Unimolecular Reaction Dynamics: Molecules, Radicals and Networks

Hanna Reisler
Chemistry Department, USC

Herschbach Medal Talk, DMC, 2017

Outline

- My winding road to a faculty position at USC
- Past research: What I still find exciting
- Fast forward: current and continuing research
- On being a woman in science:
  The WiSE program at USC
- A few lessons learned

Funding: NSF, DOE, AFOSR, ARO, PRF

First paper in Physical Chemistry

Hydrated Electron Reactions in View of Their Temperature Dependence

M. Anbar Z. B. Alfassi, H. Bregman-Reisler
The Weizmann Institute of Science Rehovot, Israel, and The Soreq Nuclear Research Center Yavne, Israel
JACS , 89, 1263 (1967)

Michael Anbar, 1927-2014

Weizmann Institute

The Ph.D. Years at the Soreq Nuclear Research Center

Advisor: Saadia Amiel, 1930-1978

How to build an ion beam machine with almost no equipment:

Inspiration: Cermak and Herman in Czechoslovakia.

Our idea: use soft electron impact ionization to create molecular ions without fragment ions.

Thesis topic:
Charge transfer reactions of molecular ions

What I gained:
Independence
Mentoring by accomplished women

What I missed:
Interactions with challenging colleagues

Zdeněk Herman

Postdoc years, 1972-1974

The Johns Hopkins University
Advisor: John P. Doering
1938-2010

IAEA Fellowship for underdeveloped countries

Electronic and vibrational excitation induced by inelastic collisions of positive ion beams

What I gained:
Research with up-to-date equipment
Doering's advice: Get the best data. They will stay!
What I regret:
Not going to Canada to observe the Aurora Borealis

Independent project back at Soreq

Group leader of chemical lasers: Cl + HI (1974-1977)

Our son in 1977

1977: Arrival at USC to work in Curt Wittig's group

First projects: (i) E-V energy transfer of Br*

(ii) Kinetics and dynamics of bimolecular reactions of free radicals.

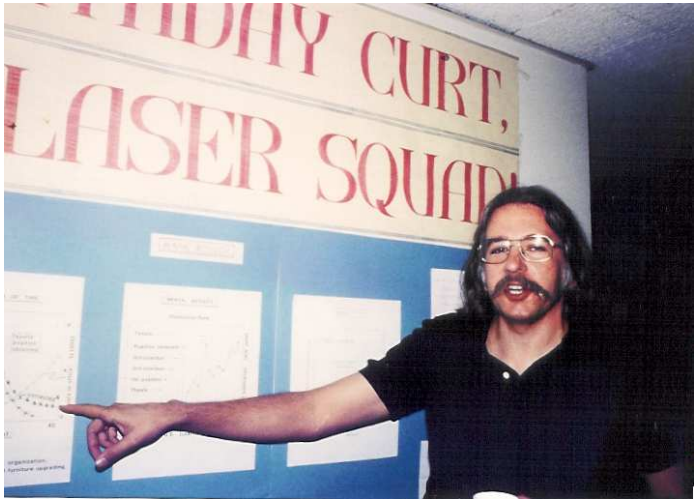
The hardest thing: Leaving at a fixed time because of child care.

Benefits: Organizational and time management skills

The Wittig years:

(i) Unimolecular reactions on the ground state

(ii) Photodissociation dynamics on excited states



Curt Wittig (1983)

(i) NCNO: State-resolved studies of a barrierless unimolecular reaction

The power and limitations of statistical theories

Near dissociation threshold

Near threshold photodissociation of expansion cooled NCNO: nascent CN(X2S+) without internal excitation I. Nadler, H. Reisler, M. Noble, and C. Wittig, Chem. Phys. Lett. **108**, 115 (1984).

CN and NO products distributions at higher energies: Tightening of the transition state

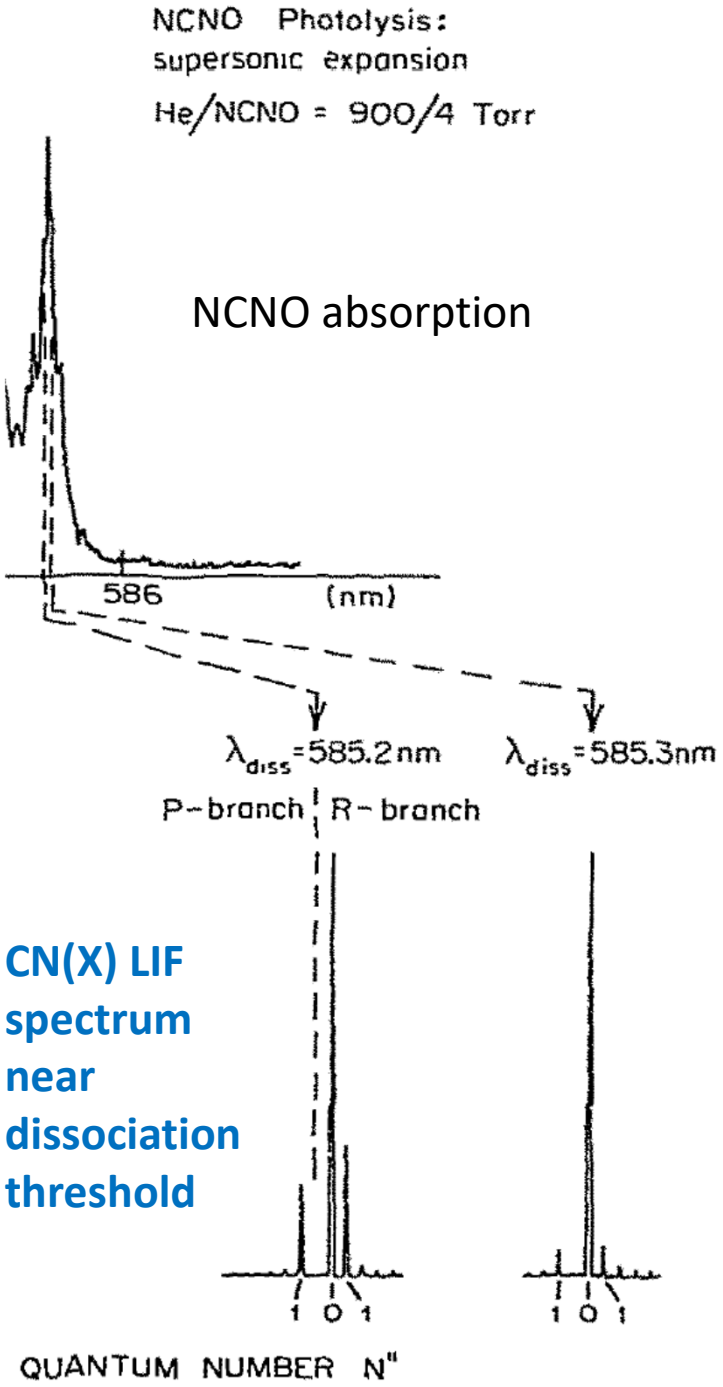
NCNO → CN+NO: complete NO(E,V,R) and CN(V,R) nascent population distributions from well-characterized monoenergetic unimolecular reactions C.X.W. Qian, M. Noble, I. Nadler, H. Reisler, and C. Wittig, J. Chem. Phys. **83**, 5573 (1985).

