Adventures at interfaces: Molecules, Atmospheres and Community

An alumni appreciation event

The group started at Harvard in 1978, moved to the University of Colorado, Boulder in 1984 where it ended in 2023.

This event is possible thanks to support from CIRES and the CU foundation. Many thanks especially to:
Event coordination team: Linda Pendergrass, Lornay Hansen , Wendy Elder.
IT support Nate Campbell and his team
CU foundation: Amanda Nugent, Ashton Pickard

Remembering group collaborators who have died

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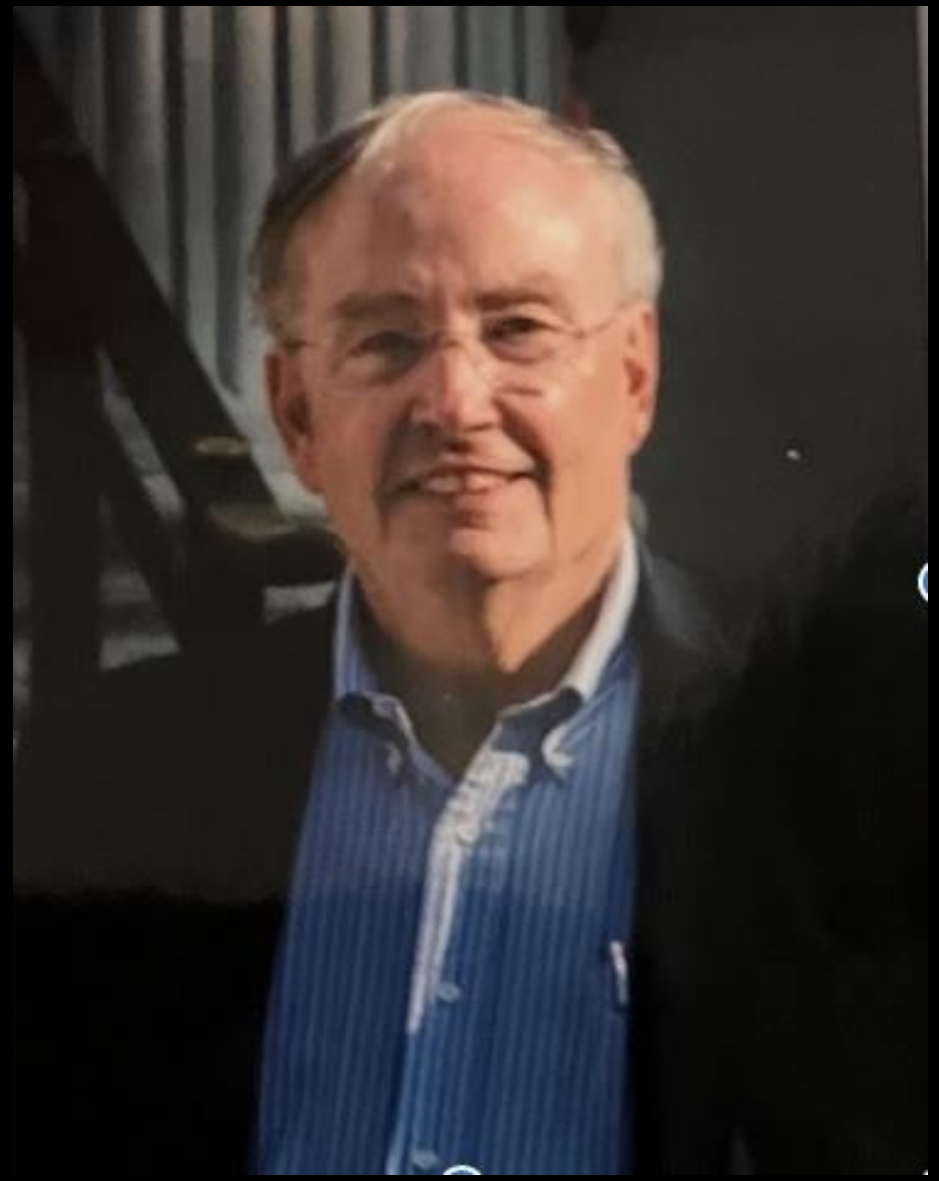
In Memory of our Past Collaborators

Kevin Peters

Harvard University,
University of Colorado, Boulder

Ultrafast reaction dynamics in solution

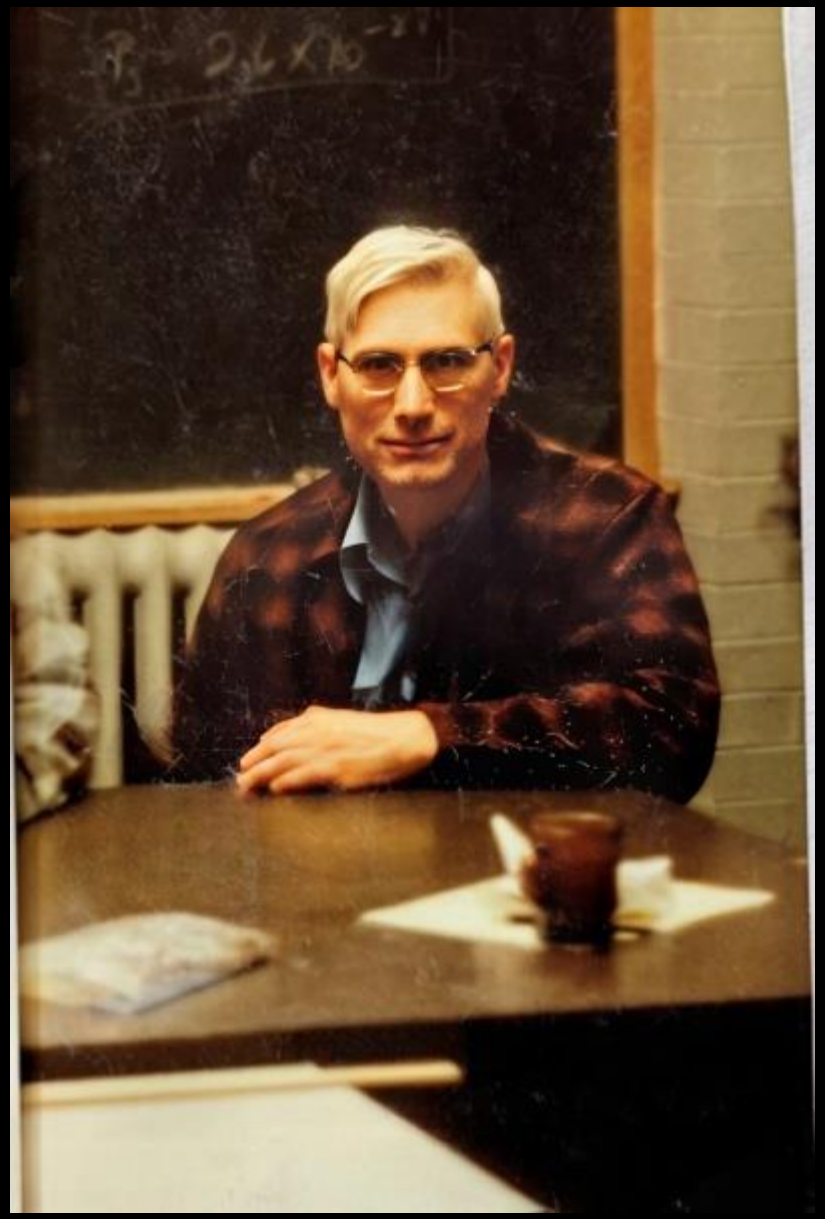


Kevin Peters 1949-2025

John Roebber

Northeastern University, Boston MA
Chemistry Department

Physical Chemistry,
Electronic spectroscopy



John Roebber 1930-2023

Martin Karplus

Harvard University, Cambridge MA

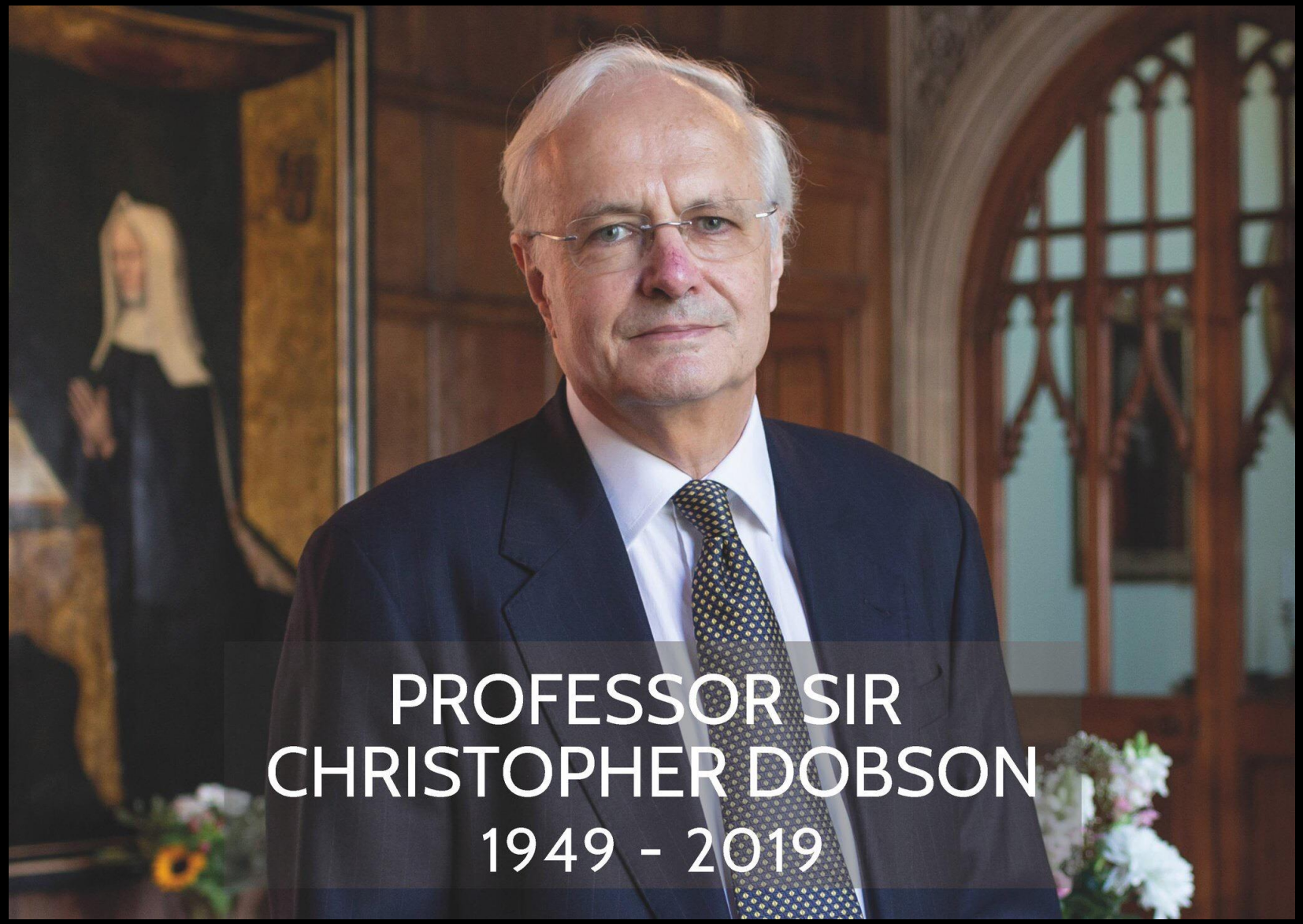
Theoretical and Computational chemistry
Computer models of chemical reactions

Martin Karplus 1930-2024

Chris Dobson

The John Humphrey Plummer Professor of Chemical and Structural Biology Cambridge University

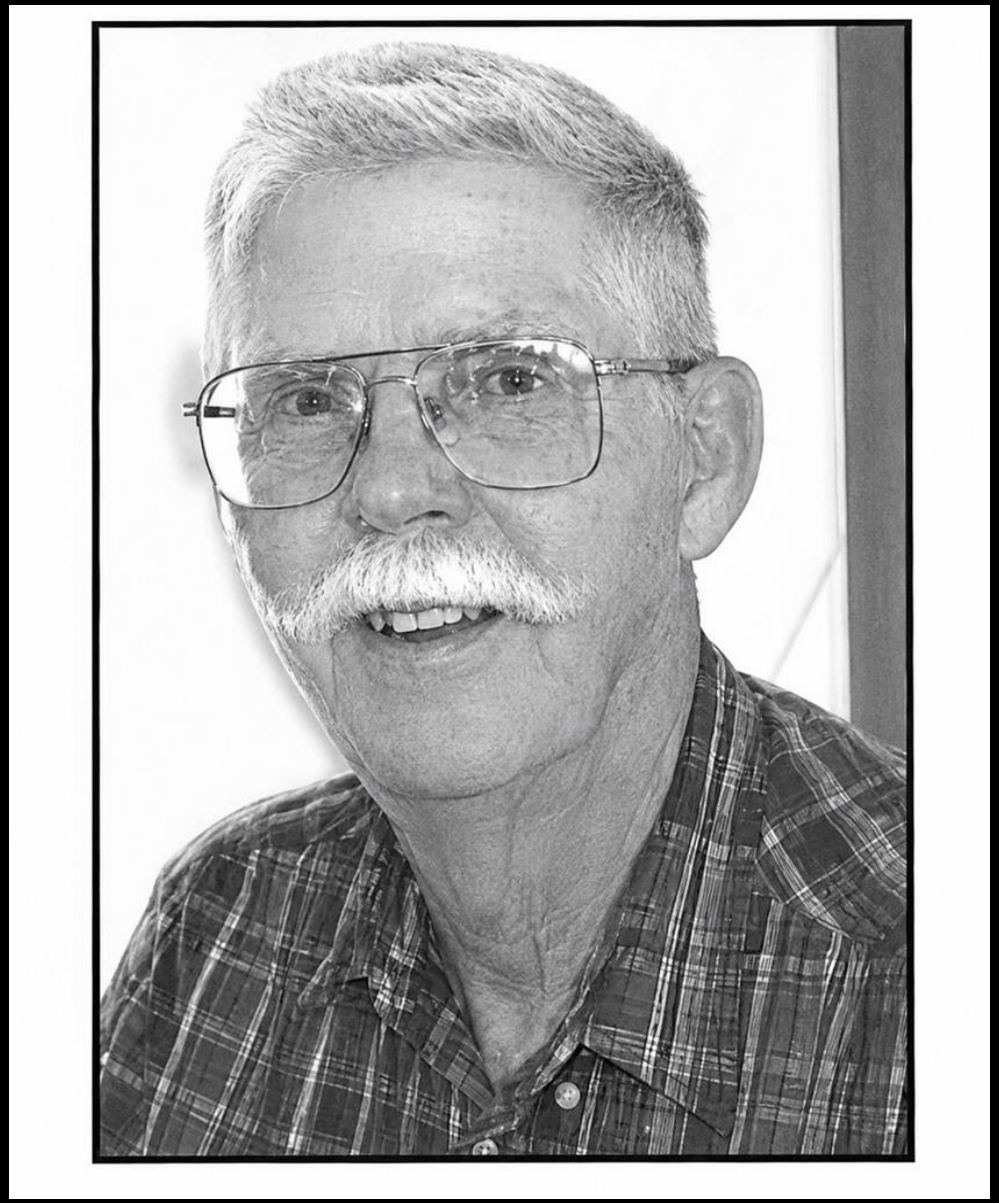
Biophysics, - protein “folding” and “aggregation” phenomena



Stew Strickler

University of Colorado, Boulder
Department of Chemistry

Molecular Spectroscopy
Photophysical properties of molecules



Pavel Rosmus

Professor Fachbereich Chemie der Universität D-6000 Frankfurt

Theoretical spectroscopy. Computational chemistry to interpret molecular properties

Martina Roeselová

Czech Academy of Sciences

Theoretical physical chemist working at the interface of fundamental physical chemistry and atmospheric science.

Martina Roeselovà 1965 - 2015

Richard Bernstein

Colombia University
UCLA

Chemical dynamics studied with molecular beam techniques.
Femtochemistry

1923 - 1990

Dan Havey

PhD 2006 Chemistry University of Colorado
James Madison University

Physical Chemistry, interaction of light and molecules, particles in the Earth's atmosphere

Dan Havey 1978 - 2013

Jim Brault

Kitt Peak Observatory
NOAA, Boulder

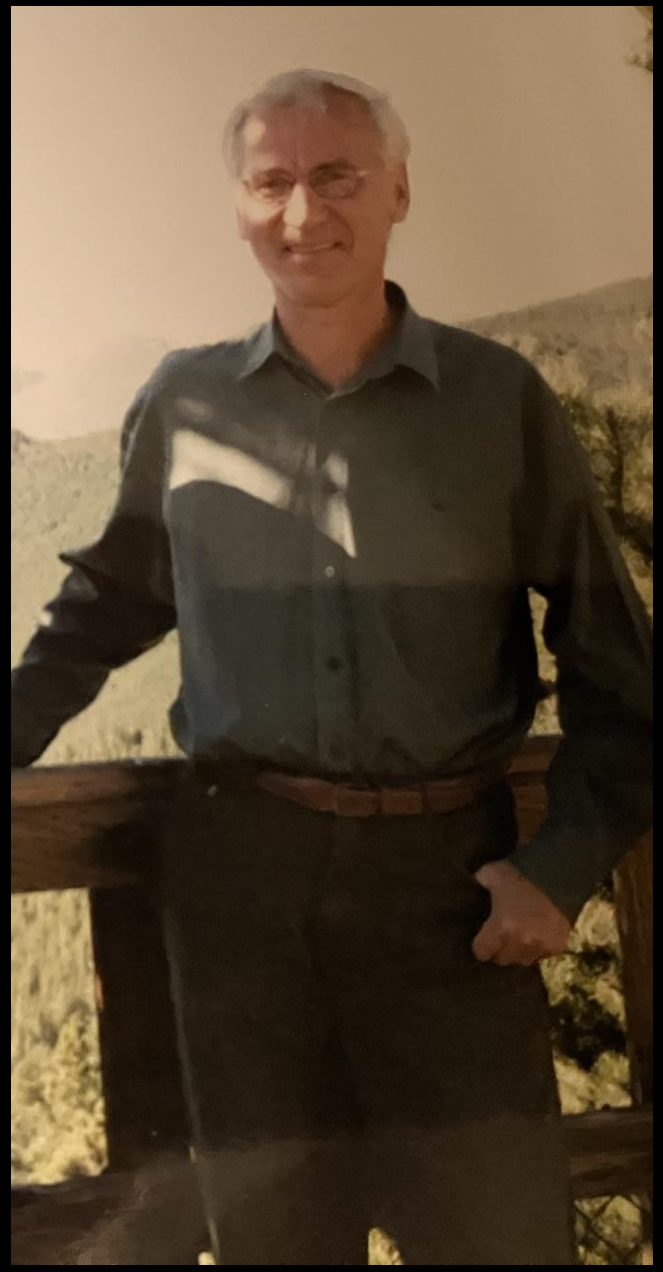
High Resolution Atomic and Molecular Spectroscopy
Fourier Transform Spectroscopy

Jim Brault 1932 - 2008

Heikki Tervahattu

Helsinki University, Helsinki, Finland

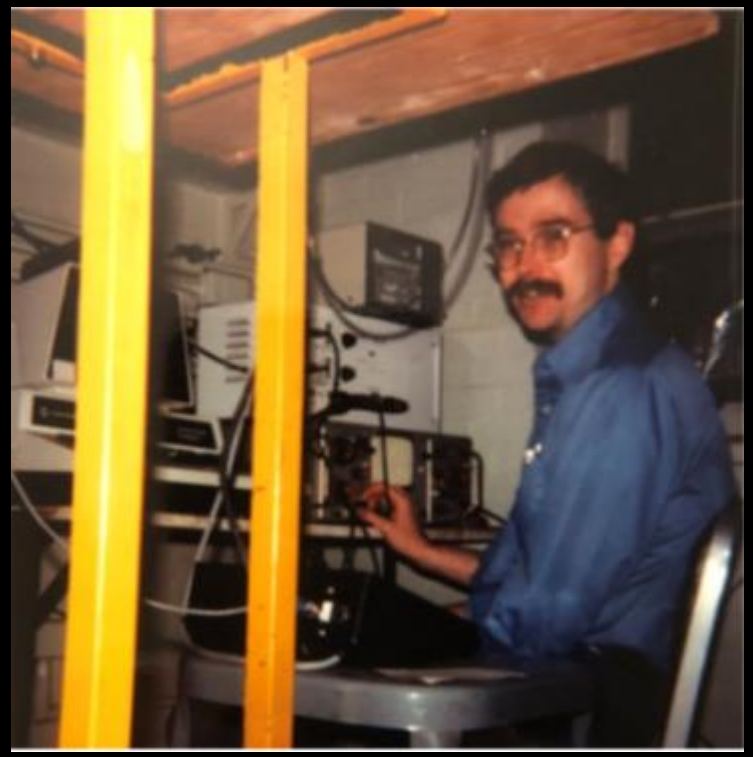
Atmospheric aerosol - field measurements
TOF- SIMS



Rex Pendley

Harvard University

Experimental Physical Chemistry Spectroscopy



Rex Pendly 1954 - 2019

Adventures at interfaces: Molecules, Atmospheres and Community

An alumni appreciation event

Interfaces, interactions and collaborations shaped our work on increasing chemical complexity in planetary atmospheres including the contemporary and prebiotic Earth. We will look at the group's scientific history through stories of the way things were, serendipitous moments, challenges, obstacles and opportunities and most of all the people who made it happen.

Session 1: Chair Rory McClish **9:00am-10:30am**

- Spectroscopy and dynamics of reactive molecules
- Light initiated chemistry in the Earth's atmosphere

Coffee break: **10:30am -11:00am**

Session 2: Chair Denver Talley **11:00am - 12:15pm**

- Complex Chemical Environments: Complexes, aqueous solutions, aerosols and water-air interfaces in the atmosphere of the contemporary and ancient Earth

Session 3: Chair Veronica: **2:00pm – 4:00pm**

- What comes after a Chemistry PhD. Accounts from those holding a chemistry PhD.

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1) Spectroscopy and dynamics of reactive molecules

The context and idea: high resolution electronic spectroscopy was a powerful tool for determining electronic structure. However, molecules undergoing efficient nonradiative processes such as reaction, with short excited state lifetimes could not be studied with the sensitive methods being developed for symmetric and stable molecules.
Develop spectroscopic methods to study (photo)reactive molecules.

The techniques

a) Absorption spectroscopy of jet-cooled molecules where inhomogeneous effects could be eliminated
b) Develop sensitive methods (MPI, LIF, etc.) to look for forbidden molecular states and spectroscopic identification of photoproducts.

Sensitive spectroscopic methods (MPI, LIF, etc.) developed to look for forbidden molecular states and spectroscopic identification of photoproducts

Metal Atoms Produced in the Photodissociation of Group VI Hexacarbonyls, D. P. Gerrity, L. J. Rothberg and V. Vaida, *Chem. Phys. Lett.*, (1980).
Picosecond Dynamics of Solution Phase Photofragmentation of Mn2(CO)10," L. J. Rothberg, N. J. Cooper, K. S. Peters and V. Vaida, *J. Am. Chem. Soc.*, 1982
Production of Gas Phase Bare Transition-Metal Clusters by Laser Photodissociation of Organometallic Cluster Compounds, V. Vaida, N. J. Cooper, R. J. Hemley and D. G. Leopold, *J. Am. Chem. Soc.*, (1981).
Mass Spectrometry of Transition-Metal Complexes: Mn2(CO)10 and Re2(CO)10," D.A. Lichtin, R.B. Bernstein and V. Vaida, *J. Am. Chem. Soc.* (1982).
Multiphoton Dissociation of Transition-Metal Carbonyl Complexes: A Novel Route to Gas Phase Metal Clusters, D. G. Leopold and V. Vaida, *J. Am. Chem Soc.*, (1983).
Photofragmentation of Transition-Metal Cluster Carbonyls in the Gas Phase," W. E. Hollingsworth and V. Vaida, *J. Phys. Chem.*, (1986).
Wavelength Dependent Photofragmentation of Gas Phase Mn2(CO)10. D. A. Prinslow and V. Vaida, *J. Am. Chem. Soc.*, (1987).

The search for the totally symmetric states of $Cr(CO)_6$ → **Generated metal atoms! Lewis Rothberg & Dan Gerrity**
Generate bare transition metal clusters Doreen Leopold, Jeanne Welsh, Prof Richard Bernstein
Generate Metal-S clusters Doug Prinslow, Will Hollingsworth
Study the psec dynamics of solution phase transition metal carbonyls with the Kevin Peters & John Cooper groups at Harvard and in Colorado

Spectroscopy of dissociating molecules: effects of clusters formation

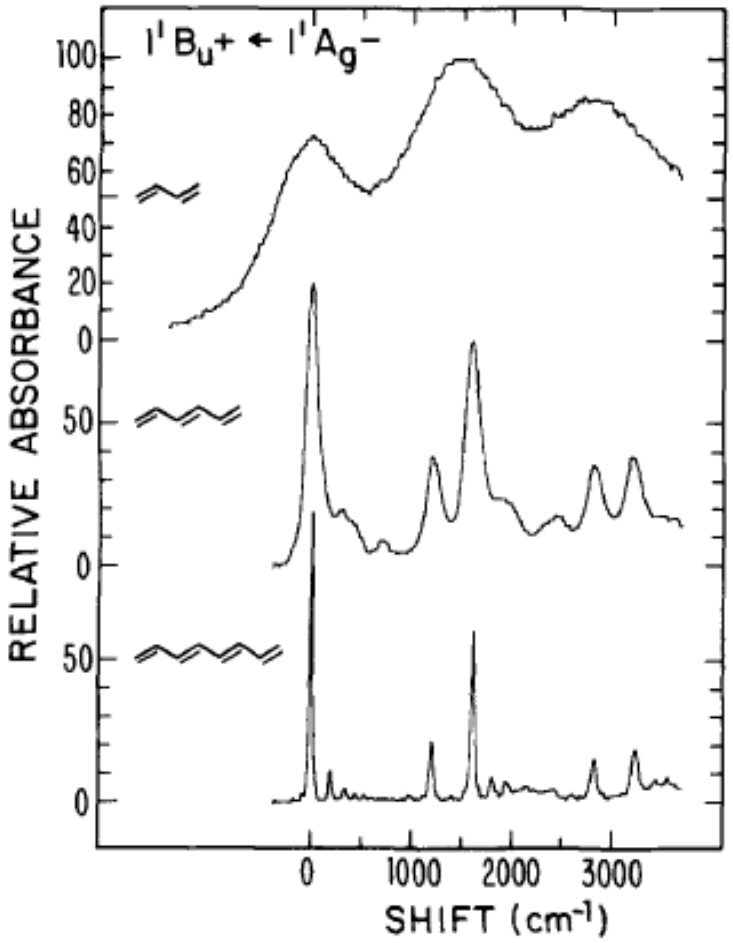
Ultraviolet Absorption Spectroscopy of Dissociating Molecules: Effects of Cluster Formation on the Photodissociation of **CH_3I**," D. J. Donaldson, V. Vaida and R. Naaman, *J. Chem. Phys.*, (1987).
Surface Crossings and Predissociation Dynamics of Methyl Iodide Rydberg States, D. J. Donaldson, M. S. Child and V. Vaida, *J. Chem. Phys.*, (1988).
Spectroscopic and Photochemical Perturbations of Weak Interactions on Electronic Surfaces of Methyl Iodide, V. Vaida, D. J. Donaldson, S. P. Sapers and R.Naaman, *J. Chem. Soc., Faraday Trans.*, (1990).

Spectroscopic effects of weak interactions on the spectra and reaction dynamics of strong bonds
$(CH_3I)_2$
Which bonds break when clusters are excited in the UV?
$(O_2)_2$ odd oxygen Laura Brown
$O_3.H_2O \rightarrow 2OH$? Greg Frost (collaboration with Ron Naaman, Yinon Rudich
Spectroscopy of water clusters – radiative transfer
$(H_2O)n$ IR and near IR
Jill Headrick, Lisa Goss, Henrick Kjaergaard, Adrian Tuck, John Daniel

Physicochemical Properties of Hydrated Complexes in the Earth's Atmosphere" V. Vaida and J. E. Headrick *J. Phys. Chem.* (2000)
Atmospheric absorption of near infrared and visible solar radiation by the hydrogen bonded water dimer V. Vaida, A.F. Tuck, L.M. Goss, J.S. Daniel, and H. Kjaergaard *Q. J. Roy. Met. Soc*. (2001)

Absorption Spectroscopy of Jet-Cooled Molecules

Direct absorption spectroscopy of jet-cooled **polyenes**; Leopold, Hemley, Roeber, Pendley, Granville JCP 1984
Franck-Condon analysis Hemley, Dawson, Dinur, Lasaga, Karplus 1983, 1988
The Singlet State of **Styrene**: theoretical vibrational analysis of the ultraviolet spectrum" R. J. Hemley, D. G. Leopold, V. Vaida and M. Karplus, *J. Chem. Phys.*(1985).
The Direct Ultraviolet Absorption Spectrum of the 1∑+ ® 1∏ Transition of Jet-cooled **CS_2**," R. J. Hemley, D. G. Leopold, J. L. Roebber and V. Vaida, *J. Chem. Phys* (1983).
Direct Absorption Spectroscopy of Jet-Cooled **H_2S**," K. O. Lanz and V. Vaida, *Chem. Phys. Lett.*, (1993).
Near Ultraviolet Absorption Spectrum of the A2A2 ¬ X2B1 Transition of Jet-Cooled **Chlorine Dioxide**" E. C. Richard and V. Vaida, *J. Chem. Phys.*, (1991).



