I. A Laboratory Study of the $H^+_3$-$e^-$ Recombination Rate

In a collaboration with the Mats Larsson group from Stockholm, we carried out a new measurement of the rate of dissociative recombination of $H^+_3$, using a new pulsed supersonic beam source of rotationally cold $H^+_3$. This source was first designed and characterized in our lab by IR cavity ringdown spectroscopy, determining a rotational/translational temperature of 20-60K, depending on conditions. This new source was then taken to Stockholm for the recombination rate studies at the CRYRING storage ring. The recombination rate constant measured against temperature yields values consistent with the most recent calculations, whereas previous experimental measurements varied over a range of $10^4$ and were poor agreement with theory.

This is a crucial achievement for understanding the ion chemistry of diffuse clouds. Moreover, this result in combination with recent observations implies a greatly enhanced (factor of 40) cosmic ray ionization rate in a diffuse cloud ($\zeta$ Persei) relative to previous studies. The implications of this are discussed in our recent Nature paper [B.J. McCall, A.J. Huneycutt, R.J. Saykally, T.R. Geballe, N. Djuric, G.H. Dunn, J. Sernak, O. Novotny, A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas, F. Osterdahl, and M. Larsson, "An enhanced cosmic-ray flux towards $\zeta$ Persei inferred from a laboratory study of the $H^+_3$-$e^-$ recombination rate," Nature 422, 500-502 (2003)].
II. **IR Cavity Ringdown Spectroscopy of Carbon Clusters**

We have continued to develop the requisite technology for extending cavity ringdown methods throughout the mid-IR – a necessary step for a systematic study of carbon clusters. Our pulsed high resolution (Alexandrite laser-based) system has been refurbished with a new technology for triggering the flashlamps while in cavity lock. This has resulted in much improved reliability and spectral bandwidth (now < 60 MHz), but somewhat degraded ability for externally locking to the laser vaporization source. We are currently working on schemes to improve the latter. A paper describing the design, construction, and performance of our pulsed, high resolution mid-IR cavity ringdown system (largely based on a study of the C₉ cluster) was published [R.N. Casaes, R.A. Provencal, J.B. Paul, and R.J. Saykally, "High resolution pulsed infrared cavity ringdown spectroscopy: Application to laser ablated carbon clusters," *J. Chem. Phys.* **116**, 6640-6647 (2002)].

III. **Mid-IR Water Recombination Lasers**

We reported the discovery of a large number of mid-IR lasing transitions in pulsed supersonic plasmas containing helium and H₂O [*Chem. Phys. Lett.* **338**, 277-284 (2001)]. This work has now been extended to pure hydrogen discharges, where over 12 IR laser lines have been discovered. Moreover, additional transitions in He/H₂O discharges have been found and tentatively assigned to the H₂O⁺ ion. We believe that these lasers are driven by electron-ion recombination, and that this mechanism may be operative in appropriate interstellar sources.

IV. **Single Photon Infrared Emission Spectroscopy (SPIRES) of PAHs and PAH Cations**

We have published the first detection of laboratory IR emission spectra from gaseous PAH cations [*Phys. Rev. Lett.* **86**, 5691 (2001)]. The spectra of pyrene cation, measured by our SPIRES spectrometer in an ion beam, generally agree well with both UIR bands and with matrix isolating spectra. We have also published a detailed report on this work, additionally describing spectra of dehydrogenated PAH cations observed in the SPIRES experiment, as well as the design of the experiment itself [H.-S. Kim, and R.J. Saykally, "Single Photon Infrared Emission Spectroscopy of Gaseous Polycyclic Aromatic Hydrocarbon Cations: A Direct Test for Proposed Carriers of the Unidentified Infrared Emission Bands," *Astrophys. J. Supp. Series*, **143**:455-467 (2002); H.-S. Kim, and R.J. Saykally, "An ion beam reflectron/ single photon infrared emission (SPIRE) spectrometer for the study of gas phase PAH ions: testing proposed carriers of the unidentified infrared emission bands (UIRs)," *Rev. Sci. Instrum.* **74**, 2488 (2003)].
Graduate Students Supported by this Grant
Raphael Casaes (Ph.D. expected 8/03)
Alex Huneycutt (Ph.D. expected 6/03)
Don Wagner (Ph.D. 2001)

Postdoctorals Supported by this Grant
H.-S. Kim (Northwestern)
E.A. Michael (U. Cologne)

Publications Supported by NASA (numbers correspond to complete list)
of the Nobel Symposium 117 on The Physics and Chemistry of Clusters, Visby, Sweden,

Provencal, F.N. Keutsch, A. Van Orden, and R.J. Saykally, "Detection of the Linear

*Cover Article.