Dr. Israel Nadler-Niv

Charles Qian

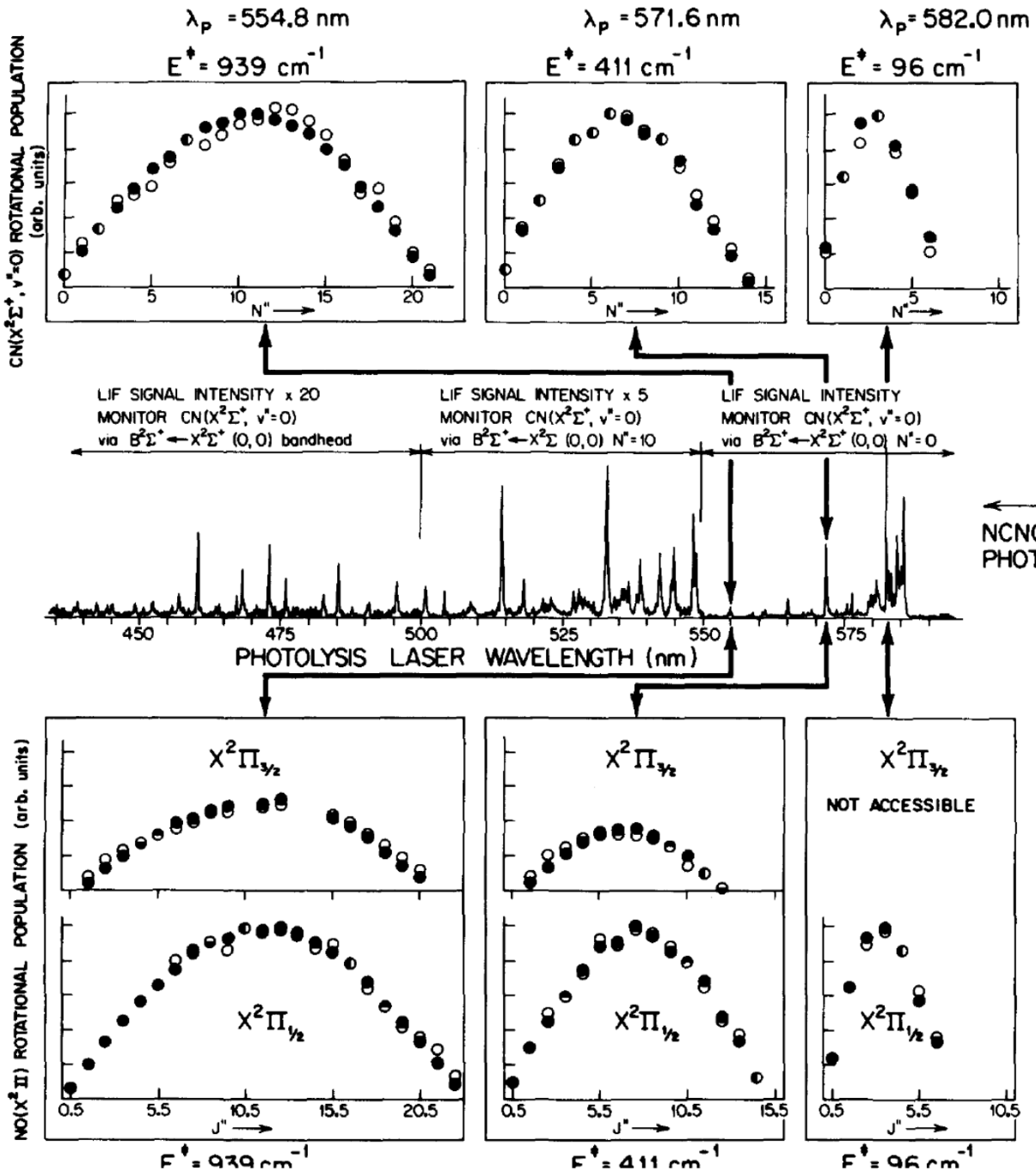
Prof. J. Pfab came from Scotland to teach us how to make NCNO without explosions.

Main observation: No internal energy in the products near threshold. Results agree with PST.



CN(X) LIF spectrum near dissociation threshold

NCNO → CN + NO



Conclusion:
Good agreement with PST
not too far from threshold

Transition to tenured position at USC, 1987

Center for the Study of Fast Transient Processes headed by Curt Wittig:
Collision Induced dissociation of highly vibrationally excited molecules in the gas phase and on surfaces (NO_2)

Spectroscopy and dynamics of fast evolving states
Properties that are sensitive to the shape of the potential energy surfaces

Collaboration with theoreticians
First: Reinhard Schinke, Keiji Morokuma, Moshe Shapiro, Uri Peskin/Bill Miller

Later: Stephen Klippenstein, Anna Krylov, David Yarkony, Joel Bowman, Hua Guo

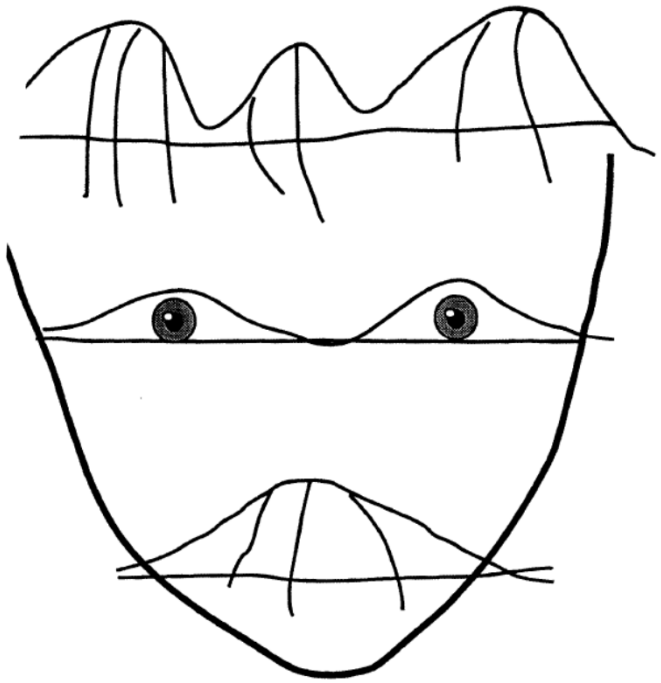
New experimental tool: Photofragment Imaging (Chandler and Houston, 1987)

Experimental probes of potential energy surfaces

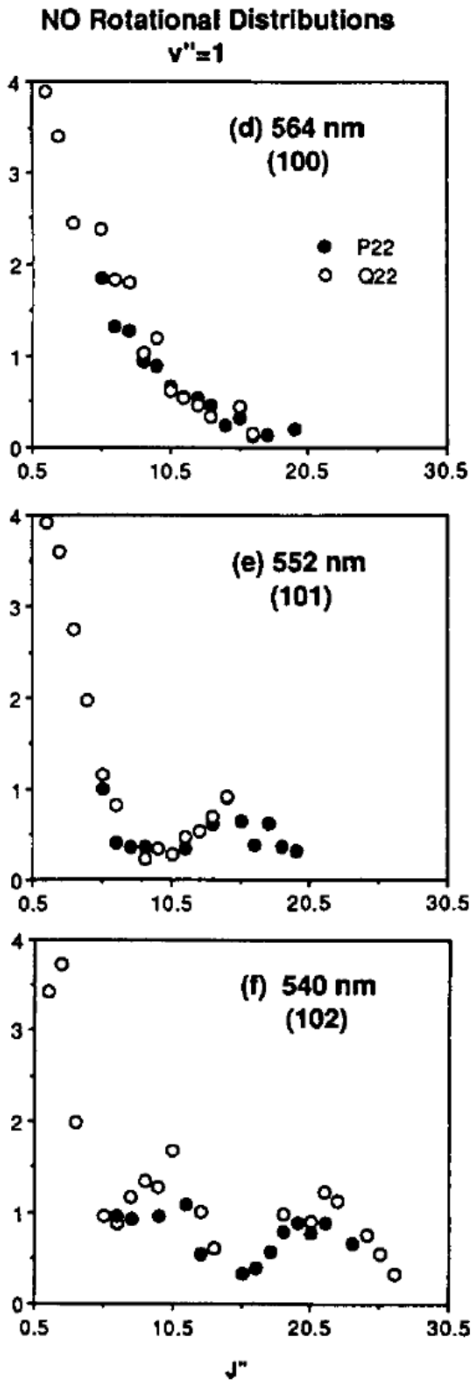
Mapping excited state transition state wavefunctions into rotational distributions: ClNO on T_1

