

E. Bright Wilson, Jr.



Linus Pauling

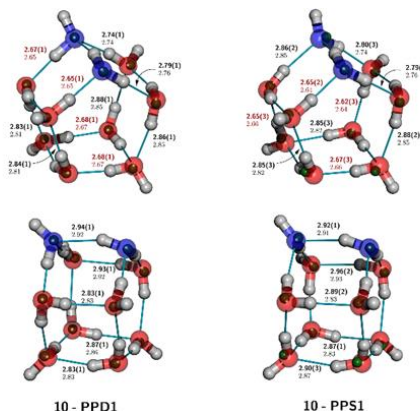
Broadband Molecular Rotational Spectroscopy for Chemical Dynamics and Molecular Structure

E. Bright Wilson, Jr (1986)

“You said earlier that microwave hasn’t played the role that NMR has. Of course it’s nowhere near playing the role that NMR does. It’s a little hard to say what should have been done, but we could have done better. Still, it’s a marvelous tool, and I still love it, quite frankly. I wish I could go on and do more with it.”

Raymond C. Ferguson interview for the Beckman Center for the History of Chemistry

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<http://faculty.virginia.edu/bpate-lab/>

Acknowledgements

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Frank Gupton

Pate Broadband Rotational Spectroscopy Group

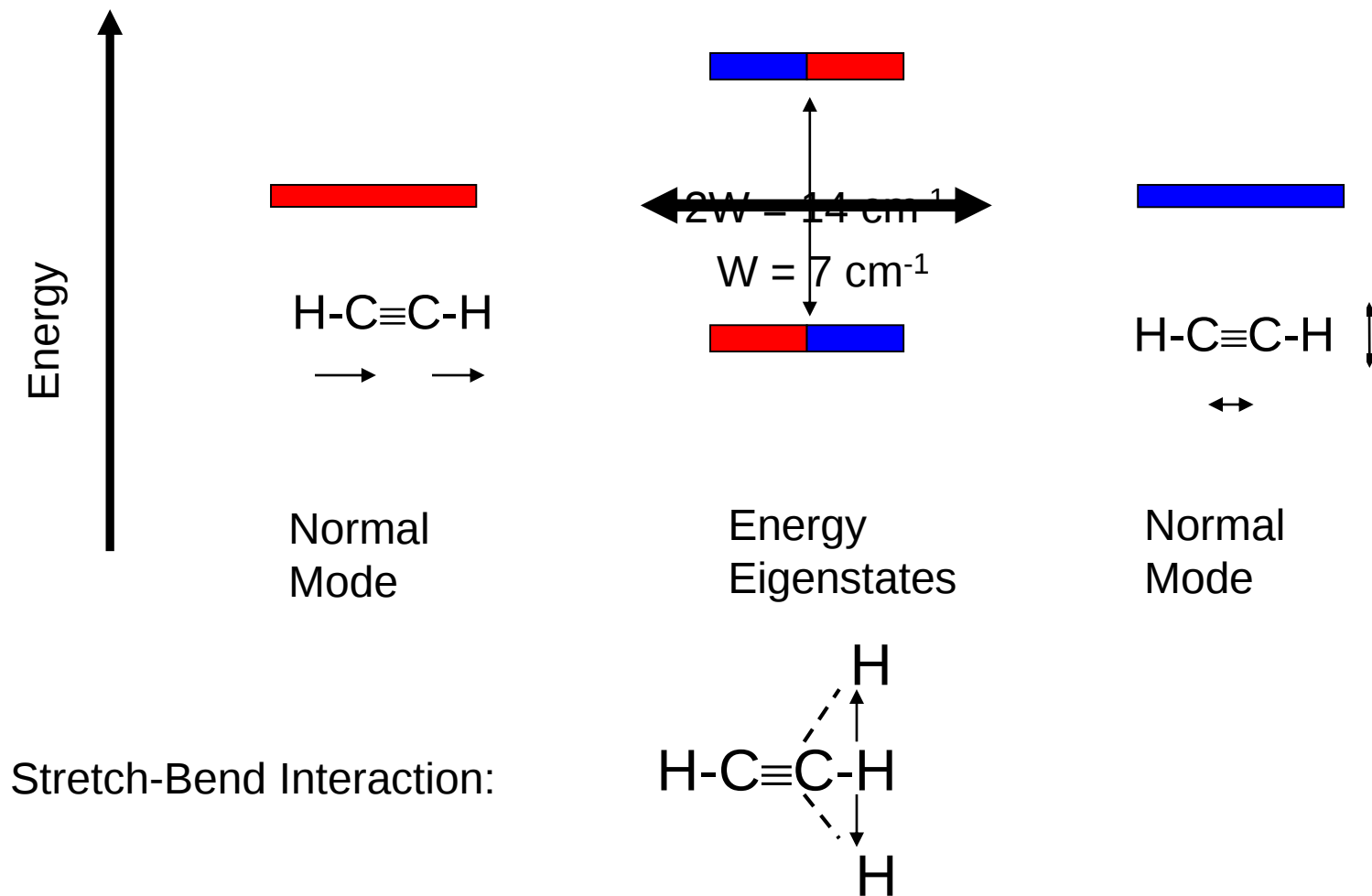
Gordon Brown, Kevin Douglass, Brian Dian, Steve Shipman

Matt Muckle, Justin Neill, Dan Zaleski, Brent Harris, Amanda Steber, Nathan Seifert,

Cristobal Perez, Simon Lobsiger, Luca Evangelisti, Lorenzo Spada, Jonathan Warren

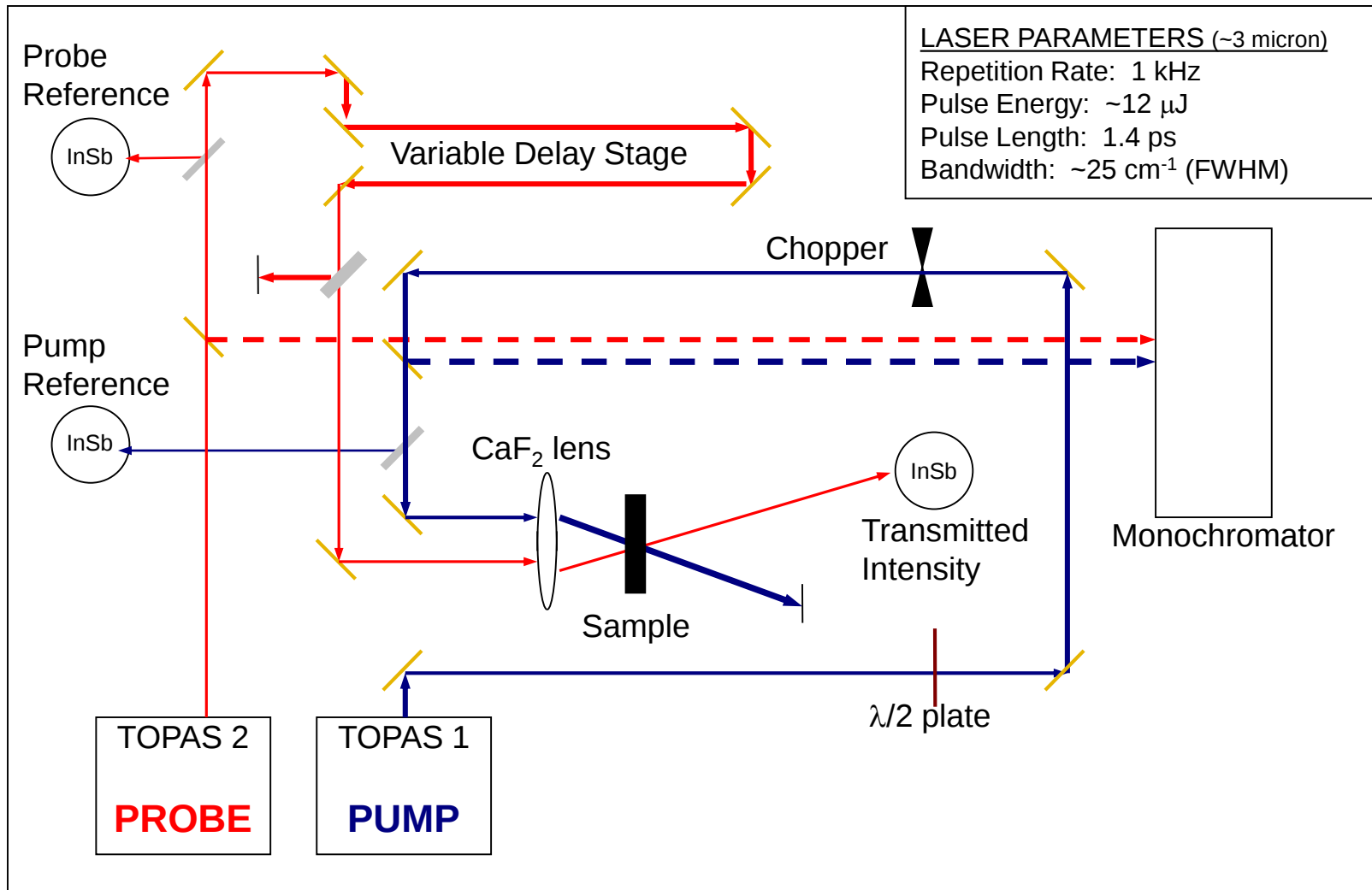
Perturbations and Quantum Dynamics

“Two State IVR” in Acetylene: $\text{H-C}\equiv\text{C-H}$

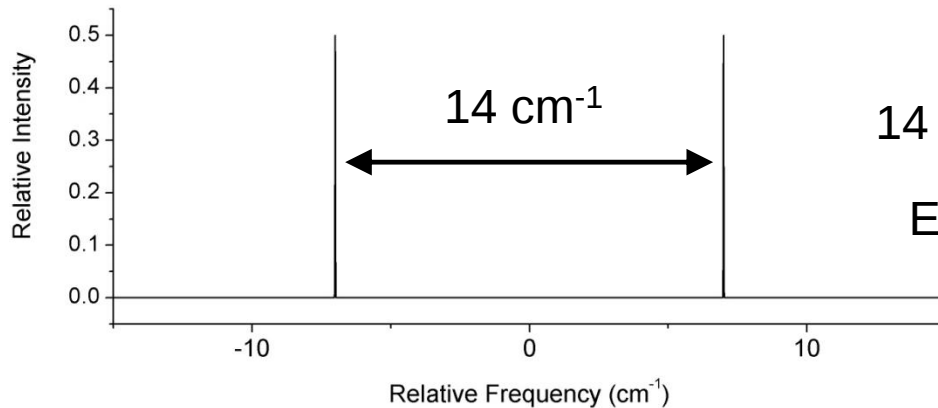
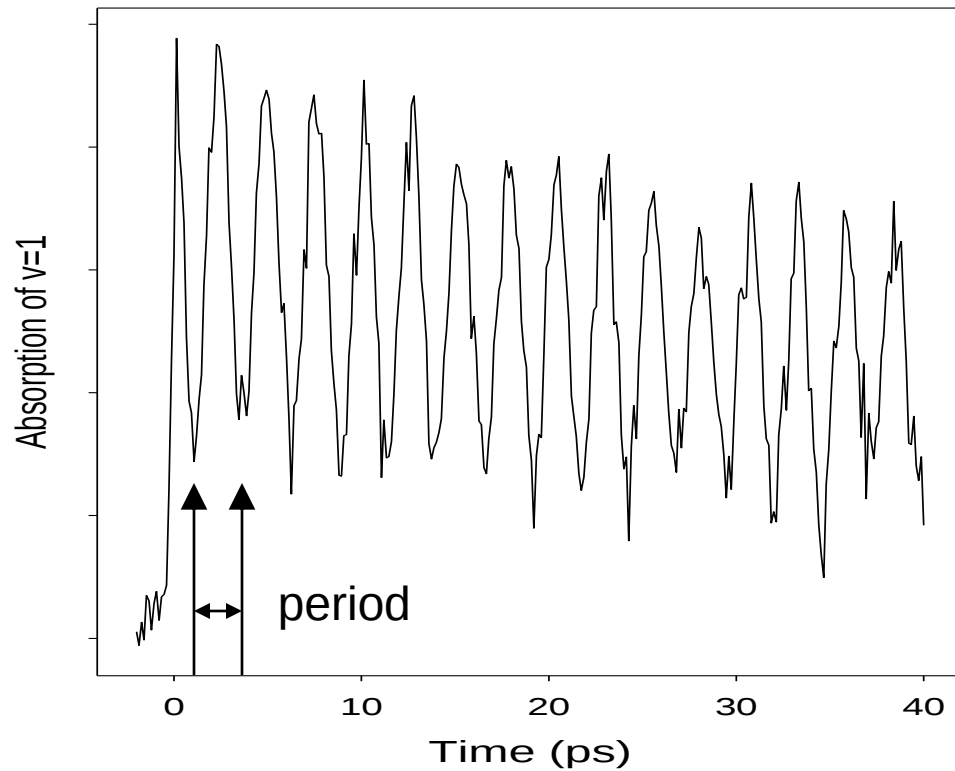


