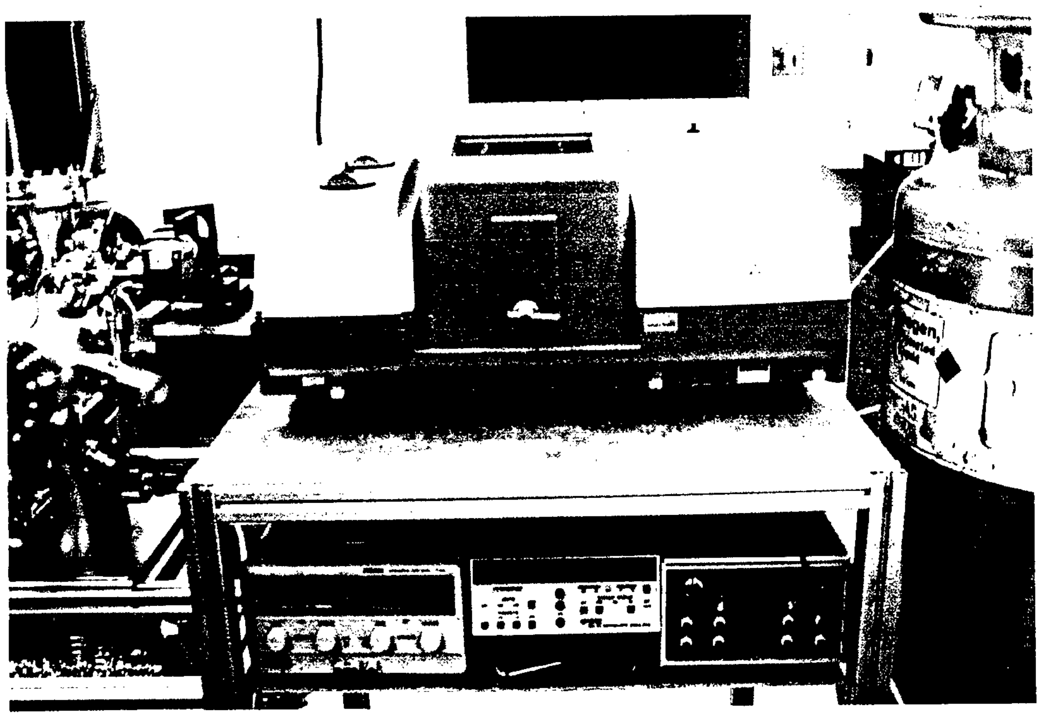

Figure 4. The PM-IRRAS experiment makes use of a Nicolet 670 FTIR bench that is equipped with dual A/D inputs, thus allowing the synchronized detection of the two signals produced from the modulation of the incident polarization.

Significance to the Field

High friction and wear are problems that plague mechanical devices, often leading to degraded performance and eventual failure. To limit these deleterious phenomena, lubrication of mechanical devices is commonplace, but the lubricant type, the inclusion of boundary additives, and the need to replenish the lubricant are factors that play a significant role in the successful design and operation of a mechanical system. The USAF obviously relies upon a vast number of machines that could all benefit from a reduction in friction and wear, in turn leading to extended lifetimes, longer intervals between service, and potentially enhanced performance. The specific devices which are most related to the proposed studies are USAF satellite mechanisms systems- specialized devices that often have very precise requirements. Such devices can represent single-point failure modes in spacecraft. Due to the inaccessibility for repair or service, these failures result in loss of mission at high strategic and financial costs. Most spacecraft mechanisms are lubricated for life during the manufacturing process with no design for "oil changes". These devices often operate under unique conditions, and therefore, lubricant loss and degradation, and the collection of wear debris may present significant problems during operation. The accumulation of wear debris in high precision bearings can affect performance by producing high torque and torque noise, and loss of precision movement capability through preload relief. There have been many documented and undocumented mechanical failures of satellite deployment devices, momentum control systems, scanners, actuators, and solar array drives; programs using such devices (essentially all USAF satellite systems) will directly benefit from the proposed work. Although the precise causes of these on-orbit failures are usually unknowable, ground testing often demonstrates that insufficient ball bearing lubrication is to blame, leading to high friction and wear. It is logical, therefore, to pursue the use of new lubricants in conjunction with new coating materials that have the potential to limit wear and extend the useful life of satellite mechanisms. Before hard coatings may be safely employed in any of these applications, suitable lubricants and additives must be identified for the range of conditions encountered. The proposed equipment seeks to expand the research to include detailed molecular level characterization of real lubricant and additive systems applied to these carbide and nitride surfaces.

Relationship to Original Goals

The original goals of the DURIP proposal have been fully realized in the completion of the UHV surface analysis system, which incorporates PM-IRRAS as a vibrational probe of molecular adsorbates on metal carbide substrates. This experimental system is now being employed to investigate the surface chemical reactivity of model lubricants and additives.

Relevance to Air Force Mission

Advanced anti-wear materials, such as hard-coated components, are beginning to find use within Air Force, DoD, and NASA spacecraft systems. Specifically, TiC-coated bearing balls are used in the filter wheel mechanisms in the NASA/GOES spacecraft and in the reaction wheels of the NASA/AXAF (Chandra) telescope. These same materials were baselined for the reaction wheels of the SBIRS-Low FDS program. In our experience, even though the hard coatings are improving performance, several questions still remain that require a fundamental understanding of the surface chemistry and tribology of these materials. In general, the same lubricants and that have been used with steel components are being used with hard coatings, with little or no insight into chemical incompatibilies or optimization of formulations. For example, the PFPE lubricant used in one of these applications appeared to chemically react with and create pits on the TiC-coated ball, making a detailed understanding of the chemical interaction of fluorocarbon species with TiC highly desirable. With our work, we seek to provide a fundamental perspective to enable these decisions to be made based on scientific principles.

Potential Applications to Air Force and Civilian Technology Challenges

In general, extensive chemical reactivity of lubricant species at tribological interfaces can be correlated with lubricant degradation. This reactivity can be potentially controlled through the use of a lubricant additive. At the same time, if there are poor interactions between a lubricant and a material, dewetting of the lubricant can occur, again leading to poor tribological performance. All of these issues are inherently related to the surface chemical interactions of lubricant and additive species, which in turn are heavily influence by the composition of the substrate materials. ***If new carbide and nitride hard coating materials are to be employed in advanced tribological settings, the interfacial properties of potential lubricant systems must be understood on a fundamental and molecular level.*** The full potential of these coating materials and the significant cost savings associated with lifetime enhancement of USAF satellite and terrestrial mechanisms can be realized only through gaining a fundamental insight into these chemical and tribological properties.

Personnel Supported by Other AFOSR Funds and Working on Project

Dr. Scott S. Perry (University of Houston)

Rebecca Guenard (University of Houston)

Publications

None to date.

Interactions/Transitions

Not applicable.

New Discoveries

Not applicable.

Honors/Awards

Scott S. Perry
University of Houston, College of Natural Science and Mathematics Teaching Excellence Award,
Spring, 2000.

Scott S. Perry (PI)
National Science Foundation CAREER Award,
April 1999.