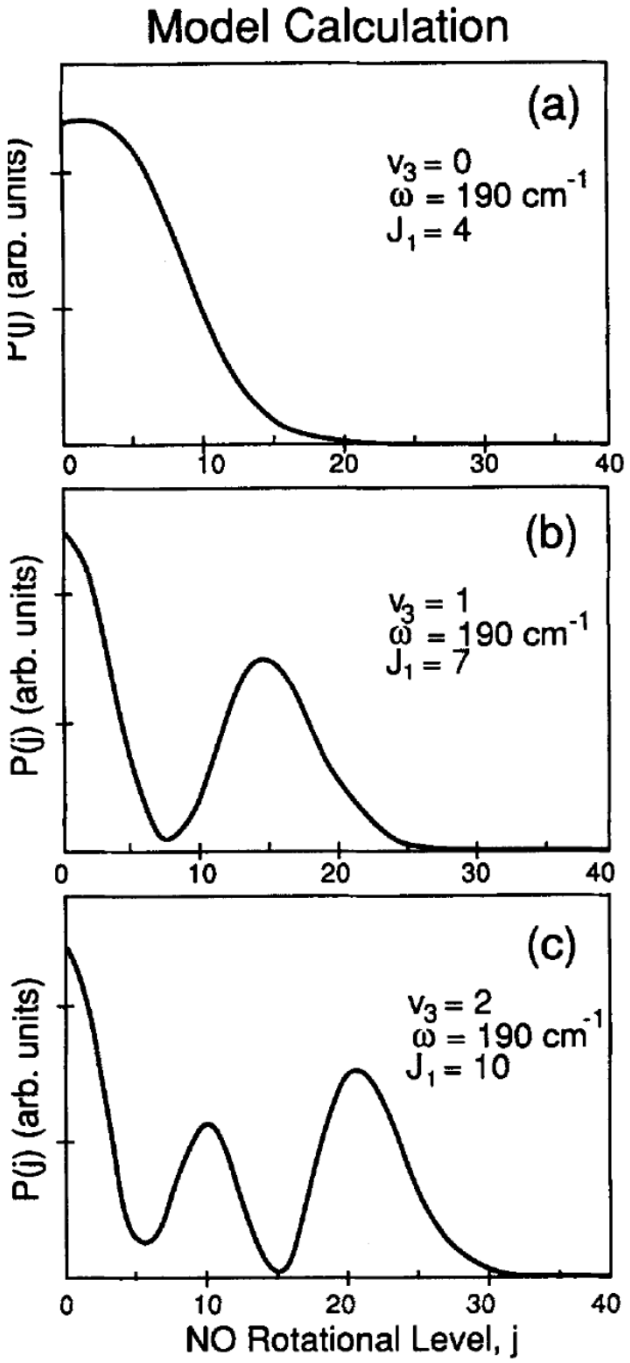
Dr. HO

By Charles Qian, 1988



C.X.W. Qian, A. Ogai, L. Iwata, and H. Reisler, J. Chem. Phys., **92**, 4296 (1990)



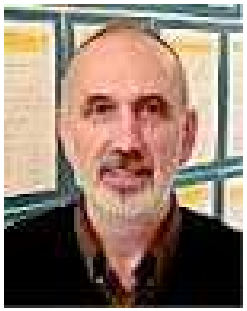


Interference Effects: *Experimental probes of dissociative states:* ***Fano profiles*** *in the state-specific photodissociation of* ***FNO***, J.T. Brandon, S.A. Reid, D.C. Robie and H. Reisler, J. Chem. Phys., **97**, 5246 (1992).

Collaboration with theoreticians

Reinhard Schinke

Moshe Shapiro

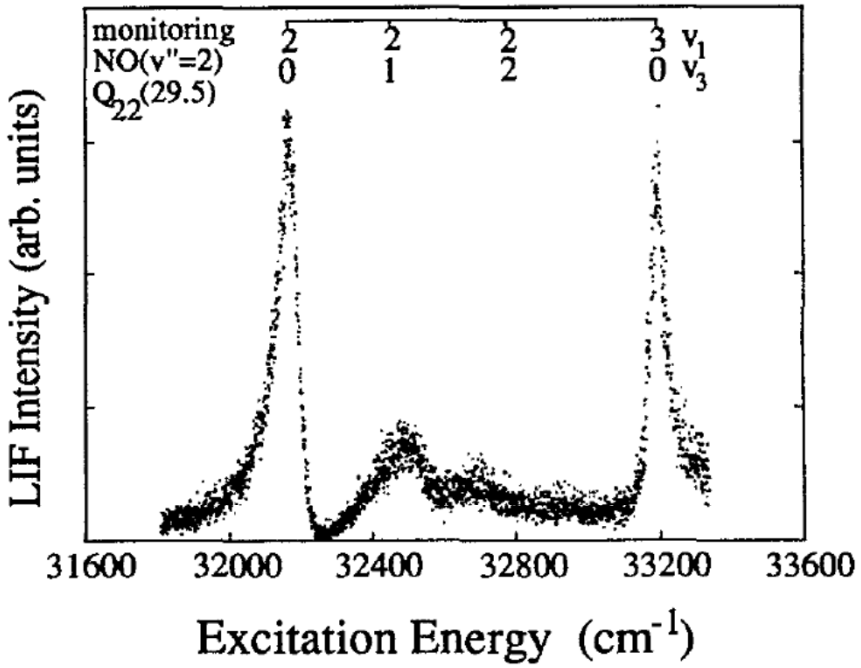


Uri Peskin

Also Moshe Shapiro
And Bill Miller

Excitation to transition state region: Interference between direct outgoing wave and recurrences to bound region

Photofragment yield spectrum of FNO absorption to S_1: monitorin NO (v,J)



$$\sigma(\tilde{\nu}) = \sigma_0(q+\epsilon)^2/(1+\epsilon^2) + \sigma',$$

where

$$\epsilon = (\tilde{\nu} - \tilde{\nu}_0)/(\Gamma/2).$$

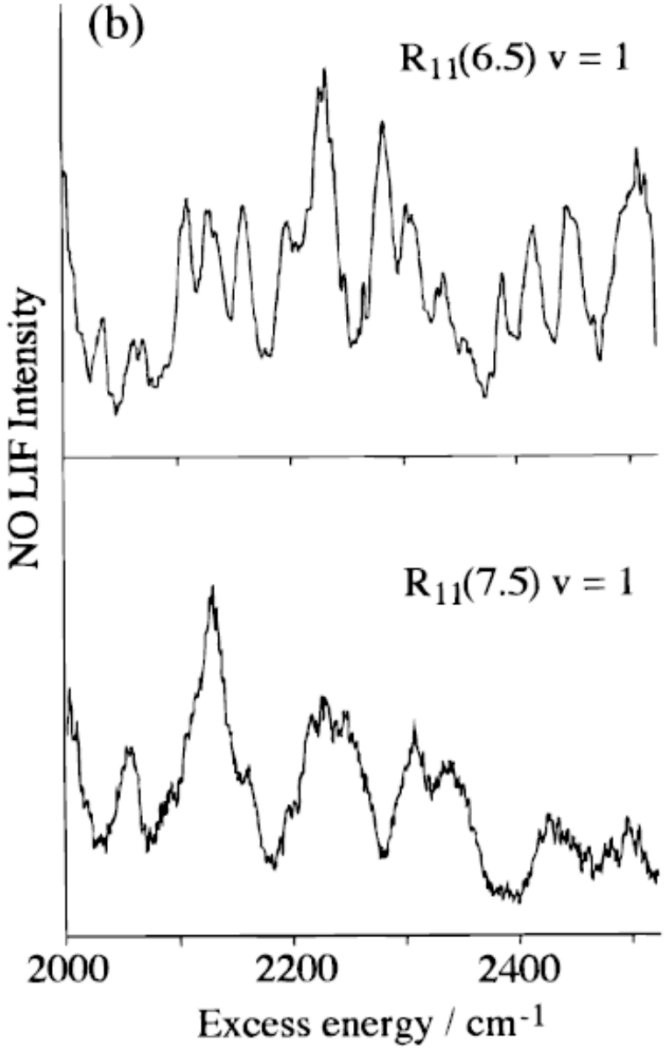
Scott Reid

The curious case of NO_2: Fluctuations and overlapping resonances in a unimolecular reaction