Experiment Setup:

Transient Absorption Spectroscopy



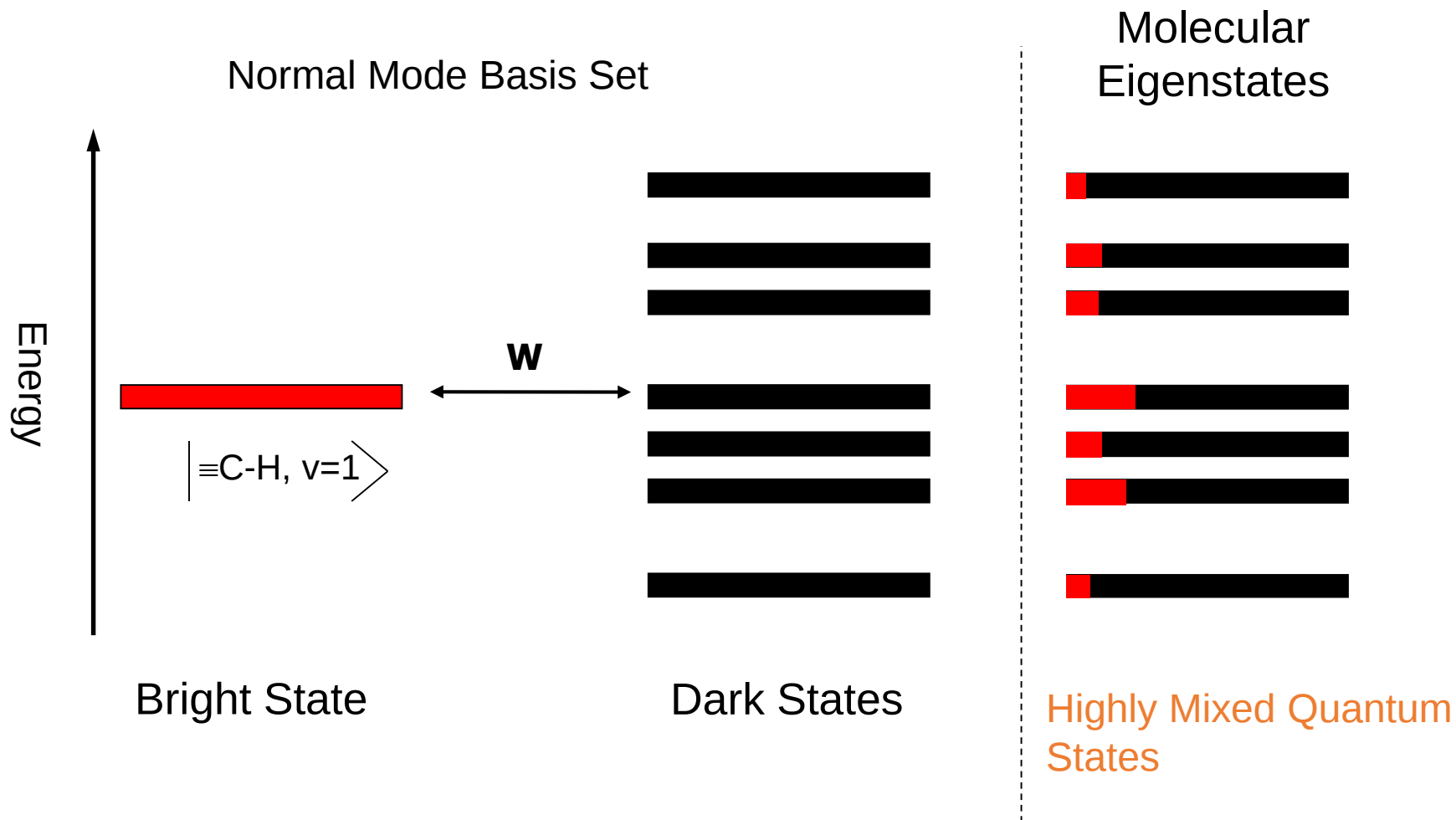
Acetylene C-H Stretch Dynamics



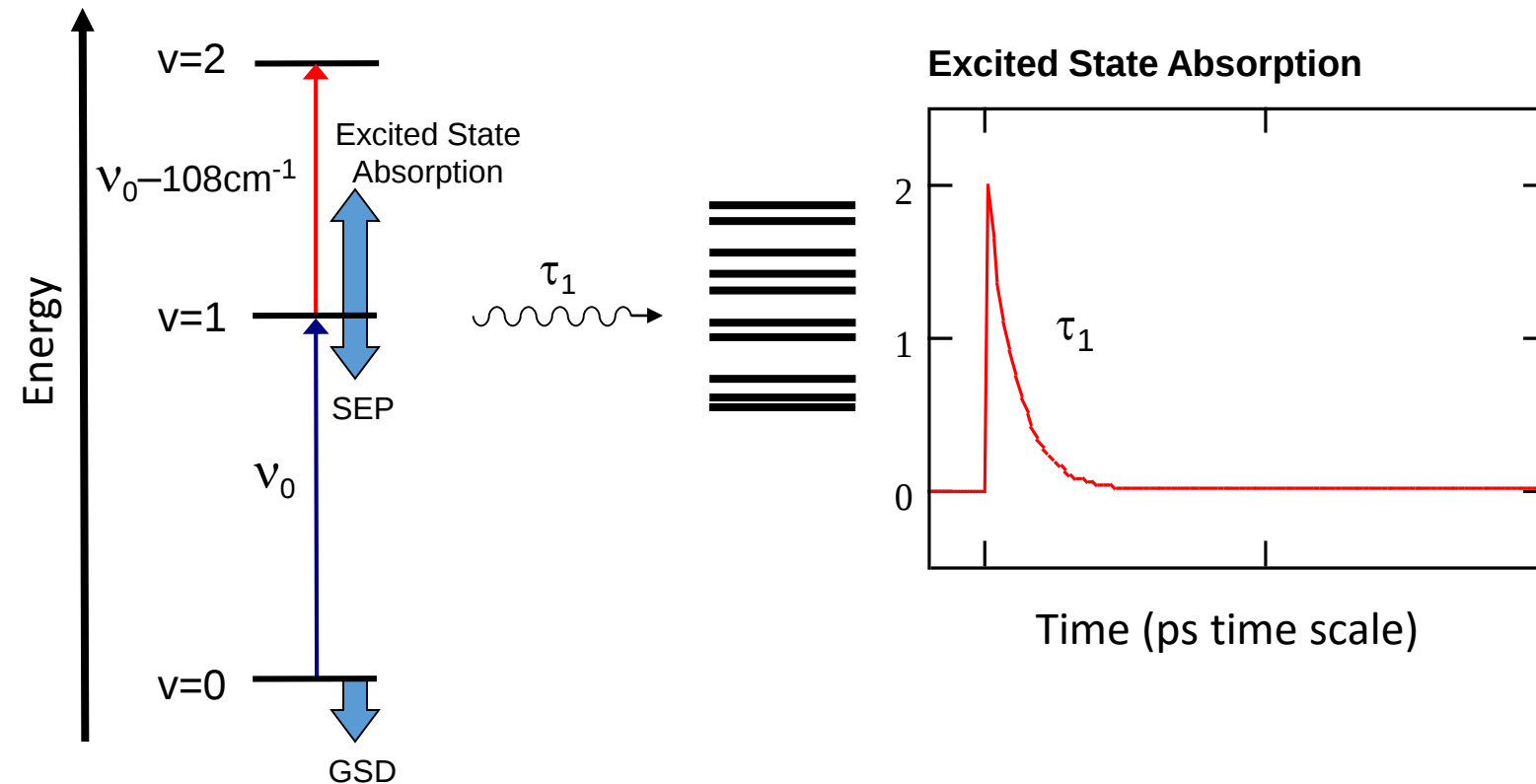
$$14 \text{ cm}^{-1} = 422 \text{ GHz} = 1/\text{period} = 1/2.37 \text{ ps}$$

Expected Frequency Domain Spectrum

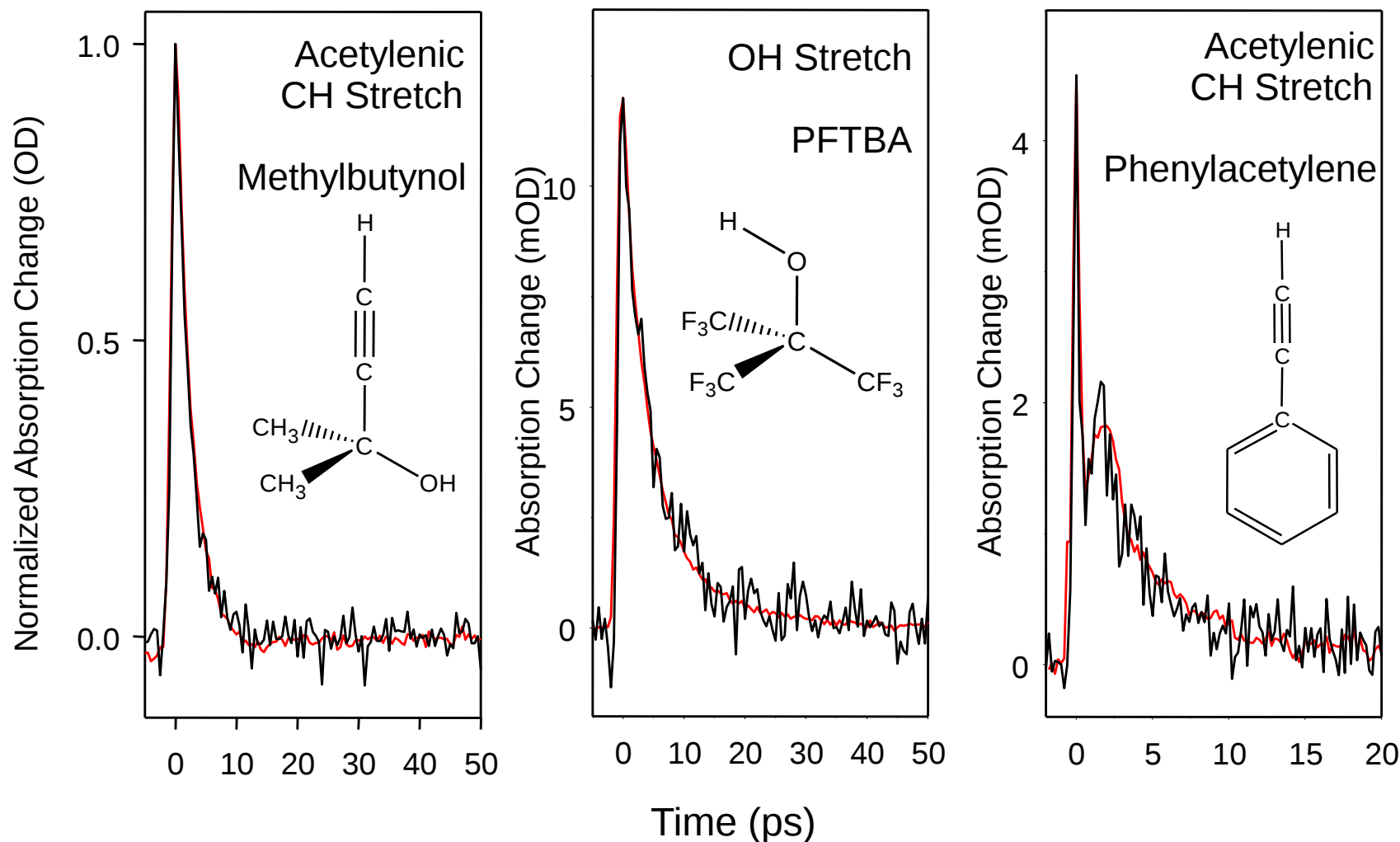
Standard Model of IVR



Transient Absorption Spectroscopy for Terminal Acetylenes



Population Relaxation in Gas and Solution (0.05 M CCl_4)

