# 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 condidates 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 molecles, in which experimental bandshapes and temperature-dependent redshifts are used inconjunction 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 UIR 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 disasterous 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!).

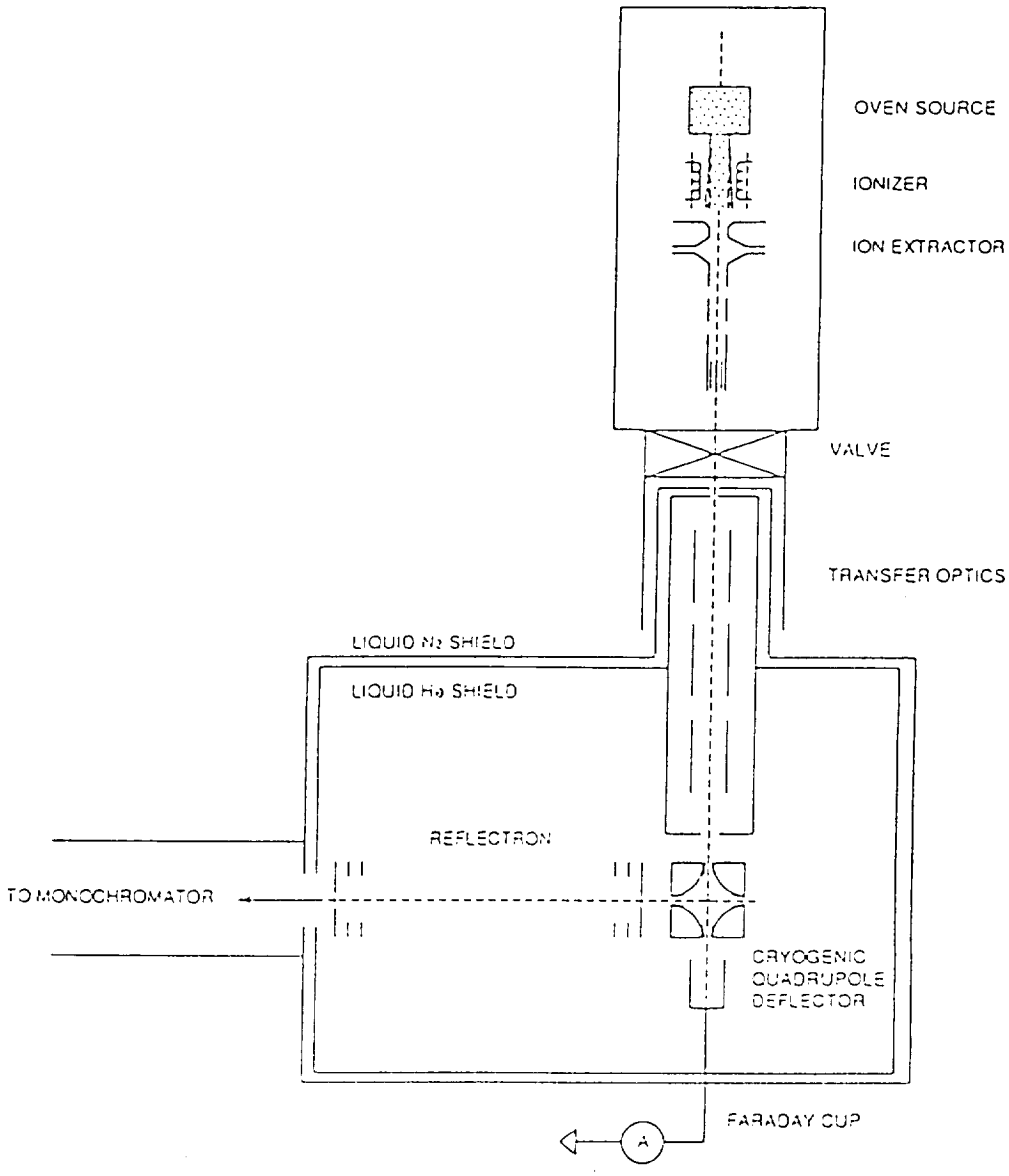


**Figure 1.** Schematic view of the Polycyclic Aromatic Hydrocarbon Ions (PAHI) experiment. The PAHs are evaporated in a two stage oven source which is heated by thermocoax heating cables. After passing the changeable nozzle orifice the vapor molecules are ionized by electron impact at around 80 eV kinetic 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.