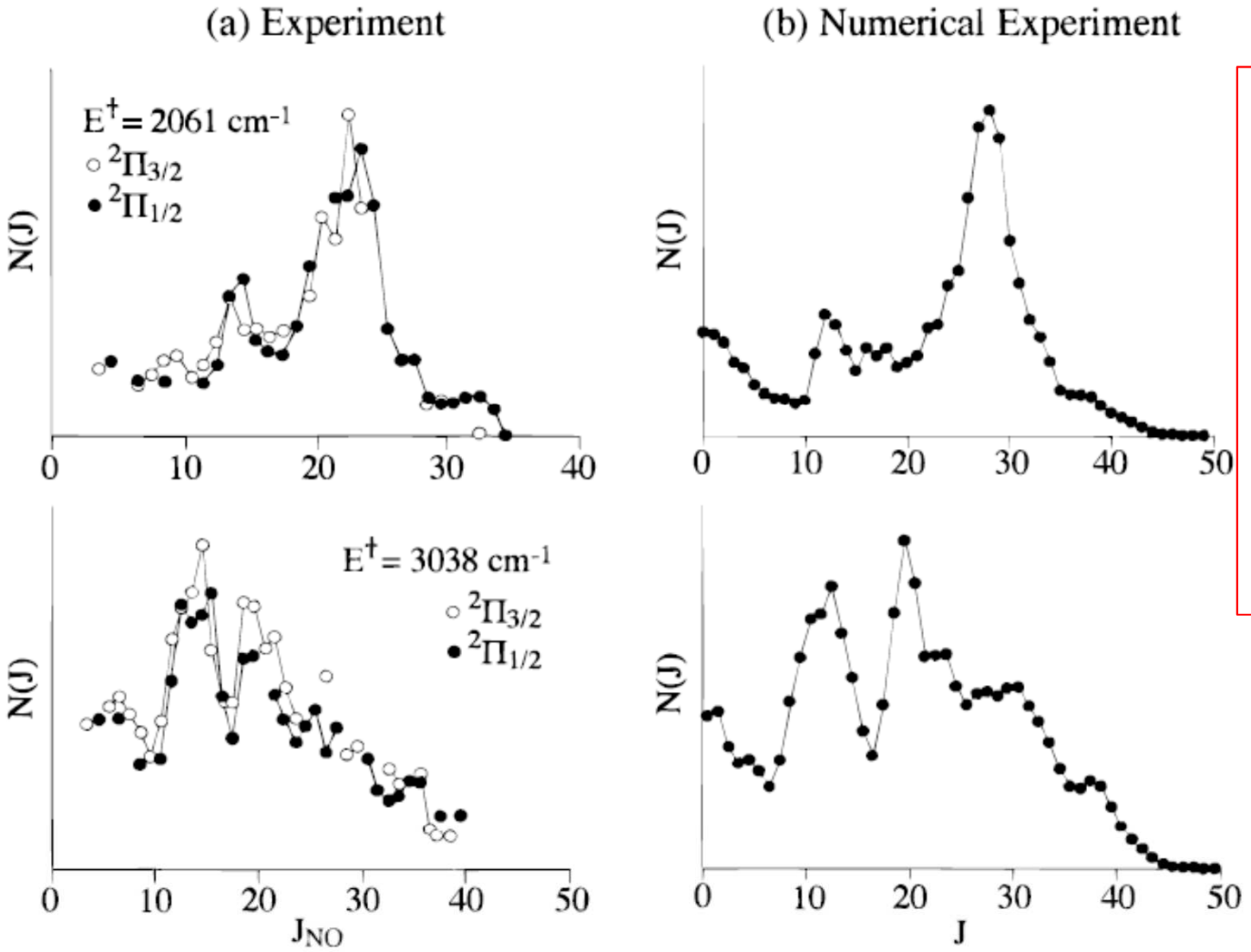
Resonances and fluctuations in the unimolecular reaction of NO_2, **S.A. Reid, A. Sanov** and H. Reisler, Roy. Soc. Chem. Faraday Discussion, **102**, 129 (1995).

Andrei Sanov

Photofragment yield spectra obtained by monitoring NO in v=1, J = 6.5 and 7.5 at excess energies 2000-2500 cm^{-1}



Final state-selected spectra in unimolecular reactions: A transition-state-based random matrix model for overlapping resonances, **U. Peskin, W.H. Miller** and H. Reisler, J. Chem. Phys., **102**, 8874 (1995).



Mapping of transition state wavefunctions, including interference effects (phase)

Average behavior is statistical (PST)

Figure 10. (a) NO($^2\Pi_{1/2}$) and ($^2\Pi_{3/2}$) rotational state distributions obtained at $E^\dagger = 2061$ and 3038 cm^{-1} following one-photon excitation. (b) Calculated distributions using Franck–Condon mapping of harmonic TS basis functions whose complex coefficients are randomly weighted, as described in the text. (From ref 22.)

Velocity map imaging

David Chandelr, Thierry Droz-Georget, Mikhail Zyrianov

Imaging

David Chandler (Sandia) fostered collaboratiions and interactions

Vladimir Dribinski: **BASEX**

The imaging technique sees it all!

Current Work

Photodecomposition of molecules and radicals
Conical Intersections

Vibrational predissociation of H-bonded clusters
State specificity

Molecular transport and reactions in amorphous solid water using nanoarrays as nanoheaters
with Curt Wittig

Radical Adventures

Rydberg-valence interaction
Interacting Rydberg and valence states in radicals and molecules: Experimental and theoretical studies, H. Reisler and A.I. Krylov, Int. Rev. Phys. Chem., **28**(2) 267-308 (2009)

Conical Intersections: David Yarkony

The long saga of CH_2OH on the ground and excited states

First generation: David Conroy and Victor Aristov

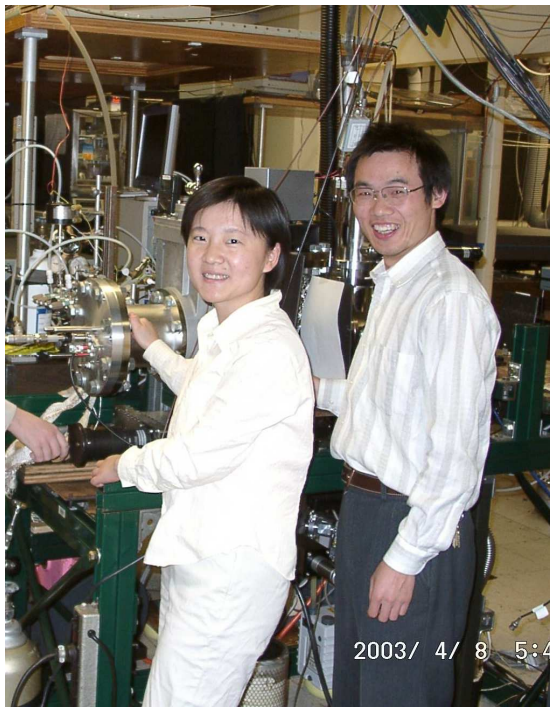
Second Generation: Lin Feng, Boris Karpichev, Dr. Andrei Demyanenko, Dr. Jie Wei

Third Generation: Mikhail Ryazanov, Subhasish Sutradhar, Dr. Chirantha Rodrigo

Experiment: Hudgens (UV), Nesbitt (IR),

Theory: Marenich and Boggs, Bruna and Grein, Anna Krylov and Joel Bowman, David Yarkony and Hua Guo. The tale is not complete yet!