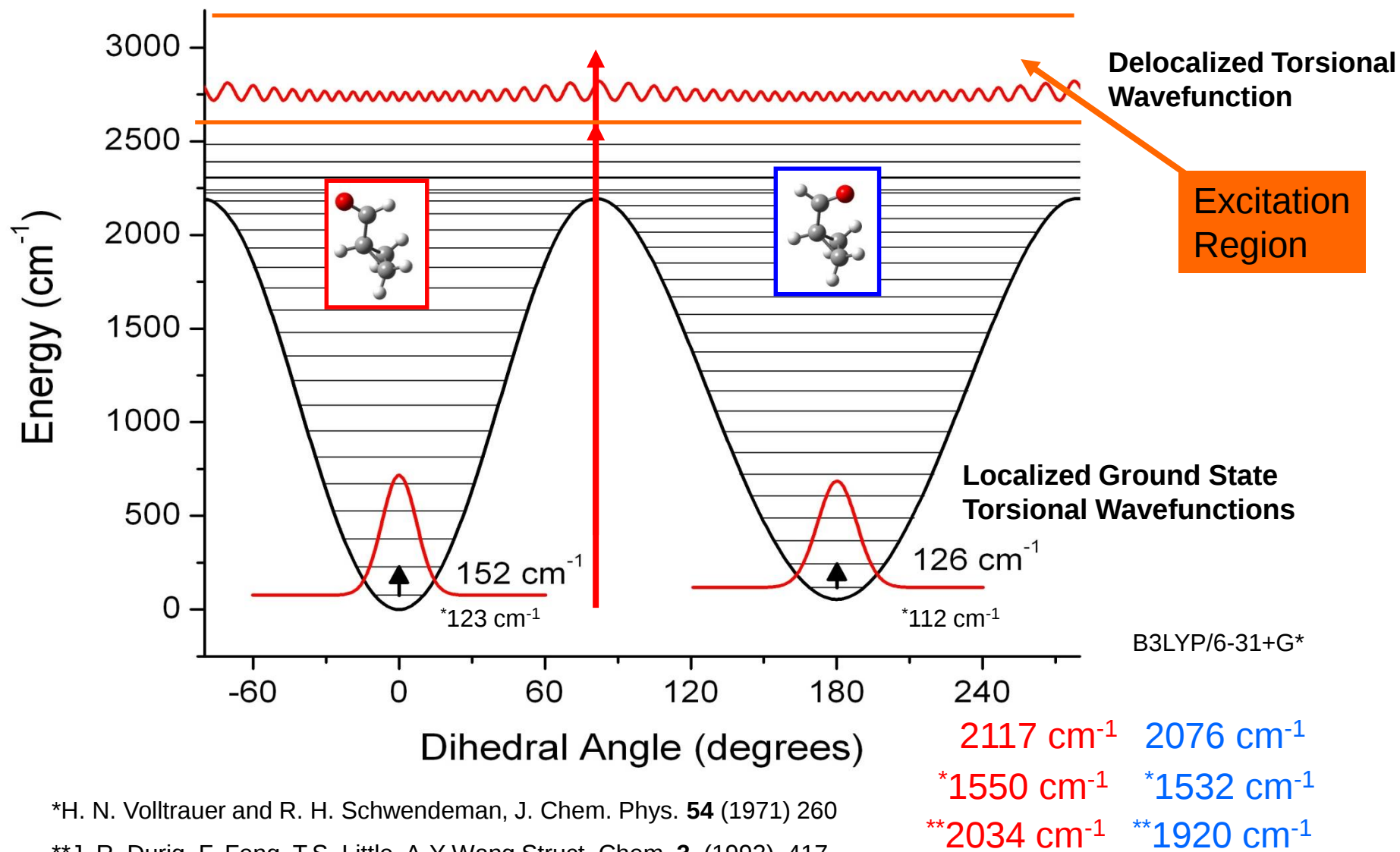


IVR and Isomerization

Measuring Picosecond Isomerization Kinetics via Broadband Microwave Spectroscopy

Brian C. Dian,* Gordon G. Brown, Kevin O. Douglass, Brooks H. Pate†

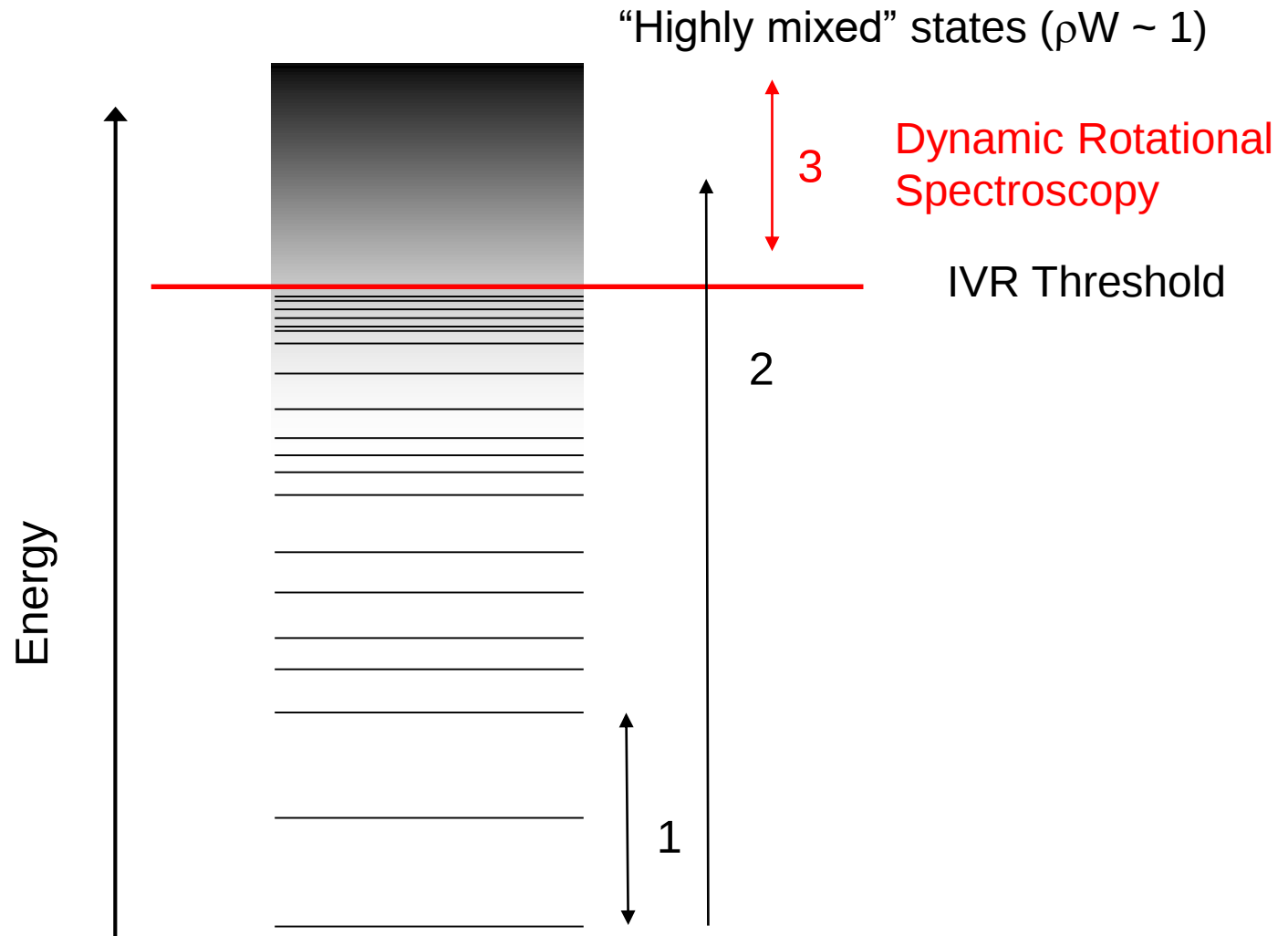
16 MAY 2008 VOL 320 SCIENCE www.sciencemag.org



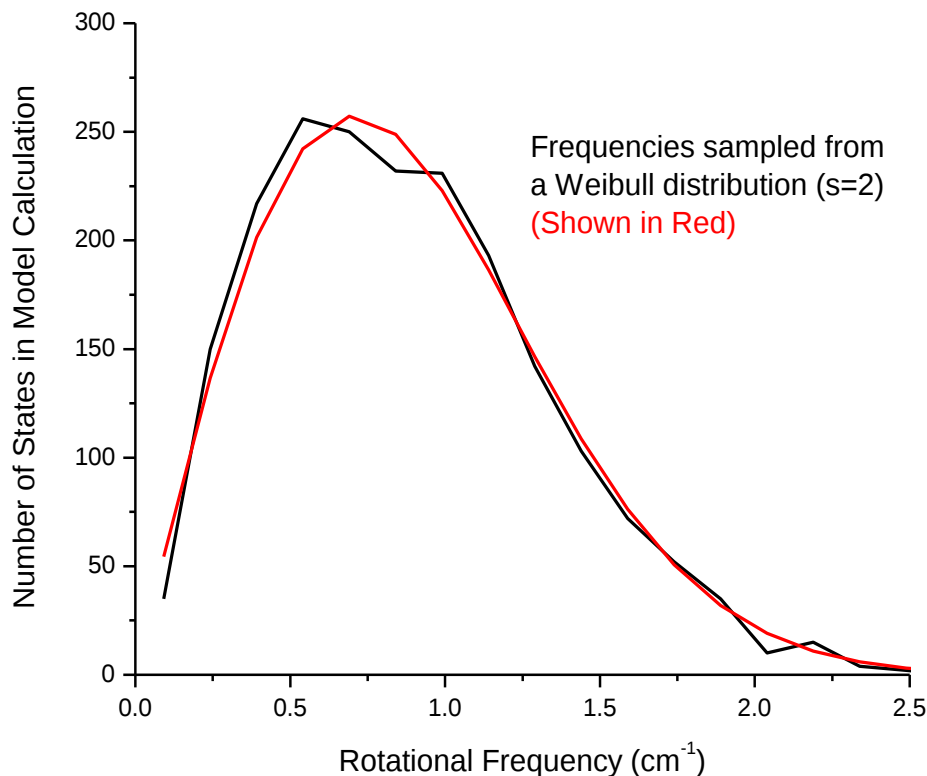
*H. N. Volltrauer and R. H. Schwendeman, J. Chem. Phys. **54** (1971) 260