## II. *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 $C_{60}^+$ 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 ($C_{24}H_{12}$) and ovalene ($C_{32}H_{14}$) 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 ($C_{48}H_{20}$) 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***


1. A. Van Orden and R.J. Saykally, "Carbon," in *The 1997 McGraw-Hill Yearbook of Science & Technology*, Sybil P. Parker, editor, pp. 71-73 (McGraw-Hill, Inc. 1996).

2. A. Van Orden, R.A. Provencal, F.N. Keutsch, and R.J. Saykally, "Infrared Laser Spectroscopy of Jet-Cooled Carbon Clusters: The $\nu_5$ Band of Linear $C_9$," *J. Chem. Phys.* **105**, 6111 (1996).

3. J.R. Heath and R.J. Saykally, "Space Carbon: Neutral Pathways?," *Science* **274**, 1480 (1996).

4. D.J. Cook and R.J. Saykally, "Simulated Infrared Emission Spectra of Highly Excited Polyatomic Molecules: A detailed model of the PAH-UIR hypothesis," (in preparation 1997). *PREPRINT ATTACHED.*

5. D.J. Cook, S. Schlemmer, N. Balucani, D.R. Wagner, J.A. Harrison, B. Steiner, and R.J. Saykally, "Single Photon Infrared Emission Spectroscopy: A Study of UV Laser Excited PAHs from 3 to 10 μm," (in preparation 1997). *PREPRINT ATTACHED.*


*Invited Lectures*

N/A

*Contributed Talks and Posters*

1. "Polycyclic Aromatic Hydrocarbons and the Interstellar Unidentified Infrared Emission Bands: Infrared Photon Counting Fluorescence Study," Western Spectroscopy Association, 43rd Annual Meeting, Asilomar Conference Center, Pacific Grove, CA; January 31-February 2, 1996.

Year 3

## Budget Summary

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

| | | NASA USE ONLY | |
|---|---|---|---|
| | A | B | C |
| 1. Direct Labor (salaries, wages, and fringe benefits) | $42,120 | | |
| 2. Other Direct Costs: | | | |
| a. Subcontracts | | | |
| b. Consultants | | | |
| c. Equipment | | | |
| d. Supplies | $2,578 | | |
| e. Travel | $1,000 | | |
| f. Other | $1,000 | | |
| 3. Indirect Costs | $23,302 | | |
| 4. Other Applicable Costs | | | |
| 5. Subtotal--Estimated Costs | $70,000 | | |
| 6. Less Proposed Cost Sharing (if any) | | | |
| 7. Carryover Funds (if any) | | | |
| a. Anticipated amount | | | |
| b. Amount used to reduce budget | | | |
| 8. Total Estimated Costs | $70,000 | | XXXXXXX |
| APPROVED BUDGET | XXXXXXX | XXXXXXX | |

## 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.

---------- ADDITIONAL INSTRUCTIONS ON REVERSE ----------

*NASA Exobiology Program*
*(Grant #NAGW-4847)*

*Project Title: Carbon in The Universe: PAHs and Clusters*

*PROPOSED BUDGET*

SALARIES AND WAGES

| No. | Classification | Amount of Time | | Month | Monthly Rate | 8/1/97-7/31/98 |
|---|---|---|---|---|---|---|
| 1 | Postdoctoral | 100% | for | 12 | 3,000 | $36,000 |
| 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
Bourke Medal, U.K. Royal Society of Chemistry - 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 ($S_4ST$)," NSF Summer Training Institute for Junior High School Science Teachers - 1989-93
Co-Director - "Prime Science," NSF Junior High School Curriculum Development Project - 1992-present
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)
Journal Editorial Review Boards - Journal of Chemical Physics (1993-95),

Molecular Physics (1983-present), Chemical Physics Letters (1987-present), Spectroscopy (1986-present), Review of Scientific Instruments (1987-90), Journal of Molecular Spectroscopy (1995-present)

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*

151. J.J. Scherer, J.B. Paul, A. O'Keefe, and R.J. Saykally, "CRLAS: A New Analytical Technique for Cluster Science," in *Advances in Metal and Semiconductor Clusters, Volume 3*, M.A. Duncan, editor, pp. 149-180 (JAI Press Inc. **1995**).

155. J.J. Scherer, J.B. Paul, A. O'Keefe, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy: History, Development, and Application to Pulsed Molecular Beams," *Chemical Reviews* **97**, 1, 25-51 (**1997**).

163. M.J. Elrod and R.J. Saykally, "Vibration-Rotation-Tunneling Dynamics Calculations for the Four Dimensional $(HCl)_2$ System: A Test of Approximate Models," *J. Chem. Phys.* **103**, 921 (**1995**).