Collaborations:

a) Experiment: The Herschbach Klemperer, Peters groups. Chuck Joyner, Gary McClelland, John Roebber (Norteastern University).
b) Spectroscopy: Stew Strickler, Paul Engelking
c) Theory: The Karplus group
Ammonia: Pavel Rosmus, Hans-Joakim Werner, Peter Botschwina

Ammonia

Ground electronic state → Excited electronic state ($NH_3 \rightarrow NH_2 + H$)

Pyramidal

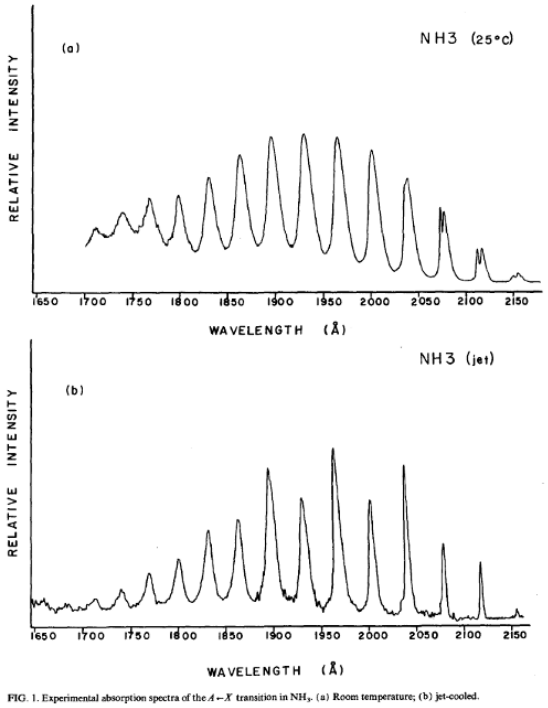


FIG. 1. Experimental absorption spectra of the $A \leftarrow X$ transition in NH_3. (a) Room temperature; (b) jet-cooled.

Planar

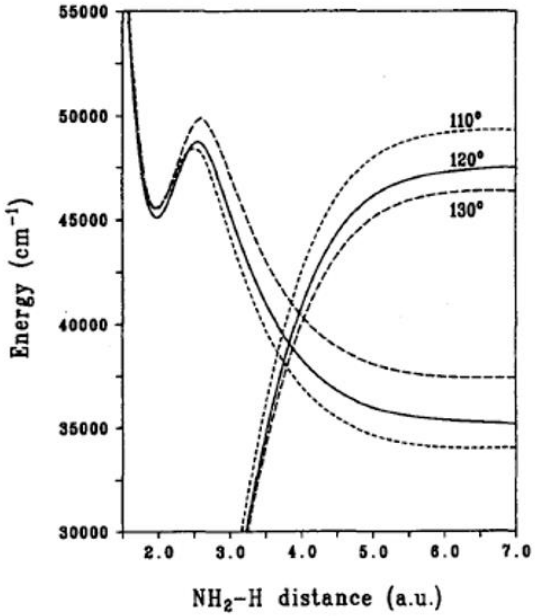


FIG. 3. Potential energy functions of the $\tilde{X}$ and the $\tilde{A}$ states for planar NH_3 (C_{2v} symmetry) as functions of the R_{NH} distance for various angles α_{HNH}. The distance r_{NH} in NH_2 is 2.0 a.u.

Maureen McCarthy PhD Thesi

Alternation in intensity of NH_3 and inverse in ND_3
Explanation E. B. Wilson JCP 1936: nuclear spin statistics

The Direct Ultraviolet Absorption Spectrum of the A'A"2 ¬ X'A1 Transition of Jet-Cooled Ammonia
Vaida, Hess and Roebber, *J. Phys. Chem.*, (1984).

The ultraviolet spectrum of ammonia
Vaida, McCarthy, Engelking, Rosmus, Werner, Botschwina JCP 1987

Theoretical absorption and emission spectrum of ammonia
Rosmus, Botschwina, Werner, Vaida, Engelking, McCarthy JCP 1987

Treat NH_3 dissociation as a two mode system
McCarthy, Rosmus, Werner, Botschwina, Vaida JCP 1987

Photoreactive molecules
Vibrational mode coupling a prelude to reaction

Lewis Rothberg

Early Year Reminiscences

“Have you ever turned a wooden table into an optical table?”

Lewis Rothberg

First Experiment

Electronic spectra of butadiene and its methyl derivatives: A multiphoton ionization study

L. J. Rothberg, D. P. Gerrity, and V. Vaida

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
(Received 9 May 1980; accepted 19 August 1980)

The multiphoton ionization (MPI) spectra of *trans*-1,3-butadiene and three of its methyl substituted derivatives have been recorded using a tunable visible dye laser. The effect of methyl substitution on the electronic structure of butadiene is investigated, resulting in a reassignment of the spectra of these molecules. Quantum defects are found to be independent of principal quantum number, indicating little mixing between Rydberg and core orbitals. The validity of retaining conventional s, p, d, and f descriptions of Rydberg orbitals in these quasilinear molecules is demonstrated. Two electronic states of butadiene, assigned to the $3d$ and $4s$ Rydberg states, are observed for the first time in optical spectroscopy. No evidence for an excited ^1A_g valence state is found in the MPI spectra.

J. Chem. Phys. 1980

I am sure at the time I could have given a long-winded discussion about Rydberg states in substituted butadienes and their significance … not any more

What I remember now is how cold my apartment was as I wrote this manuscript over Christmas … and how distinctively terrible is the smell of isoprene

Lewis Rothberg

“Breakthrough experiment??”

MULTIPHOTON IONIZATION OF METAL ATOMS PRODUCED IN THE PHOTODISSOCIATION OF GROUP VI HEXACARBONYLS

D P. GERRITY, L J. ROTHBERG and V. VAIDA
Department of Chemistry Harvard University, Cambridge, Massachusetts 02138, USA

Received 15 April 1980

Chem. Phys. Lett. 1980

“Dan – I think you are going to find five peaks under there if you scan more slowly”

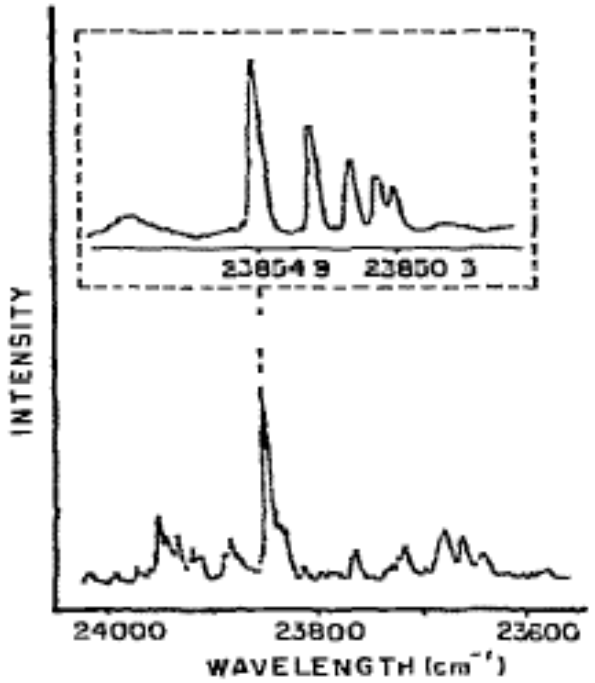
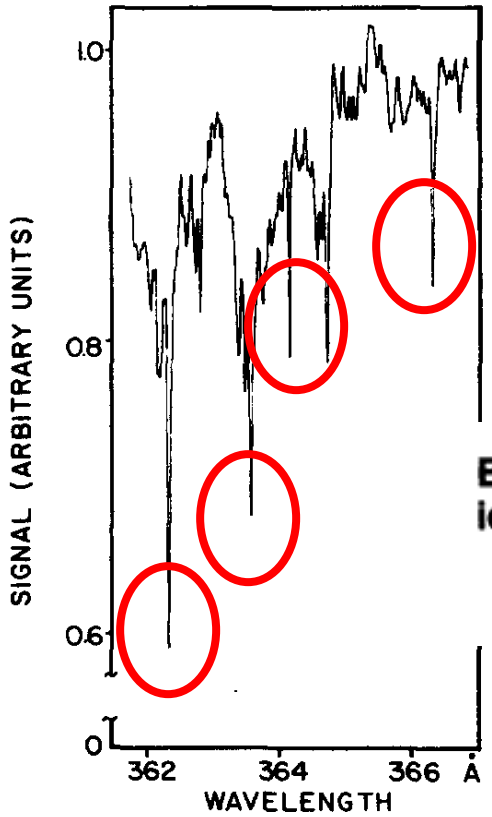


Fig. 1. The multiphoton ionization spectrum of Cr(I) obtained by the multiphoton dissociation of $Cr(CO)_6$ with excitation energies of 24000 to 23600 cm^{-1}

Lewis Rothberg

Multiphoton ionization in CS_2

"Please go back to the lab, Dan. How can there possibly be less photoionization on resonance?"



Effects of nonresonant ionization on multiphoton ionization line shapes

Lewis J. Rothberg, Daniel P. Gerrity, and Veronica Vaida[a)]

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

(Received 1 July 1981; accepted 17 July 1981)

J Chem Phys1981

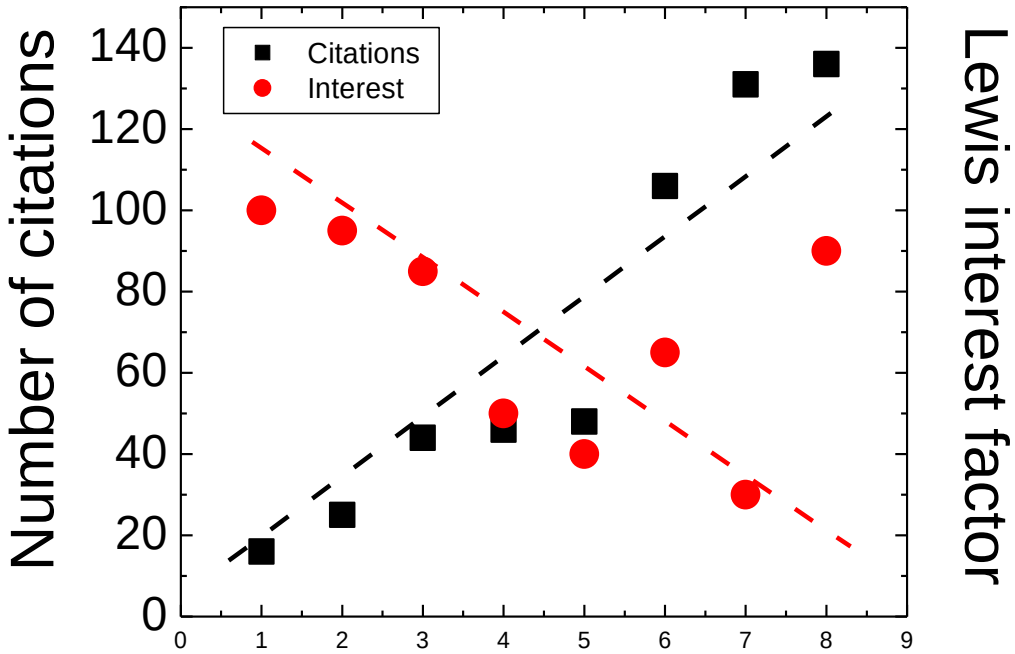
FIG. 7. MPI spectrum of CS_2 at room temperature vapor pressure between 361 and 368 nm.

"Yes, I will refill the sample cell, Dan"

Lewis Rothberg

A Major Conclusion:

The intervening years provide compelling evidence that Veronica's scientific taste is much better than mine!



Depletion of nonresonant ionization

Picosecond photoacoustic

Statistical fragmentation

Mn2(CO)10 MPI

Butadiene Rydberg states

Cr(CO)6 MPI to atoms!!

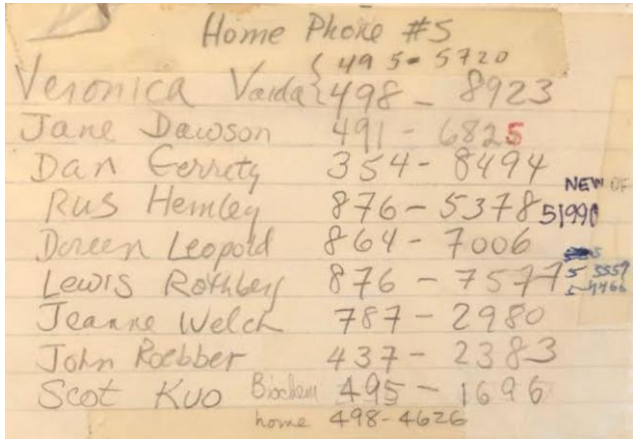
Solution Mn2(CO)10 dissn

Photoacoustic calorimetry

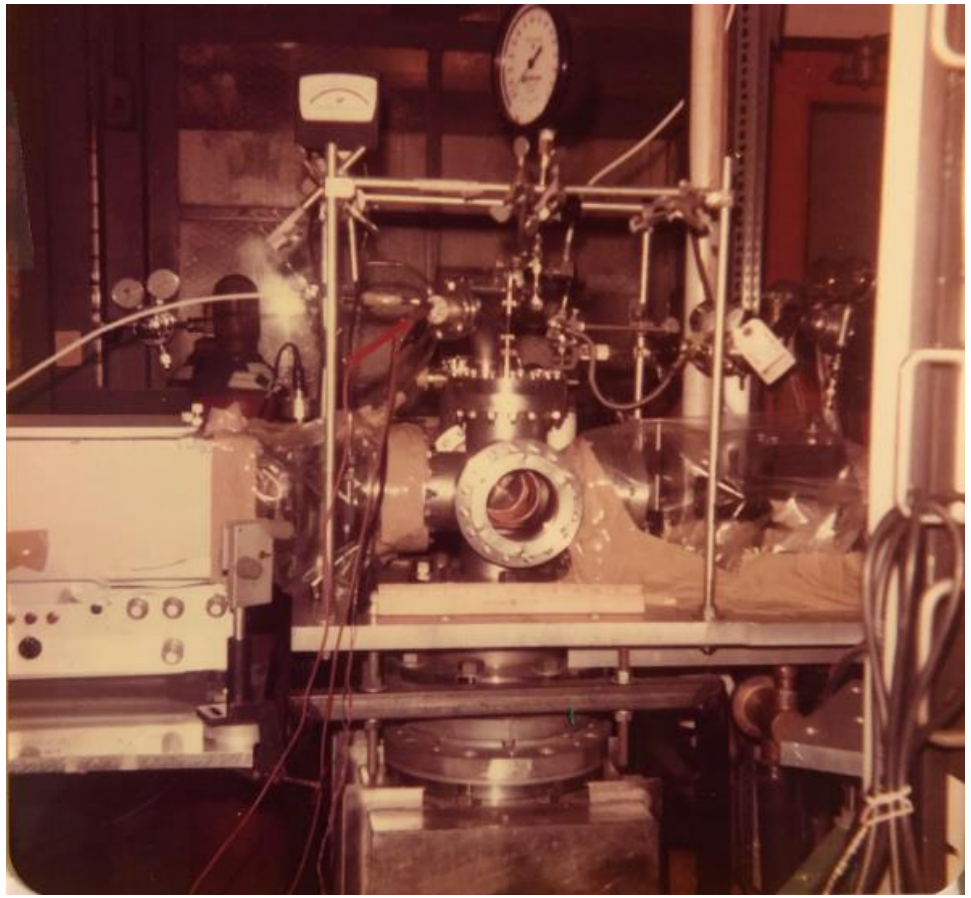
Joint with Peters group

Doreen Leopold

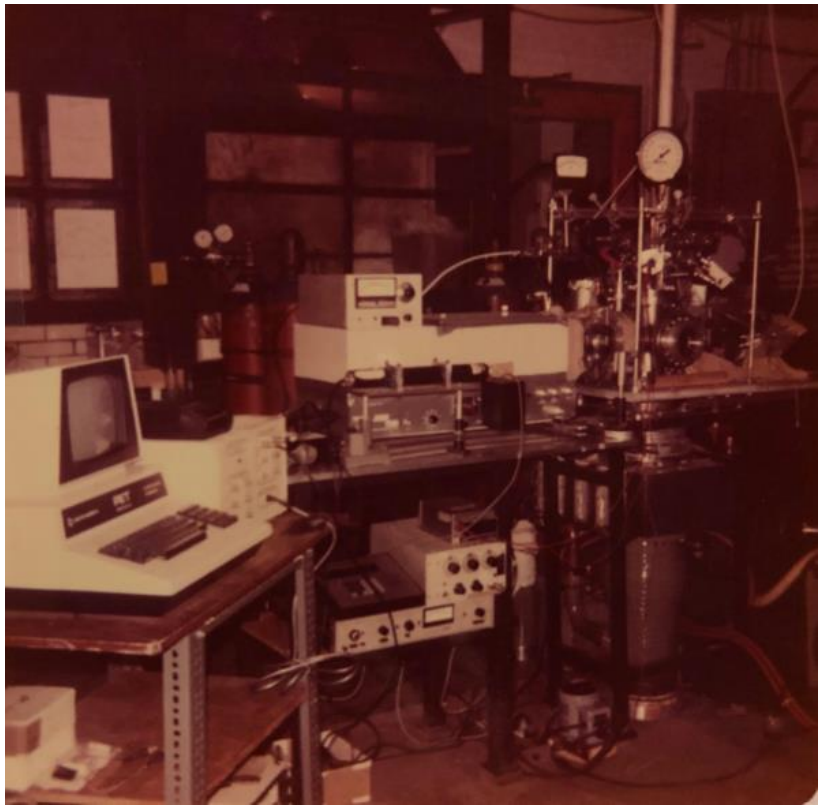
Some of the members of
Veronica's group at
Harvard
circa 1981 - 1982


Home Phone #5
(495-5720
Veronica Vanda 498-8923
Jane Dawson 491-6825
Dan Gerrety 354-8494
Rus Hemley 876-5378
Doreen Leopold 864-7006
Lewis Rothlein 876-7577
Jeanne Welch 787-2980
John Roebber 437-2383
Scot Kuo Boston 495-1696
home 498-4626

Doreen Leopold

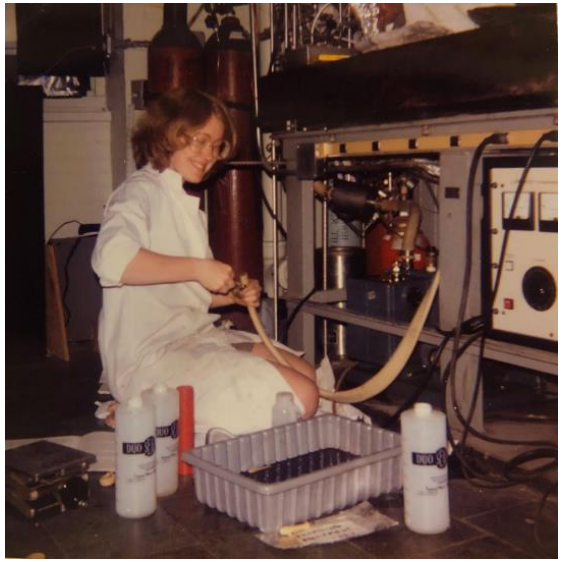


Homemade VUV Spectrometer (CS_2 1981)



Commodore PET Computer
1978 model, *32 KB RAM, 1 MHz*
8-bit processor, machine code

Doreen Leopold



The day the excimer laser flooded!
Top right: Jane Dawson

Bottom left (on better days):
Dan Gerrity, Jeanne Welch

Katherine Ann
b. Feb. 22, 1981

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Four ‘Molecular Lessons’ I Learned from Veronica…

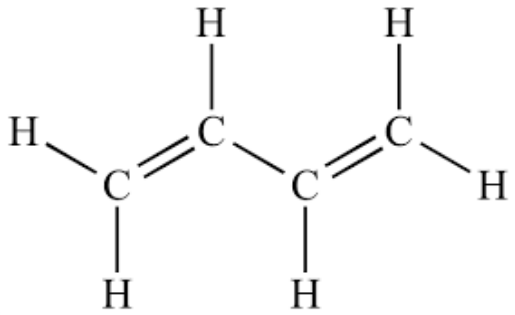
Rus Hemley

J. Chem. Phys. 78(6), Part I, 15 March 1983

Franck–Condon analysis of the $1\,^1A_g^- \rightarrow 1\,^1B_u^+$ transition of 1,3-butadiene from absorption and Raman intensities

R. J. Hemley, J. I. Dawson, and V. Vaida[a)]

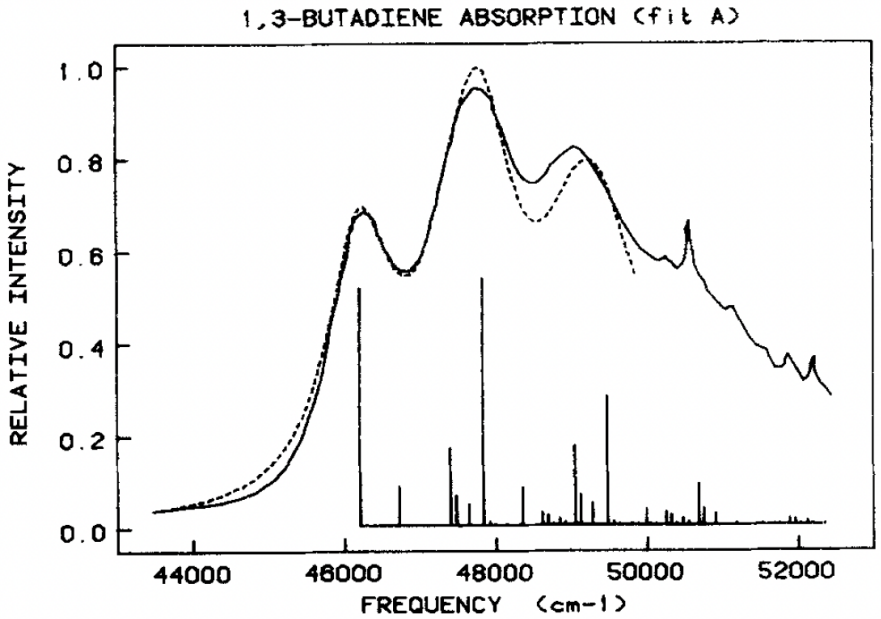
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
(Received 11 October 1982; accepted 7 December 1982)

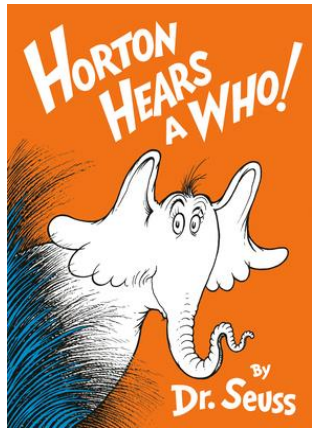


1980 BMW Fuel Injector

1974 Ford Pinto Car Battery

Impersonating Early Shoegaze Band





1980 CIA Microphone

State-of-the-art Electronics

1. Be scrappy, resourceful, and get the job done!

Four ‘Molecular Lessons’ I Learned from Veronica…

Rus Hemley

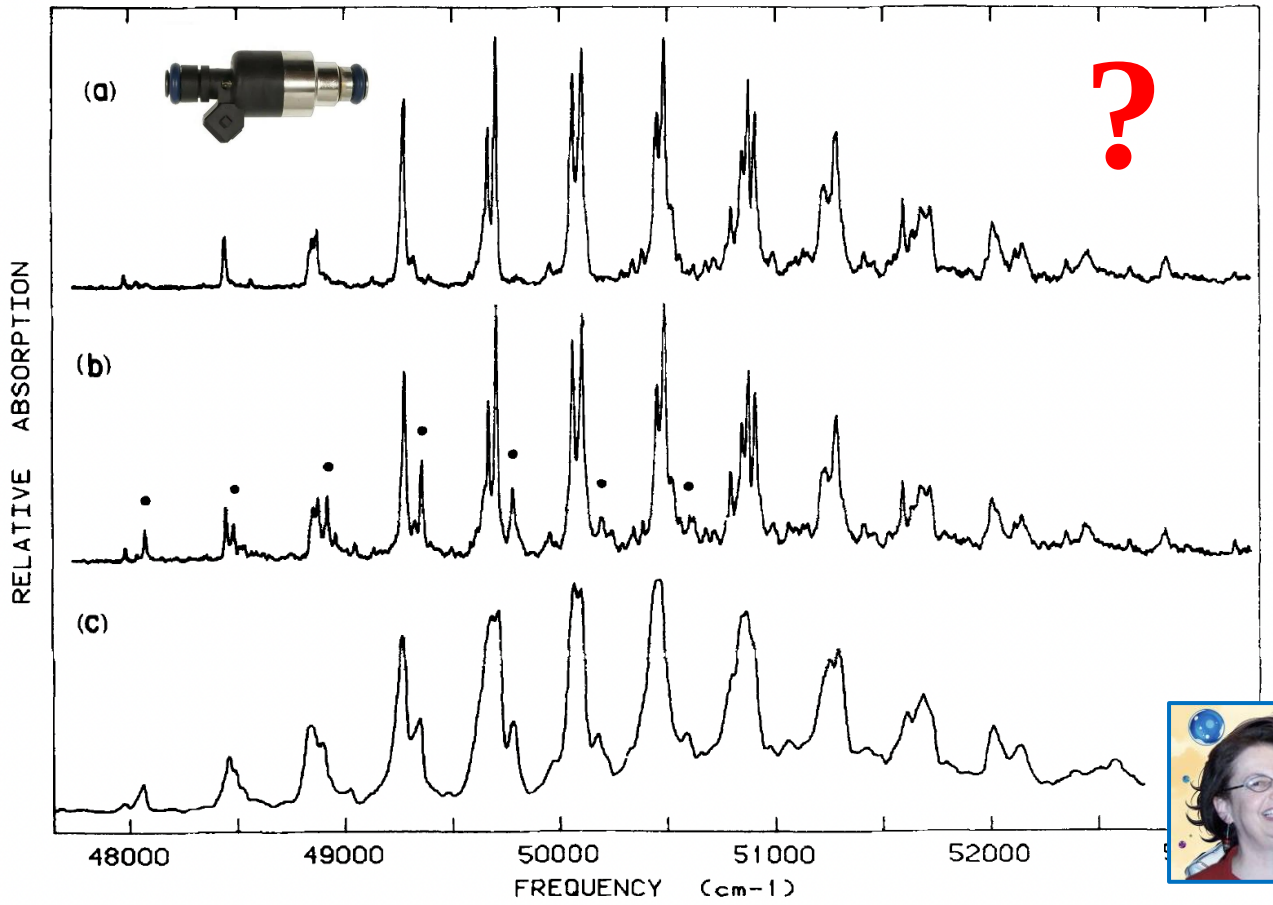
J. Chem. Phys., 79(11), 1 Dec. 1983

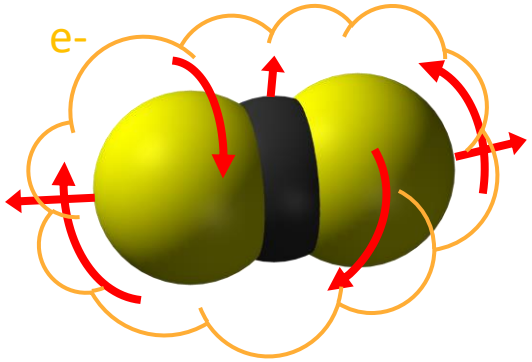
The direct ultraviolet absorption spectrum of the $^1\Sigma_g^+ \rightarrow {}^1B_2(^1\Sigma_u^+)$ transition of jet-cooled CS_2

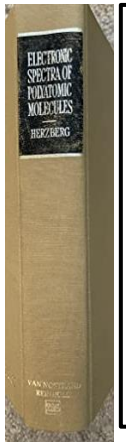
R. J. Hemley, D. G. Leopold, J. L. Roebber,[a] and V. Vaida[b]

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

(Received 15 June 1983; accepted 29 July 1983)







Dec. 24, 1982

Dear Prof. Vaida,

“Good luck with that one…”

(I paraphrase)

Gerhard Herzberg (Nobel 1971)

2. Work on hard problems, tackle tough questions, and seek out smart minds!

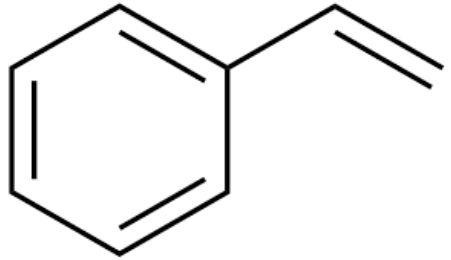
Four ‘Molecular Lessons’ I Learned from Veronica…

Rus Hemley

J. Chem. Phys. **82** (12), 15 June 1985

The singlet states of styrene. Theoretical vibrational analysis of the ultraviolet spectrum[a)]

R. J. Hemley,[b)] D. G. Leopold,[c)] V. Vaida,[d)] and M. Karplus
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138



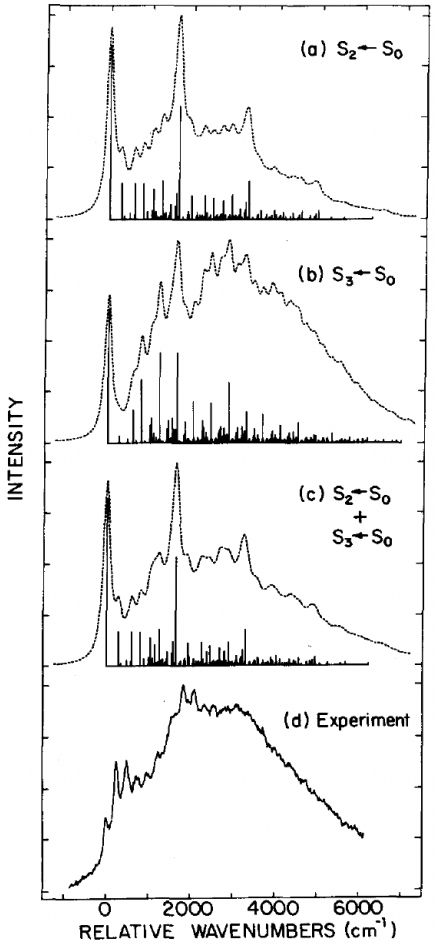


TABLE I. Styrene ground state vibrations.