Lin Wei



Boris

Andrei

David

Mikhail

Chiranta

Subhasish

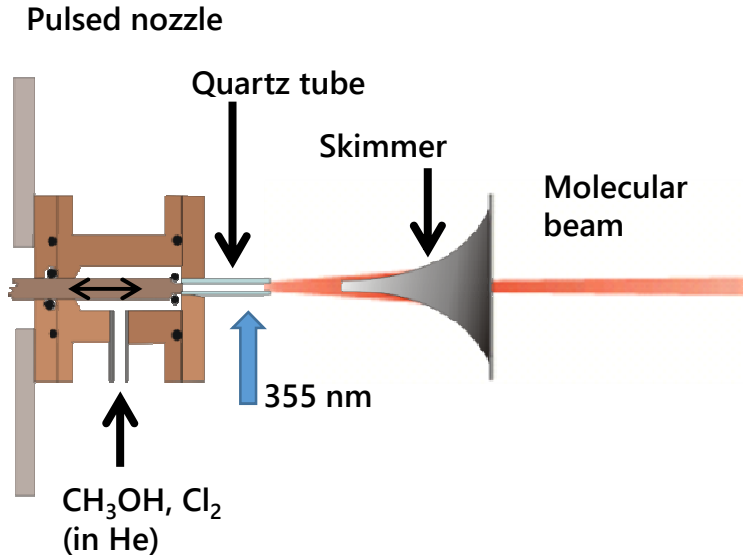
•**Translational energy of H(D) ions recorded using sliced velocity map imaging (Design: Mikhail Ryazanov)**

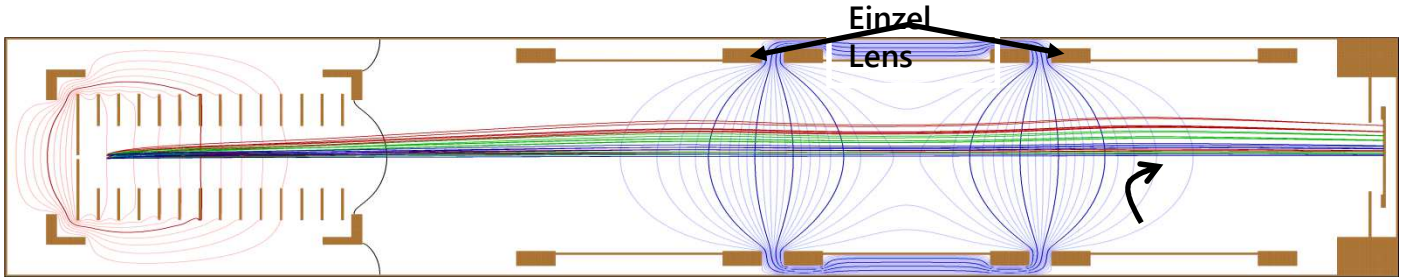
$CH_3OH + Cl \rightarrow CH_2OH$

- Photololysis: UV or near IR.

$CH_2OH \rightarrow H + H_2CO, HCOH$

•H detected by ionization (121.59 nm + 365 nm).





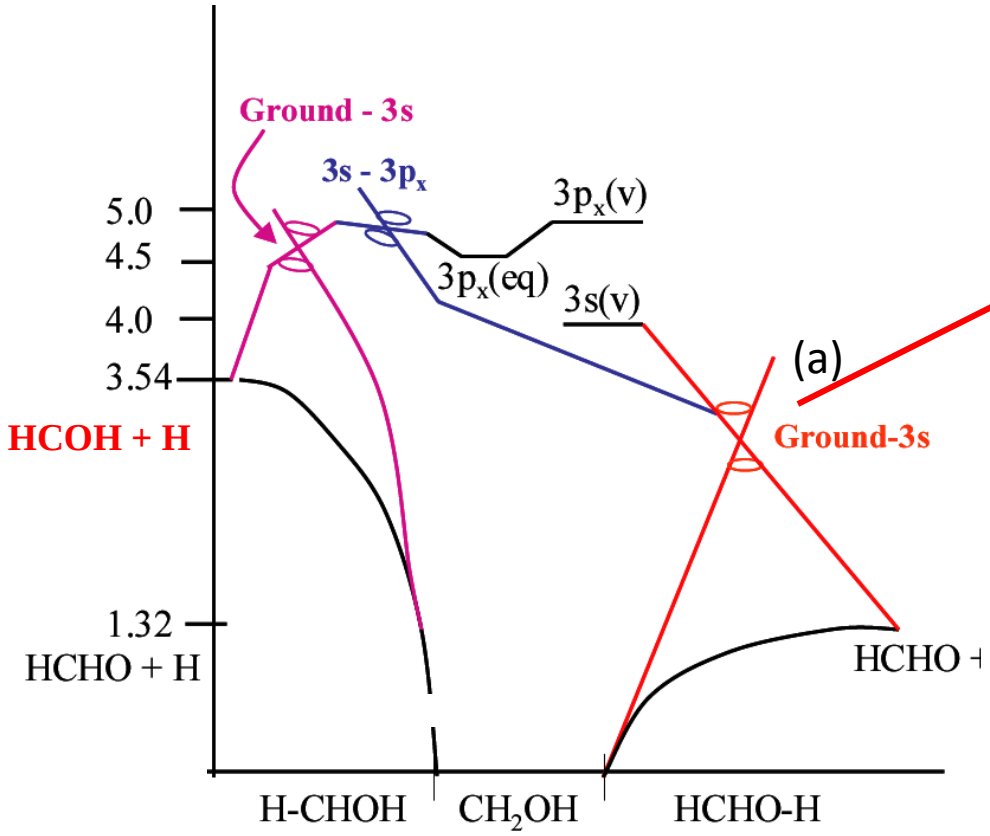
Slicing: 5 ns pulse Ion detection + Magnification control; Ryazanov and Reisler, J. Chem. Phys. *138*, 144201 (2013).

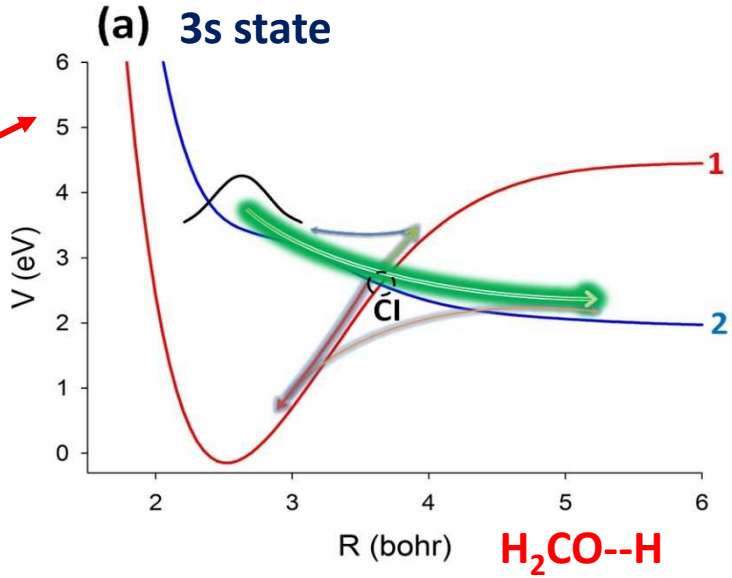
Ground state: $CH_2O + H \leftarrow CH_3O \Leftrightarrow CH_2OH \rightarrow CH_2O + H$

Experiments and calculations: E. Kamarchik, C. Rodrigo, J.M. Bowman, H. Reisler, and A. I. Krylov. J. Chem. Phys. **136**, 084304 (2012); Ryazanov, Rodrigo and Reisler, J. Chem. Phys. **136**, 084305 (2012).