J. R. Durig, F. Feng, T.S. Little, A-Y Wang Struct. Chem. **3, (1992) 417.

Types of Molecular Spectroscopy



Model Calculation for Dynamic Rotational Spectroscopy: IVR Exchange Narrowing

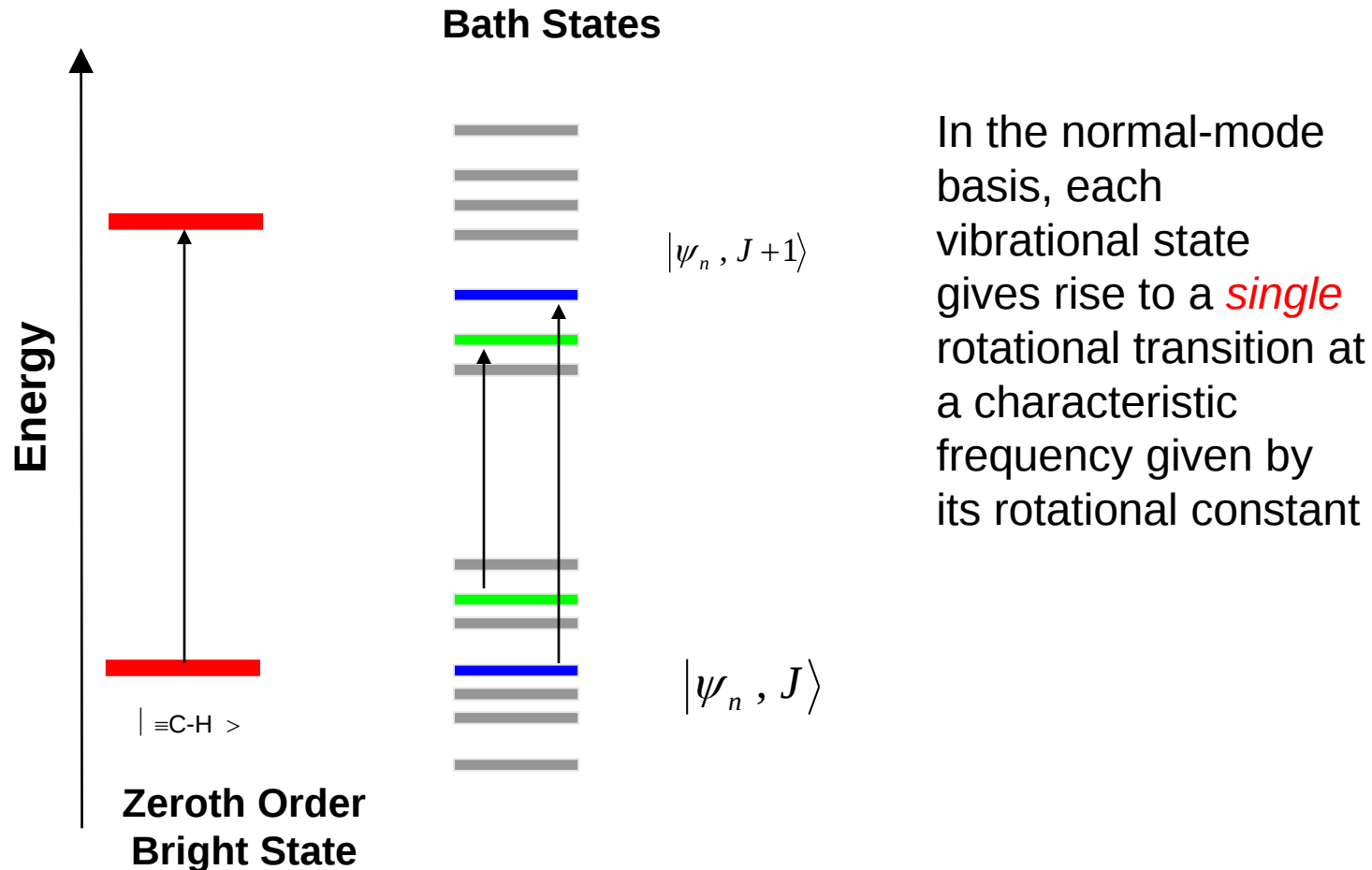


Model Includes:

- 1) Set of 2000 normal-mode vibrational states
- 2) The rotational frequencies for each normal mode vibrational state are sampled from an asymmetric distribution
- 3) The vibrational states are coupled by anharmonic interactions with a variable IVR rate.

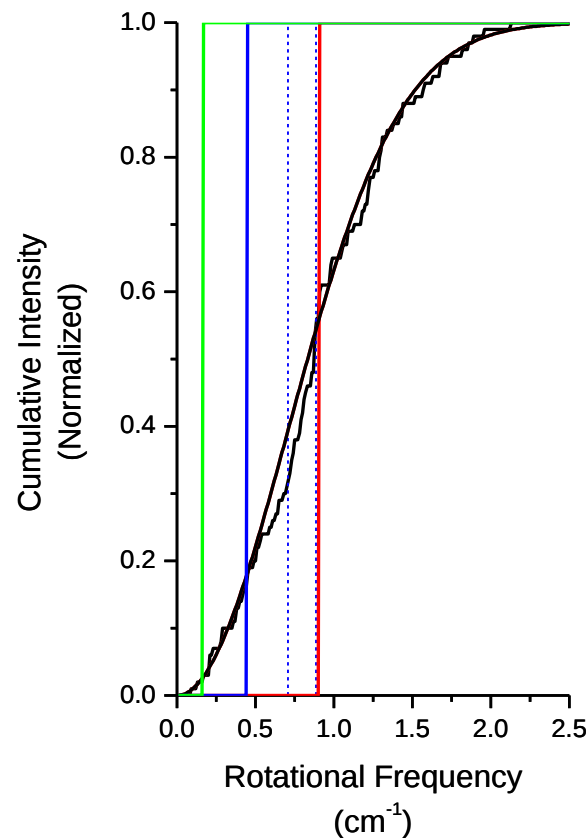
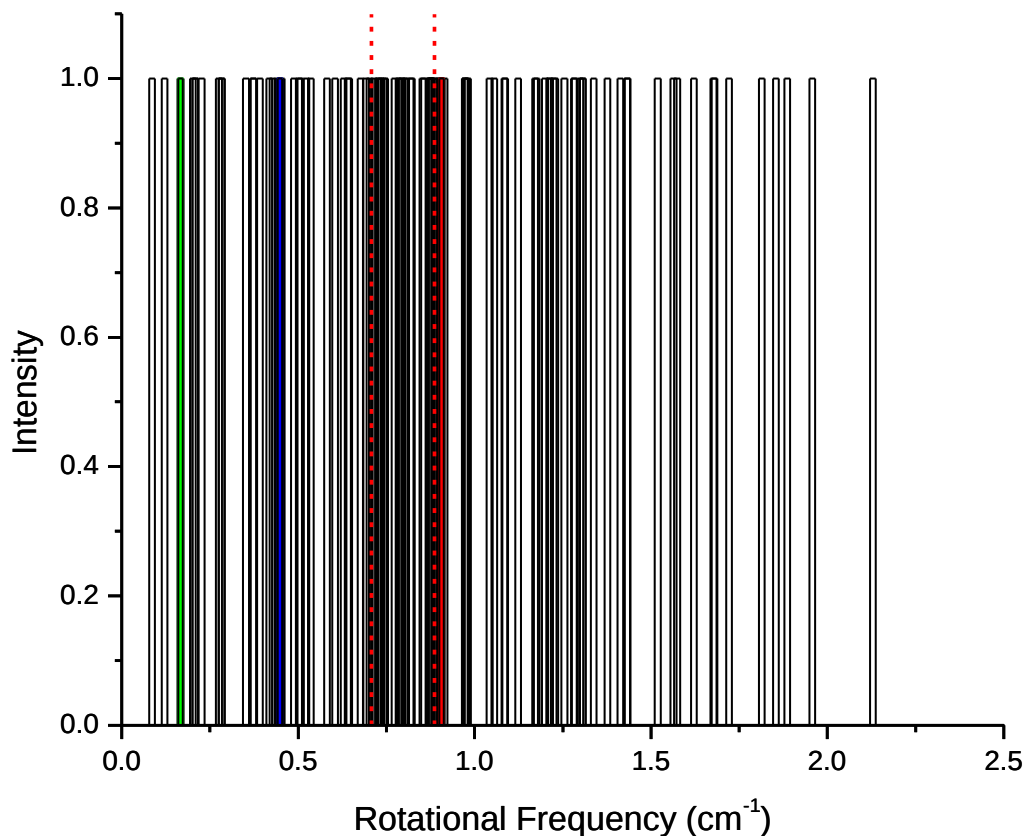
$$B_{\bar{v}} = B_e - \sum_{v=1}^{3N-6} \alpha_v \left(v + \frac{1}{2} \right)$$

Dynamic Rotational Spectroscopy



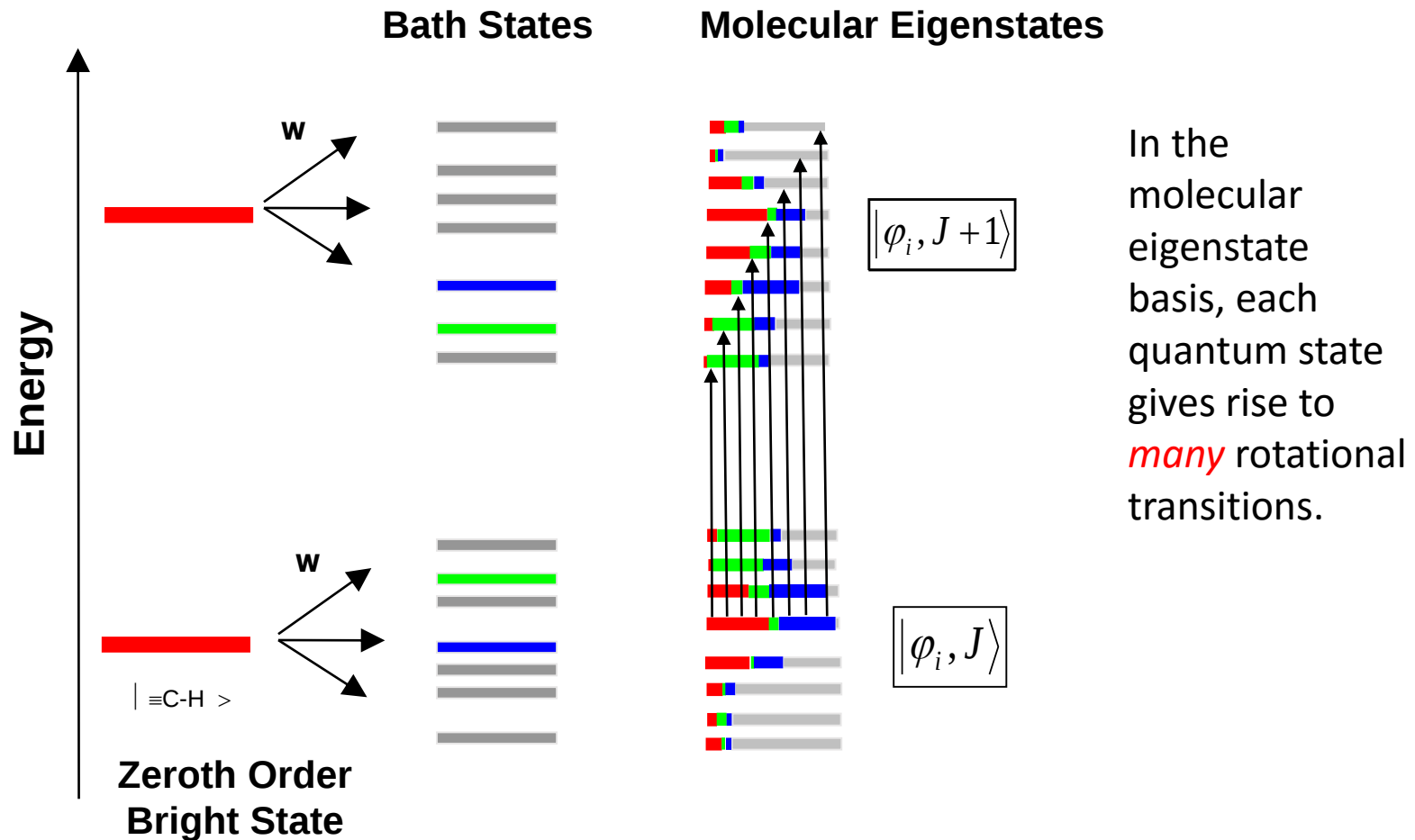
Initial Distribution of Uncoupled Normal-Mode Vibrational States