Calc.[a] ν (cm^{-1})	Expt.[b] ν (cm^{-1})	Expt.[b] Assign.	Internal coordinate contribution[c]
			a′
3093	3106	ν_1	1.00 ring C–H stretch
3090	3084	ν_3	0.97 ring C–H stretch; 0.03 subst. C–H stretch
3089	3061	ν_4	0.99 ring C–H stretch; 0.01 subst. C–H stretch
3088	3055	ν_5	1.00 ring C–H stretch
3087	3029	ν_6	0.91 ring C–H stretch; 0.09 subst. C–H stretch
3084	3009	ν_7	0.84 ring C–H stretch; 0.16 subst. C–H stretch
3063	3091	ν_2	0.96 subst. C–H stretch; 0.04 ring C–H stretch
2988	2981	ν_8	0.99 subst. C–H stretch; 0.01 ring C–H stretch
1665	1630	ν_9	0.33 C_1–C_2 stretch; 0.32 ring C–C stretch; 0.16 subst. bend; 0.14 ring bend; 0.0
1625	1600	ν_{10}	0.57 ring C–C stretch; 0.28 ring bend; 0.09 C_1–C_2 stretch; 0.04 subst. bend; 0.0
1597	1575	ν_{11}	0.46 ring C–C stretch; 0.22 ring bend; 0.18 C_1–C_2 stretch; 0.11 subst. bend; 0.0
1523	1450	ν_{13}	0.52 ring bend; 0.42 ring C–C stretch; 0.04 C_2–C_3 stretch; 0.01 subst. bend; 0.0
1496	1494	ν_{12}	0.41 ring bend; 0.39 ring C–C stretch; 0.19 subst. bend; 0.01 C_1–C_2 stretch
1438	1411	ν_{14}	0.65 subst. bend; 0.14 ring bend; 0.07 ring C–C stretch; 0.07 C_1–C_2 stretch; 0.0
1398	1334	ν_{15}	0.70 ring C–C stretch; 0.24 ring bend; 0.03 subst. bend; 0.02 C_2–C_3 stretch; 0.0
1371	1289	ν_{17}	0.76 ring bend; 0.20 ring C–C stretch; 0.02 subst. bend; 0.02 C_2–C_3 stretch
1304	1303	ν_{16}	0.61 subst. bend; 0.22 C_1–C_2 stretch; 0.07 C_2–C_3 stretch; 0.07 ring bend; 0.03 ri
1259	1203	ν_{18}	0.31 subst. bend; 0.31 ring bend; 0.22 C_2–C_3 stretch; 0.16 ring C–C stretch
1160	1181	ν_{19}	0.80 ring bend; 0.19 ring C–C stretch; 0.01 subst. bend
1144	1156	ν_{20}	0.92 ring bend; 0.08 ring C–C stretch
1094	1083	ν_{21}	0.56 ring bend; 0.37 ring C–C stretch; 0.06 subst. bend; 0.01 C_1–C_2 stretch
1059	1001[d]	ν_{24}	0.61 ring C–C stretch; 0.36 ring bend; 0.02 subst. bend
1046	1019	ν_{23}	0.55 ring bend; 0.41 ring C–C stretch; 0.03 subst. bend; 0.01 C_2–C_3 stretch
1022	1032	ν_{22}	0.66 subst. bend; 0.28 ring C–C stretch; 0.05 ring bend; 0.01 C_1–C_2 stretch
817	775[d]	ν_{25}	0.35 ring bend; 0.32 ring C–C stretch; 0.20 C_2–C_3 stretch; 0.12 subst. bend; 0.0
675	621	ν_{26}	0.82 ring bend; 0.12 C–C stretch; 0.06 subst. bend
611	553[d]	ν_{27}	0.45 ring bend; 0.37 subst. bend; 0.14 ring C–C stretch; 0.04 C_2–C_3 stretch
471	437[d]	ν_{28}	0.43 ring bend; 0.21 subst. bend; 0.19 C_2–C_3 stretch; 0.13 ring C–C stretch; 0.0
281	228[d]	ν_{29}	0.62 ring bend; 0.33 subst. bend; 0.04 ring C–C stretch; 0.01 C_1–C_3 stretch
			a″
1015	985	ν_{31}	0.48 ring o.o.p.; 0.40 ring torsion; 0.08 C_1–C_2 torsion; 0.04 subst. o.o.p.
1011	992	ν_{30}	0.54 C_1–C_2 torsion; 0.29 subst. o.o.p.; 0.09 ring o.o.p.; 0.05 ring torsion
993	970	ν_{32}	0.58 ring o.o.p.; 0.41 ring torsion; 0.01 C_1–C_2 torsion
953	909	ν_{33}	0.99 subst. o.o.p.; 0.01 C_1–C_2 torsion
912	909	ν_{34}	0.79 ring o.o.p.; 0.20 ring torsion; 0.01 subst. o.o.p.
825	841	ν_{35}	1.00 ring o.o.p.
732	776	ν_{36}	0.90 ring o.o.p.; 0.06 subst. o.o.p.; 0.03 C_1–C_2 torsion; 0.01 ring torsion
649	699	ν_{37}	0.46 ring o.o.p.; 0.25 subst. o.o.p.; 0.16 ring torsion; 0.12 C_1–C_2 torsion; C_2–C_3 torsion
584	640	ν_{38}	0.33 ring torsion; 0.27 ring o.o.p.; 0.24 subst. o.o.p.; 0.16 C_1–C_2 torsion
427	433	ν_{39}	0.62 ring o.o.p.; 0.28 ring torsion; 0.06 subst. o.o.p.; 0.04 C_1–C_2 torsion
395	399[d]	ν_{40}	0.59 ring torsion; 0.40 ring o.o.p.; 0.01 C_2–C_3 torsion
217	199[d]	ν_{41}	0.48 ring torsion; 0.35 ring o.o.p.; 0.17 C_2–C_3 torsion
109	38[d]	ν_{42}	0.75 C_2–C_3 torsion; 0.10 ring torsion; 0.08 ring o.o.p.; 0.07 subst. o.o.p.

TITLE: The singlet states of styrene. Theoretical vibrational analysis of the ultraviolet spectrum

AUTHOR(S): R.J. Hemley, D.G. Leopold, V. Vaida, and M. Karplus

TENTATIVE ISSUE: 15 May 1985

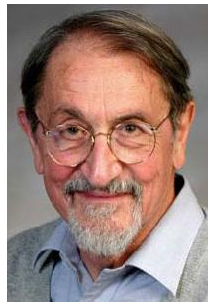
CATEGORY: Article

Professor Martin Karplus
Department of Chemistry
Harvard University
12 Oxford Street
Cambridge, MA 02138

Finally,
MK

Dear Professor Karplus:

The above manuscript has been accepted for publication in the Journal of Chemical Physics and is being forwarded



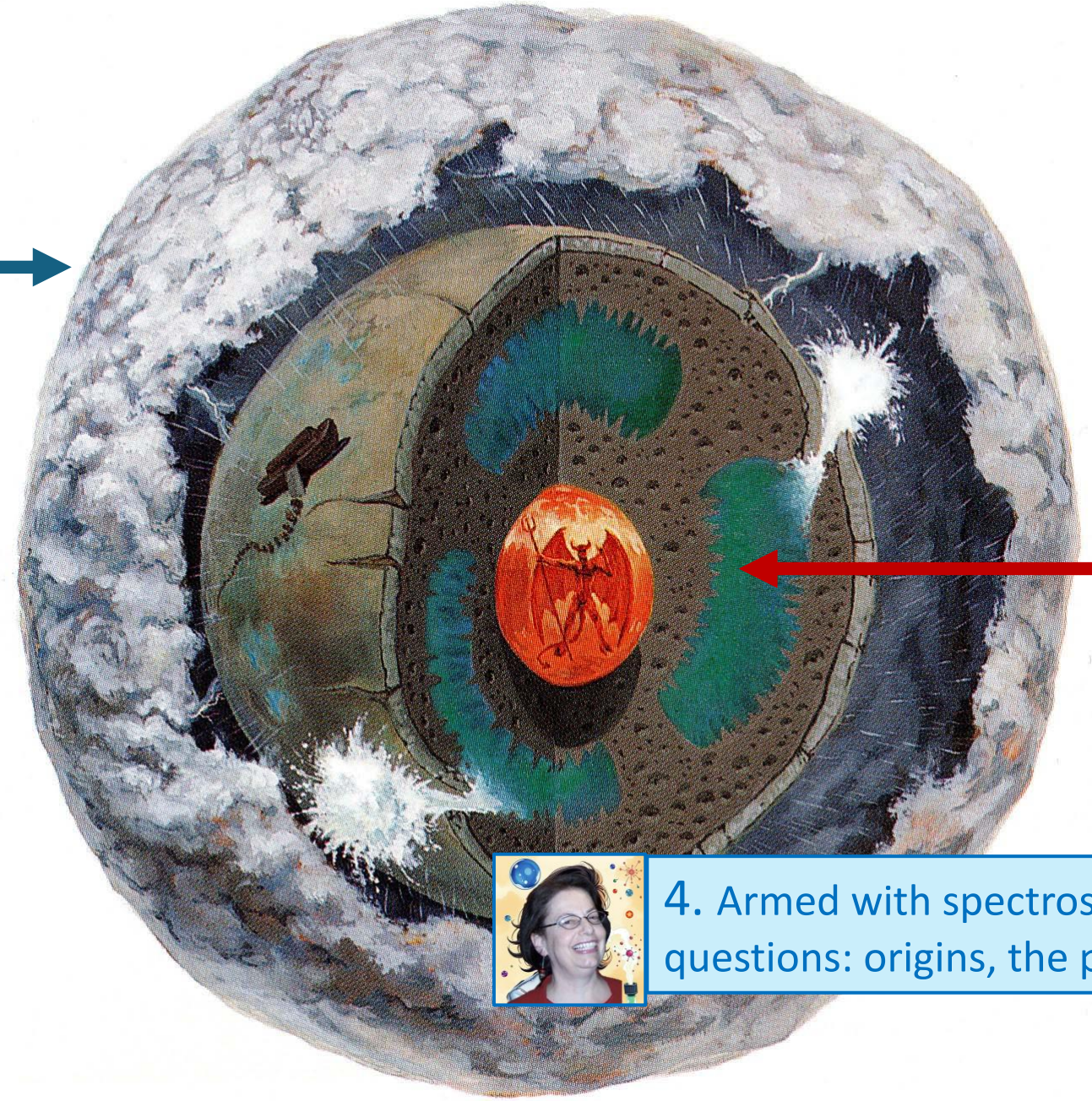
3. Don’t stifle debate, but remember: the molecules have the final word!

Four ‘Molecular Lessons’ I Learned from Veronica…

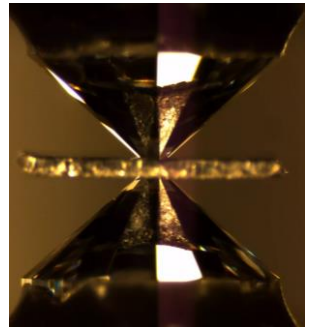
Rus Hemley

VERONICA ASCENDING

NAS, Amer. Acad. Arts Sci., Langmuir Award, E. B. Wilson Award, Guggenheim, AAAS . . .



OTHERS DESCENDING



Courtesy of Steve Jacobsen

4. Armed with spectroscopy, tackle bold questions: origins, the planet, and beyond

Setting up the lab in Boulder. The lab was not renovated I found cabinets, sinks, etc. and set it up before VV arrived in Boulder (June 1984)
The move: optical tables set in place.
The people, skiing, interactions.
The story of backfilling the lab with sewage

Maureen McCarthy

Maureen McCarthy

- Controversy at the time about the electronic spectrum of NH_3. The issue was that models available at the time did not consider mode coupling which turned out to be important in this molecule where the pyramidal ground state becomes planar on excitation and dissociates.
- Theory was necessary to understand the spectra. Potential energy surfaces were needed first, before one could do dynamics. You set up theory collaborations to get the potentials needed for dynamics with Pavel et. al. whom you found at JILA. Maureen does computation in Frankfurt!

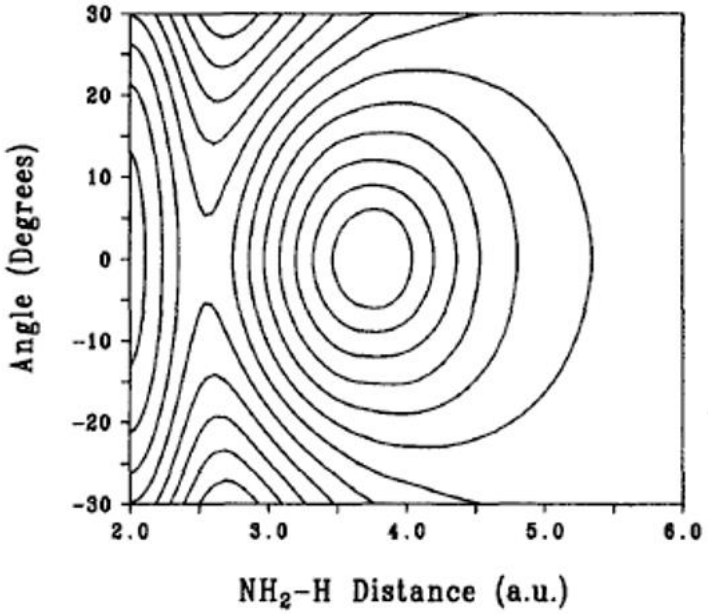


FIG. 6. Contour plot of the potential energy surface of the A state as functions of the bending angle Θ and the R_{NH_2-H} distance. The contours are plotted with energy increments of 0.005 a.u.

"The Ultraviolet Absorption Spectrum of the A'A"2 ¬ X'A1 Transition of Jet-Cooled Ammonia," V. Vaida, M. I. McCarthy, P. C. Engelking, P. Rosmus, H. J. Werner, P. Botschwina, *J. Chem. Phys.*, **86**, 6669-6676 (1987).

"Theoretical A'A"2 ¬ X'A1 Absorption and Emission Spectrum of Ammonia," P. Rosmus, P. Botschwina, H. J. Werner, V. Vaida, P. C. Engelking and M. I. McCarthy, *J. Chem. Phys.*, ***86***, 6677-6692 (1987).

"Dissociation of NH3 to NH2 + H," M. I. McCarthy, P. Rosmus, H. J. Werner, P. Botschwina and V. Vaida, *J. Chem. Phys.*, **86**, 6693-6700 (1987).

Mode coupling can be read from the jet-cooled absorption spectra and inform on the reaction dynamics

Anne Jefferson

Steve Sapers

Boulder, the first years

Grad students

- Maureen McCarthy
- Steve Sapers (me)
- Doug Prinslow
- Erik Richard
- Ann Jefferson
- Kathy Lantz

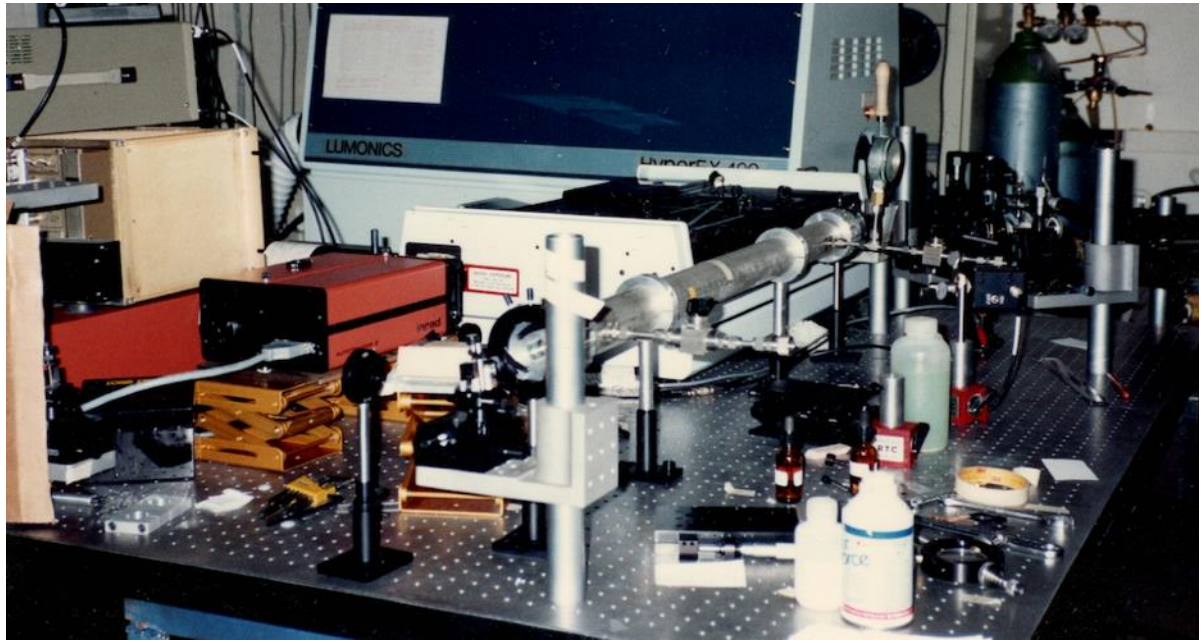
Undergrads

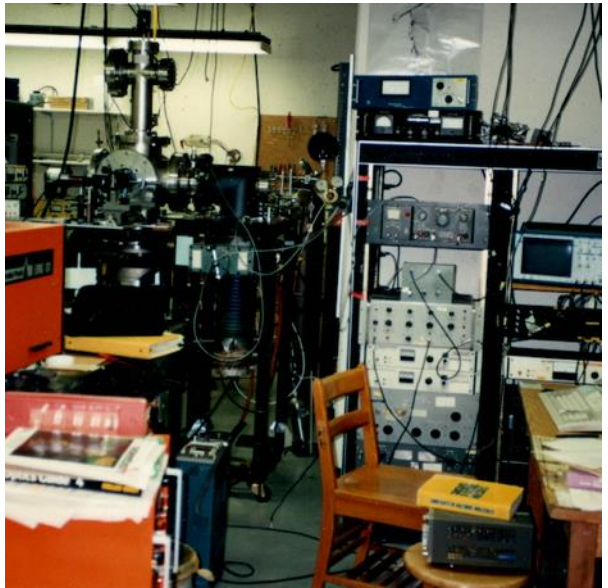
- Geoff Gaines

Post Docs and Collabs/Sabaitcal

- William Hollingsworth
- Jamie Donaldson
- Eckart Rühl
- Tom Wickham-Jones
- Ron Naaman
- Mark Child

Steve Sapers





Steve Sapers

Steve Sapers

The CH_3I collaborators: Effects of weak interactions on the spectra and photoreaction dynamics. CH_3I and $(CH_3I)_2$

Multiphoton Ionization Study of Intra and Intermolecular Effects on the Photodissociation of Methyl Iodide," S. P. Sapers, V. Vaida and R. Naaman, *J. Chem. Phys.*, **88**, 3638-3645 (1988).

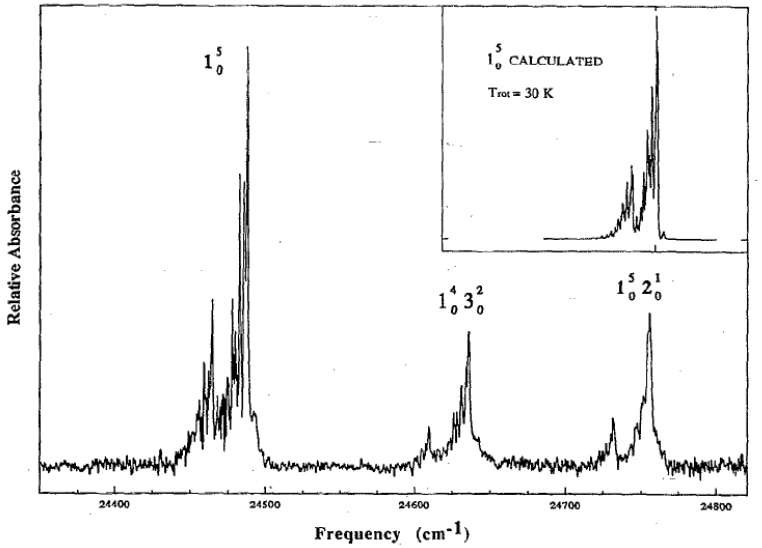
"Spectroscopic Probe of Intramolecular Predissociation Dynamics," V. Vaida, D.J. Donaldson, S. P. Sapers, R. Naaman and M. S. Child, *J. Phys. Chem.*, **93**, 513-520 (1989).

"Spectroscopic and Photochemical Perturbations of Weak Interactions on Electronic Surfaces of Methyl Iodide," V. Vaida, D. J. Donaldson, S. P. Sapers and R.Naaman, *J. Chem. Soc., Faraday Trans.*, **86**, 2043-2048 (1990).

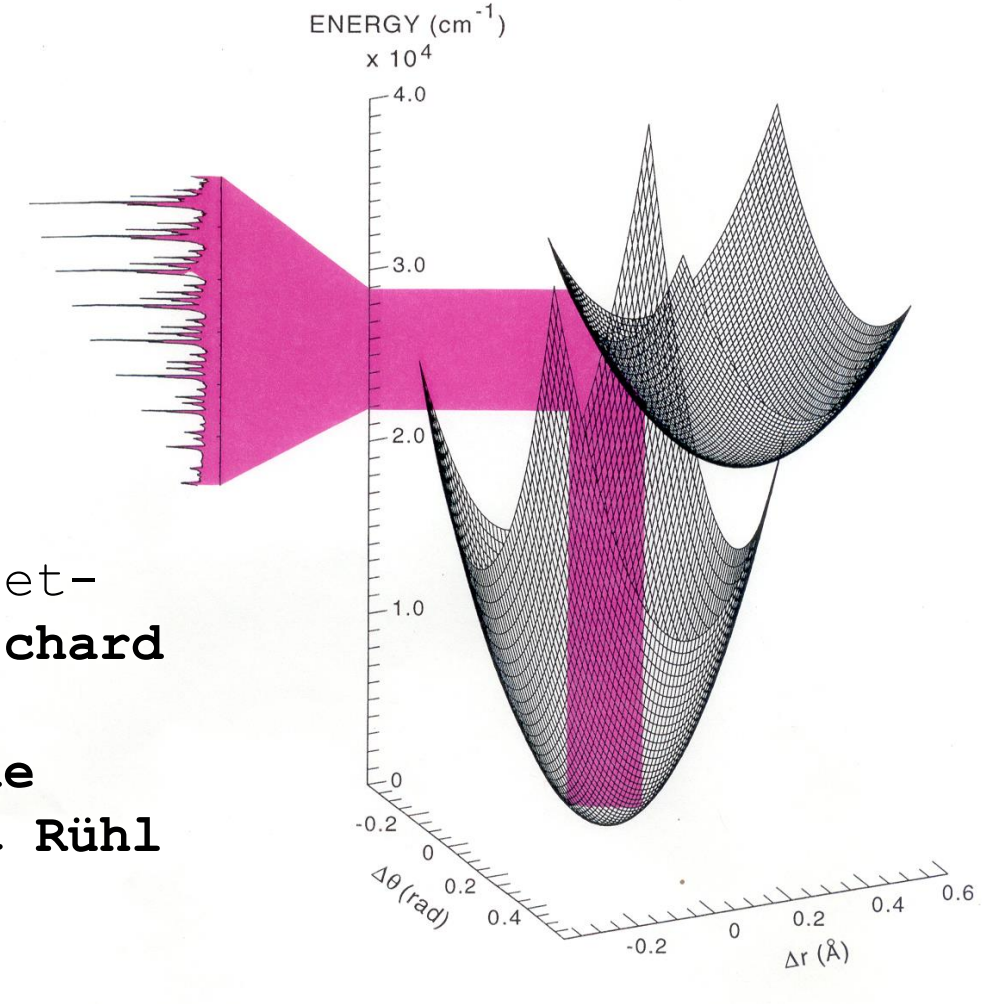
2) Light initiated chemistry in the Earth's atmosphere

"The Direct Near Ultraviolet Absorption Spectrum of the A2A2 ¬ X2B1 Transition of Jet-Cooled **Chlorine Dioxide**" E. C. Richard and V. Vaida, *J. Chem. Phys.*, (1991)
"The Photochemical Dynamics of the A^2A^2 State of Chlorine Dioxide," E. C. Richard and V. Vaida, *J. Chem. Phys* (1991).

OClO → ClO + O induced by the asymmetric stretch
OClO → Cl + O_2 coupling of symmetric stretch and
k



UV spectroscopy of jet-cooled OClO- **Erik Richard**
REMPI MS for product identification – **Anne Jefferson and Echart Rühl**



This chemistry is completely different in condensed phase:
Aqueous solutions with John Simon (UCSD)
Photochemistry of OClO on ice: Laura Brown with Jeff Roberts (U Minnessota) and Dave Hansen (NOAA)

2) Light initiated chemistry in the Earth's atmosph

UV spectroscopy of jet-cooled OClO- **Erik Richard**

REMPI MS for product identification – **Anne Je**

Rü

This chemistry is completely different in condensed phase:

Aqueous solutions with John Simon (UCSD)

Photochemistry of OClO on ice: Laura Brown with Jeff

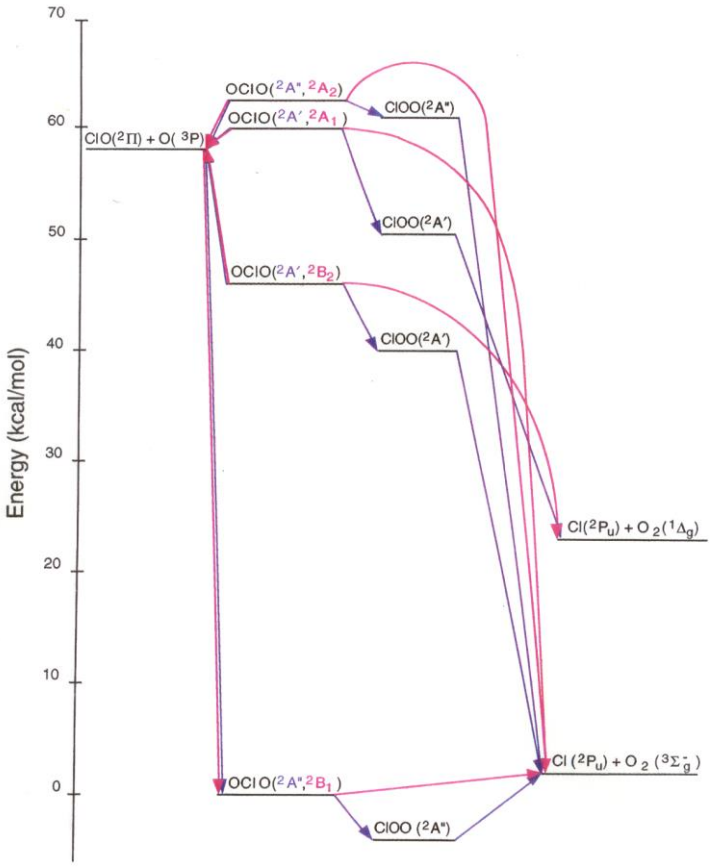
The OClO photochemistry is completely different in condensed phase:

Aqueous solutions with John Simon (UCSD)

"The Photoreactivity of Chlorine Dioxide," V. Vaida and J. D. Simon, *Science*, **268**, 1443-1448 (1995).