Vibrational energies: using IR-UV double resonance REMPI detection (Wei et al. JCP 2006)

Dissociation on the 3s state: Conical intersection





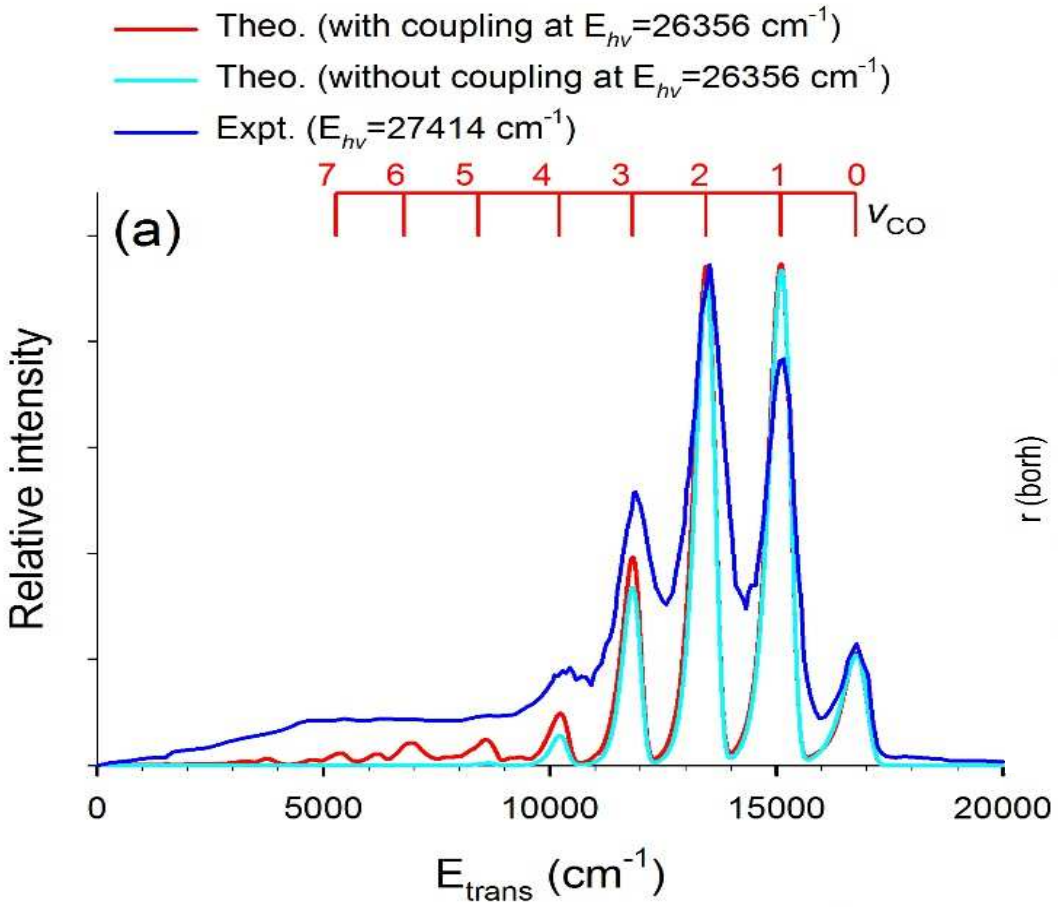
B. C. Hoffman and D. R. Yarkony, JCP 116, 8300 (2002).
Yarkony, JCP 122, 084316 (2005); JPCA, 2015
Feng, Demyanenko, Reisler, JCP, **118**, 9623 (2003).

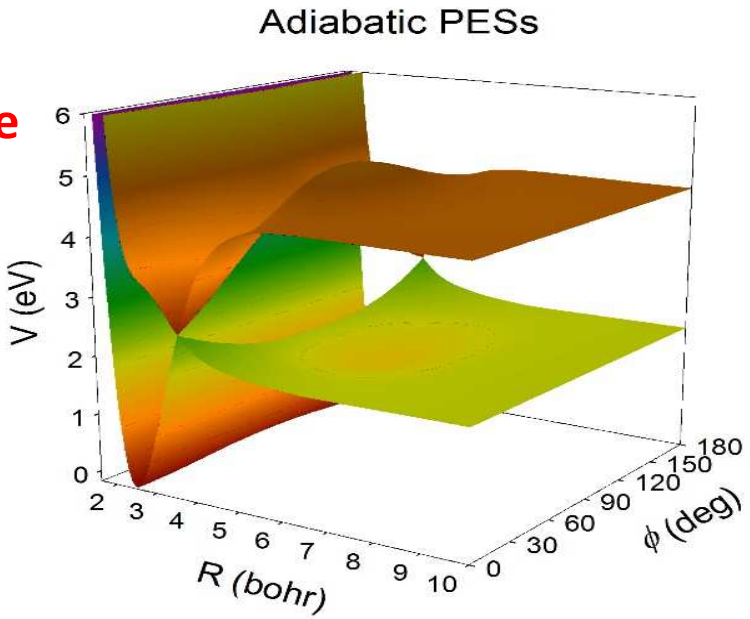
Nonadiabatic photodissociation dynamics of the hydroxymethyl radical *via* the $2^2A(3s)$ Rydberg state: A four-dimensional quantum study, Xie, Malbon, **Yarkony, Guo**, JCP, 2017

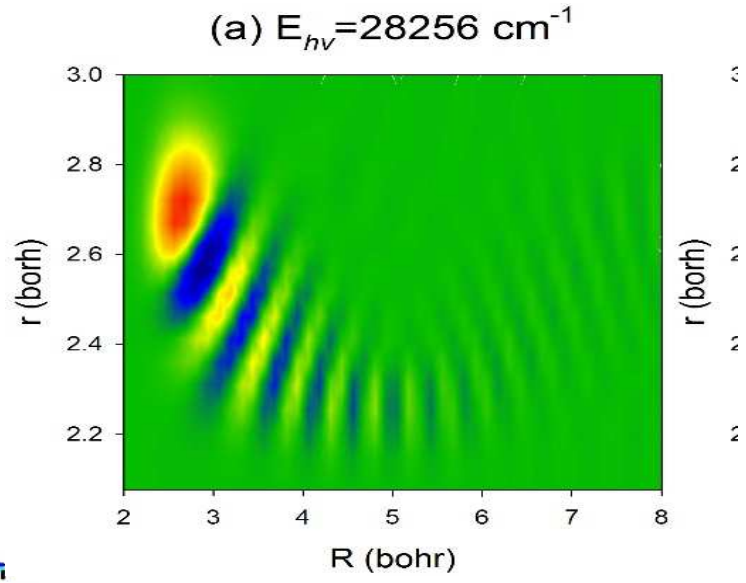
Dissociation on 3s dissociative state:
With and without coupling to the ground state

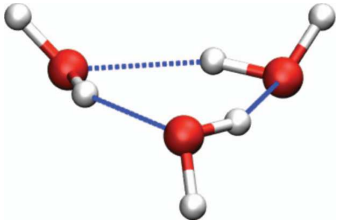
Breaking the O-H bond: H_2CO + H channel

Experiment: Rodrigo, Zhou, Reisler, J. Phys. Chem. A (Wittig Festschrift) **117**, 12049-12059, 2013.