$$\rho W_{\text{rms}} = 0 \quad \tau_{\text{IVR}} = 0$$



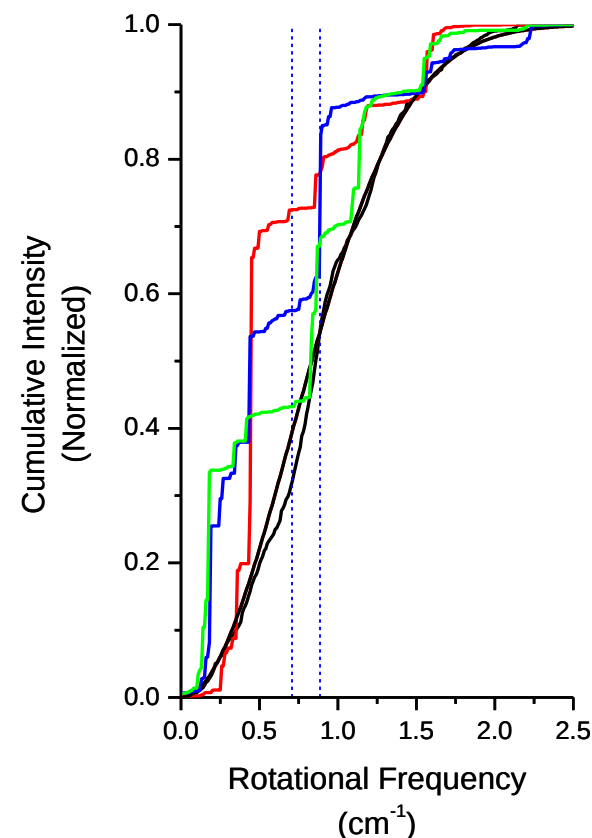
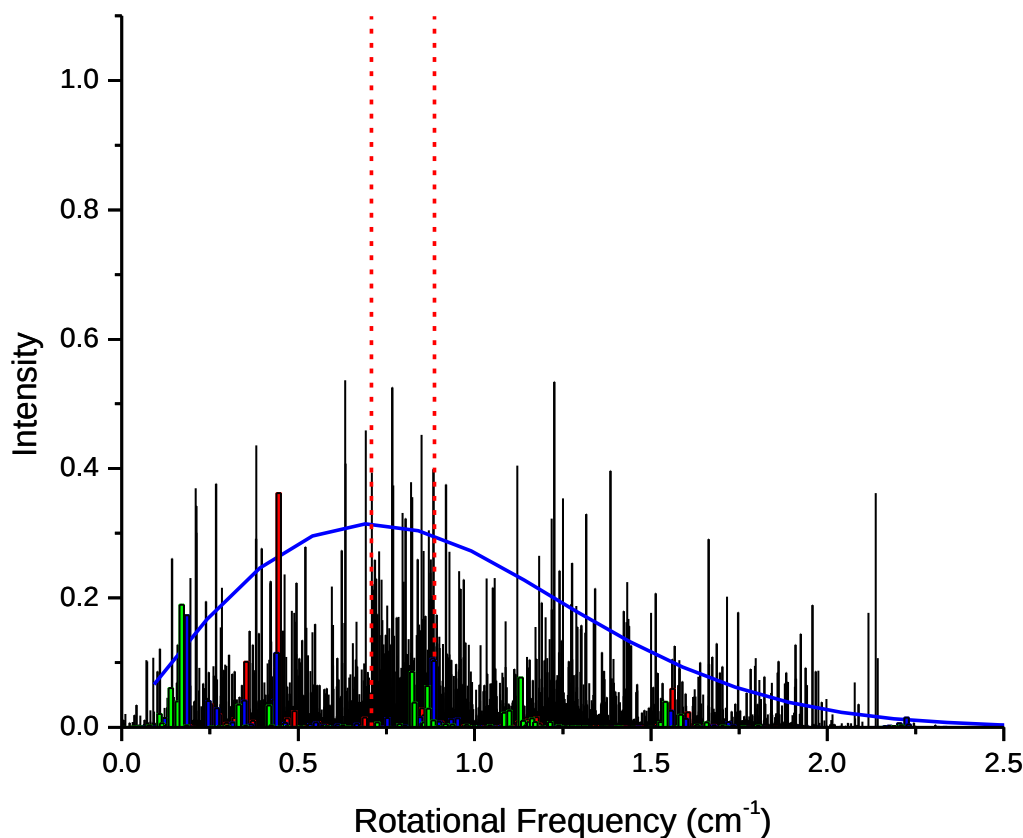
“Assignable” by traditional methods: Vibrational and Rotational Quantum Numbers

Dynamic Rotational Spectroscopy



Limited Vibrational State Mixing

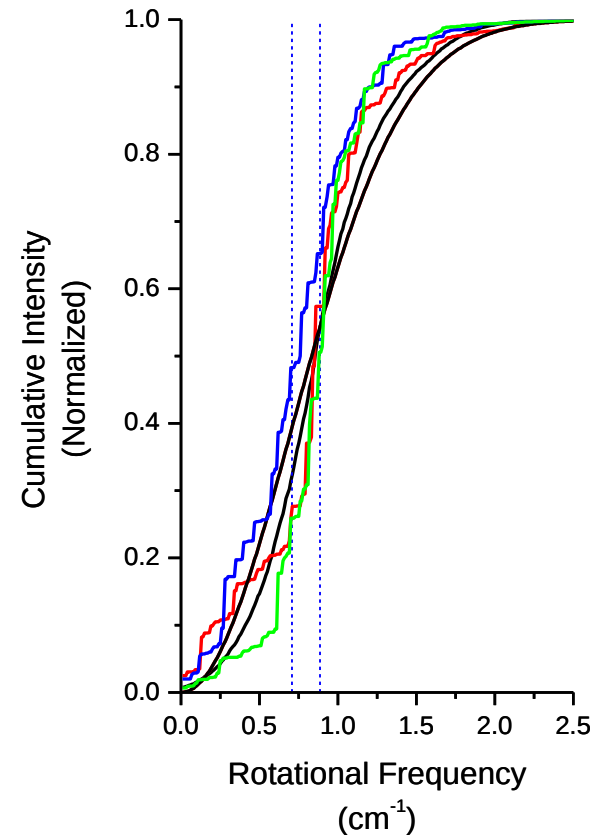
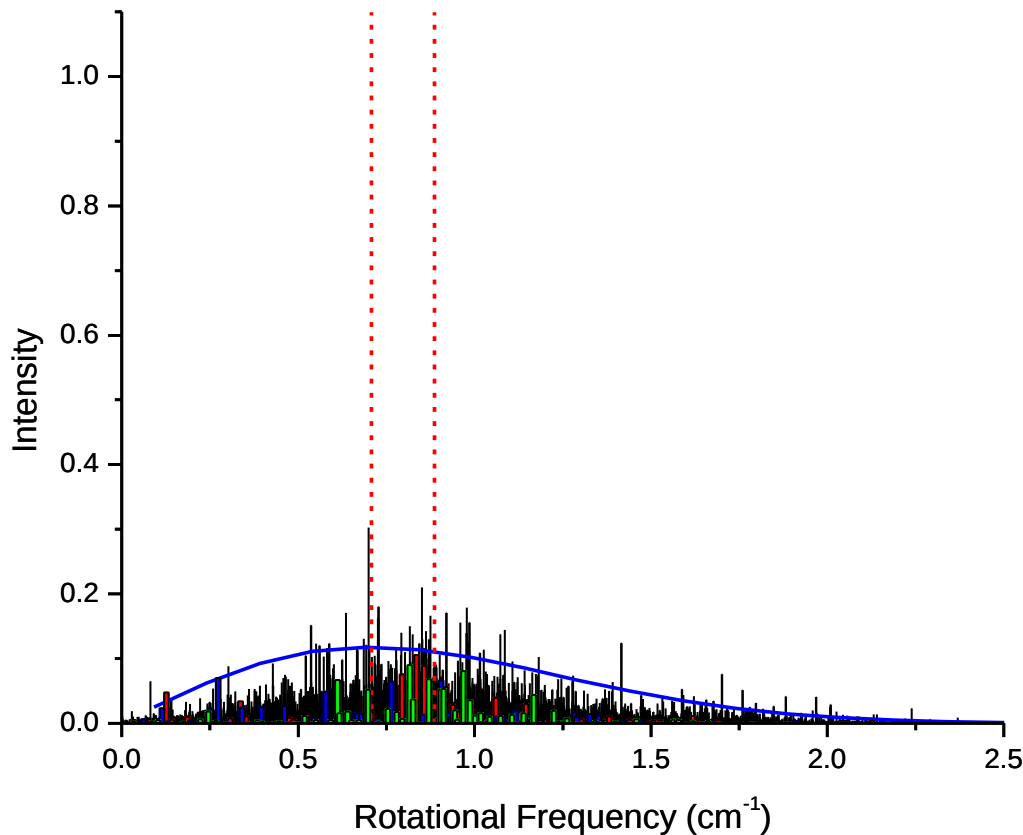
$$\rho W_{\text{rms}} = 0.53 \quad \tau_{\text{IVR}} = 200 \text{ ps}$$



Normal Mode Ensemble Properties Transferred to Each Molecular Eigenstate
No traditional “assignment” (highly vibrationally mixed): J remains a good QN

Extensive State Mixing with Limited IVR Exchange Narrowing

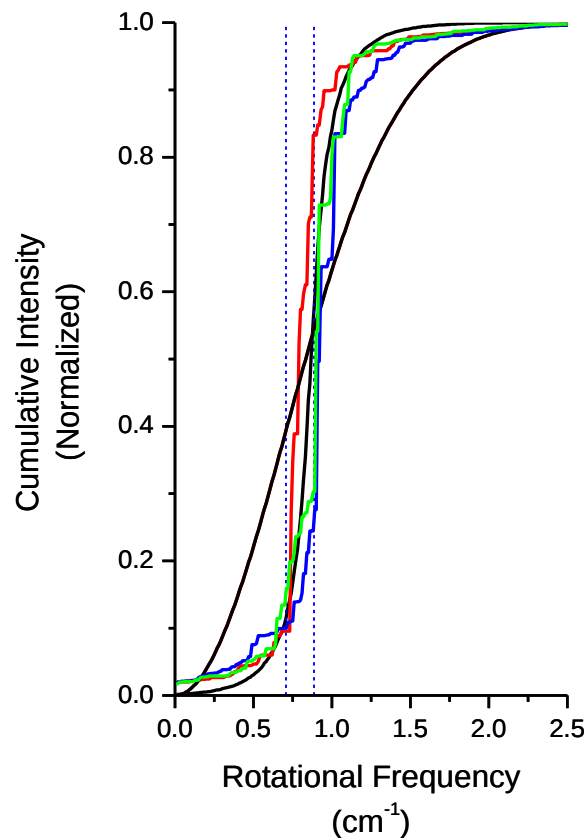
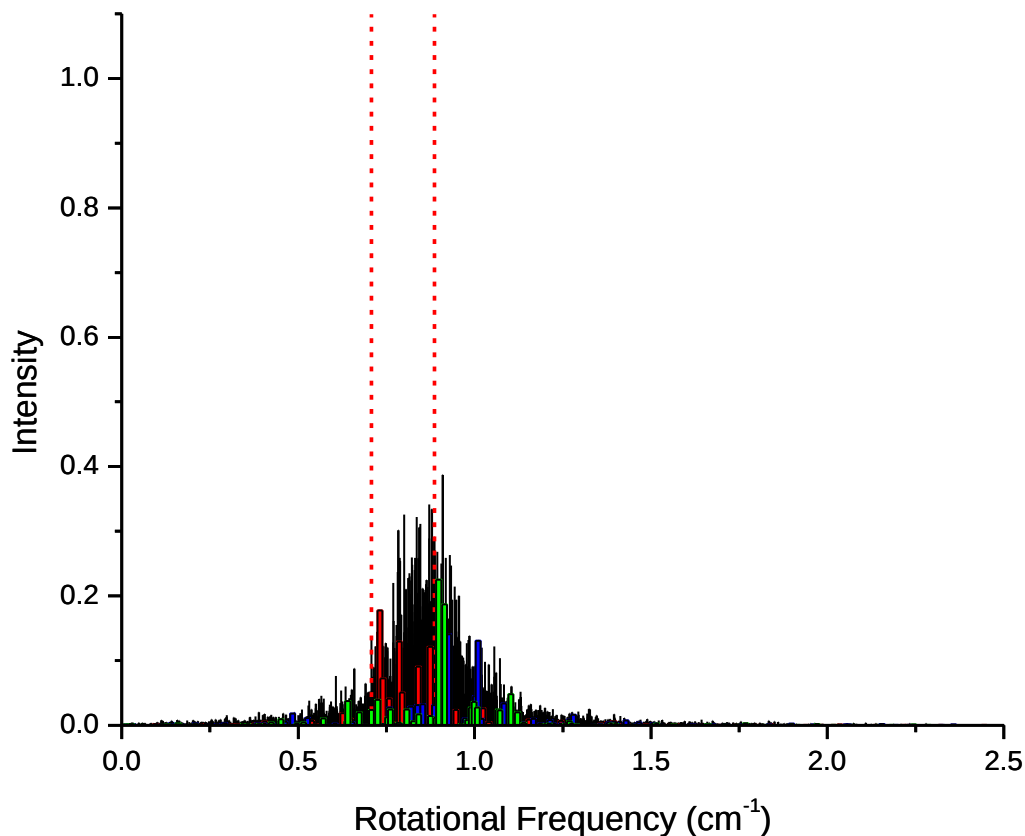
$$\rho W_{\text{rms}} = 1.69 \quad \tau_{\text{IVR}} = 20 \text{ ps}$$