"Competing Photochemical Pathways of OClO in Polar Solutions," R. C. Dunn, E. C. Richard, V. Vaida, and J. D. Simon, *J. Phys. Chem.*, **95**, 6060-6063 (1991).

Photochemistry of OClO on ice: Laura Brown with Jeff Roberts (U Minnesota) and Dave Handson (NOAA)



"Uptake of Chlorine Dioxide by Model Polar Stratospheric Cloud Surfaces: Ultrahigh Vacuum Studies," J. D. Graham, J. T. Roberts, L. Brown and V. Vaida, *J. Phys. Chem.*. **100**, 3115-3120 (1996)

"Uptake of Chlorine Dioxide by Model PSC's Under Stratospheric Conditions," L. A. Brown, V. Vaida, D. R. Handson, J. D. Graham and J. T. Roberts, *J. Phys. Chem.*. **100**, 3121-3125 (1996)

OClO and polar ozone

"Photoisomerisation of OClO: a Polar Ozone Depletion Mechanism?" V. Vaida, S. Solomon, E. C. Richard, E. Ruhl and A. Jefferson, *Nature*, (1989)

$OClO \rightarrow ClO + O$ do nothing cycle with respect to polar ozone loss

$OClO \rightarrow Cl + O_2$ potential catalytic polar ozone loss

How our program changed - opportunities at the interface with atmospheric science

Observe discrepancies between atmospheric measurements and model results to find the interesting problems where fundamental information is missing.

Work with aqueous environments

Technology:

Use equilibrium cells (not supersonic jets) to quantify the results for atmospheric purposes

Use solar simulators for photochemical experiments (not lasers)

Photoreactive molecules: The OClO story

E. C. Richard and V. Vaida, *J. Chem. Phys.*, (1991 a & b).
V. Vaida, S. Solomon, E. C. Richard, E. Ruhl and A. Jefferson, *Nature*, (1989)

Spectroscopy established the Molecular Framework

Exciting part was what the spectroscopy told us about the photochemistry

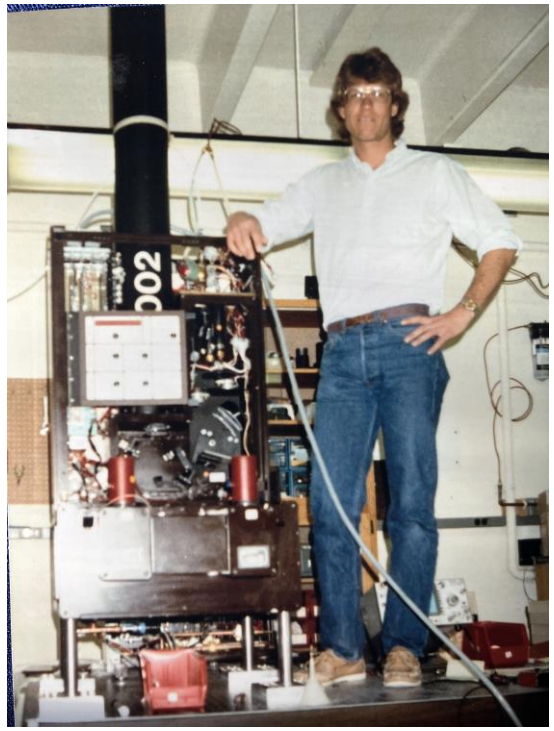
- The high-resolution jet-cooled absorption spectroscopy ultimately mapped the electronic excited state structure of OClO and characterized the excited-state PES's responsible for the photochemistry

Measurements of the vibrationally resolved spectra linewidths revealed how specific vib. modes controlled the photochemical outcomes

- Excited-state lifetimes varied dramatically depending on vibration excited, particularly in asym. stretch and bending modes
  - Asym. Str. → ClO + O
  - Bending → Cl + O_2

Early example of what we would now call *mode-selective photochemistry*

Jet-Cooled absorption



Erik Richard

Study of Primary Photofragments," E. Ruhl, A. Jefferson & V. Vaida, *J. Phys. Chem* (1990)
Anne Jefferson & Eckart Rühl

Solvent Effects on the Spectroscopy and Ultrafast Photochemistry of OClO, Dunn, Flanders, & Simon, *J. Phys. Chem* (1995)
Rob Dunn, Bret Flanders, & John Simon

OClO increasing sym. s

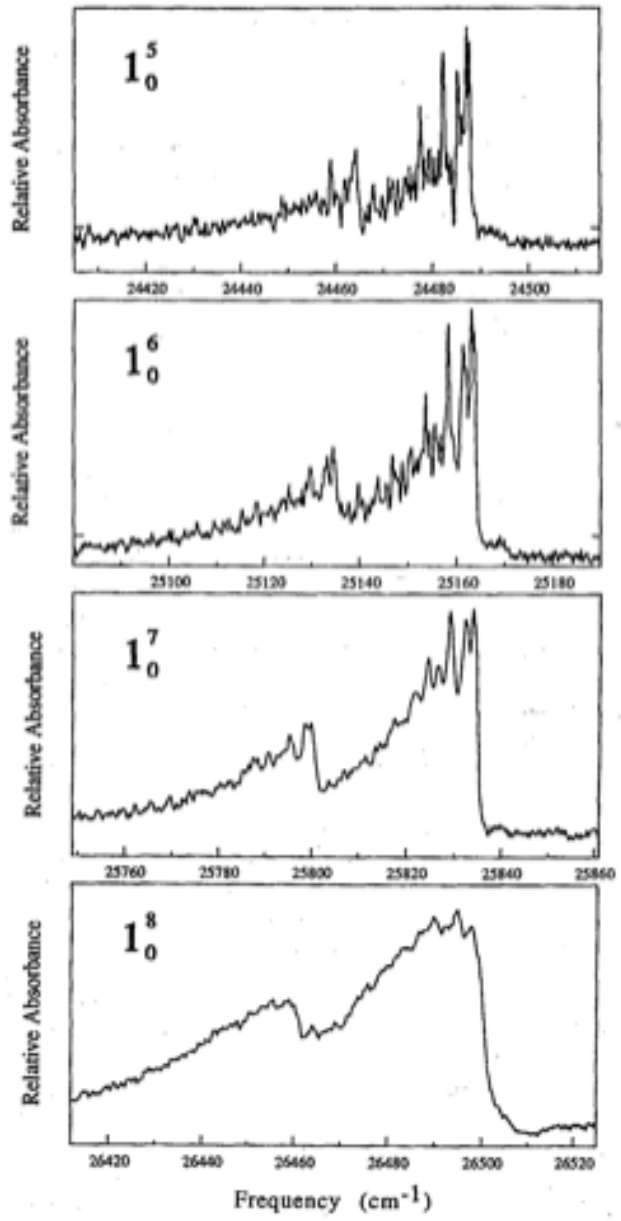
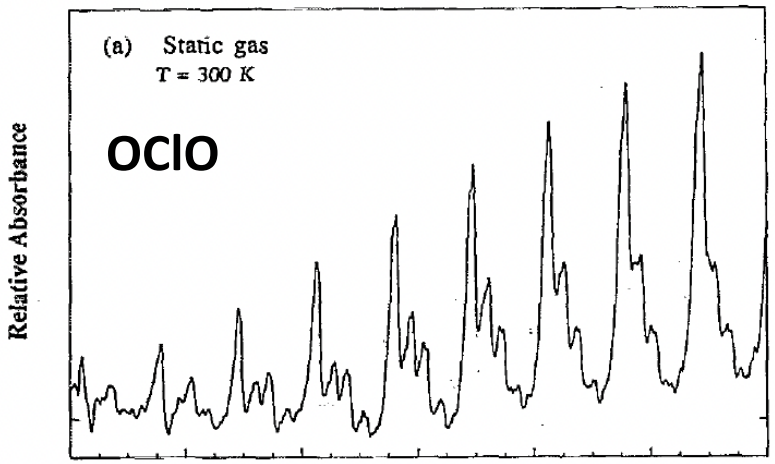
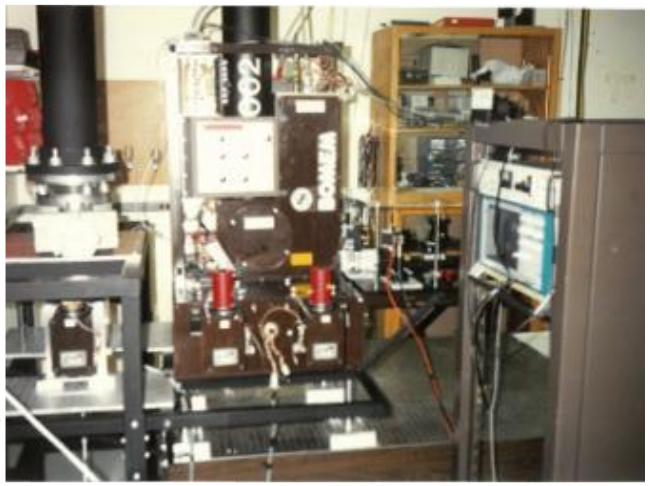
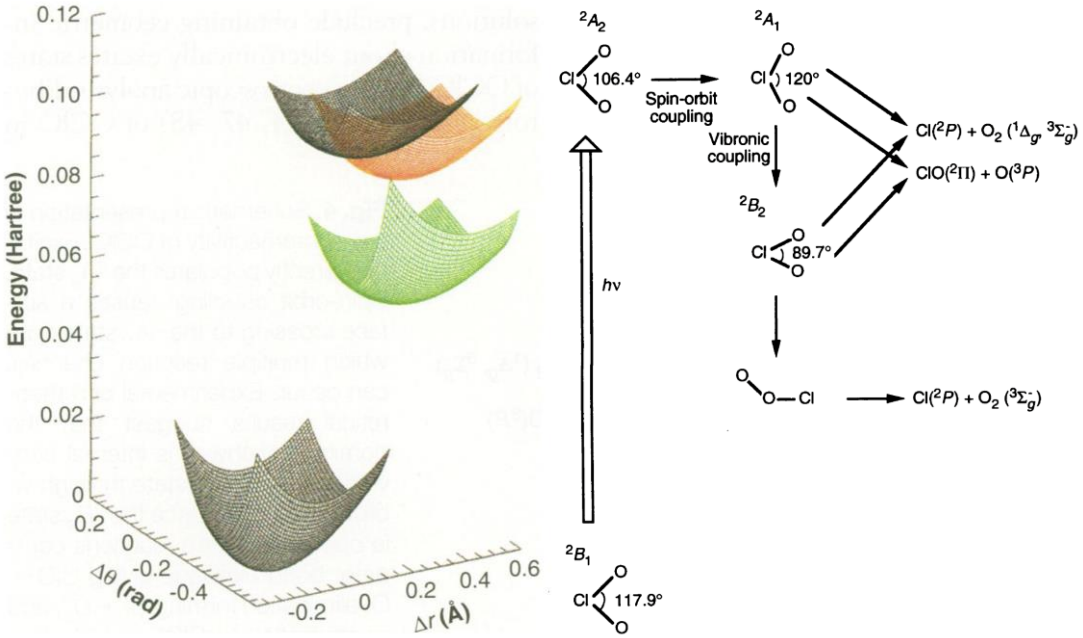


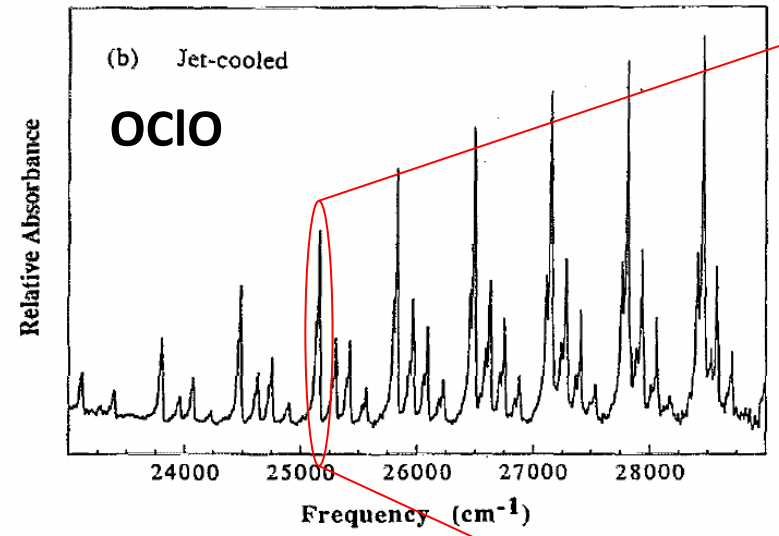
FIG. 1. Comparison of the (5,0,0), (6,0,0), (7,0,0), and (8,0,0) bands in the $\tilde{A}\,^2A_2$ state of OClO showing the homogeneous rotational line broadening occurring with increasing energy. All of the spectra were recorded at 0.25 cm^{-1} resolution under dilute expansion conditions of 3% OClO in 1.5 atm of Helium.

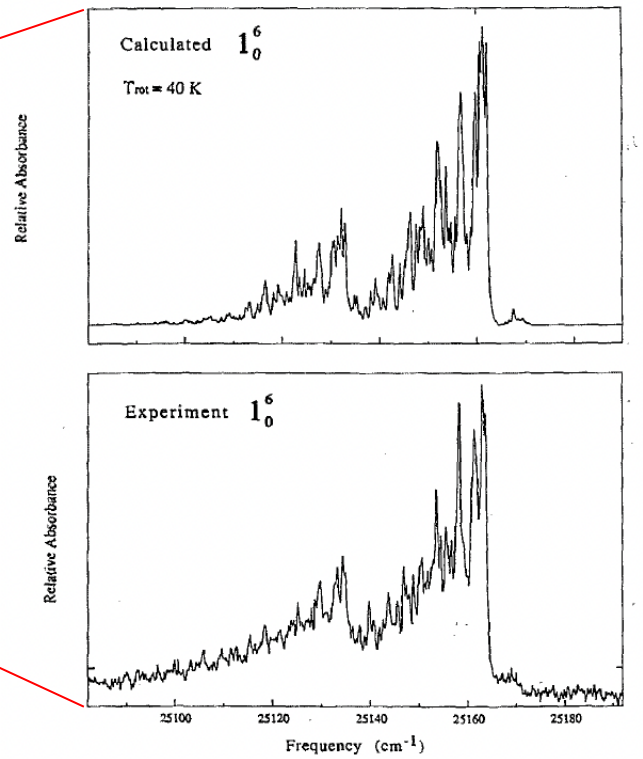
Spectroscopy → Photodynamics











Multiple Photochemical Pathways

Work demonstrated that OClO does not photodissociate through a single channel, but excitation accesses a manifold of coupled electronic states that can produce:

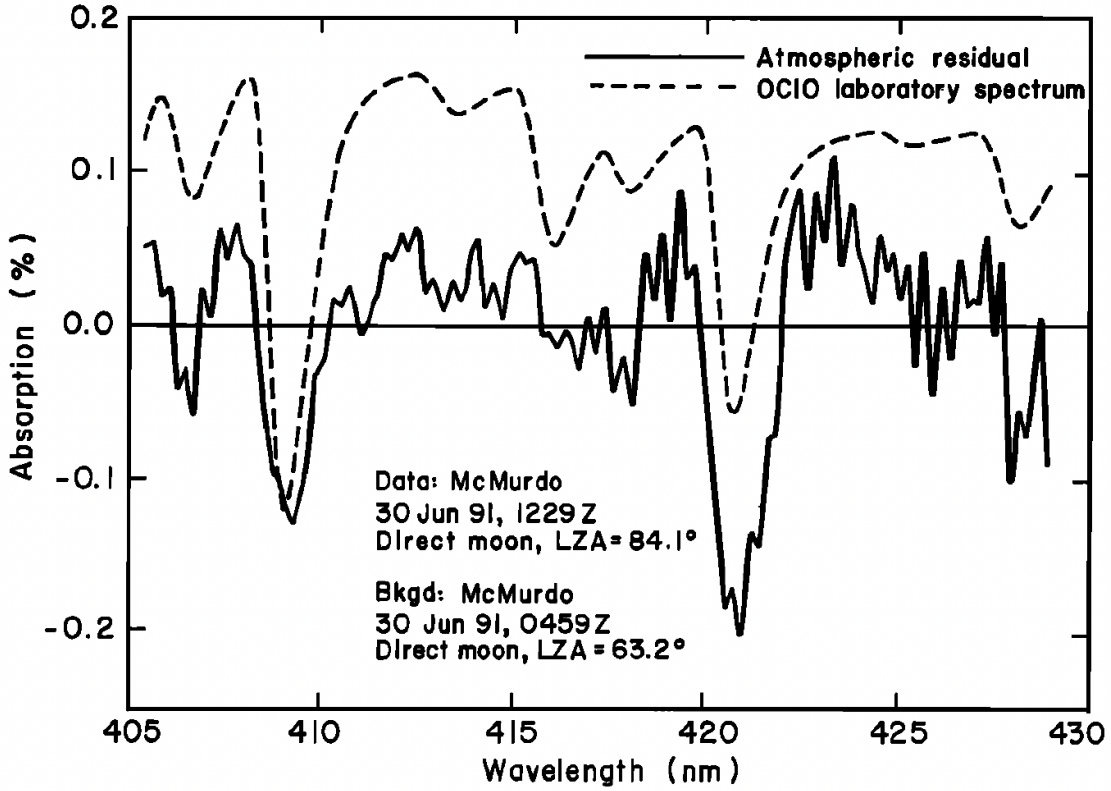
- ClO + O
- Cl + O_2
- Isomerization to ClOO → Cl + O_2

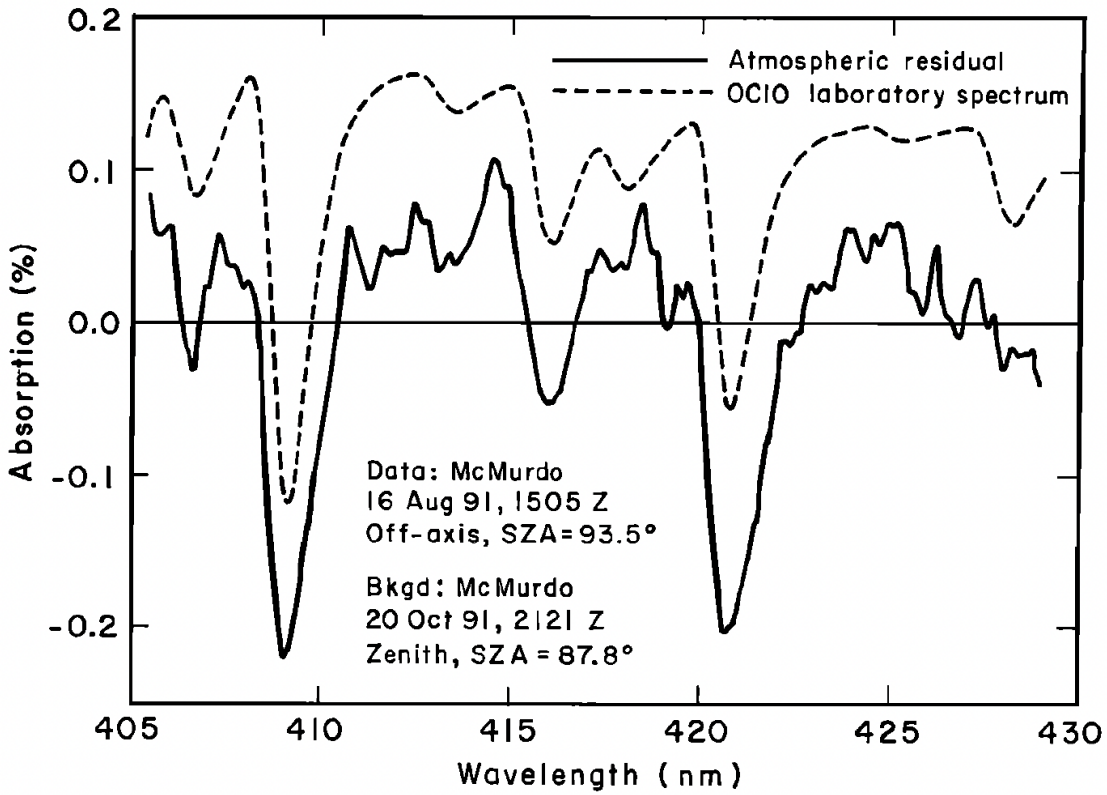
Erik Richard

Erik Richard

Observations of OClO at McMurdo Station, Antarctica

R. W. Sanders, S. Solomon, J. P. Smith, L. Perliski, H. L. Miller, G. H. Mount, J. G. Keys, and A. L. Schmeltekopf, *J. Geophys. Res.*, **98**, D4, 7219 - 7228, (1993)





OClO provided a direct observational link between PSC chemistry, chlorine activation, and ozone destruction.

Laura Brown

Collaborations

J. Phys. Chem. **1996** DOI: 10.1021/jp951664b

Uptake of Chlorine Dioxide by Model PSCs under Stratospheric Conditions

Laura A. Brown[1], Veronica Vaida[2], David R. Hanson[3], James D. Graham[4], Jeffrey T. Roberts[5]

Abstract: The uptake of chlorine dioxide by ice at temperatures approaching those needed for PSC formation in the Antarctic stratosphere was studied. The two approaches used in this investigation involved modeling the surface coverage using kinetic parameters obtained in an ultrahigh-vacuum surface experiment and comparing these results to the uptake measured in a flow tube apparatus. For an OClO gas phase concentration of 5 × 1010 molecules/cm3, a surface coverage of ≈2 x 10-4±1 monolayers of OClO was estimated on the ice at 189 K from both methods. For an average OClO concentration in the Antarctic stratosphere of 2 x 109 molecules/cm3, a surface coverage of 7 × 10-6±1 monolayers of OClO on PSCs is predicted.

The Journal of Physical Chemistry › Vol 100/Issue 8 › Article

ARTICLE | February 22, 1996

Uptake of Chlorine Dioxide by Model Polar Stratospheric Cloud Surfaces: Ultrahigh-Vacuum Studies

James D. Graham, Jeffrey T. Roberts, Laura A. Brown, and Veronica Vaida

Hide Author Information

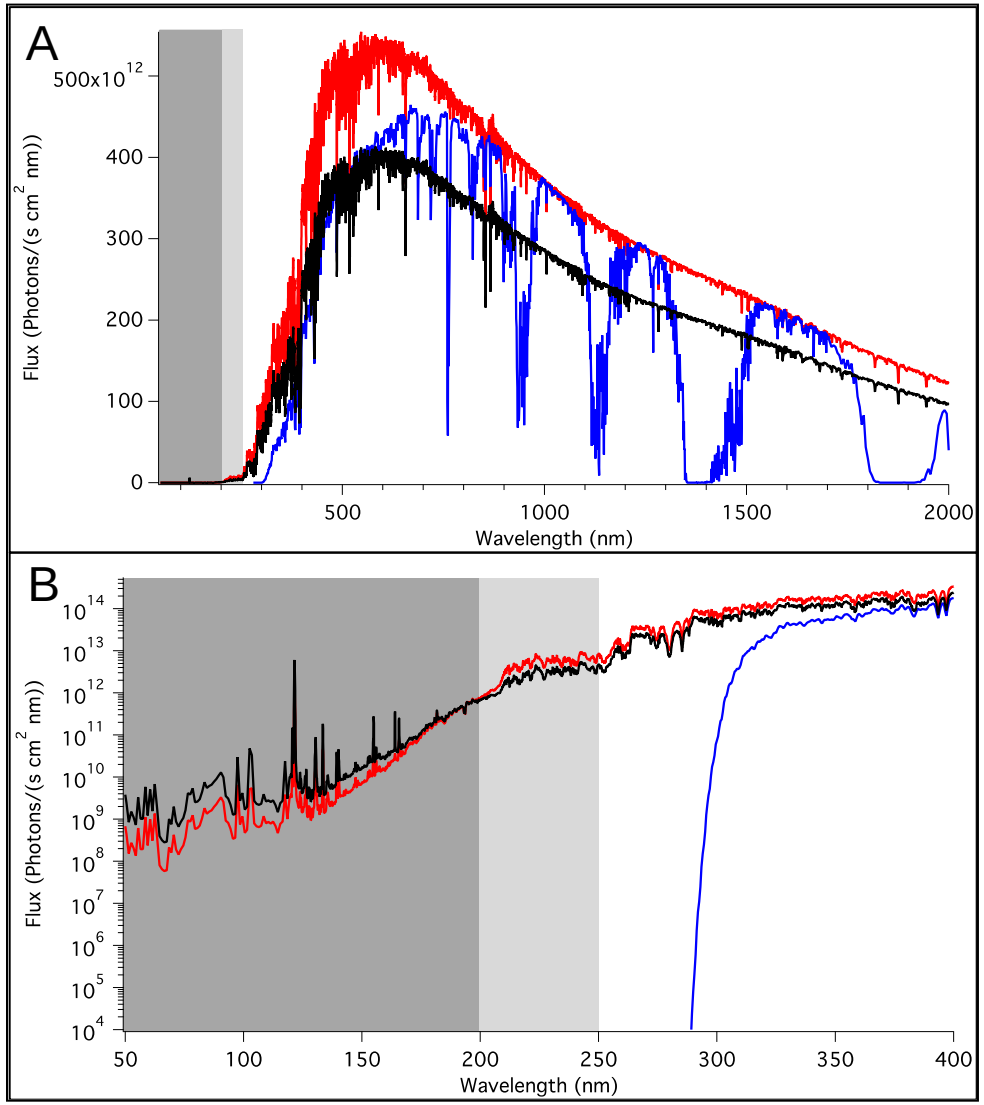
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Laura Brown

Collaborations

Sunlight - the energy source in the natural environment
Solar simulators used in the lab and in simulation chambers –Xe lamp with appropriate filters



Modern Solar Spectrum[1]

3.8 Gya Solar Spectrum[1]

Current Surface Spectrum[2]

Prebiotic Atmospheric Filter:

Completely Attenuated[3]

Modestly Attenuated[3]

Figure From:
Rapf & Vaida *PCCP* 2016, *18*, 20067-20084

Data From:

[1]Claire et al. *Astrophys. J.*, 2012, 757, 95

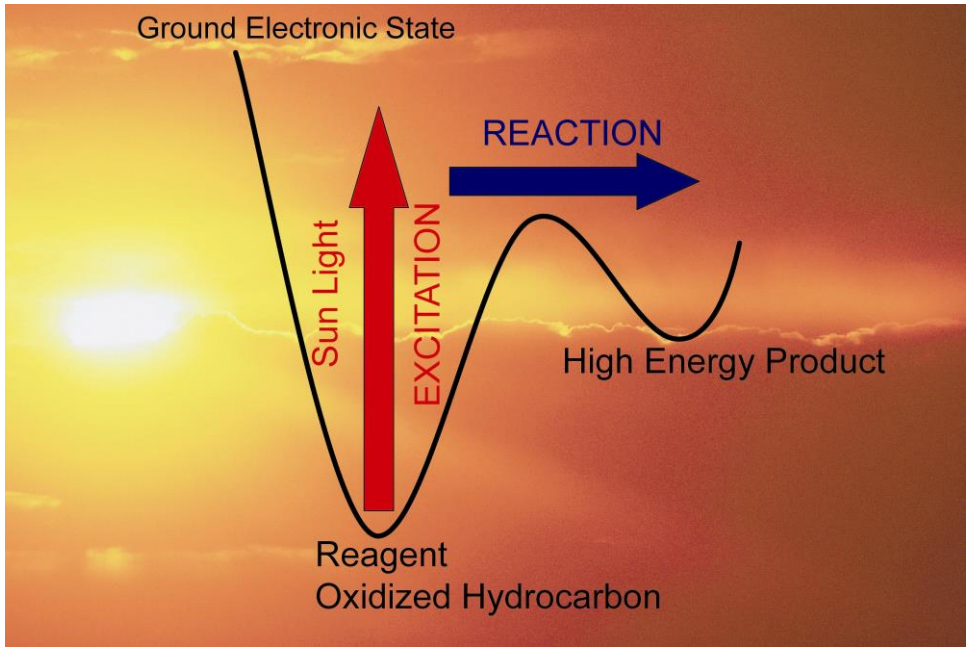
[2]NREL Reference AM 1.5 Atmosphere

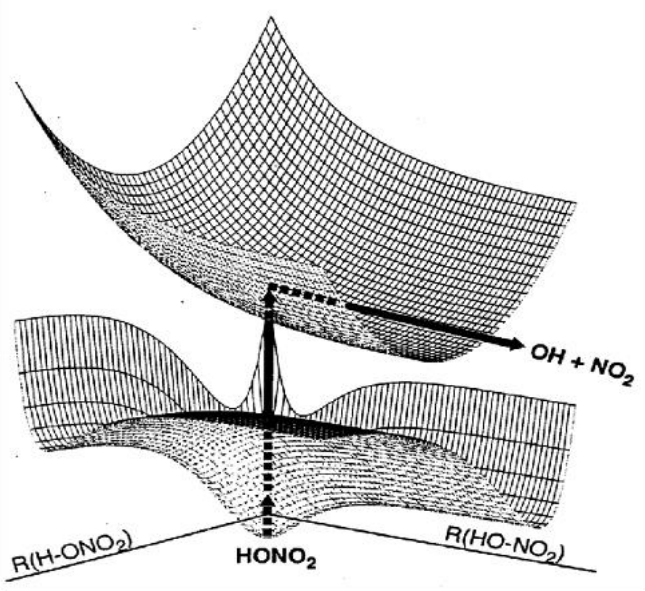
[3]Ranjan & Sasselov *Astrobio.*, 2016, 16, 68-88

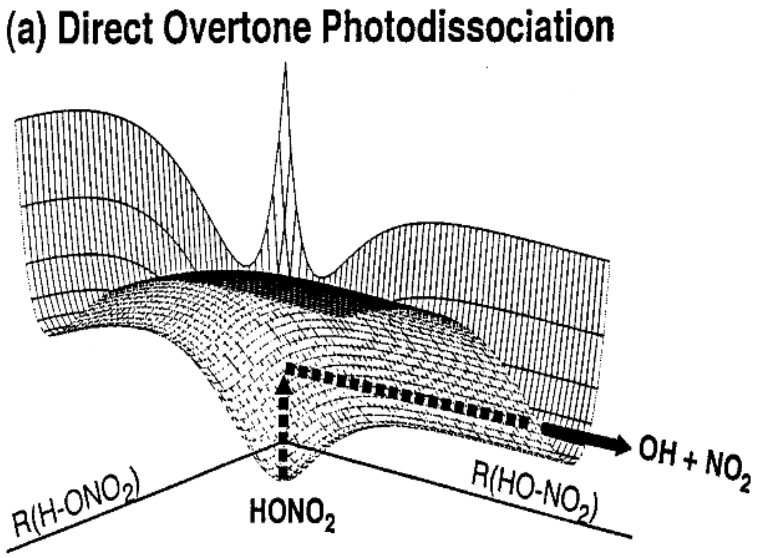
Red light initiated photochemistry

Chemistry through vibrationally excited states was well known in physical chemistry but not expected to be important in the atmosphere with the Sun as the light source because of the low IR absorption cross sections. The UV photochemistry will always win!
At dusk and dawn UV is suppressed by the long absorption path of radiation but visible light gets through. Vibrational overtones can be excited and react.