164. M.J. Elrod and R.J. Saykally, "Determination of the Intermolecular Potential Energy Surface for $(HCl)_2$ from VRT Spectra," *J. Chem. Phys.* **103**, 933 (**1995**).

165. A. Van Orden, J.D. Cruzan, R.A. Provencal, T.F. Giesen, R.J. Saykally, R.T. Boreiko, and A.L. Betz, "A Search for the $C_3$ Carbon Cluster in the Interstellar Medium," *Proceedings of the 1994 Kuiper Airborne Astronomy Symposium, NASA-Ames Research Center, Moffett Field, CA, Astron. Soc. Pac. Conf. Ser.*, **73**, 67-70 (**1995**).

166. J.J. Scherer, J.B. Paul, C.P. Collier, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy and Time-of-Flight Mass Spectroscopy of Jet-cooled Copper Silicides," *J. Chem. Phys.* **102**, 5190 (**1995**).

167. A. Van Orden, R.A. Provencal, T.F. Giesen, and R.J. Saykally, "Characterization of Silicon-Carbon Clusters by Infrared Laser Spectroscopy: The $\nu_1$ Band of $SiC_4$," *Chem. Phys. Lett.* **237**, 77-80 (**1995**).

168. J.J. Scherer, J.B. Paul, C.P. Collier, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) and Time-of-Flight Mass Spectroscopy of Jet-cooled Silver Silicides," *J. Chem. Phys.* **103**, 113 (**1995**).

169. J.J. Scherer, J.B. Paul, C.P. Collier, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) and Time-of-Flight Mass Spectroscopy of Jet-cooled Gold Silicides," *J. Chem. Phys.* **103**, 9187 (**1995**).

170. D.J. Cook, S. Schlemmer, N. Balucani, D.R. Wagner, B. Steiner, and R.J. Saykally, "Infrared emission spectra of candidate interstellar aromatic molecules," *Nature* **380**, 227 (**1996**).

171. J.J. Scherer, J.B. Paul, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy of the Jet-cooled Aluminum Dimer," *Chem. Phys. Lett.* **242**, 395-400 (**1995**).

172. J.D. Cruzan, L.B. Braly, K. Liu, M.G. Brown, J.G. Loeser, and R.J. Saykally, "Quantifying Hydrogen Bond Cooperativity in Water: VRT Spectroscopy of the Water Tetramer," *Science* **271**, 59 (**1996**).

173. J.B. Paul, J.J. Scherer, C.P. Collier, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy and Time-of-Flight Mass Spectroscopy of Jet-cooled Platinum

Silicides," *J. Chem. Phys.* **104**, 2782 (**1996**).

174. J.J. Scherer, D. Voelkel, D.J. Rakestraw, J.B. Paul, C.P. Collier, A. O'Keefe, and R.J. Saykally, "Infrared Cavity Ringdown Laser Absorption Spectroscopy (IR-CRLAS)," *Chem. Phys. Lett.* **245**, 273-280 (**1995**).

175. M.R. Viant, R.S. Fellers, R.P. McLaughlin, and R.J. Saykally, "Infrared Laser Spectroscopy of Uracil in a Pulsed Slit Jet," *J. Chem. Phys.* **103**, 9502 (**1995**).

176. K. Liu, M.G. Brown, J.D. Cruzan, and R.J. Saykally, "VRT Spectra of the Water Pentamer: Structure and Dynamics," *Science* **271**, 62 (**1996**).

177. A. Van Orden and R.J. Saykally, "Carbon," in *The 1997 McGraw-Hill Yearbook of Science & Technology*, Sybil P. Parker, editor, pp. 71-73 (McGraw-Hill, Inc. **1996**).

178. K. Liu, R.S. Fellers, M.R. Viant, R.P. McLaughlin, M.G. Brown, and R.J. Saykally, "A Long Path Length Pulsed Slit Valve Appropriate for High Temperature Operation: Infrared Spectroscopy of Jet-cooled Large Water Clusters and Nucleotide Bases" *Rev. Sci. Instrum.* **67**, 410 (**1996**).

179. K. Liu, J.D. Cruzan, and R.J. Saykally, "Water Clusters," *Science* **271**, 929 (**1996**) - Invited Article.

180. K. Liu, M.G. Brown, and R.J. Saykally, "Far-Infrared VRT Spectroscopy of Two Water Trimer Isotopomers: Vibrationally Averaged Structures and Rearrangement Dynamics," *Molecular Physics* **89**, 1373 (**1996**).

181. J.J. Scherer, J.B. Paul, C.P. Collier, A. O'Keefe, D.J. Rakestraw, and R.J. Saykally, "Cavity Ringdown Laser Spectroscopy: A New Ultrasensitive Absorption Technique," *Spectroscopy* **11**, 46-50 (**1996**).