Eigenstate-to-Eigenstate Transition Strength Decreases: Fragmentation
Total Intensity of Each Eigenstates Rotational Spectrum is Conserved

Onset of IVR Exchange Narrowing

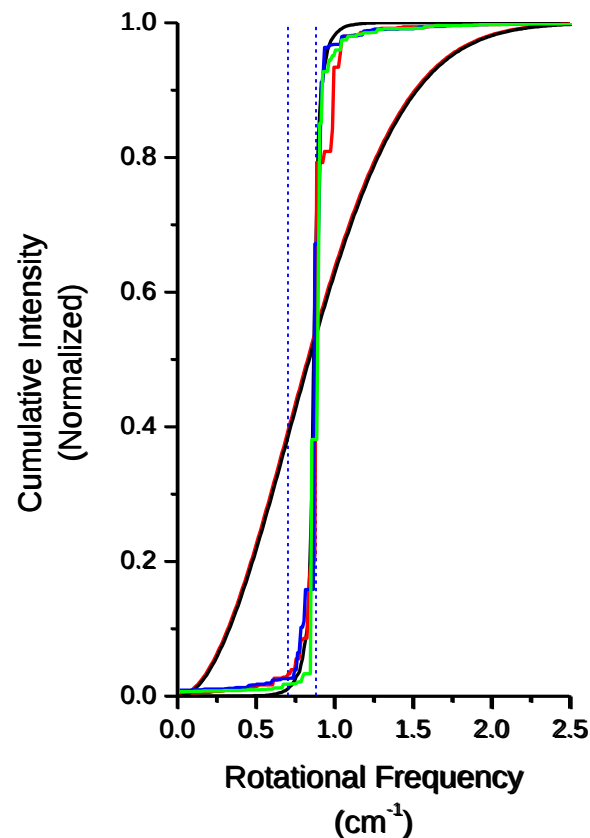
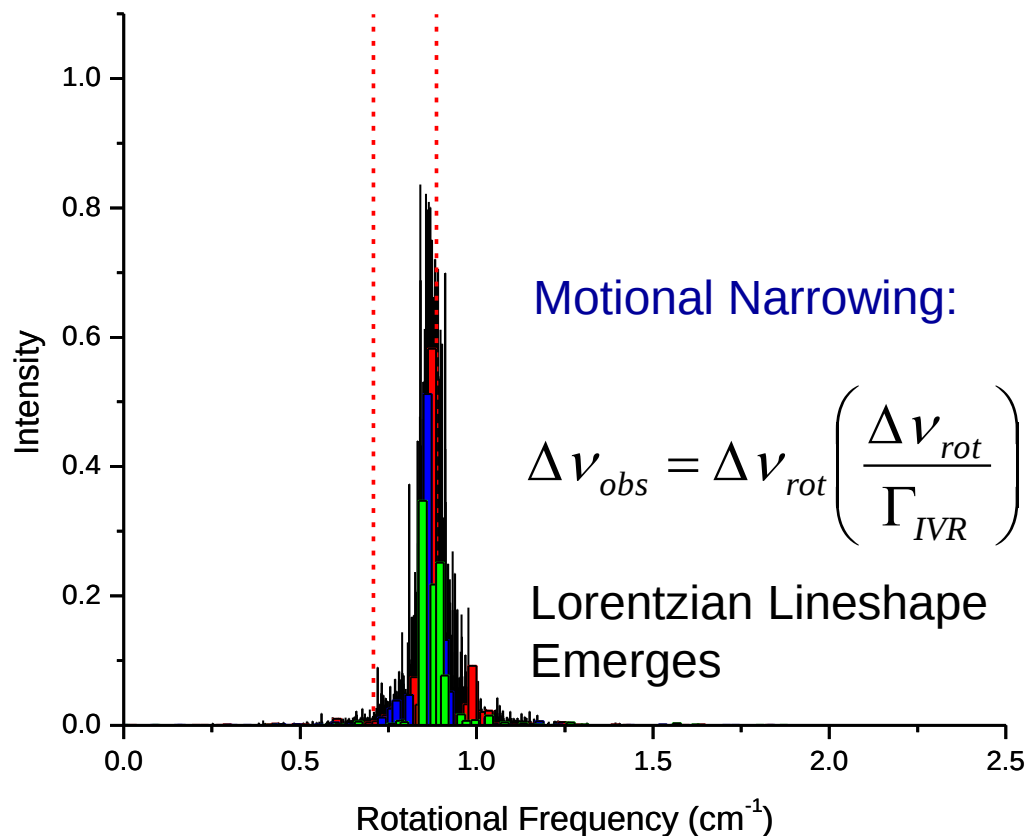
$$\rho W_{\text{rms}} = 5.3 \quad \tau_{\text{IVR}} = 2.0 \text{ ps}$$



Dynamics information encoded in the overall rotational line shape.
The spectrum is composed of discrete transitions because the quantum system is bound.

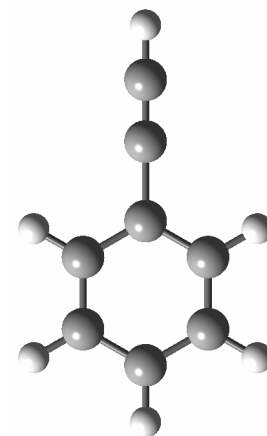
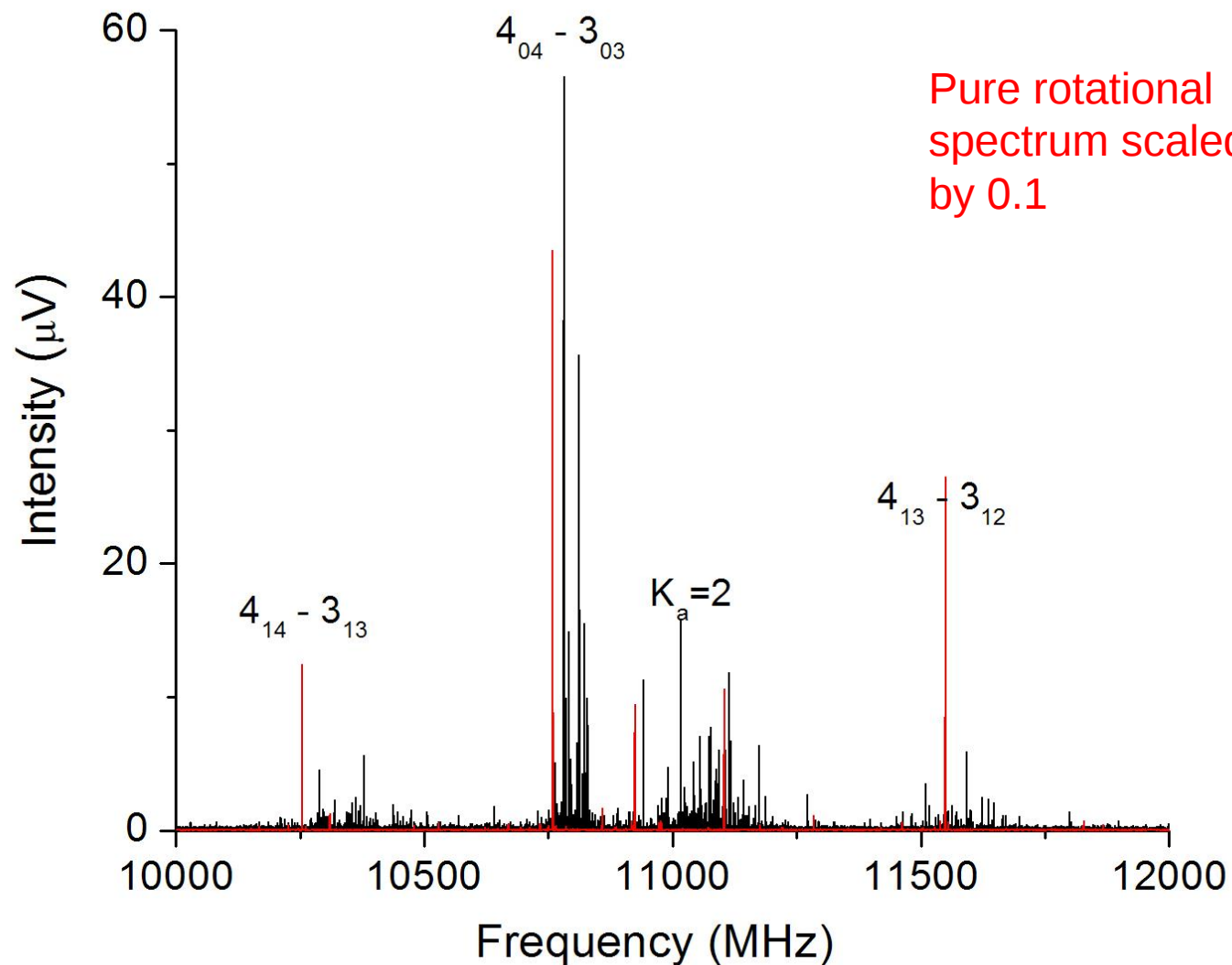
Extreme IVR Exchange Narrowing