"Atmospheric Radical Production by Excitation of Vibrational Overtone Absorption"
D.J.Donaldson, G.J.Frost, K.H.Rosenlof, A.F.Tuck and V.Vaida *Geophys. Res.Lett.* **24**, 2651-2654 (1997)

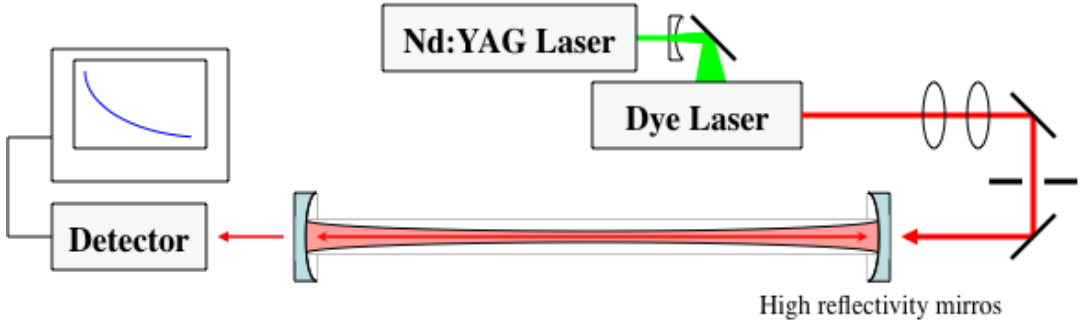


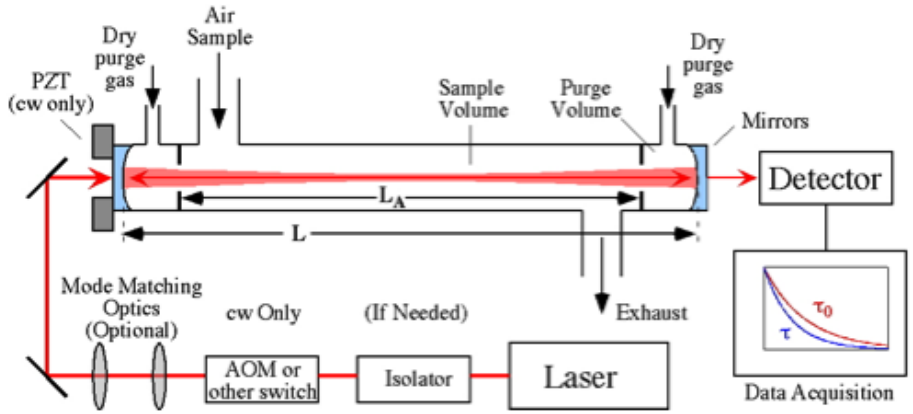


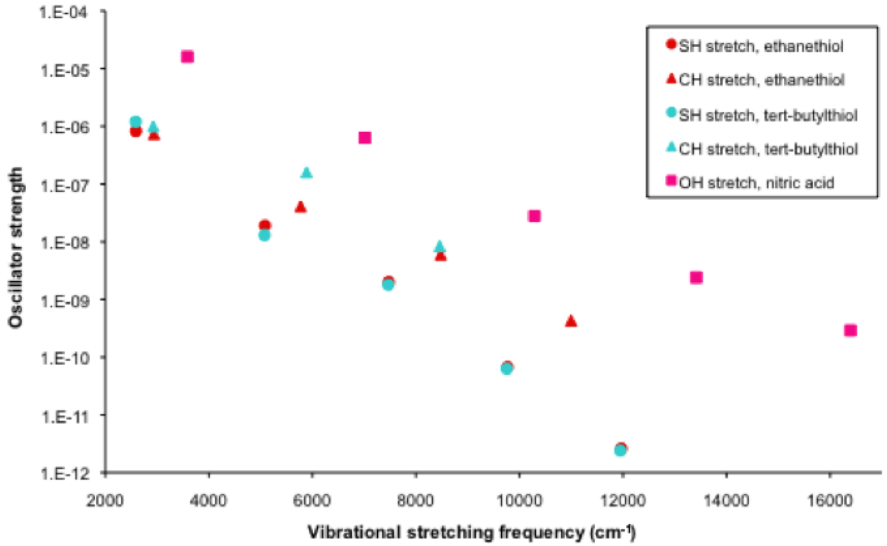


The mechanism involves excitation of v=5 of the OH stretch in molecules with a weak bond such as H_2O_2, HNO_3, HNO_4 followed by energy transfer to the weak bond and reaction.

Dynamics on the ground potential energy surface: gas phase



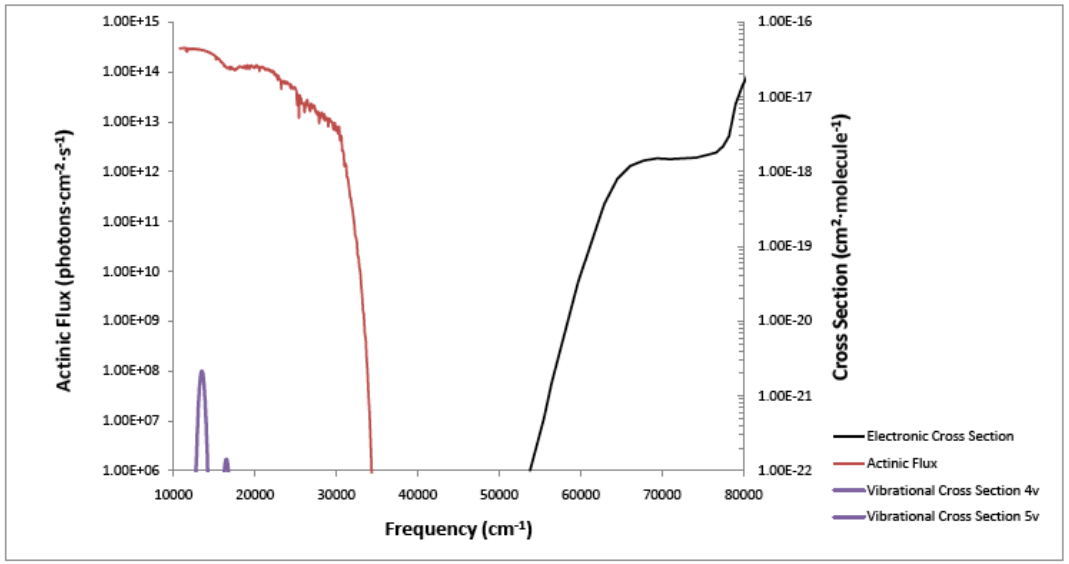




Cross sections for vibrational overtone transitions (formally forbidden) are several orders of magnitude smaller than electronic cross sections. OH stretching transitions have the largest X sections and vibrational frequencies and are therefore a gate way to chemistry.

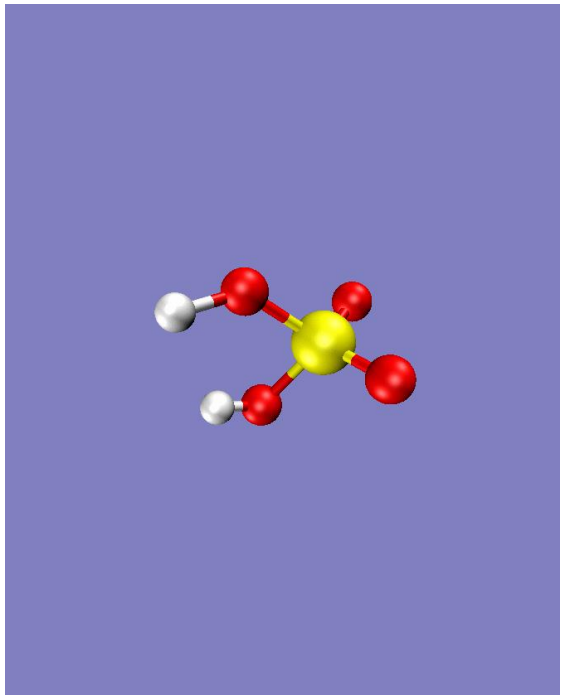
Red-light initiated chemistry should be much more important if no competing UV process exists (Donaldson & Vaida).

Atmospheric photochemistry of H_2SO_4. The mechanism used for H_2O_2, HNO_3, HNO_4 could not work in H_2SO_4 because no weak bond existed. We discovered that this chemistry occurred with a concerted mechanism and a very high energy of concert.



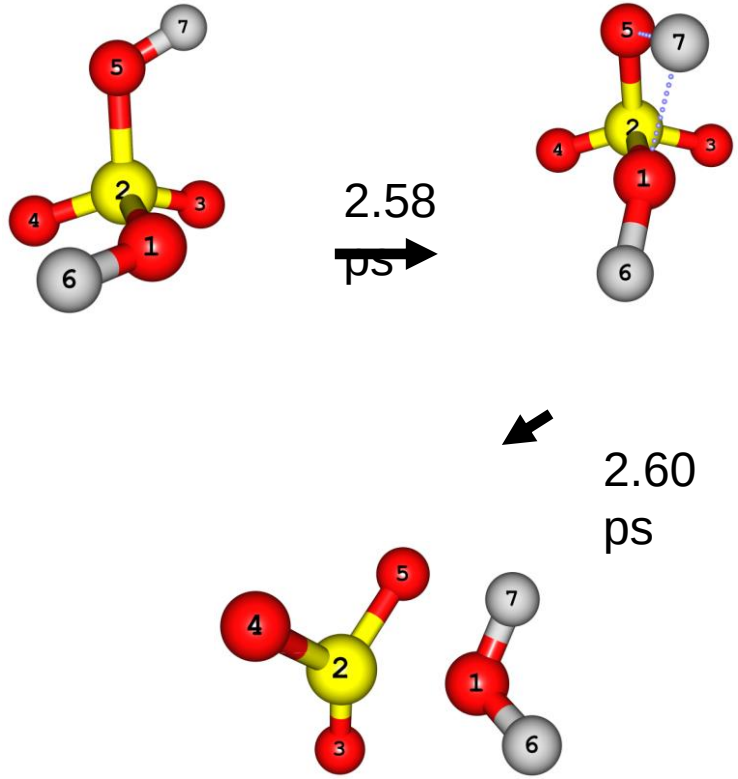
Photolysis of sulfuric acid vapor by visible solar radiation V. Vaida, D. J. Donaldson, H. G. Kjaergaard, P. E. Hintze *Science* 299, 1566-1568 (2003)

Photodissociation yields for vibrationally excited states of sulfuric acid under atmospheric conditions Y. Miller, R. B. Gerber and V. Vaida *Geophys. Res. Lett.* 34(16),



mean time scale ~9 ps

Miller, R.B. Gerber, *JACS*, 2006



Photolysis of H_2SO_4

- **We propose a photochemical mechanism for H_2SO_4 photo-decomposition based on vibrational OH stretching cross sections reported here.**

Vaida, V., H. G. Kjaergaard, P. E. Hintze, D. J. Donaldson Science **299**, 156 (2003)

- **The estimated J values are sufficiently large to explain SO_2 stratospheric and mesospheric concentrations and the related observation of the sulfate layer, solving a long-standing question raised by field measurements.**

Mills, M., O.B. Toon, V. Vaida, P.E. Hintze, H.G. Kjaergaard, D.P. Schofield, T.W. Robinson JGR (2005)

- **This chemistry was used to explain the mesospheric sulfate aerosol layer and vertical SO_2 atmospheric concentrations in the Earth's atmosphere**

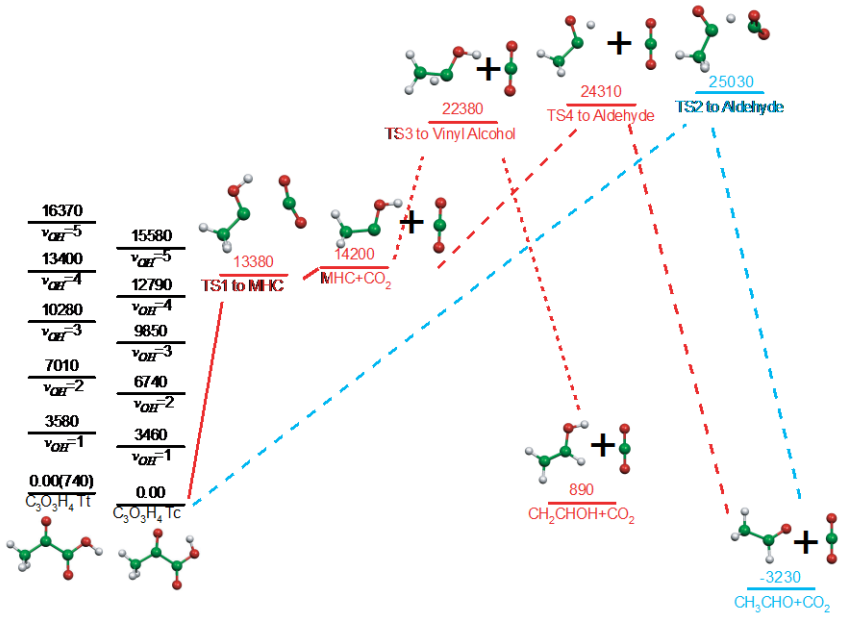
Mills, M.J., O.B. Toon, G.E. Thomas JGR **110**, D24208 (2005)

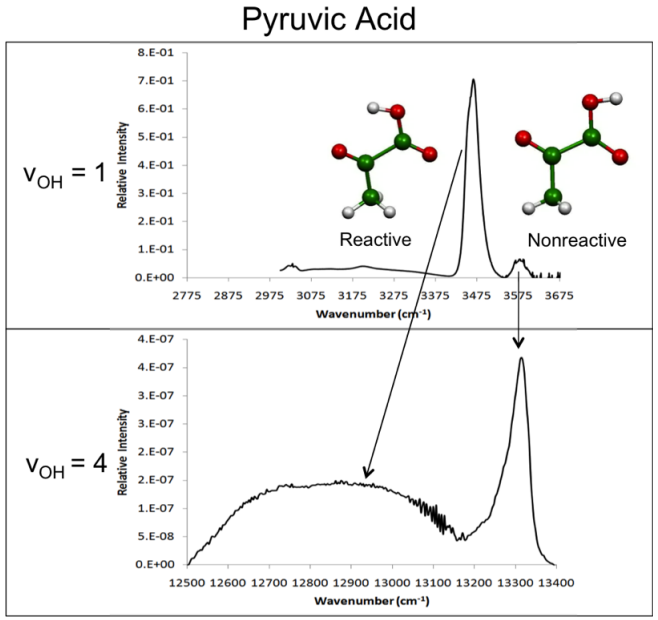
- **The consequences of photochemical decomposition as described here are not limited to Earth's atmosphere, but are expected to be important in planetary atmospheres containing H_2SO_4 - for example, the atmosphere of Venus.**

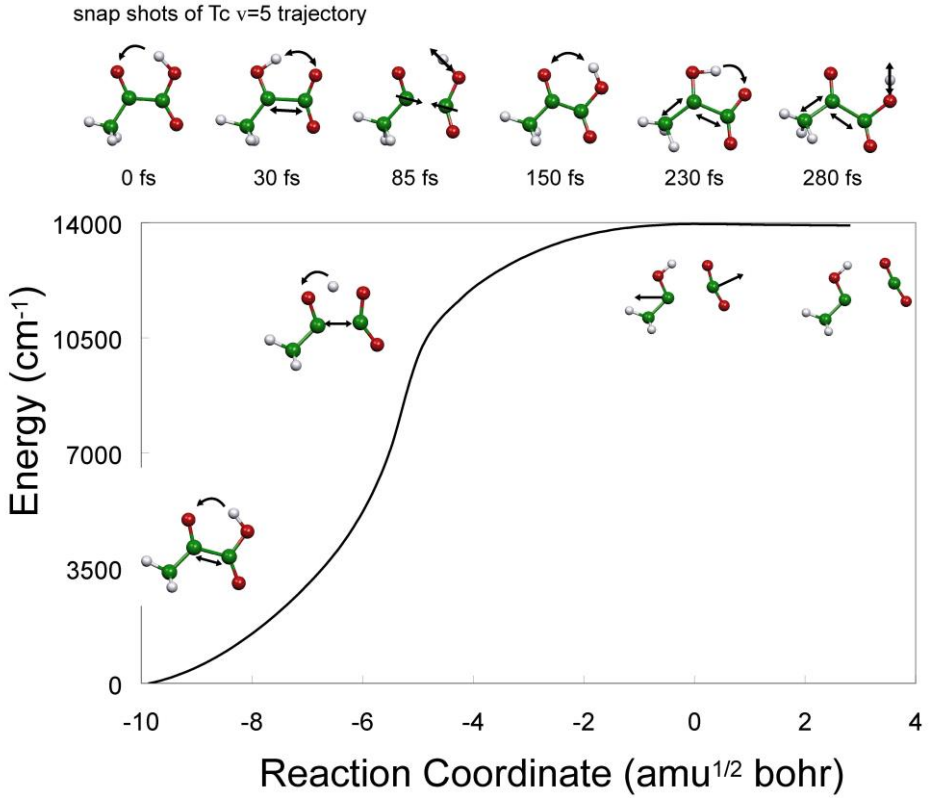
Red light initiated (OH vibrational overtone pumping)reactions by concerted mechanisms

Collaboration of the Vaida group (Dan Havey, Karl Feierabend, Nabilah Rontu-Carlon, Katy Plath, Jess Axson, Megan Dunn) with Jamie Donaldson, Adrian Tuck, Greg Frost, Karen Rosenlof, Steve Brown, Rex Skodje, Kaito Takahashi, Zeb Kramer, Gaylan Nelson, Henrik Kjaergaard, George Shields

This chemistry can be driven by a concerted mechanism in organic acids organic acids: the story of pyruvic acid - The Dynamics of Vibrational Overtone Excited Pyruvic Acid in the Gas Phase: line broadening through hydrogen-atom chattering" K. Takahashi, K. L. Plath, R. T. Skodje and V. Vaida *J. Phys. Chem A* **112** 7321-7331 (2008)

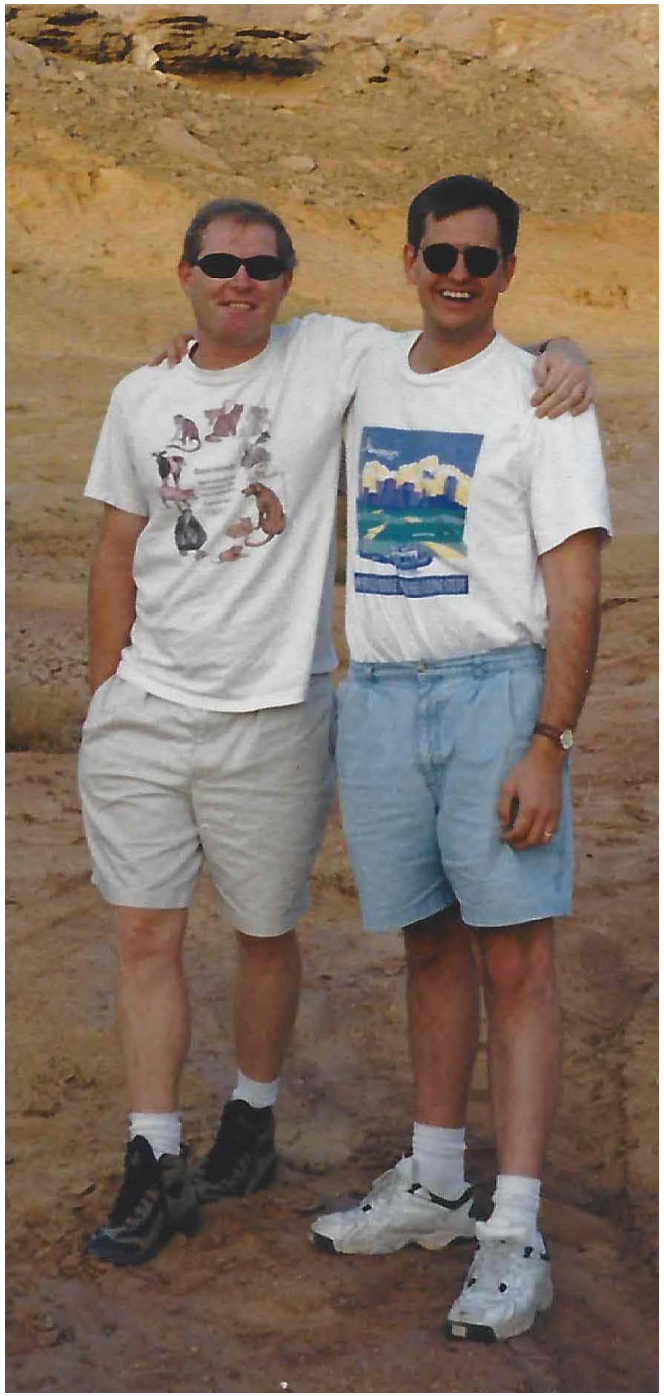






Dynamics on S_0 surface: H atom chattering in a concerted reaction on sub-psec timescales
Takahashi, Skodje, Plath, Vaida

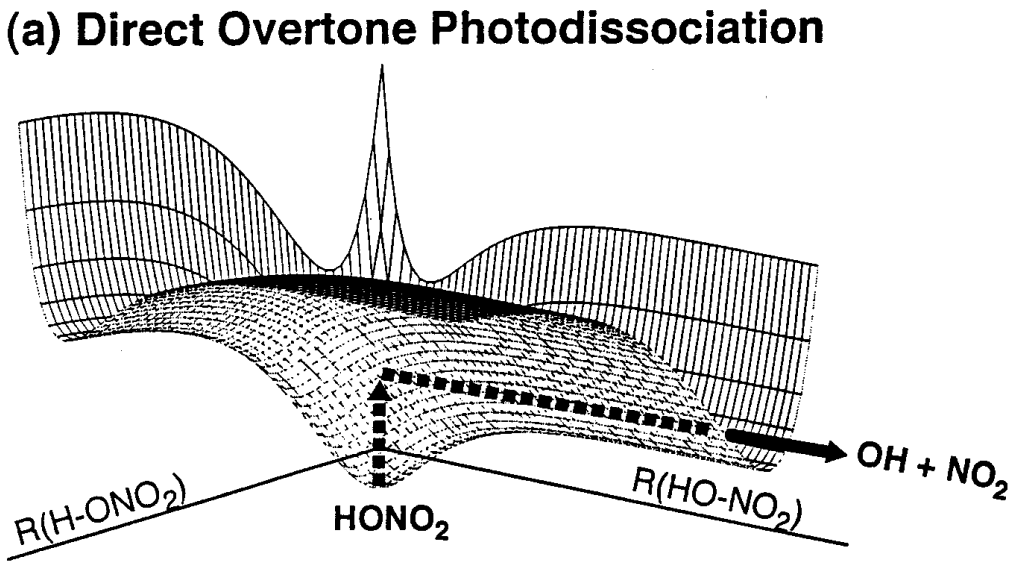
Greg Frost



- Stories of the group, its people, work & play
- Collaborations with Naaman group on clusters
- Collaborations at NOAA on overtone pumping

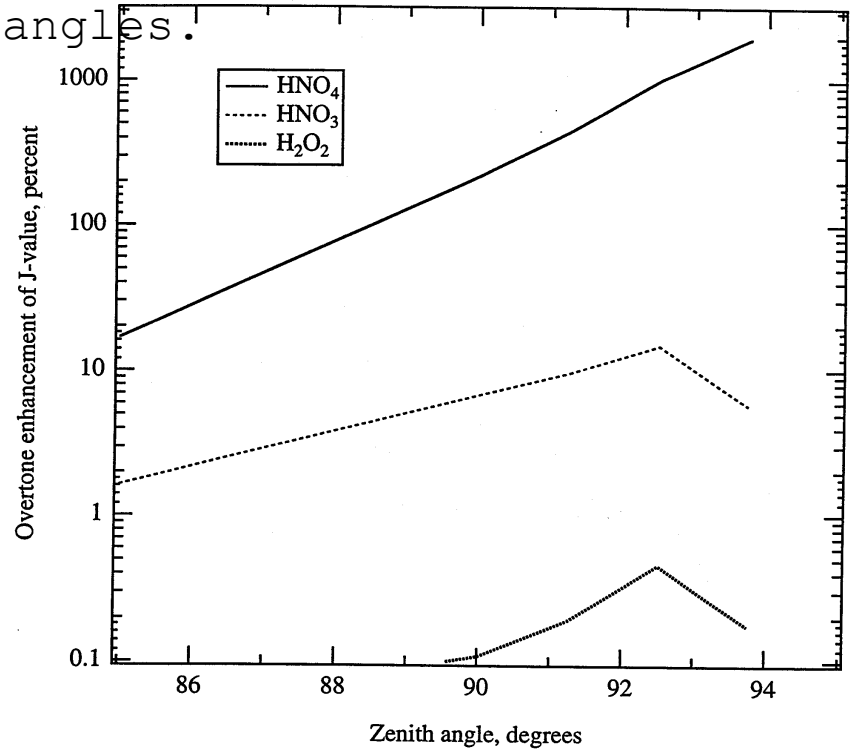
Greg Frost

Vibrational overtone pumping



Mechanism: Red light initiated reaction by excitation of OH stretching vibrational overtones. Energy transfer to the weak bond, here N-O, followed by dissociation.

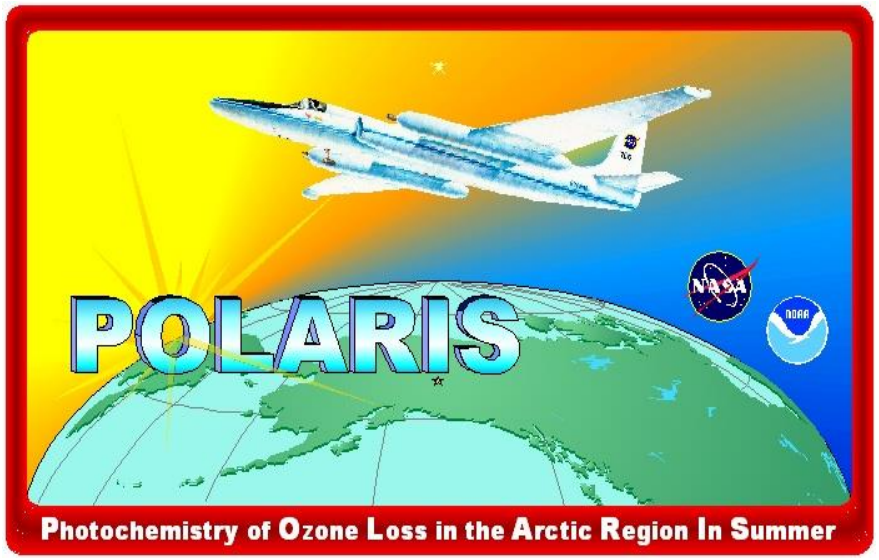
The story of modeling overtone pumping and the need to go beyond the flat Earth approximation to capture these effects at high zenith angles.