241. T.F. Giesen, A.O. Van Orden, J.D. Cruzan, R.A. Provencal, R. Gendriesch, F. Lewen,
G. Winnewisser, R.T. Boreiko, A.L. Betz, and R.J. Saykally, "Interstellar Detection of


244. R.J. Saykally and R. Casaes, "Cavity ringdown technique measures absorption," Laser
Focus World 37, 159-162 (2001).

Spectroscopy of the Gas Phase Pyrene Cation: Support for a Polycyclic Aromatic
Hydrocarbon Origin of the Unidentified Infrared Emission Bands," Phys. Rev. Lett. 86,
5691 (2001).


*Invited Lectures (numbers correspond to complete list)*


300. “Carbon Chains and PAH Ions in Space and in the Lab,” CIPS Workshop, Space Sciences Laboratory, UC Berkeley, CA; November 13, 2002.
CURRICULUM VITAE

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

• Professional Interests: Laser spectroscopy, X-ray spectroscopy, astrophysics, liquid surface chemistry, clusters, intermolecular forces, femtosecond chemical imaging microscopy, biophysics, water, science education.
• Research advisor for 41 Ph.D. and 6 M.S. Graduates and 25 Postdoctorals.
• Coauthor of over 250 Scientific Articles.

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, LECTURESHP
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
Bomem 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 – 1997-98
Pittsburgh Spectroscopy Award – 1999
Bryce Crawford Lectureship, University of Minnesota – 1999
Frontiers in Chemical Research, Distinguished Lecturer, Texas A&M University – 1999
Member – National Academy of Sciences – 1999
Sesquicentennial Colloquium Lecturer in Chemistry, University of Utah – 2000
Irving Langmuir Award in Chemical Physics (ACS) – 2000
Rayson Huang Distinguished Lecturer, University of Hong Kong – 2000
Dreyfus Distinguished Lecturer in Chemistry, Dartmouth College – 2001
Fellow – American Association for the Advancement of Science – 2001
Moses Gomberg Lecturer, University of Michigan – 2002
Distinguished Lecturer, Molecular Sciences Forum, Chinese Academy of Sciences – 2002
PROFESSIONAL ACTIVITIES
Co-Director - "Science for Science Teachers (SST)," NSF Summer Training Institute for Junior High School Science Teachers – 1989-93
Advisory Committee – Radio Astronomy Laboratory (UCB) – 1996-present
Canvassing Committee – Irving Langmuir Award (ACS) – 1996-2001
Executive Committee – Division of Chemical Physics (APS) – 1995-1999
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, UC-Berkeley 1983-86
Member – American Association of University Professors, American Association for the Advancement of Science, American Chemical Society
University of California – Committee on Teaching, Committee on Research, Committee on Committees, Budget Committee

PROFESSIONAL EXPERIENCE
Assistant Professor, University of California-Berkeley (1979-83)
Associate Professor, University of California-Berkeley (1983-86)
Principal Investigator, Lawrence Berkeley Laboratory (1983-91)
Professor, University of California-Berkeley (1986-99)
Vice Chairman, University of California-Berkeley (1988-91)
Class of 1932 Distinguished Chair, UC-Berkeley (1999-present)
PUBLICATIONS 2000-present (numbers correspond to complete list)

Richard J. Saykally


*Cover Article.


*Cover Article.


*Cover Article.


*Cover Article.


*Cover Article.


**Featured by Science as “Editors’ Choice.”**


250. F.N. Keutsch, and R.J. Saykally, “Water Clusters: Untangling the mysteries of the liquid,


*Cover Article.
**Featured by Science as “Editors’ Choice.”

253.**K.R. Wilson, M. Cavalleri, B.S. Rude, R.D. Schaller, A. Nilsson, L.G.M. Pettersson, N.
acceptor molecules at the water surface using near-edge x-ray absorption fine-structure
spectroscopy and density functional theory,” *J. Phys.: Condens. Matter* 14, L221-L226
(2002).
**Featured by Science as “Editors’ Choice.”


255. D. Kraus, V.E. Bondybey, and R.J. Saykally, “Cavity-Ringdown Spectroscopy Studies of

Saykally, “Spectroscopic Determination of the Water Dimer Intermolecular Potential

257. J.C. Johnson, H. Yan, R.D. Schaller, P.B. Petersen, P. Yang, and R.J. Saykally,
"Near-Field Imaging of Nonlinear Optical Mixing in Single Zinc Oxide Nanowires," *Nano

"Nonlinear Chemical Imaging Nanomicroscopy: From Second and Third Harmonic
Generation to Multiplex (Broad-Bandwidth) Sum Frequency Generation Near-Field
*Invited Cover Article.

259. P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, and


261. R.D. Schaller, J.C. Johnson, K.R. Wilson, L.F. Lee, L.H. Haber, and R.J. Saykally,
"Characterization of biological structures with nonlinear chemical imaging
SPIE Vol. 4633, p. 62-68, Commercial and Biomedical Applications of Ultrafast and Free-
Electron Lasers, Glenn S. Edwards; Joseph Neev; Andreas Ostendorf; John C. Sutherland; Eds. (2002).