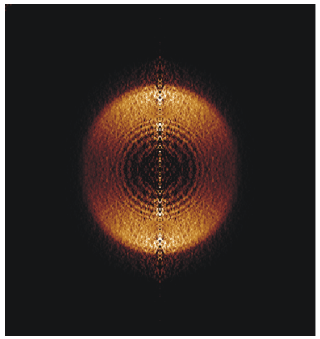








Imaging Bond Breaking and Energy Transfer Pathways in Small H-bonded Networks



Vibrational Predissociation of dimers, trimers and tetramers

First: Jessica Parr, Dr. Guosheng Li
Second: Blithe Rocher, Dr. Andrew Mollner
Third: Lee Ch'ng, Dr. Amit Samanta
Fourth: Dan Kwasniewski, Kristen Zuraski

Theory Collaboration: Prof. Joel Bowman and coworkers

Review: Chem. Rev. 2016, 116 (9) 4913

Jessica

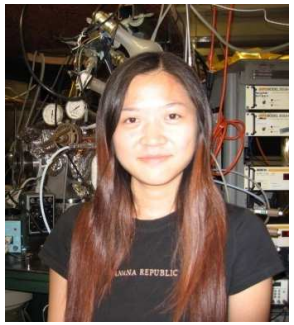
Guosheng

Kristen

Daniel

Amit

Lee



Blythe Andrew

Imaging H-Bond Breaking

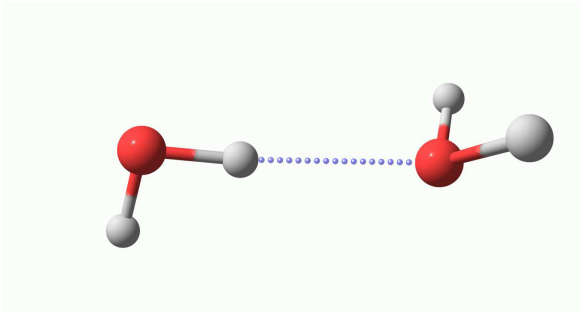
Dissociation Energy

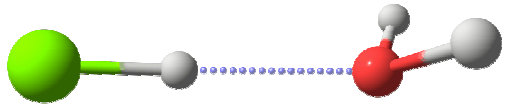
Mechanism of predissociation

Product Energy Distributions

Propensity rules

Prof. Joel Bowman



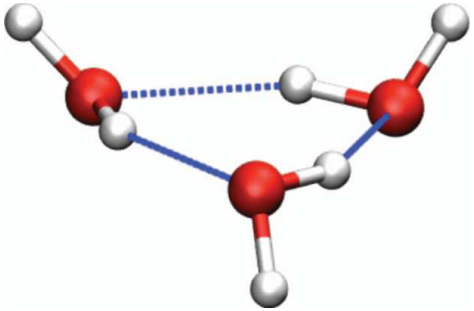


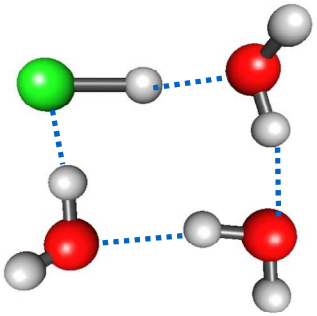
…and for cyclic networks:

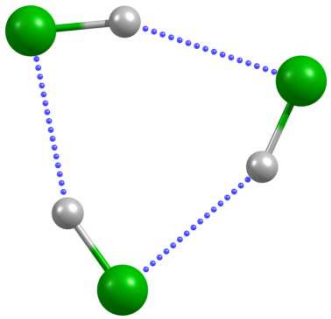
Energy transfer mechanism in a ring

Quantitative contributions of cooperativity

Timescales of IVR and dissociation



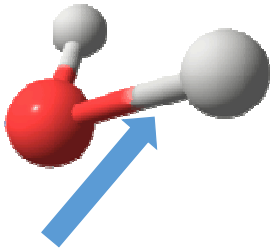




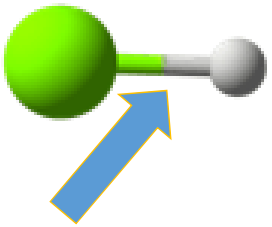
Samanta, Wang, Mancini, Bowman, Reisler, special issue on Non-covalent Interactions, *Chem. Rev.*, 2016, 116 (9), 4913

H_2O-HCl: Structured velocity distributions

$$h\nu + E_{rot}(HCl - H_2O) = D_o + E_{vib,rot}(H_2O) + E_{rot,vib}(HCl) + E_{Trans}$$

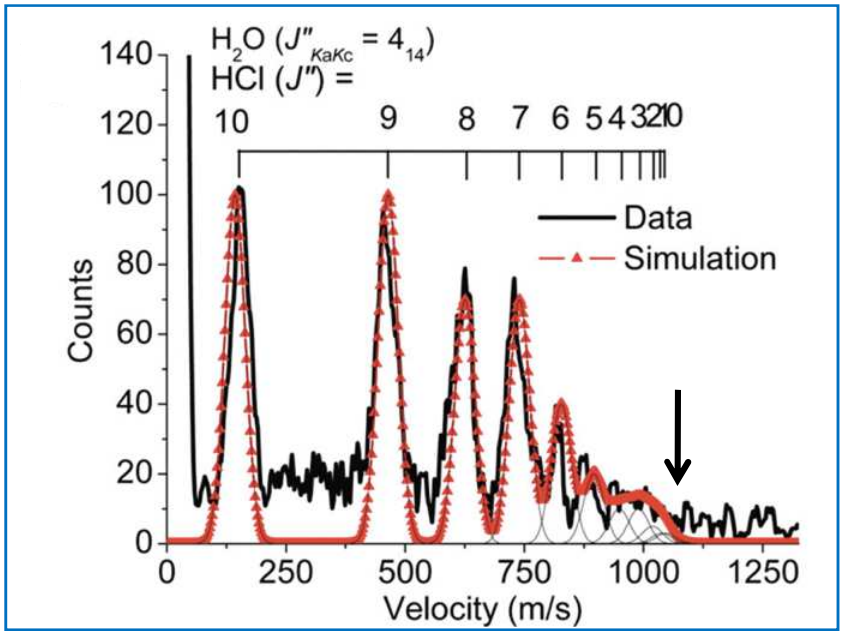


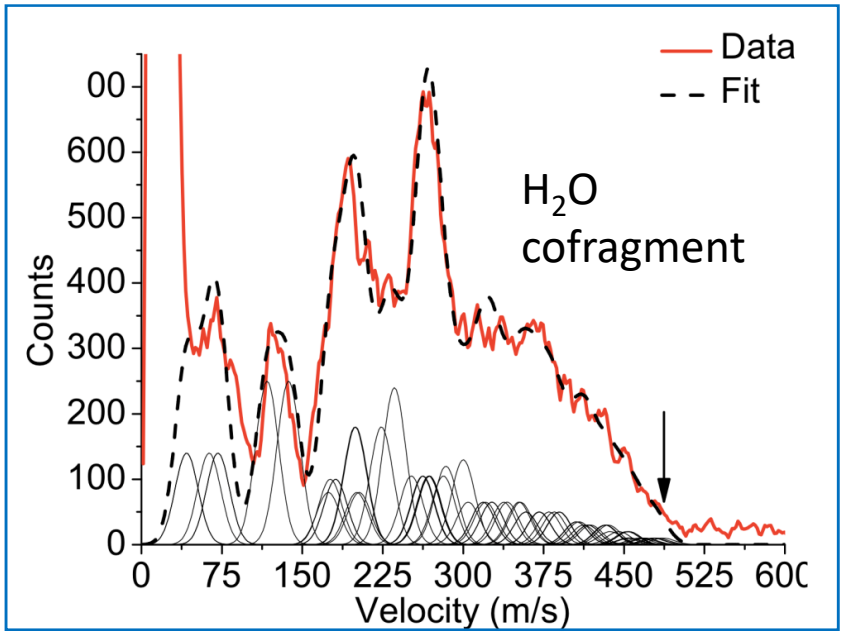
D_0 = 1334 ± 10 cm^{-1}



Monitoring H_2O (J_{KaKc})