Vibrational overtones of HNO_3 excited by visible solar radiation contribute significantly to OH and HO_2 production at dawn and dusk.

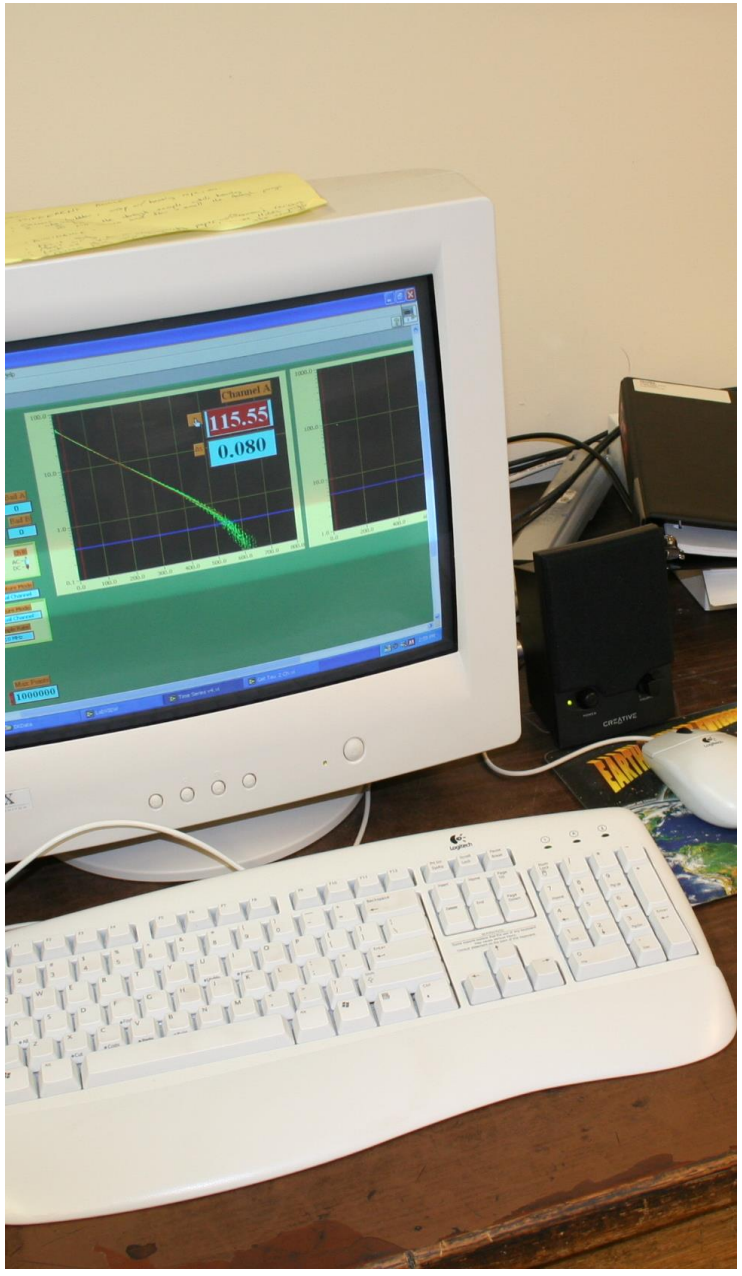
Visible light initiates a number of different reactions, all of which contribute to dusk and dawn HO_X.

Overtone photodissociation of HNO_4 has been shown to be a large contribution to HO_X, even at very low excitation energies.



- Lee, A. C. L., A study of the continuum absorption within the 8–13 μm atmospheric window. Q. J. R. Meteorol. Soc., 99, 490–505, 1973.
- Harries, J. E., Measurements of some hydrogen-oxygen-nitrogen compounds in the stratosphere from Concorde 002. Nature, 241, 515-518, 1973.
- Donaldson, D. J., Frost, G. J., Rosenlof, K. H., Tuck, A. F., Vaida, V., Atmospheric radical production by excitation of vibrational overtones via absorption of visible light. Geophysical Research Letters, 24, 2651-2654, 1997.
- Vaida, V., Daniel, J.S., Kjaergaard, H.G., Goss, L.M., Tuck, A.F., Atmospheric absorption of near infrared and visible solar radiation by the hydrogen bonded water dimer. Q.J.R. Meteorol. Soc., 127, 1627-1643, 2001.

Karl Feieabend



Veronica's Version:

Katy Plath

2004

Katy and Nabilah join the group.
Other members:
Theresa, Jessica,
Dan, Karl, Josh

Build Cavity Ring Down Spectrometer
(with significant help from Steve Brown)

Collaboration with Henrik Kjaergaard
and Joseph Lane on sulfonic acids

2006

Laura joins

Start work on
pyruvic acid

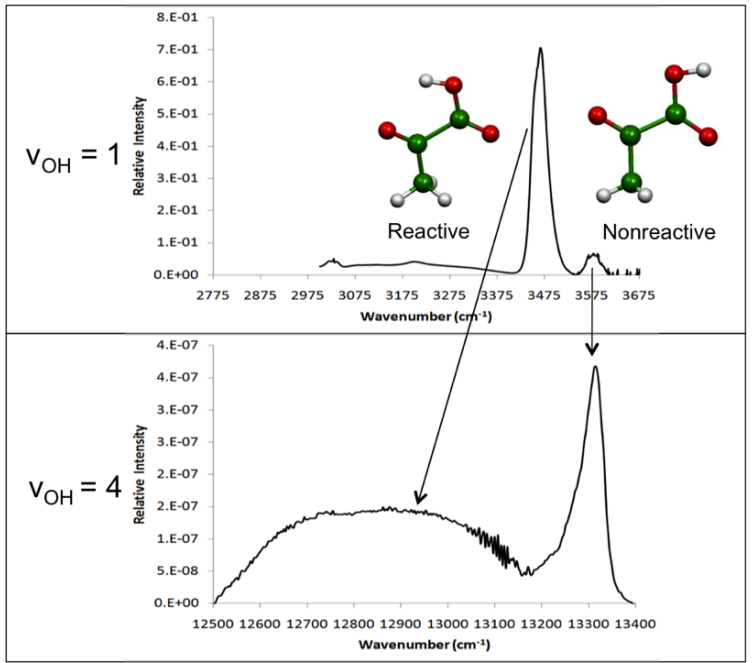
Marta and Meghan join

2008

Jess joins

Collaboration with Rex Skodje, Kaito
Takahashi, and Zeb Kramer

Pyruvic Acid



2010

Molly joins

Elizabeth joins

The lab moves out
of the basement!

We say goodbye
to the Bomem

Katy's Version:

Katy Plath

Only women join the group until after Nabilah and I leave.

2004 2006 2008 2010

The group book exchange means Nabilah and I are ahead of the curve on Game of Thrones.

One day Veronica came down to the lab to find it completely empty because we had treated ourselves to pedicures for the afternoon.

I started a small fire on a cabinet and worried Jess would never return to the lab.

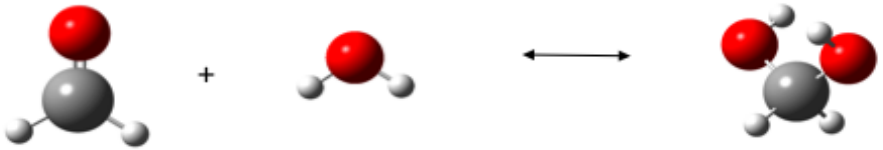
Jess, Molly, and I start every morning drinking coffee and chatting about life and science.

Water, aqueous solutions and water – air interfaces

Water catalyzed reactions: Jess Axson, Katy Plath, Martha Maron, Molly Larsen, Jay Kroll, Jamie Donaldson, the Kjaergaard group, Rex Skodje, Kaito Takahashi, Zeb Kramer

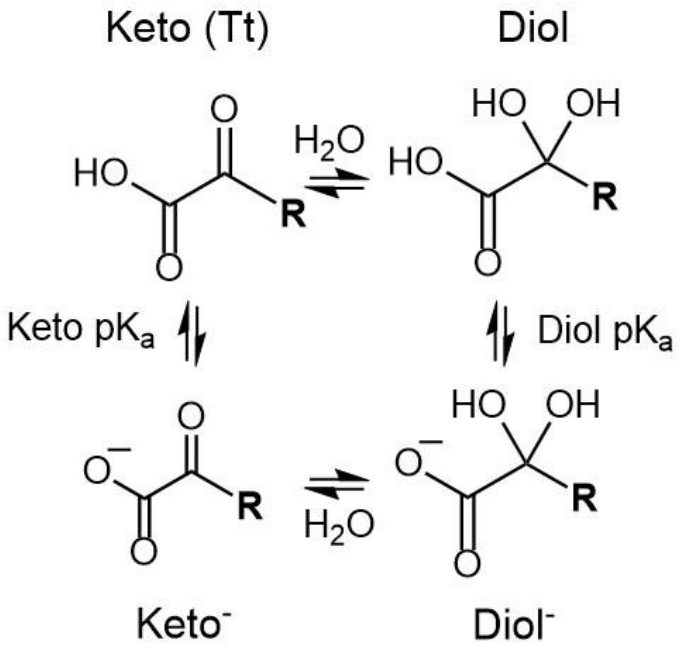
Water-air interfaces: Allison Reed Harris, Becky Rapf, Lexi Deal, Jean-Francois Doussin and the CESAM group

Hydration of aldehydes and to a lesser extent ketones lead to formation of gem diol not only in aqueous solutions but in gas phase with trace amounts of water present.



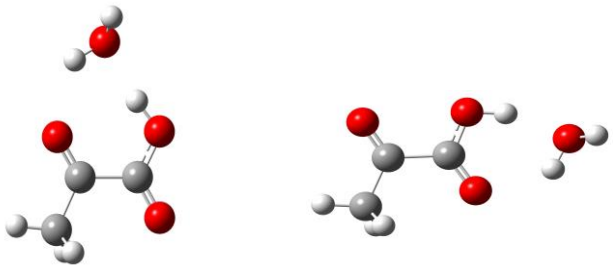
Hydration of aldehydes is water catalyzed! Examples formaldehyde, methylglyoxal, pyruvic acid, glyoxilic acid

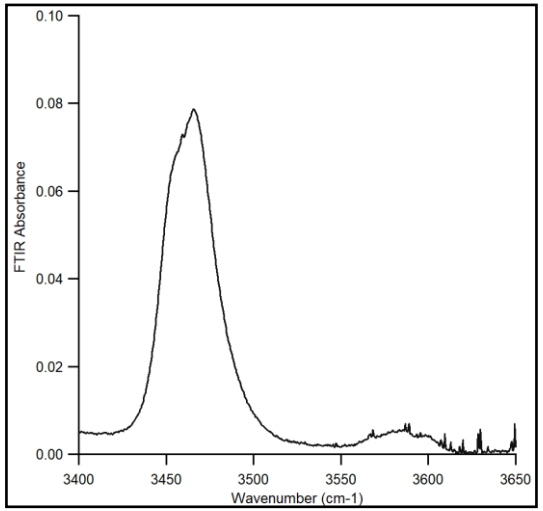
Hydration of aldehyde and ketones:
Jess Axson, Katy Plath, the Skodje group, Jay Kroll, Becky Rapf

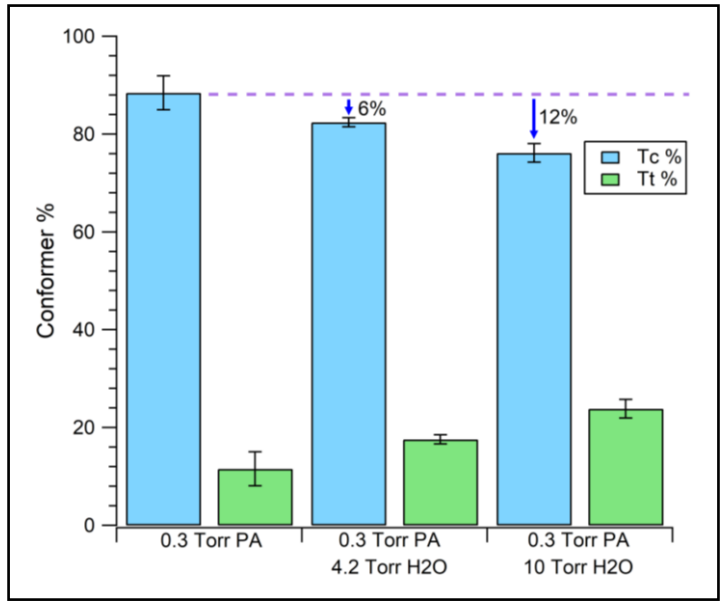


Addition of water: even one water molecule matters

Gas phase: effective and very fast S_1 reaction by H atom chattering of the Tc conformer, reaction promoted by the intramolecular H bond. Hydrogen bonding in water clusters, or at a surface disrupts the Tc conformer's intramolecular H bond allowing for competing of Tt







Tc % > Tt %; Tc % decreases with addition of H_2O

The effect of water- aqueous solutions

Changes the Tc ⇔ Tt equilibrium
Predominantly Tc in gas phase
and Tt in aqueous phase

Hydration: controls the
keto-diol equilibrium
Pyruvate is seen as
pH increases

Solvation of the singlet and triplet states changes the photochemistry: S_1 coupled to T_2 followed by internal conversion to T_1 where chemistry happens. Andrew Orr-Ewing (Bristol Univ.) unpublished

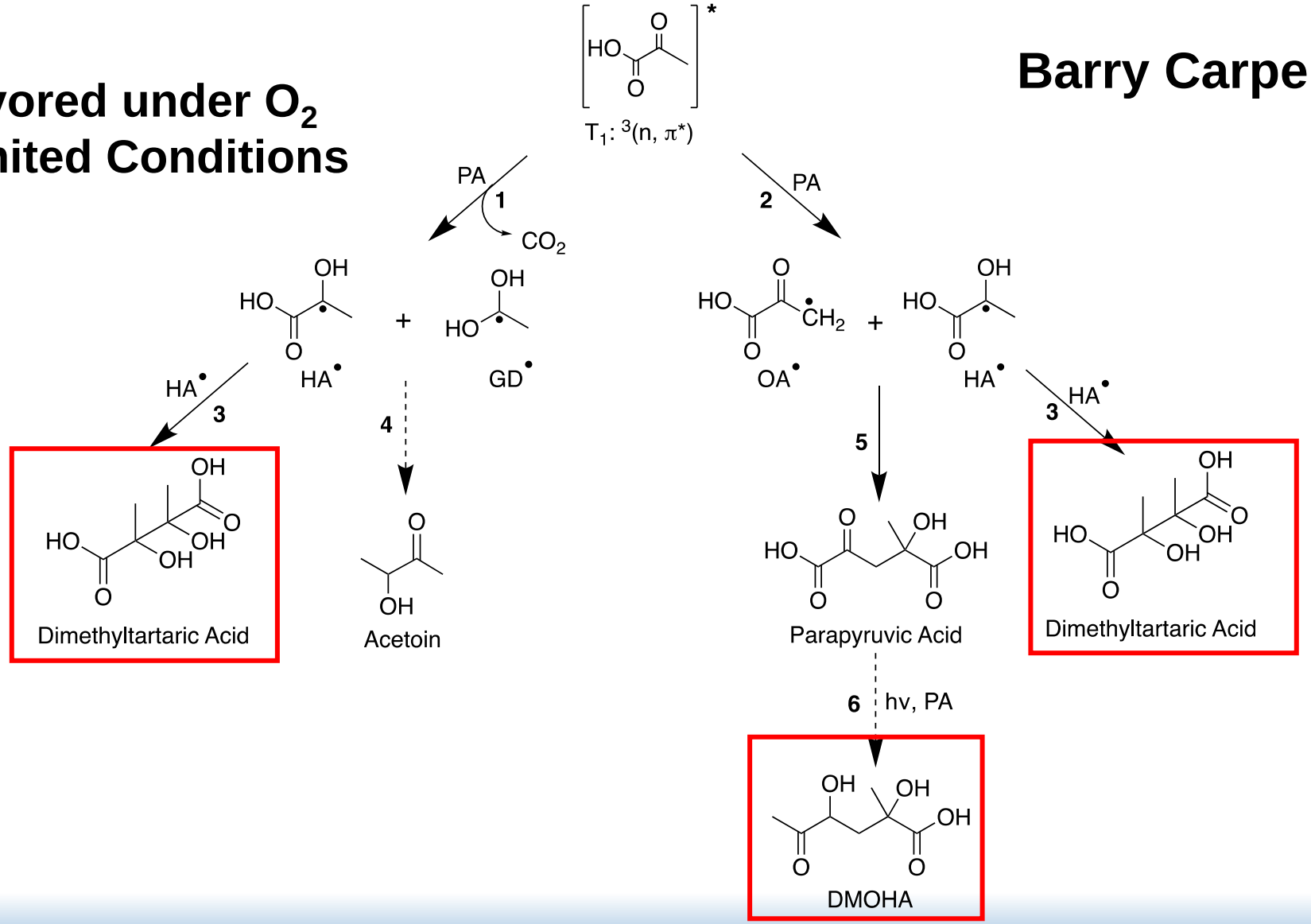
Chemistry is sensitive to O_2 and pH

Blair, S L., Reed Harris A E., Frandsen B N., Kjaergaard H G., Pangui E., Cazaunau M, Doussin J-F, Vaida V *J. Phys. Chem A*, **124**(7), 1240-1252 (2020)

Photochemical Mechanism

Favored under O_2 Limited Conditions

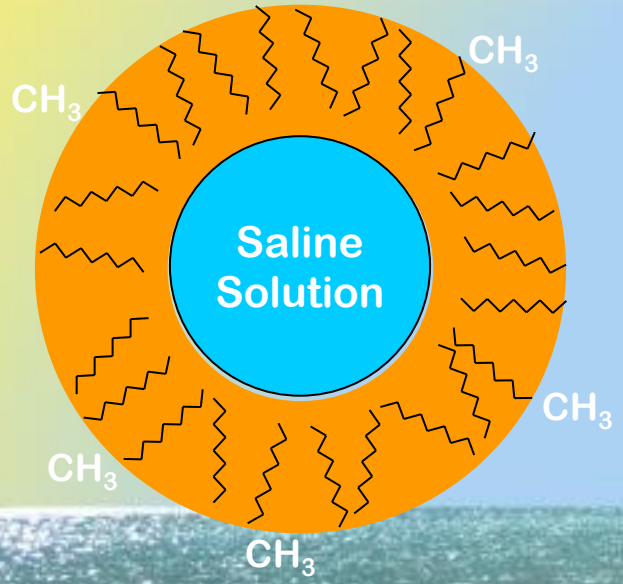
Barry Carpenter



Reed Harris, A.E., et al. *J. Phys. Chem. A.*, *118*, 8505–8516, 2014.

Griffith, E.C., et al., *PNAS*, 2013.

Atmospheric aerosols as chemical reactors



Inspiration: atmospheric measurements of the composition of single aerosol particles (Murphy et.al. Science 1998) showed organic content even to high altitude in contrast to the expectation at the time that insoluble organics will not be found on aerosol particles.

Model developed: Aqueous, saline solution encapsulated in an organic film which is processed in the atmosphere by radiation and oxidation reactions (OH, HO_2, etc.).

Ellison, Tuck, Vaida JGR 1999;
Dobson, Ellison, Tuck, Vaida PNAS 2000

The aerosol surface is an important chemical environment!

Test: TOF-SIMS experiments Heikki Tervahattu

"New Evidence of an Organic Layer on Marine Aerosols" H. Tervahattu, K. Hartonen, V-M. Kerminen, V. Vaida, A.F. Tuck, K. Kupiainen, P. Aarnio and T. Koskentalo, *J. Geophys. Res.* (2002)

Aerosols in the Contemporary and ancient Atmosphere

Atmospheric measurements found organics on aerosols even to high altitude where due to the fact that these molecules are little soluble in water, they were not expected.

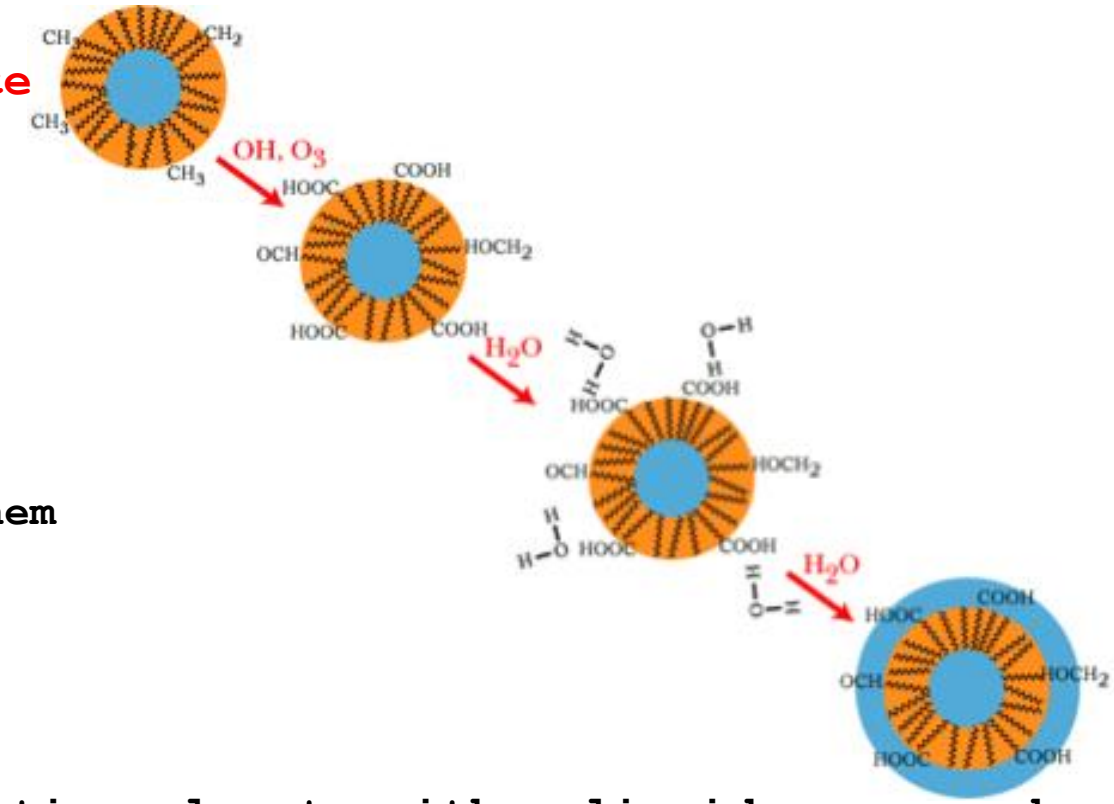
Contemporary atmosphere: Aerosols influence climate by absorption and scattering of solar radiation.

Ellison, Tuck, Vaida J. Geophys. Res. 1999

Donaldson, Vaida Chem. Rev. 2006

Griffith, Tuck, Vaida Acc Chem Res 2012

Deal, Rapf Vaida J. Phys. Chem. 2021



Ancient Earth

Aerosols form on any rotating planet with a liquid ocean and have a very large surface area (several orders of magnitude larger than the sea surface.

They could have provided prebiotic reactors for biopolymer and protocell formation.

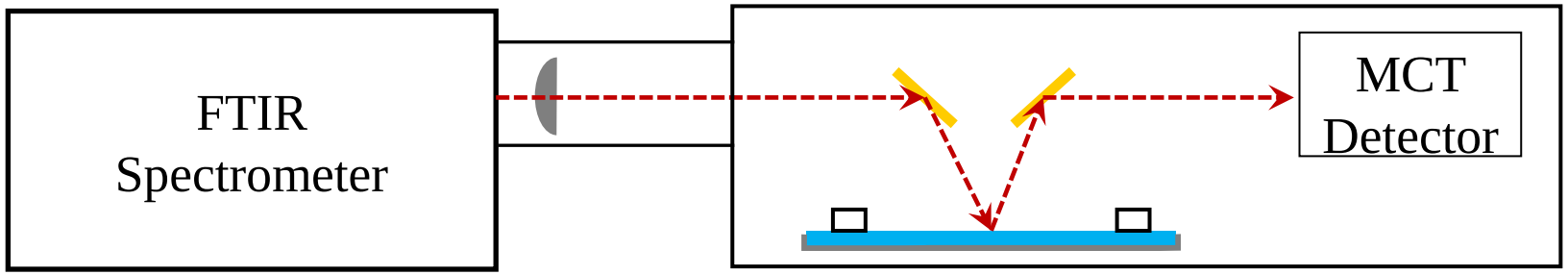
Techniques

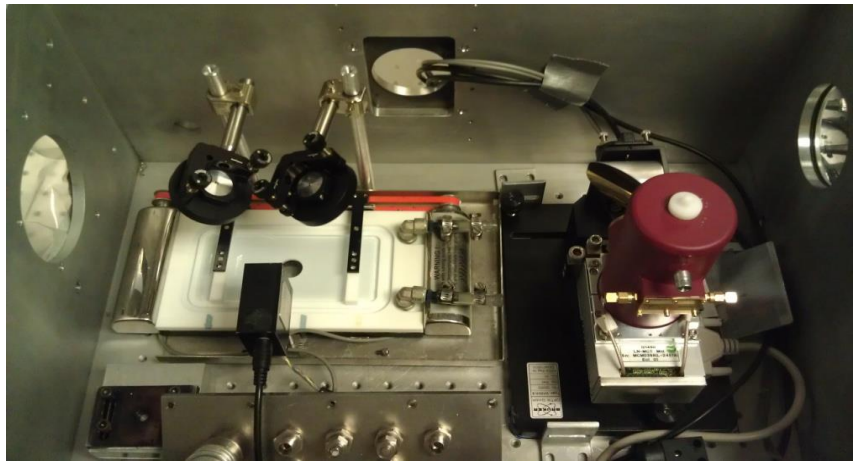
Gas Phase: IR and UV Vis spectroscopy & light initiated reactions (photochemistry).