$$\rho W_{\text{rms}} = 16.7 \quad \tau_{\text{IVR}} = 0.2 \text{ ps}$$



“High Resolution” Spectrum in the Presence of Fast IVR Dynamics

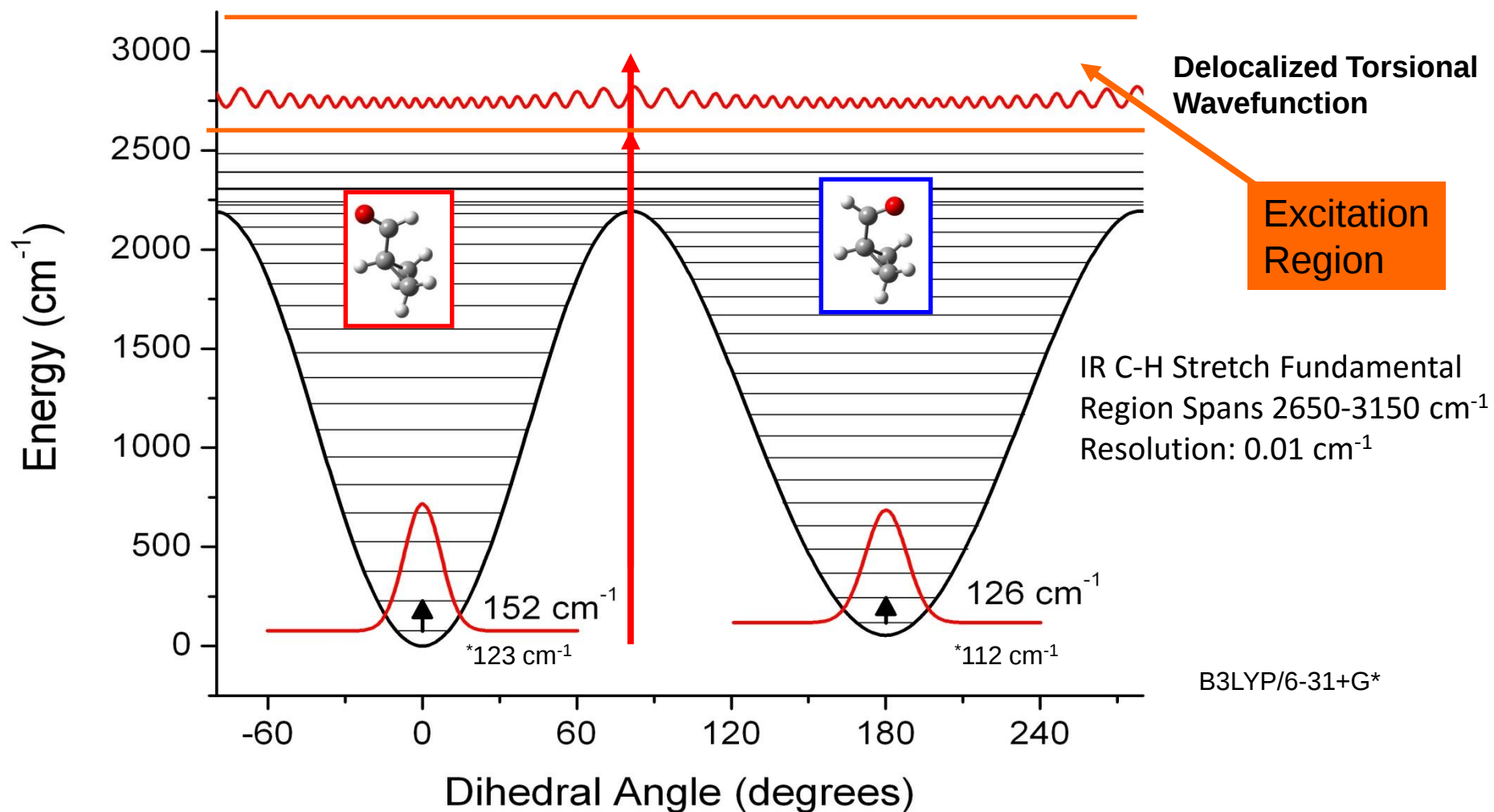
DRS for Phenylacetylene



Laser Pumps
R(3) at 3324 cm^{-1}

All asymmetric
top rotational
levels

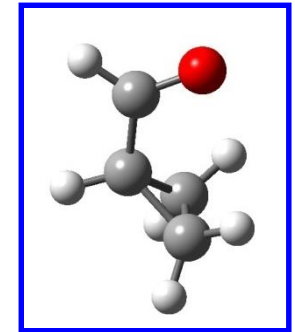
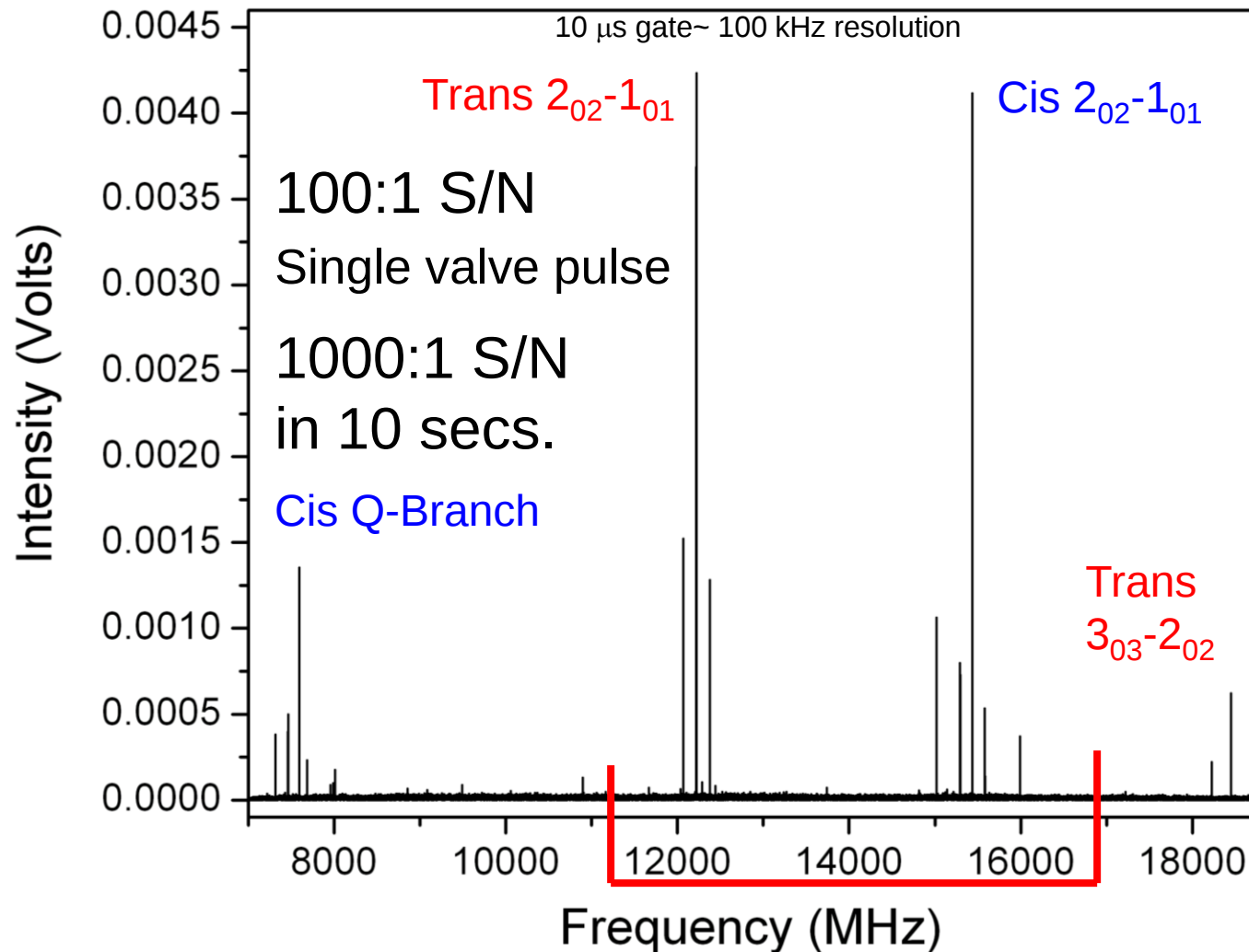
Unimolecular Conformational Isomerization of Cyclopropane Carboxaldehyde



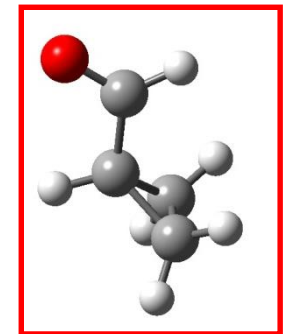
*H. N. Volltrauer and R. H. Schwendeman, J. Chem. Phys. **54** (1971) 260

J. R. Durig, F. Feng, T.S. Little, A-Y Wang Struct. Chem. **3, (1992) 417.

Ground State Rotational Spectrum of Cyclopropane Carboxaldehyde

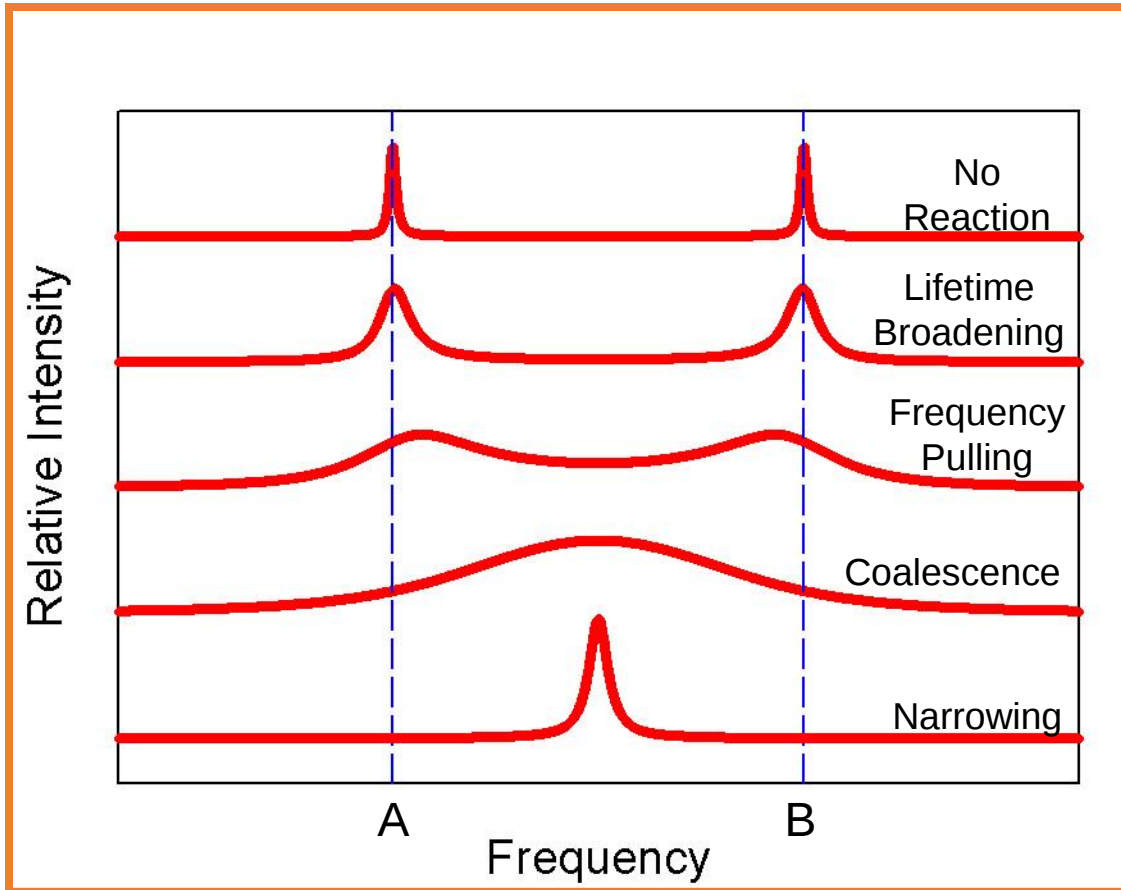


Cis



Trans

Coalescence Phenomenon in Dynamic Rotational Spectroscopy

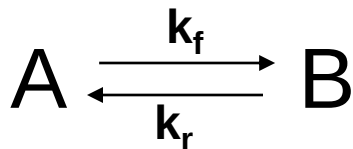


Increasing
Reaction Rate

$$k_{\text{coal}} \sim 2.2 \times \text{frequency splitting } (\delta\nu)$$

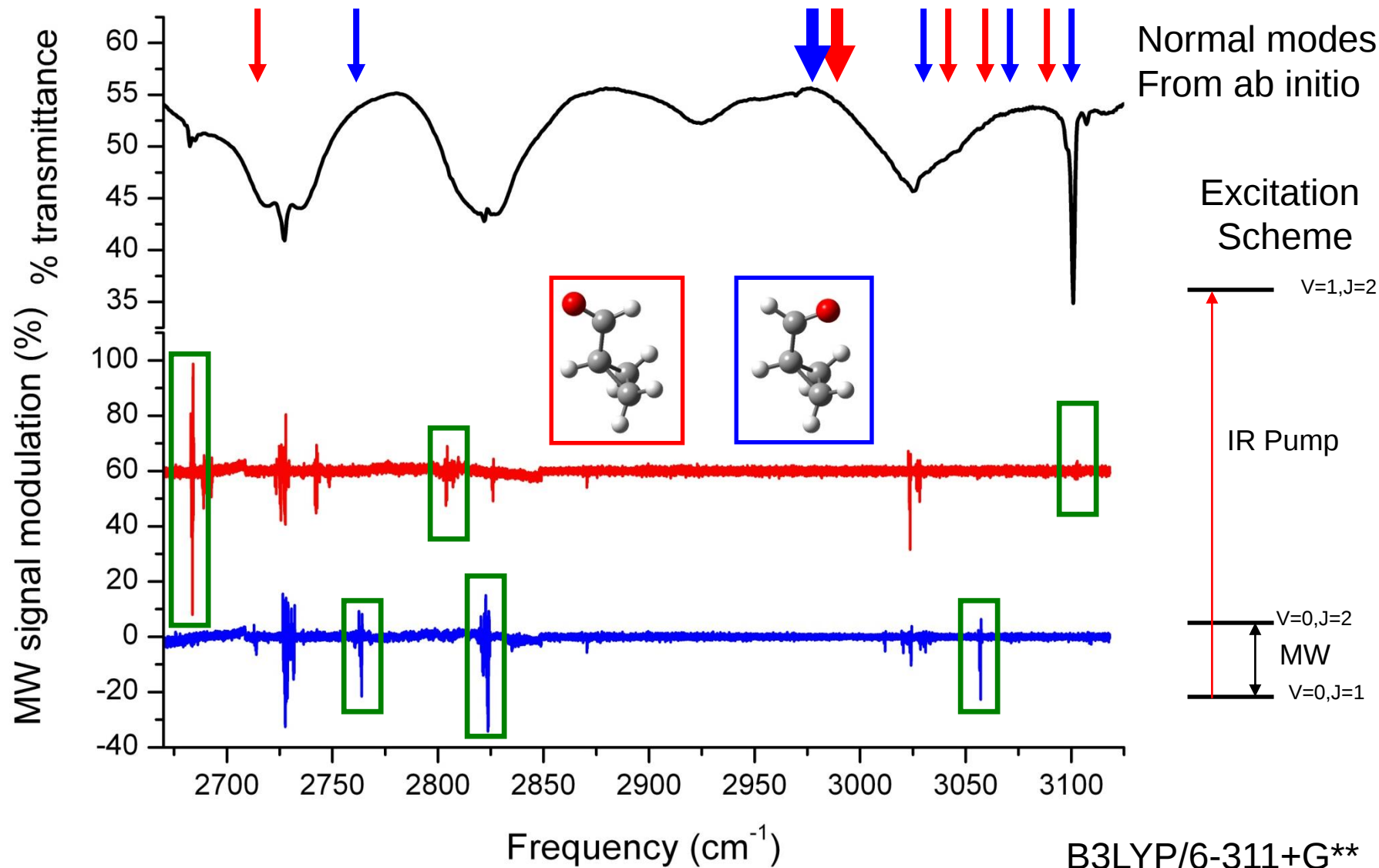
NMR: $\delta\nu \sim 1 \text{ kHz}$
 $\tau_{\text{isom}} \sim 10^{-3} \text{ s}$

MW: $\delta\nu \sim 1 \text{ GHz}$
 $\tau_{\text{isom}} \sim 10^{-9} \text{ s}$



Ground State Depletion Spectrum

45,000 Rotational Spectra (72 years!)



