PROGRESS REPORT FOR NASA GRANT #NAGW-4847

"Carbon in The Universe: PAHs and Clusters"
(Year 2: 08/01/96 - 07/31/97)

Richard J. Saykally - Principal Investigator
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460

I. Progress Report
A. Single Photon Infrared Emission Spectroscopy (SPIRES) Studies of PAHs: Are They Carriers of The UIR Bands?

Following the initial demonstration of this new technique [Science 265, 1686 (1994)] and its application to a series of neutral PAHs which have been proposed as candidates for the UIRs [Nature 380, 227 (1996)], we have concentrated on two major aspects of this project.

1. Developing a detailed model for infrared emission spectra of a collection of highly excited PAH molecules, in which experimental bandshapes and temperature-dependent redshifts are used in conjunction with ab initio vibrational frequencies and intensities to simulate the UIR bands. This shows that a collection of nine different cations (as large as ovalene) reproduce the I.FIR features better than do a collection of the corresponding neutrals, but a detailed match with the UIRs is not obtained. PREPRINT ATTACHED.

2. Construction of SPIRES apparatus for the study of PAH ion emission spectra. The design of this experiment is shown and described in Figure 1.

Unfortunately a disastrous accident occurred just as we were preparing to start the testing of the ion apparatus. A vacuum implosion occurred, destroying the liquid He cooled monochromator. It has taken us nearly one full year to reconstruct this, and we are only now in the final testing of the new system. We expect to try the ion experiments by the end of summer.

B. IR Laser Spectroscopy of Carbon Clusters

We have spent most of the past year incorporating the new pulsed laser vaporization/supersonic jet source of carbon clusters into our new infrared cavity ringdown spectrometer [Laser Focus World 33, 71-80 (1997)]. We hope to test this new system by the end of June. It promises a large increase in the sensitivity and frequency coverage and should lead to exciting new results for carbon clusters (hopefully the cyclic ones!).
Figure 1. Schematic view of the Polycyclic Aromatic Hydrocarbon Ions (PAHI) experiment. The PAHs are evaporated in a two stage oven source which is heated by thermocoax heating cables. After passing the changeable nozzle orifice the vapor molecules are ionized by electron impact at around 80 eV kinetic electron energy in the high current ionizer. The ions are extracted from the ionizer by a double pierce optics and focussed with an einzel lens to the entrance aperture of the transfer optics. The transfer optics adapts the hot ionizing region of the experiment to the cryogenic cool sample chamber and can be separated by a gate valve. The small entrance and exit apertures reduce the gas load of the sample chamber as well as reducing the black body radiation into the viewing region of the monochromator which has to stay at cryogenic temperatures. The transferred PAH ions are deflected by a cryogenic quadrupole deflector which is mounted onto the inner Helium shield of the doubly cold shielded sample chamber. The deflector can therefore be cooled down to approximately 5K. The bended ions are travelling towards the monochromator entrance after a deceleration region to expand the ion beam and adapts its diameter to the viewing region of the monochromator. The ions are bounced back in front of the monochromator by a simple multiple stage gridless reflectron field. This field provides a reasonable protection of the monochromator chamber from being deposited with PAHs as well as it increases the time interval in which the IR fluorescence can be detected.
11. **Future Plans**

A. **Single Photon Infrared Emission Spectroscopy (SPIRES) Studies of PAHs: Are They Carriers of The UIR Bands?**

PAH molecules will first be vaporized in an oven (200-600°C), then electron impact ionized. The ions will be extracted from the source and accelerated. All of this will occur in a room temperature vacuum chamber. Ions will then pass through a carefully baffled transfer optics system into a 4 K chamber, where they will be bent by 90° and directed along the optic axis of the SPIRES spectrometer. This will avoid a direct path for hot blackbody radiation into the spectrometer. The PAH ions will be directed into a reflectron located at the entrance to the monochromator, which will reflect the ions away from the spectrometer. Emission spectra of the PAH ions will be measured as a function of ionizing conditions, and pulsed UV lasers will be introduced as in the neutral PAH experiments. SPIRES data will be acquired as a function of both time and frequency, permitting temperature as well spectral characterization of the excited PAH ions. These same experiments will be subsequently extended to C₆₀⁺ and other Fullerene ions, noting some good matrix work for guidance.

Langhoff has calculated IR spectra for a variety of PAH cations, indicating that encouraging matches with the UIRs exist, both with regard to spectral band positions and relative intensities. Coronene and ovalene cations are two good cases, and these will be specifically addressed.

The measurement of SPIRES spectra from UV-laser excited neutral PAHs will be extended to larger systems. Unfortunately, coronene (C₂₄H₁₂) and ovalene (C₃₂H₁₄) are the largest PAHs that are commercially available in gram quantities at affordable prices. Therefore we are collaborating with Dr. J.C. Fetzer of Chevron Inc. in order to obtain specially synthesized large PAHs. We currently have a sample of benzo-dicoronene (C₄₈H₂₀) from him, which did not work well in preliminary laser vaporization experiments. Further such work is needed to perfect the laser desorption of these large PAHs. However, we feel the problems are solvable, and that we can (with the help of Dr. Fetzer) address a number of these systems.

Work from the d'Hendecourt laboratory contends that the UIRs probably arise from PAHs with 60 or more carbons. Hence it is important to pursue this extension to large molecules in order to thoroughly test the PAH hypothesis.

B. **IR Laser Spectroscopy of Carbon Clusters**

We plan to search for spectra of neutral carbon clusters with IR-cavity ringdown
spectroscopy. Following detection and characterization of new spectral features, we will use diode lasers to perform high resolution analysis.

We are writing a detailed paper on our detection of C$_3$ in interstellar sources, and note that plans to continue our search for carbon clusters in the ISM are on hold until SOPHIA becomes operational.