Interfaces for which surface sensitive methods were developed

Langmuir troughs - thermodynamic information and sample control

Surface reflection spectroscopy IRRAS, UVRAS





Multiphase chemistry relevant to the environment studied in environmental chamber. CESAM Paris Est, France

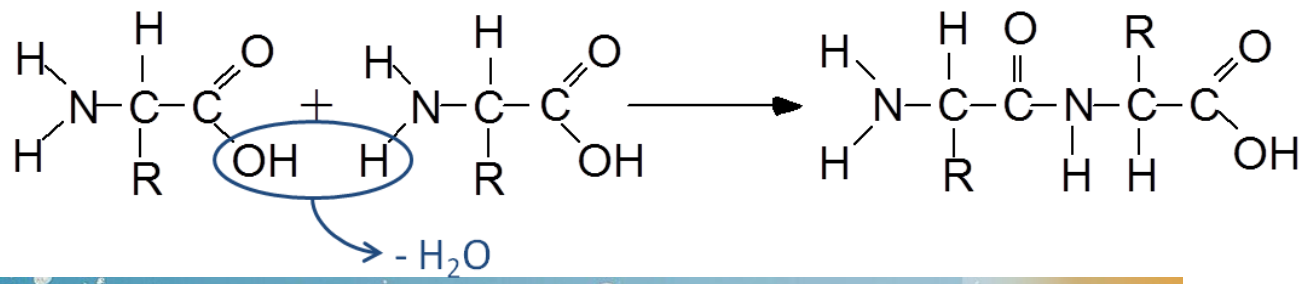
CESAM – atmospheric chamber at Université Paris-Est Créteil (UPEC) Jean-François Doussin[1]

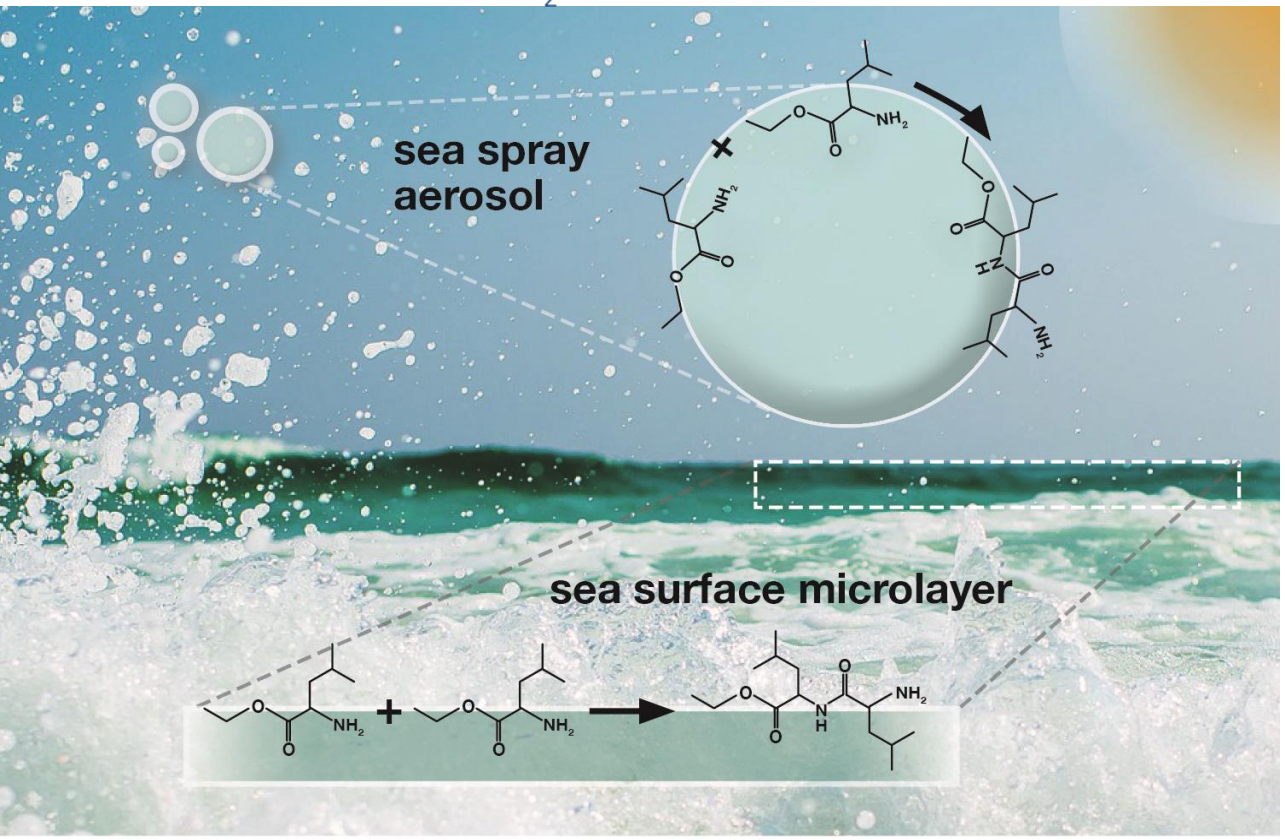
- 4000 L stainless steel chamber
- gas and particle injection ports
- control of relative humidity, temperature, pressure, gas phase species (O_2, N_2, etc.)
- three 4000 W Xe lamps (1/2 photon flux of the sun)
- 192 m path length FTIR spectrometer to detect gas phase products *in situ;* Particle analyzer

Wang, J.; Doussin, J. F.; Perrier, S.; et al. ATMOSPHERIC MEASUREMENT TECHNIQUES 4, 2465-2494 (2011)

Univ. Paris Est, MEREIA, LISA
Prof. Jean-Francois Doussin

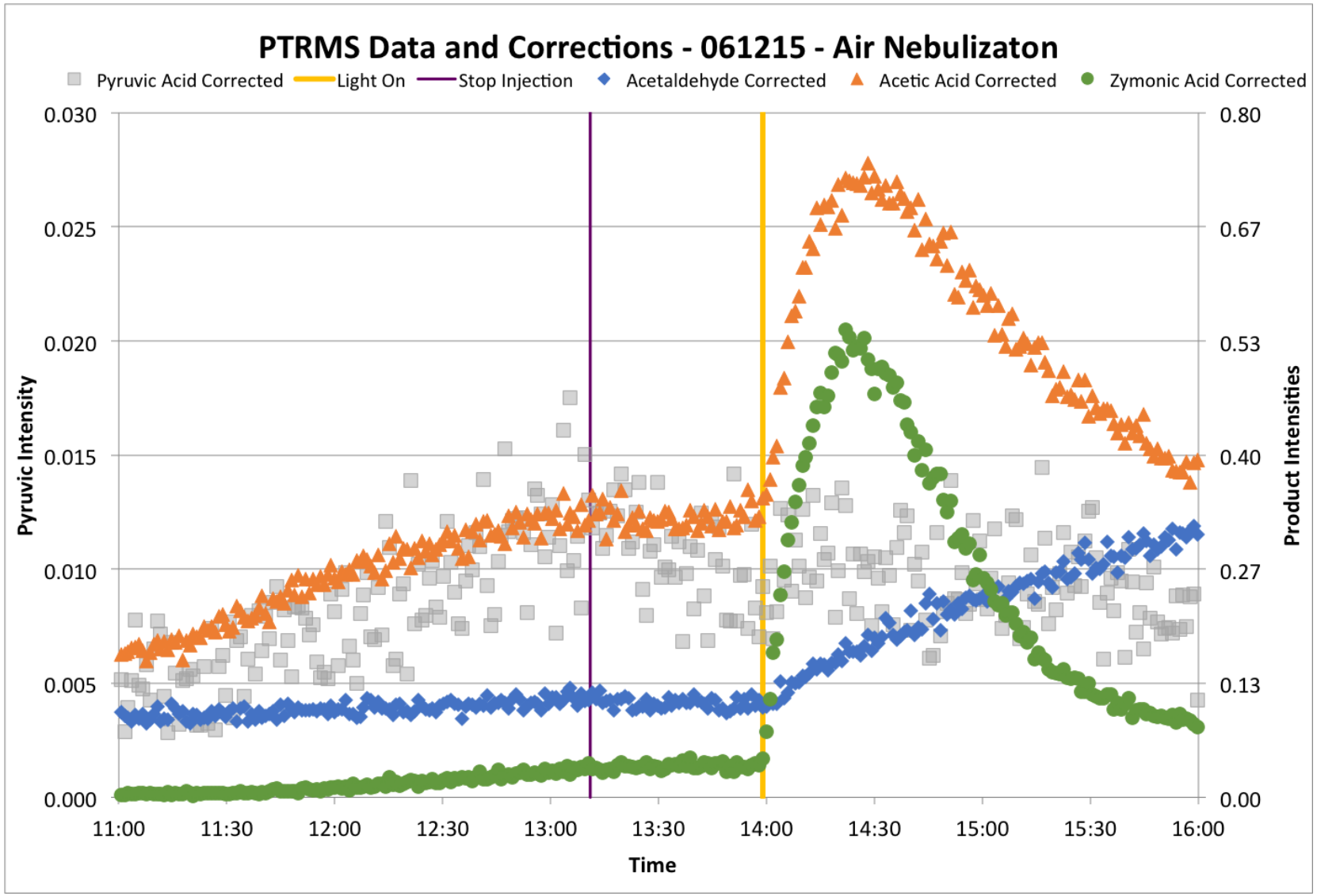
Condensation reactions favored at the water-air interface (aerosols, microdrops, etc) over bulk aqueous phase



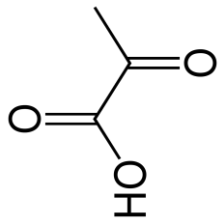


Peptide bond formation at the water-air interface
Griffith & Vaida PNAS 2013

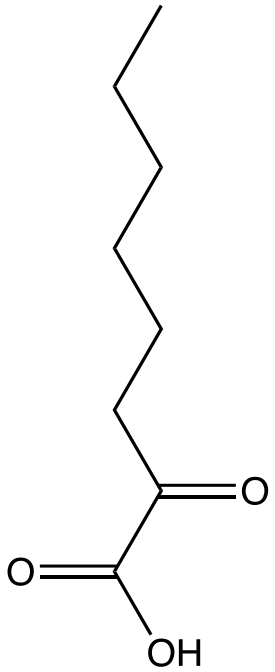
Polymers are formed in both aerobic and anaerobic conditions: CESAM results of products seen by PTR MS on sample nebulized in high relative humidity air



2-OOA as a Model System (building complexity with C-C bonds)



Pyruvic Acid

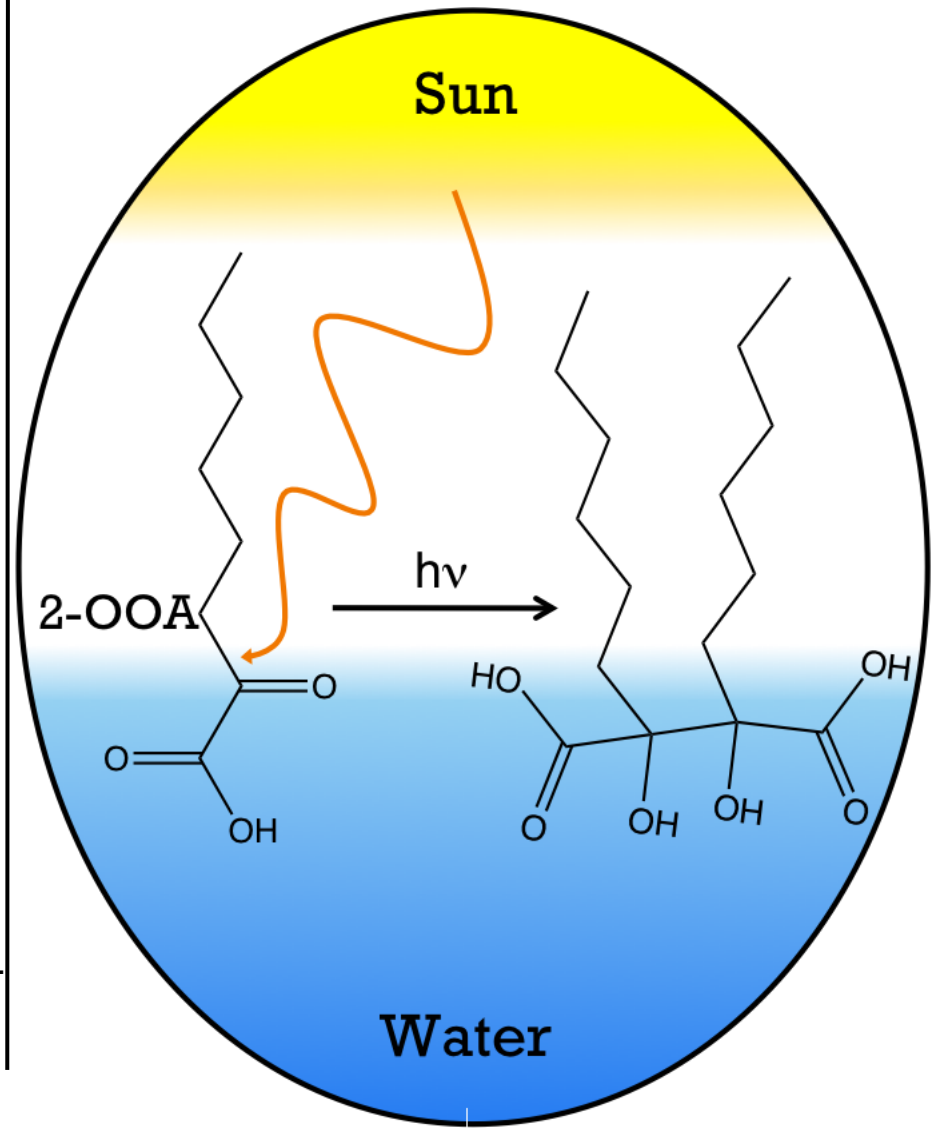


2-Oxooctanoic Acid

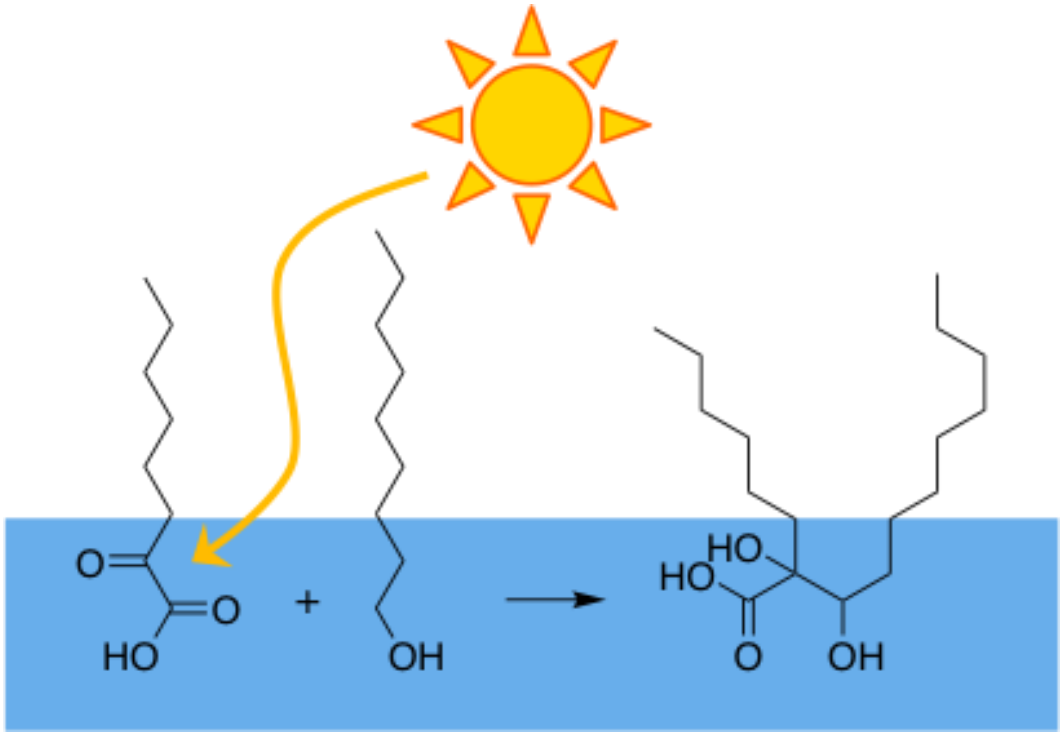
Prebiotically Plausible:

Oxo-acids found in meteorites

Fischer-Tropsch synthesis of lipids (C7-C9)



Building chemical complexity with Sunlight

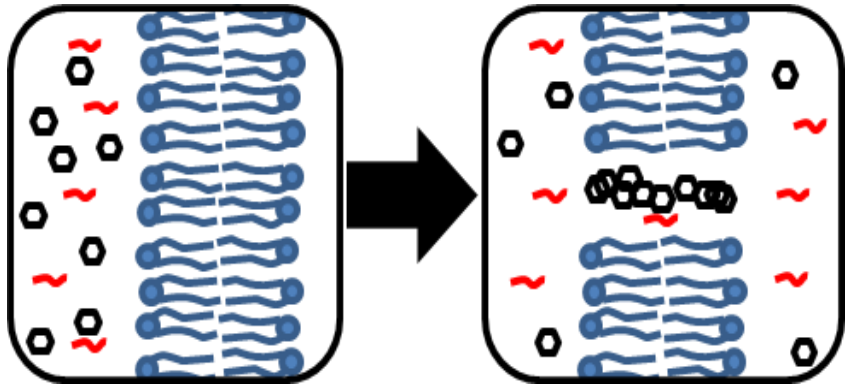


Environmental processing of lipids driven by aqueous photolysis of α-keto acids

Rapf, Perkins, Dooley, Kroll, Carpenter, Vaida
ACS Central Science 2018

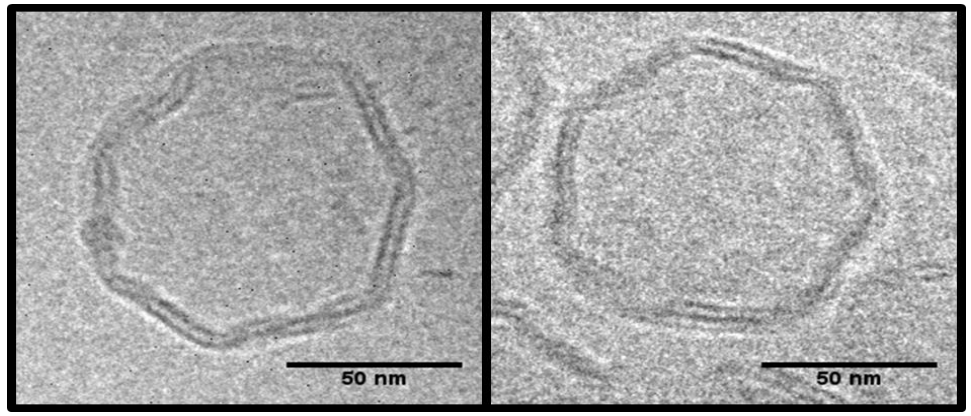
Photochemically generated organic radicals react with inert molecules at the water surface: abiotic mechanism for building complexity in the environment
Organic radicals more important in atmospheric chemistry then assumed, especially in the prebiotic atmosphere where OH scarce.

Vesicles and membranes



Russell Perkins & VV *J. Am. Chem. Soc.* 139(41), 14388-14391 (2017)

Thanks to Sheriff Mansy

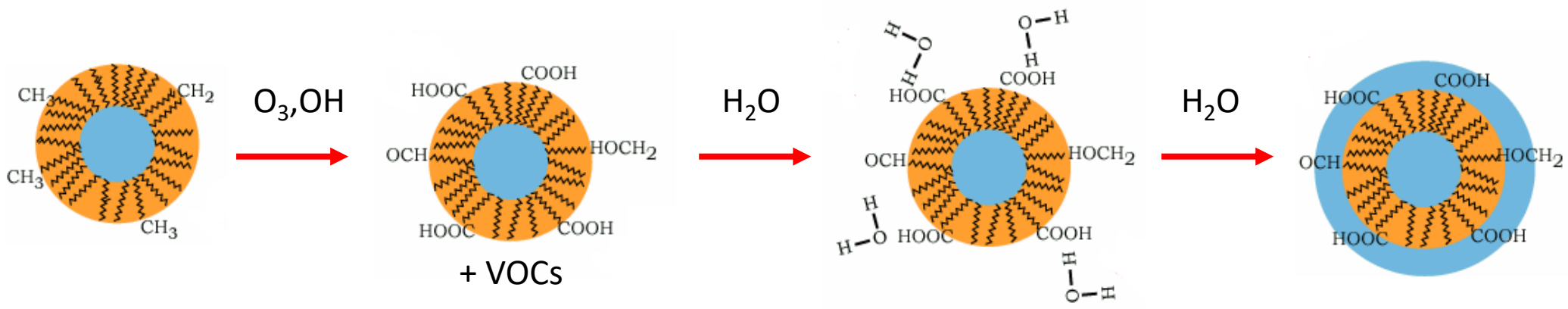


Example cryo-TEM images of unilamellar vesicles prepared without (left) and with 20 mM phenylalanine (right).

Properties of Organic Films
as proxies for organically coated aerosols

Jessica Gilman

Research based on the inverted micelle model developed by Barney Ellison, Adrian Tuck, and Veronica Vaida [1999]



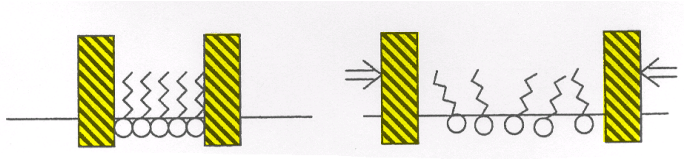
My graduate research (2001-2006) focused on the general properties and oxidation of organic films

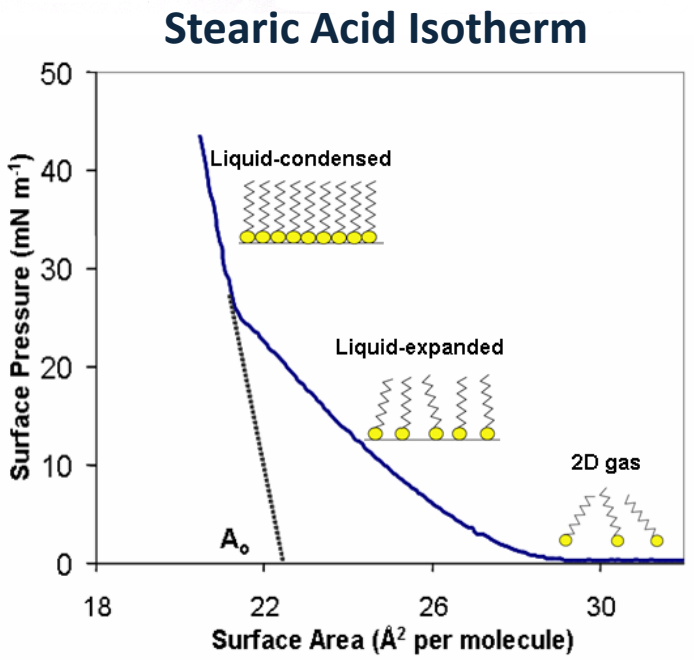
- How will oxidizing the organic film with ozone or hydroxyl radical alter the film properties?
- **Oxidation of films relevant to atmospheric aerosols**. Teresa Eliason, Jessica Gilman and Veronica Vaida, *Atmospheric Environment* **38**(9), p. 1367 (2004)
  - Hexadecane and 1-Dodecene with O_3 and O_3/•OH
- **Kinetics and products of the reaction of gas-phase ozone with anthracene adsorbed at the air-aqueous interface**. B.T. Mmereki, D.J. Donaldson, J.B. Gilman, T.L. Eliason and V. Vaida *Atmos. Environ* **38**(36), p.6091 (2004)
  - Anthracene with O_3

Properties of Organic Films
as proxies for organically coated aerosols

Jessica Gilman


Langmuir-Blodgett Trough





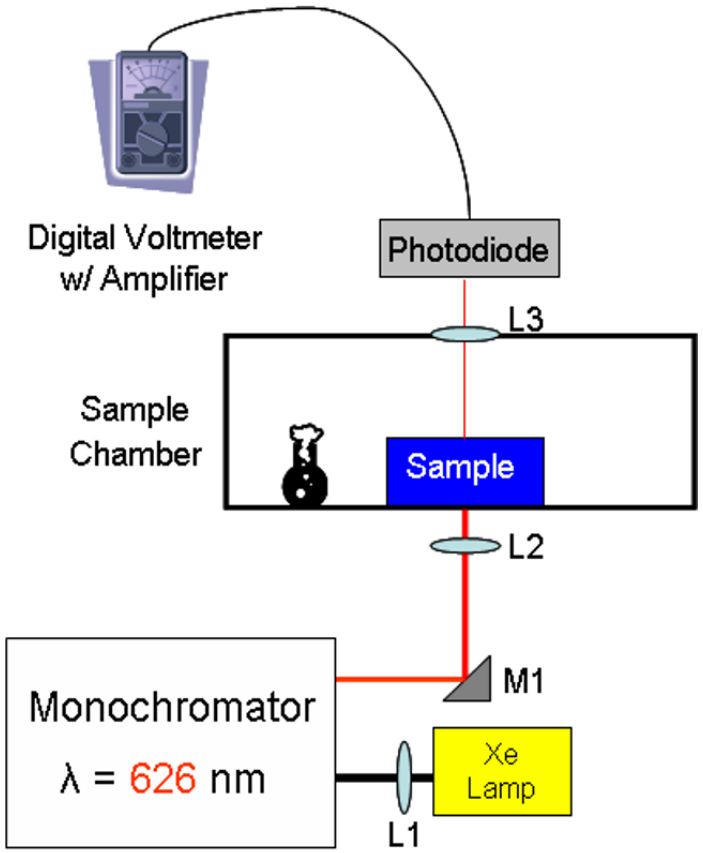
Heikki Tervahattu – University of Helsinki
Organic surfactant films at the water air interface

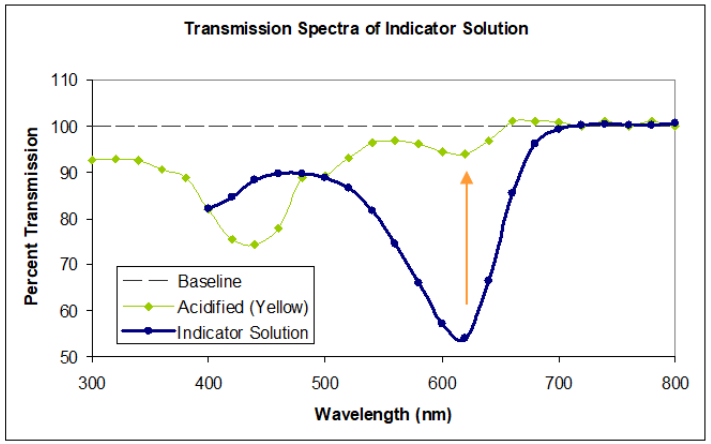
Selectivity and stability of organic films at the air-aqueous interface. Gilman JB, Eliason TL, Fast A, and Vaida V [2004]

Interfacial properties of mixed films of long-chain organics at the air-water interface. Gilman JB, Tervahattu H, and Vaida V [2006]

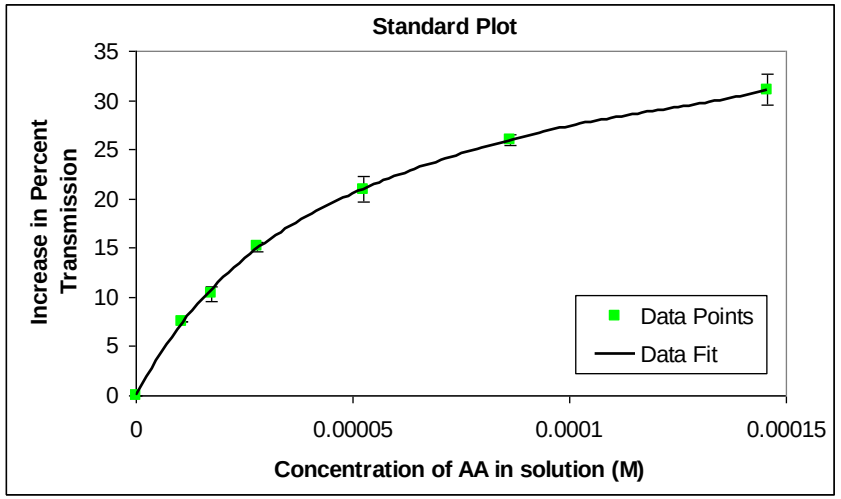
Properties of Organic Films
as proxies for organically coated aerosols

Jessica Gilman





- Sample
  - 10 ml Bromocresol green solution
- Exposure time
  - Starts when acetic acid vial is inserted; $[HAc\ (g)]_{t=0} = 0$
- Measure
  - Increase in transmission
  - Calculate $\%T = (I/I_o) \times 100\%$



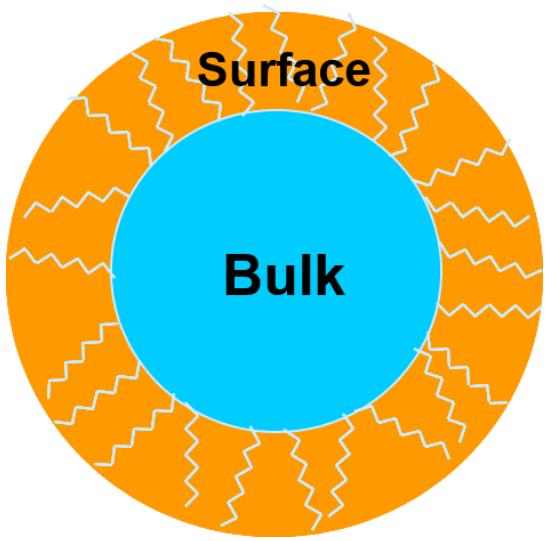
Permeability of acetic acid through organic films at the air-aqueous interface. Gilman JB and Vaida V [2006]

Properties of Organic Films
as proxies for organically coated aerosols

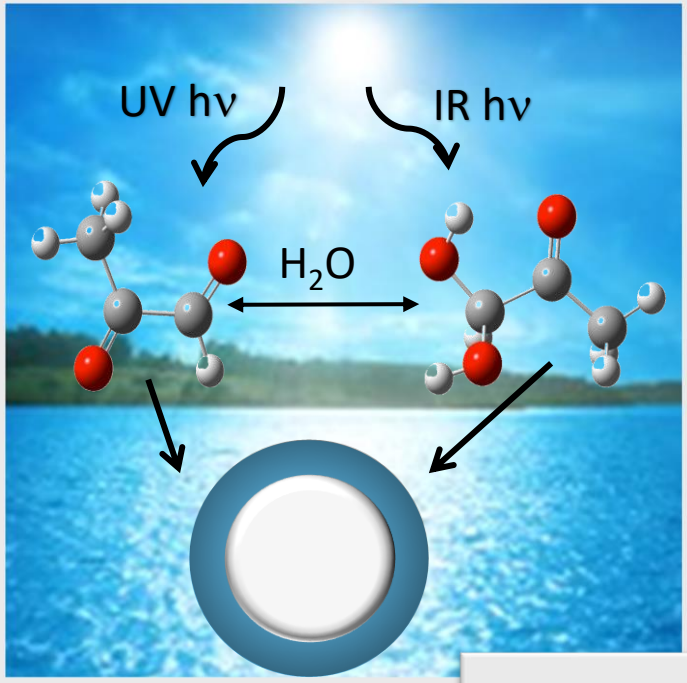
Jessica Gilman

- Organic films on aerosols can alter their physical, chemical, and optical properties

- Particle morphology is important in understanding and predicting the role that aerosols play in the atmosphere



It's All About Hydration

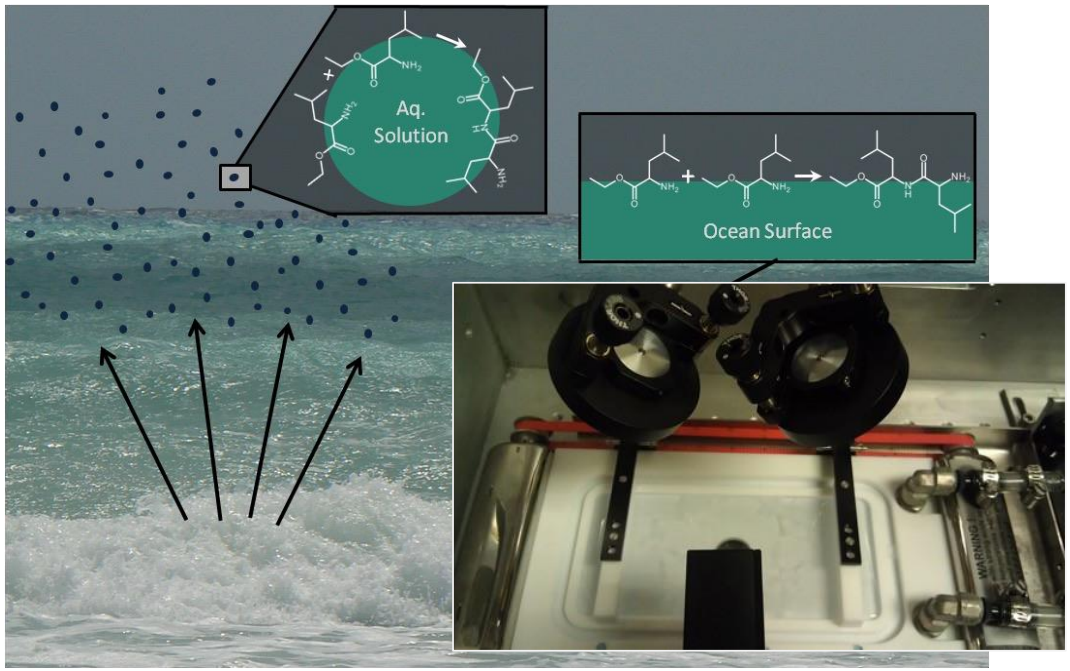


Jess Axson

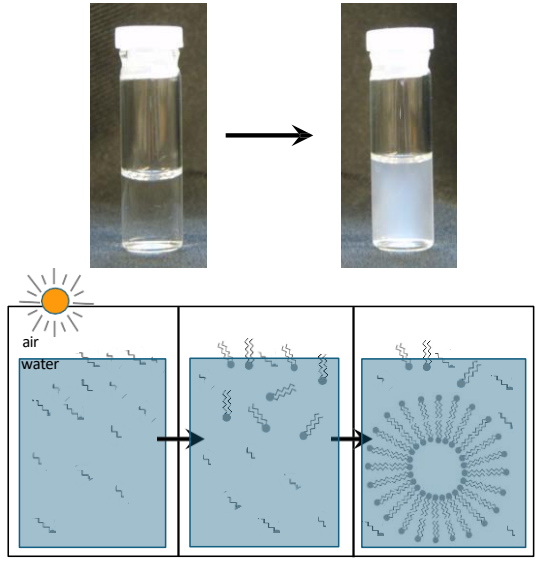
Prebiotic chemistry at the water surface

During my first meeting with Veronica as a bright-eyed, 1st year grad student, she mentioned her conceptual papers on prebiotic chemistry at the water surface – despite her warnings about potential backlash, I was sold.