182. K. Liu, M.G. Brown, C. Carter, R.J. Saykally, J.K. Gregory, and D.C. Clary, "Characterization of A Cage Form of The Water Hexamer," *Nature* **381**, 501 (**1996**).

183. E.H.T. Olthof, A. van der Avoird, P.E.S. Wormer, K. Liu, and R.J. Saykally, "Tunneling dynamics, symmetry, and far-infrared spectrum of the rotating water trimer, II. Calculations and experiments," *J. Chem. Phys.* **105**, 8051 (**1996**).

184. J.D. Cruzan, M.G. Brown, K. Liu, L.B. Braly, and R.J. Saykally, "The far-infrared vibration-rotation-tunneling spectrum of the water tetramer-*d8*," *J. Chem. Phys.* **105**, 6634 (**1996**).

185. A. Van Orden, R.A. Provencal, F.N. Keutsch, and R.J. Saykally, "Infrared Laser Spectroscopy of Jet-Cooled Carbon Clusters: The $\nu_5$ Band of Linear $C_9$," *J. Chem. Phys.* **105**, 6111 (**1996**).

186. C. Leforestier, L.B. Braly, K. Liu, M.J. Elrod, and R.J. Saykally, "Fully Coupled 6D Calculations of the Water Dimer VRT States with a Split Wigner Pseudo-Spectral Approach," *J. Chem. Phys.* **106**, 8527 (**1997**).

187. J.K. Gregory, D.C. Clary, K. Liu, M.G. Brown, and R.J. Saykally, "The Water Dipole Moment in Condensed Phases: Insights Through Cluster Studies," *Science* **275**, 814 (**1997**).

188. J.R. Heath and R.J. Saykally, "Space Carbon: Neutral Pathways?," *Science* **274**, 1480 (**1996**).

189. J.B. Paul, C.P. Collier, J.J. Scherer, A. O'Keefe, and R.J. Saykally, "Direct Measurement of Water Cluster Concentrations by Infrared Cavity Ringdown Laser Absorption Spectroscopy," *J. Phys. Chem.* (accepted **1997**).

190. J.B. Paul and R.J. Saykally, "Cavity Ringdown Laser Spectroscopy Absorption," *Analytical Chemistry A* **69**, 287 (**1997**).

191. J.B. Paul, J.J. Scherer, A. O'Keefe, and R.J. Saykally, "Cavity Ringdown Laser Absorption Spectroscopy," *Laser Focus World* **33**, 71-80 (**1997**).

192. K. Liu, M.G. Brown, and R.J. Saykally, "Terahertz Laser VRT Spectroscopy and Dipole Moment of a Cage Form of the Water Hexamer," *J. Phys. Chem.* (accepted **1997**).

193. K. Liu, M.G. Brown, J.D. Cruzan, and R.J. Saykally, "Terahertz Laser VRT Spectroscopy of the Water Pentamer: Structure and Hydrogen Bond Network Rearrangement Dynamics," *J. Phys. Chem.* (accepted **1997**).

194. J.D. Cruzan, M.R. Viant, and R.J. Saykally, "Terahertz Laser VRT Spectroscopy of the Water Tetramer," *J. Phys. Chem.* (accepted **1997**).

195. M.R. Viant, J.D. Cruzan, D.D. Lucas, M.G. Brown, K. Liu, and R.J. Saykally, "A study of pseudorotation in water trimer isotopomers using terahertz laser spectroscopy," *J. Phys. Chem.* (accepted **1997**).

196. A.I. Boldyrev, J. Simons, J.J. Scherer, J.B. Paul, C.P. Collier, and R.J. Saykally, "On the ground electronic state of copper slicide and its ions," *J. Chem. Phys.* (accepted **1997**).

197. C.P. Collier, J.J. Shiang, S.E. Henrichs, R.J. Saykally, and J.R. Heath, "Tuning of Collective Quantum Mechanical Interactions in Monolayers of Organically Passivated Silver Nanocrystals," (in preparation **1997**).

198. D.J. Cook and R.J. Saykally, "Simulated Infrared Emission Spectra of Highly Excited Polyatomic Molecules: A detailed model of the PAH-UIR hypothesis," (in preparation **1997**).

199. D.J. Cook, S. Schlemmer, N. Balucani, D.R. Wagner, J.A. Harrison, B. Steiner, and R.J. Saykally, "Single Photon Infrared Emission Spectroscopy: A Study of UV Laser Excited PAHs from 3 μm to 10 μm," (in preparation **1997**).