**Publications Supported by NASA**


**Invited Lectures**

N/A

**Contributed Talks and Posters**

### Year 3 Budget Summary

**From** 08/01/97 **to** 07/31/98

**NASA USE ONLY**

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<tr>
<th></th>
<th>Column A</th>
<th>Column B</th>
<th>Column C</th>
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<td>b. Consultants</td>
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**APPROVED BUDGET**

|          | XXXXXXXX | XXXXXXXX |

**Instructions**

1. Provide a separate budget summary sheet for each year of the proposed research.

2. Grantee estimated costs should be entered in Column A. Columns B and C are for NASA use only. Column C represents the approved grant budget.

3. Provide in attachments to the budget summary the detailed computations of estimates in each cost category, along with any narrative explanation required to fully explain proposed costs.

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**ADDITIONAL INSTRUCTIONS ON REVERSE**
**Project Title: Carbon in The Universe: PAHs and Clusters**

**PROPOSED BUDGET**

**SALARIES AND WAGES**

<table>
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<th>No.</th>
<th>Classification</th>
<th>Amount of Time</th>
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<td>Postdoctoral</td>
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TOTAL SALARIES AND WAGES $36,000

**EMPLOYEE BENEFITS**

- 17% Postdoctoral $6,120

TOTAL EMPLOYEE BENEFITS $6,120

**OTHER COSTS**

- Publication charges (various journals) $1,000
- Supplies (liquid helium, liquid nitrogen, laser gases) $2,578

TOTAL OTHER COSTS $3,578

**TRAVEL**

- Travel expenses for PI and Postdoc to attend meetings (ACS, APS, Mol. Spec. Sym. & NASA Contractors Meetings) $1,000

TOTAL DIRECT COSTS $46,698

**TOTAL INDIRECT COSTS**

- 49.90% (7/1/95-6/30/98) $23,302

TOTAL AMOUNT REQUESTED $70,000
CURRICULUM VITAE

Richard James Saykally
Professor of Chemistry
University of California, Department of Chemistry (MC 1460)
Berkeley, CA 94720-1460, U.S.A.
(September 10, 1947; Rhinelander, Wisconsin)

- Professional Interests: Laser spectroscopy, ultrasensitive detection of trace species, high energy molecules, molecular ions, clusters, intermolecular forces, molecular dynamics, molecular spectroscopy, astrophysics, astrochemistry, science education.

- Coauthor of over 200 Scientific Articles.
- Research advisor for 30 Ph.D. and 6 M.S. Graduates and 18 Postdoctorals.

Education

- B.S. (1970) University of Wisconsin - Eau Claire
- Ph.D. (1977) University of Wisconsin - Madison (with R. C. Woods)
- Postdoctoral (1977-79) NIST - Boulder (with K. M. Evenson)

AWARDS, HONORS, LECTURESHIPS

- National Research Council Postdoctoral Fellowship - 1977
- Camille and Henry Dreyfus Award - 1979
- NSF Presidential Young Investigator - 1984-88
- UC Berkeley Miller Research Professor - 1985-86
- Fellow - Royal Society of Chemistry - 1986
- UW-Eau Claire Distinguished Alumnus Award - 1987
- Bergman Lectureship, Yale University - 1987
- Merck-Frost Lectureship, University of British Columbia - 1988
- Michelson Prize for Spectroscopy (Coblentz Society) - 1989
- E.K. Plyler Prize for Molecular Spectroscopy (APS) - 1989
- Fellow - American Physical Society - 1989
- E.R. Lippincott Medal for Spectroscopy (OSA, SAS) - 1992
- Distinguished Teaching Award - University of California-Berkeley - 1992
- Harrison Howe Award (ACS-Rochester Section) - 1992
- L.J. Bircher Lectureship, Vanderbilt University - 1993
- Fellow - Optical Society of America - 1994
- Churchill Fellowship, Cambridge University - 1995
- Harry Emmett Gunning Lectureship, University of Alberta - 1995
- Fellow - American Academy of Arts and Sciences - 1995
- Humboldt Senior Scientist Award - 1995
- Samuel M. McElvain Lectureship, University of Wisconsin-Madison - 1995
- UC Berkeley Miller Research Professor - 1996

PROFESSIONAL ACTIVITIES

- Co-Director - "Science for Science Teachers (S²T)," NSF Summer Training Institute for Junior High School Science Teachers - 1989-93
- Canvassing Committee - Irving Langmuir Award (ACS) - 1996-2001
- Executive Committee - Division of Chemical Physics (APS) - 1995-present
- Laser Science Topical Group Fellowship Committee (APS) - 1993-present
- Selection Committees - E.K. Plyler Prize (APS), Ellis R. Lippincott Medal (OSA)

Triennial Oversight Committee for the NSF - 1992
Executive Committee - Western Spectroscopy Conference - 1982-85
International Steering Committee - Twelfth International Conference on Laser Spectroscopy (TWICOLS '95)

Board of Directors, Space Sciences Laboratories, U.C. Berkeley 1983-86
Member - American Association of University Professors, American Association for the Advancement of Science, American Chemical Society

PROFESSIONAL EXPERIENCE
Assistant Professor, University of California-Berkeley (1979-83)
Associate Professor, University of California-Berkeley (1983-86)
Professor, University of California-Berkeley (1986-present)
Vice Chairman, University of California-Berkeley (1988-91)
Principal Investigator, Lawrence Berkeley Laboratory (1983-91)
Visiting Professor, University of Nijmegen (1991)
Visiting Professor, Max-Planck-Institute for Fluid Dynamics-Göttingen (1991)
Visiting Professor, Cambridge University (1995)
PUBLICATIONS (1995 - present)

RICHARD J. SAYKALLY