This led to so many interesting results, some purposeful....



And some accidental....



Elizabeth Griffith

Prebiotic chemistry at the water surface

But beyond the results, it led to many collaborations and interesting interactions with people.

A few were less than pleasant…

- Failed collaboration with a group in engineering at CU but led to collaboration with Heather Allen at OSU
- Narrowly avoided fists flying at an ACS conference (thanks to Adrian Tuck for ”fighting” the battle for me)

But most were amazing. A few of the more memorable ones:

- Many trips to CESAM in Paris – found unexpected results under atmospheric conditions compared with the lab
- Barry Carpenter sniffing out acetoin as a product of the photolysis of pyruvic acid
- MD simulations with Martina Roeselová in Prague – disruption of DPPC film by phenylalanine

I was the only grad student in the lab for a while and have some extra special memories with Veronica too:

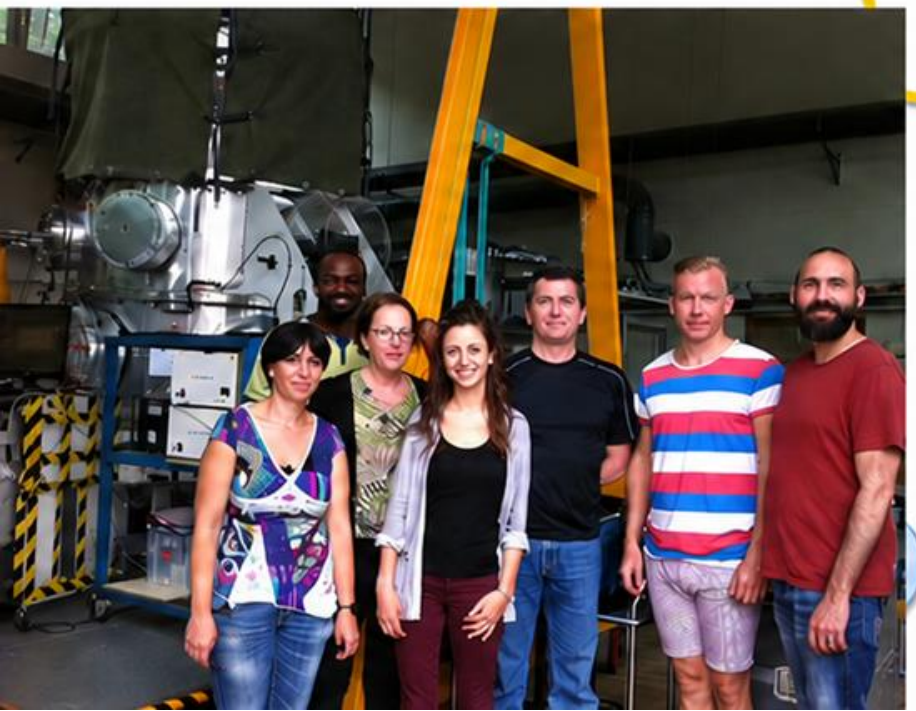
- Burning my fingerprint into the frame of a lens holder
- Veronica removing a pipet from my hand mid experiment because I was being “awkward” with it
- MANY coffees talking about science and life

Elizabeth Griffith

Allison Reed Harris

Pyruvic Acid Photochemistry:
From Isolated Phases to the Atmosphere

Barry Carpenter



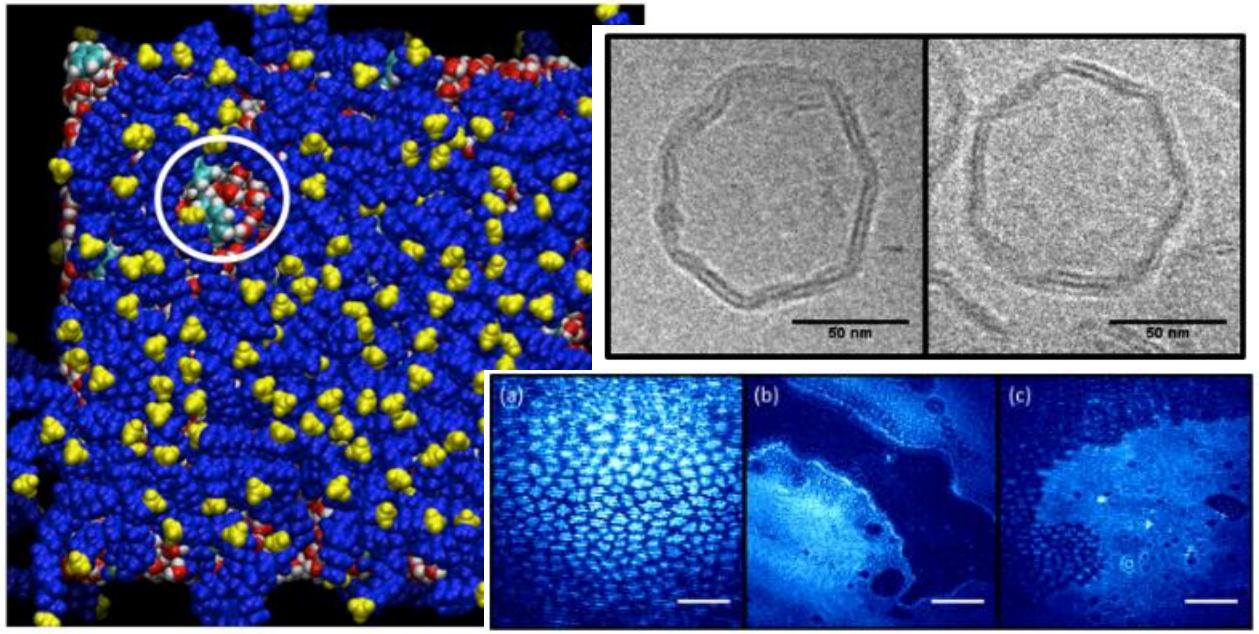
Anne Monod
Barbara Ervens
Rich Shoemaker

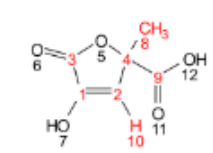
Jean
Francois-Doussin

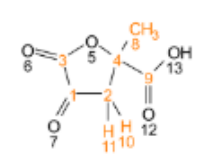
Russell Perkins

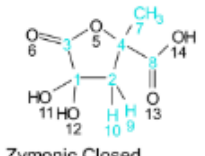
So many great opportunities and people to work with!

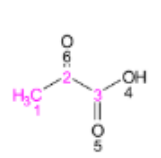
- Rich Shoemaker
- Barry Carpenter
- Molly Larson
- Annette Erbse
- Sheref Mansy
- Heather Allen
- Martina Roselová

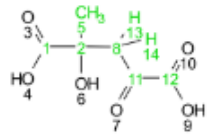


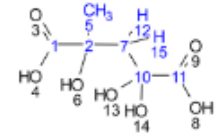

Zymonic Closed Enol (ZCE) (aka Zymonic Acid)

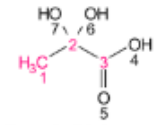

Zymonic Closed Ketone (ZCK)


Zymonic Closed Diol (ZCD)


Pyruvic Acid

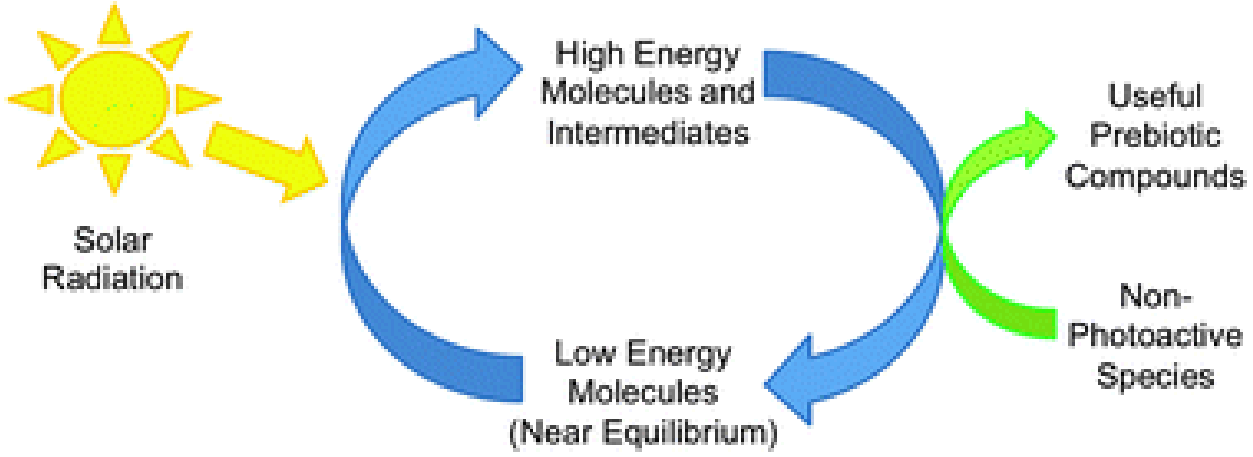

Zymonic Open Ketone (ZOK) (aka Parapyruvic Acid)

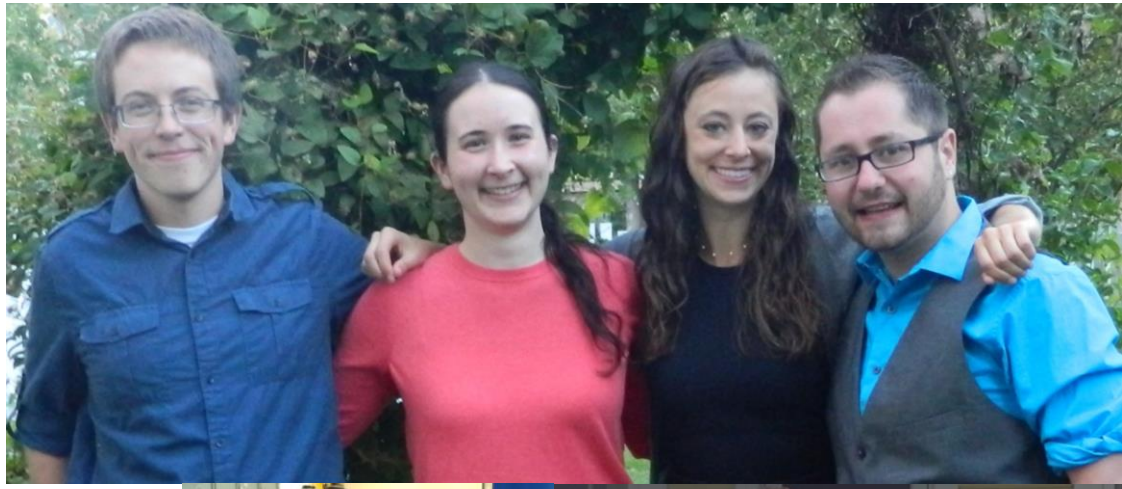

Zymonic Open Diol (ZOD)

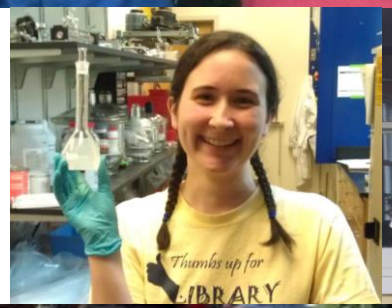

Pyruvic Diol

Building Complexity – Aqueous Environments and Sunlight

Applications to Atmospheric Chemistry, Planetary Atmospheres, and Prebiotic Chemistry







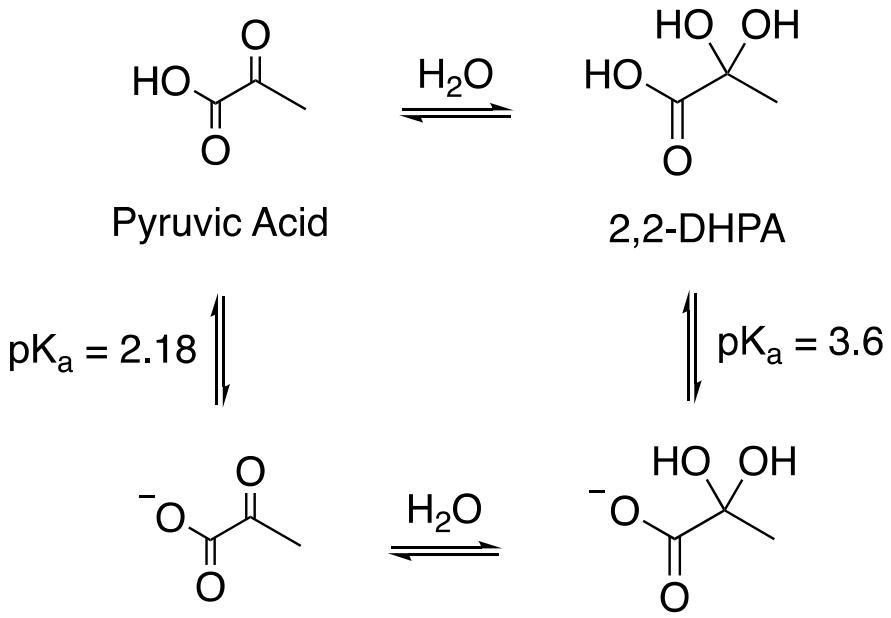
"Sunlight as an energetic driver in the synthesis of molecules necessary for life"
R.J. Rapf, **V. Vaida** *PCCP*, 2016

Becky Rapf

Building Complexity – Aqueous Environments and Sunlight

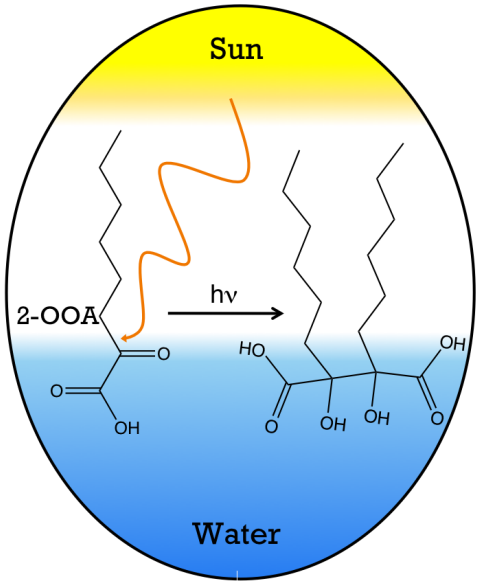
Becky Rapf

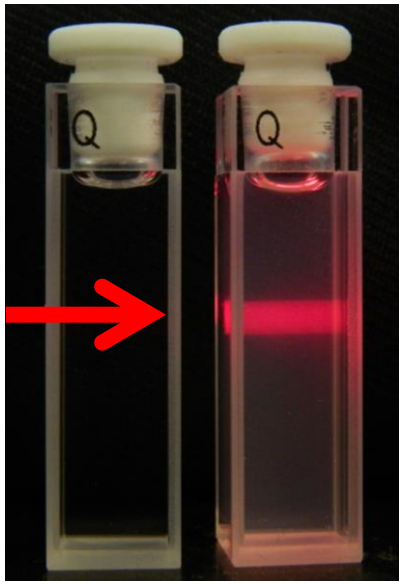
Pyruvic Acid and Alkyl α-Keto Acids



Collaborations:

Annette Erbse
Garret Miyake
Barry Carpenter
Sheref Mansy
Rob Walker
Kevin Wilson



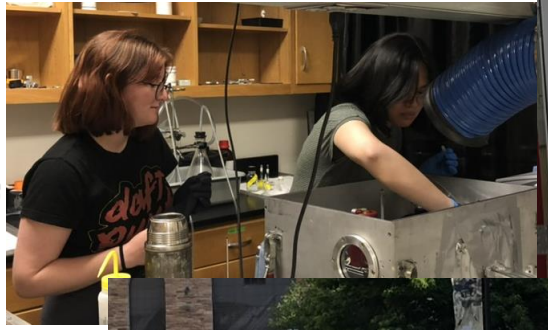


"pH Dependence of the Aqueous Photochemistry of α-Keto Acids" R.J. Rapf, M.R. Dooley,* **K. Kappes**, **R.J. Perkins**, **V. Vaida** *JPCA* 2017

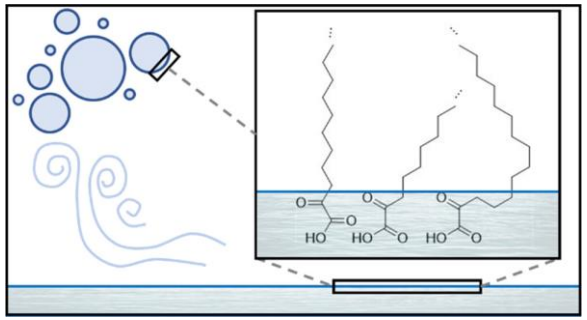
"Mechanistic description of photochemical oligomer formation from aqueous pyruvic acid" R.J. Rapf, **R. J. Perkins**, B. K. Carpenter, **V. Vaida**, *JPCA* 2017

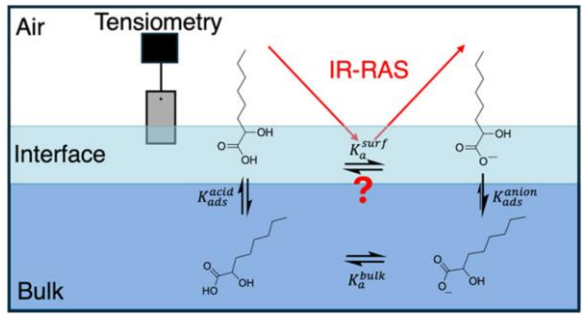
"Photochemical synthesis of oligomeric amphiphiles from alkyl oxoacids in aqueous environments" R.J. Rapf, **R.J. Perkins**, H. Yang, G.M. Miyake, B.K. Carpenter, **V. Vaida**, *JACS* 2017

Rapf Lab at Trinity University



Molecules at the water surface vs. bulk





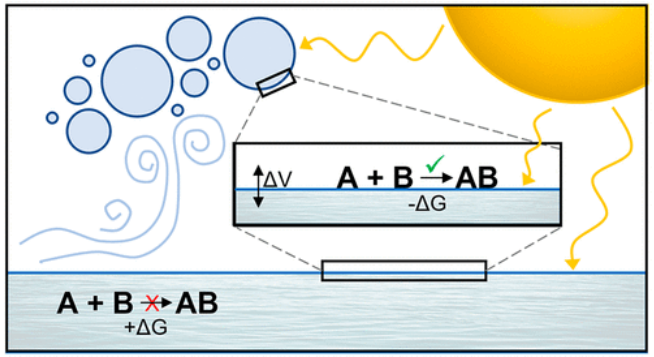
“Changes in protonation state of atmospherically relevant α-hydroxyacids at the water-air interface” Rugeley*, Holt*, Peterson*, Moulai-Khatir*, Koltun*, **Rapf**, *JPCA* 2025

“Infrared Reflection–Absorption Spectroscopy of α-Keto Acids at the Air–Water Interface: Effects of Chain Length and Headgroup on Environmentally Relevant Surfactant Films” **Deal**, Smith*, Oyala*, Campolo*, Rugeley*, Mose*, Talley*, Cooley*, **Rapf,** *JPCA* 2023

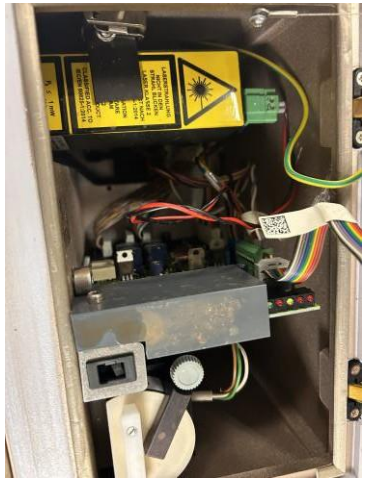
Continued connections and inspiration from Veronica!

The last graduate student, but far from alone…

"Water-Air Interfaces as Environments to Address the Water Paradox in Prebiotic Chemistry: A Physical Chemistry Perspective" Deal A.M., **Rapf** R.J., **Vaida** V. *J. Phys. Chem. A* 125(23), 4929-4942 (2021)

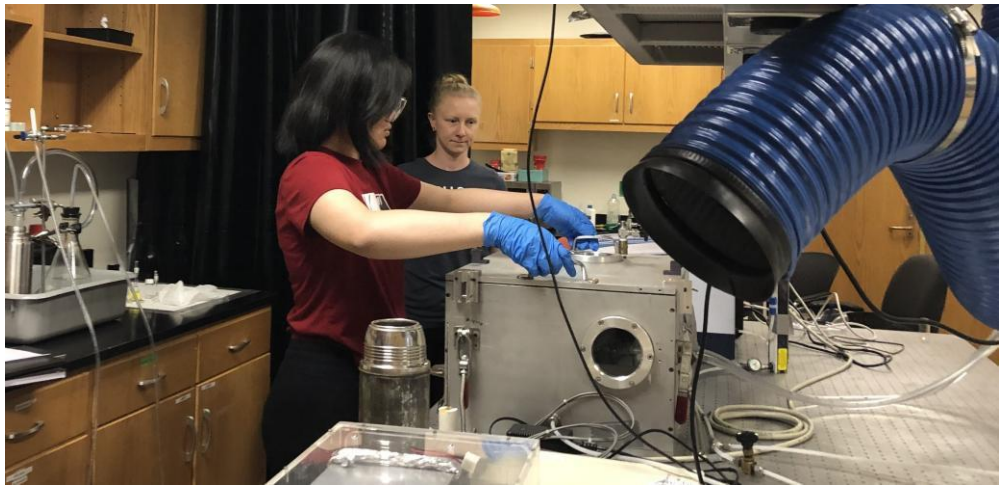


Pandemics, fires, and floods Lexi Deal



Lots of infrared reflection-absorption spectroscopy (IRRAS) and ultraviolet-visible RAS (UV-Vis-RAS)

"Infrared Reflection-Absorption Spectroscopy of α-Hydroxyacids at the Water-Air Interface" Deal A.M., Vaida V. *J. Phys. Chem. A* 126, 8280-8294 (2022)



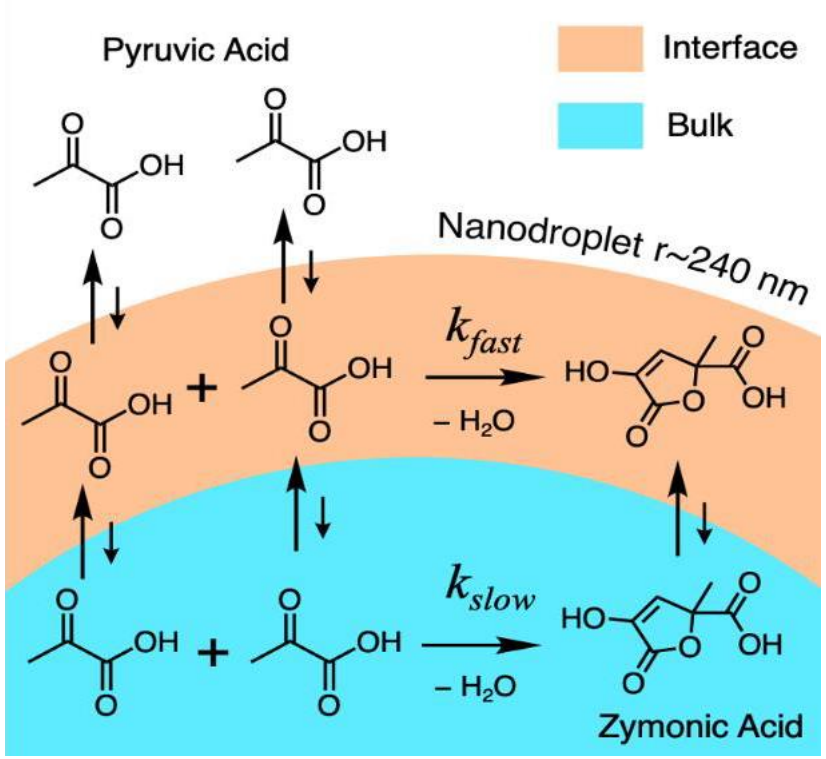
"Infrared Reflection–Absorption Spectroscopy of α-Keto Acids at the Air–Water Interface: Effects of Chain Length and Headgroup on Environmentally Relevant Surfactant Films" Deal A.M., Smith A.E., Oyala K.M. Campolo G.H., Rugeley B.E., Mose T.A., Talley D.L., Cooley C.B., **Rapf** R.J. *J. Phys. Chem. A* 127 (2023)

The Vaida legacy continues

Lexi Deal

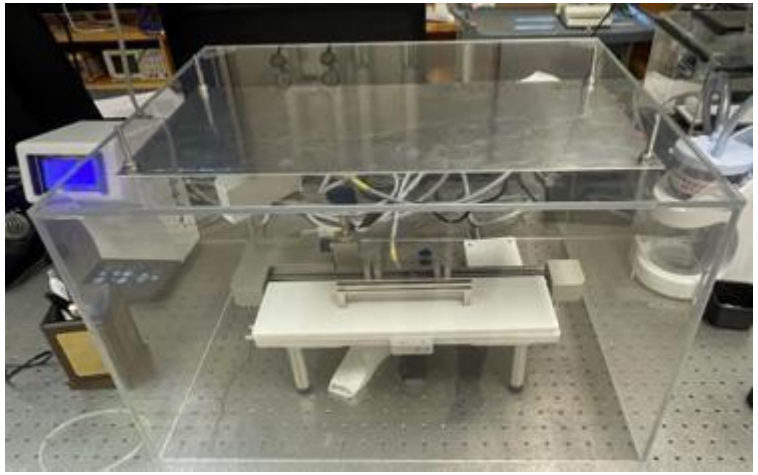
Zymonic acid from Boulder to Berkeley

Accelerated zymonic acid formation from pyruvic acid at the interface of aqueous nanodroplets- Kim P., Reynolds RS, Deal AM, **Vaida V**, Ahmed M, **Wilson KR** – J. Phys. Chem. Lett. 2004



Deal lab at the University of Michigan

Surface-specific photochem:



Next-gen IRRAS