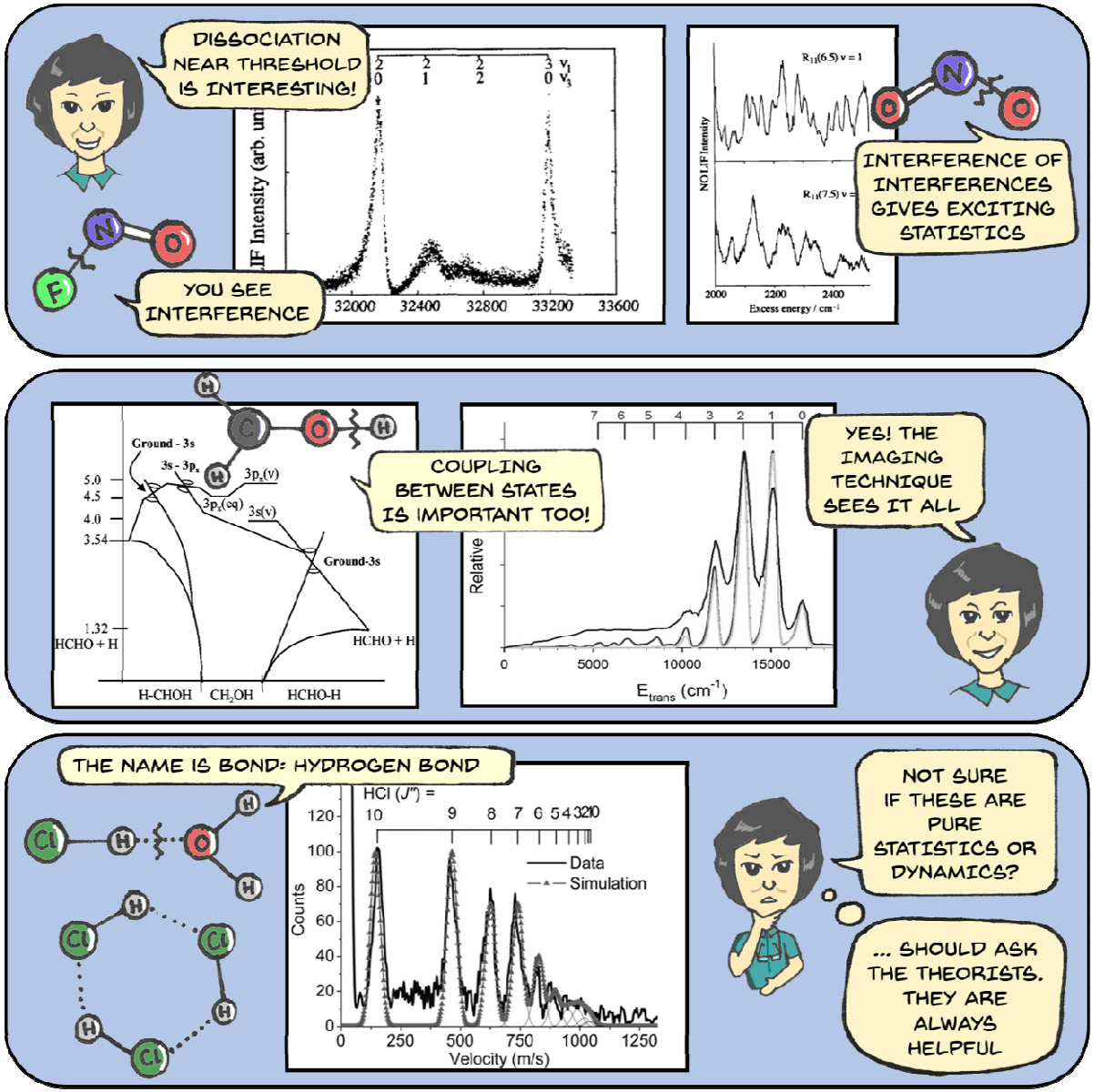
Monitoring HCl (J=5)



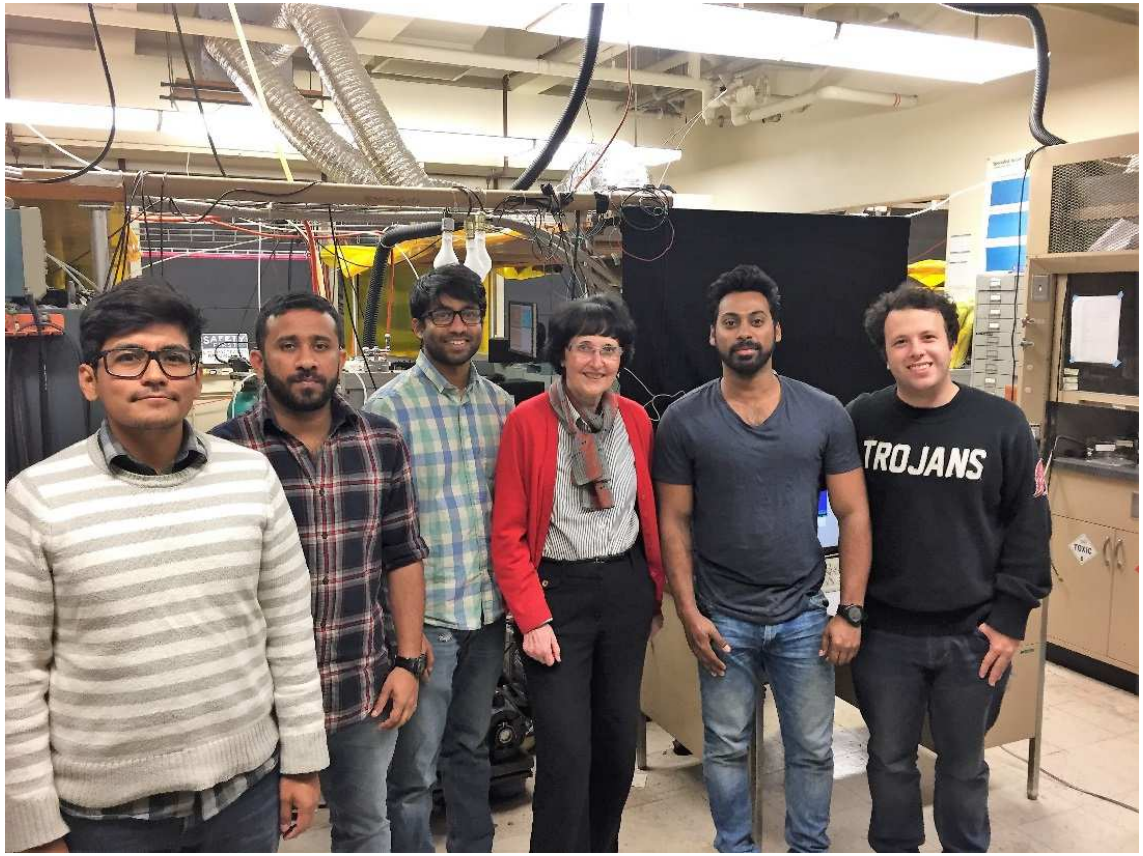


Rely on structures in an array of images to get a unique and precise value of D_0

Art work by Bibek R. Samanta, 2019



Current Group



Mixtli Ravin Bibek Subhasish Dcan

University of Southern California

wise

Women in Science: challenges and perspective (wise.usc.edu)

If you don't like something, change it.
If you can't change it; change your attitude.
Don't just complain
Maya Angelou

Much progress has been made, but cademic cultures are hard to change.

- **Both men and women need to take family leave**
- **Most women are and will remain the primary caretakers of young children.**
- **Women often have non traditional career trajectories**
- **Need to provide good mentoring and special accommodations when needed**
- **Support networks are helpful for careers (and good for health)**
- **Train women on how to succeed (COACh; www.coach.uoregon.edu)**

Geri Richmond, 2017 Priestley Medal

Richmond in honored for:

"Her pioneering research to understand the characteristics of surfaces in chemical processes has advanced studies related to energy, the environment and biological applications. **Beyond the lab, she has been a devoted advocate for women in science and a true trailblazer in assuring a diverse workforce."**

"Richmond is also the founding and current director of COACh, a grassroots organization formed in 1998 to promote career advancement for women scientists and engineers. More than 18,000 scientists worldwide have attended COACh career-building workshops since the organization began."

Some Lessons Learned (so far…)

Know who you are: I discovered my aptitude for teaching and mentoring while doing it
You can't have it all, but you can certainly have a satisfying life!

To the students:

Keep on learning
Keep your enthusiasm and get high on science
Find an environment where you can relax

What kept me going:

Excitement about science and discovery
The quality of the people around me
Keeping a sense of humor and optimistic view
Friendships and a sense of community
My family!

With Emil on our 50th wedding anniversary

There is still a lot to discover:
"…The full area of ignorance in not yet mapped; we are at present only exploring its fringes". J.D. Bernal