Conformational Isomerization Rates Measured by Dynamic Rotational Spectroscopy

Lineshape Analysis Results

Product Yields

$$P_{\text{trans}} = 42 \%$$

$$P_{\text{cis}} = 58 \%$$

Reaction Rates

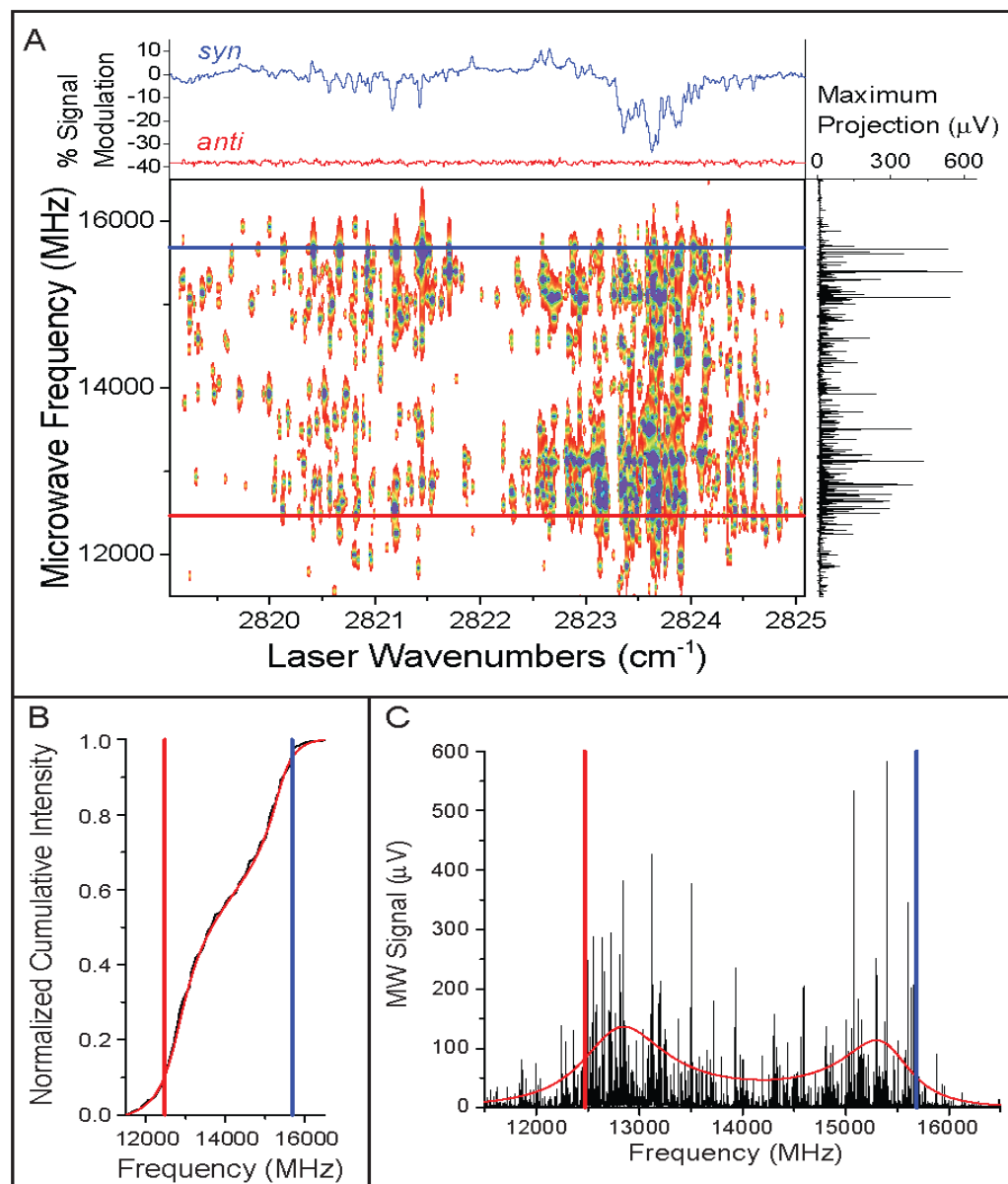
$$k_{\text{trans-cis}} = 3.08(16) \times 10^9 \text{ s}^{-1}$$

$$k_{\text{cis-trans}} = 2.52(19) \times 10^9 \text{ s}^{-1}$$

$$k_{\text{tot}} = 5.60(35) \times 10^9 \text{ s}^{-1}$$

$$\tau_{\text{isom}} = 180 \text{ ps}$$

$$\tau_{\text{RRKM}} = 11 \text{ ps}$$



Fourier Transform Rotational Spectroscopy

Fabry-Perot cavity pulsed Fourier transform microwave spectrometer with a pulsed nozzle particle source

T. J. Balle and W. H. Flygare

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 28 July 1980; accepted for publication 12 September 1980)

[Review of Scientific Instruments](#) **52**, 33 (1981)

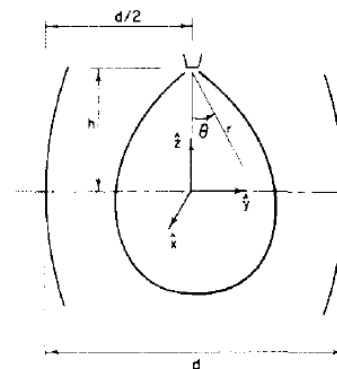


FIG. 1. Geometry and coordinate system used for the gas nozzle and Fabry-Perot cavity. The density of the gas expansion is parameterized as $(\cos^p \theta)/r^2$. The microwave radiation travels along the y axis, perpendicular to the nozzle axis.

Fast passage in rotational spectroscopy: Theory and experiment

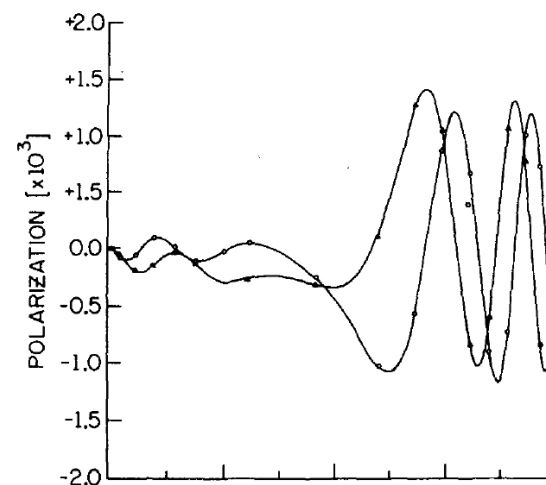
J. C. McGurk, T. G. Schmalz, and W. H. Flygare

Noyes Chemical Laboratory and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

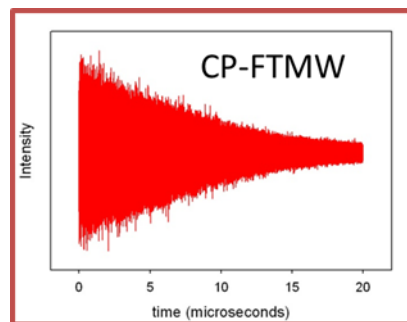
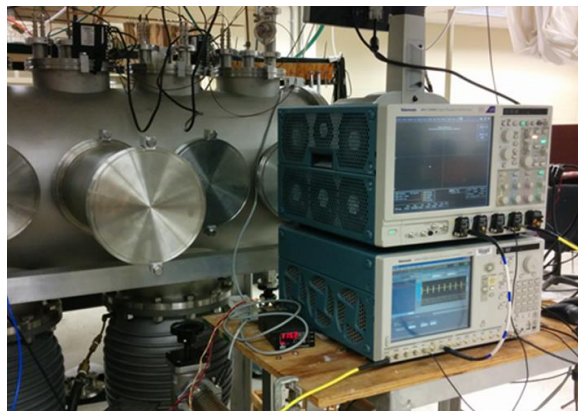
(Received 21 January 1974)

[The Journal of Chemical Physics](#) **60**, 4181 (1974)

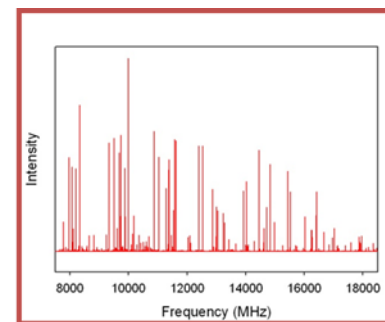
An important result of these studies is the surprisingly strong polarization achieved by fast passage. This has important consequences in applying Fourier transform techniques in microwave spectroscopy. According to the development summarized in Eq. (56), near equal polarization is achieved over a much larger band of frequencies using the fast passage method as compared to the $\pi/2$ pulse technique.



Low Frequency (2-8 GHz) Chirped-Pulse Fourier Transform Microwave Spectrometer



Free Induction Decay (FID)

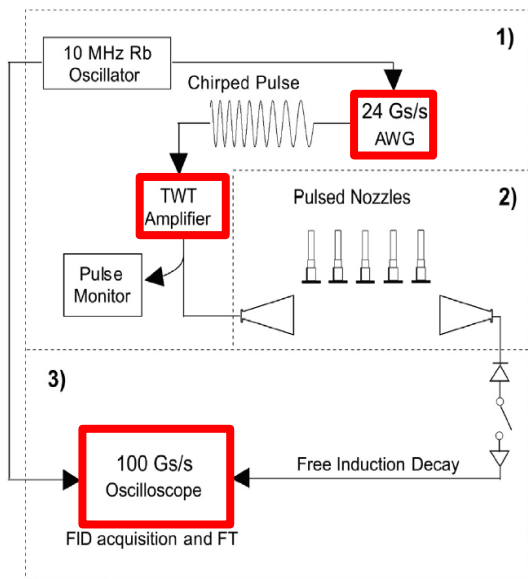


Fourier Transform

General Spectral Properties:

Measurement Bandwidth:	6000 MHz
FWHM Resolution:	60 kHz (10^5 data channels)
Transitions in a Spectrum:	20-200 (0.02-0.2% of range)
RMS Frequency Error in Fit:	6-10 kHz (~10% of FWHM)
Hamiltonian:	Watson Distortable Rotor (8 parameters)

“Simple rules, not simple patterns” – Automated Spectral Fitting



C. Perez, S. Lobsiger, N. A. Seifert, D. P. Zaleski, B. Temelso, G.C. Shields, Z. Kisiel, B. H. Pate, Chem. Phys. Lett. **571**, 1 (2013).

N.A. Seifert et al., “Autofit, an Automated Fitting Tool for Broadband Rotational Spectra, and Applications to 1-Hexanal”, J. Mol. Spectrosc. 312, 13-21 (2015).

When is Chirped Pulse Fourier Transform Spectroscopy Advantageous ?

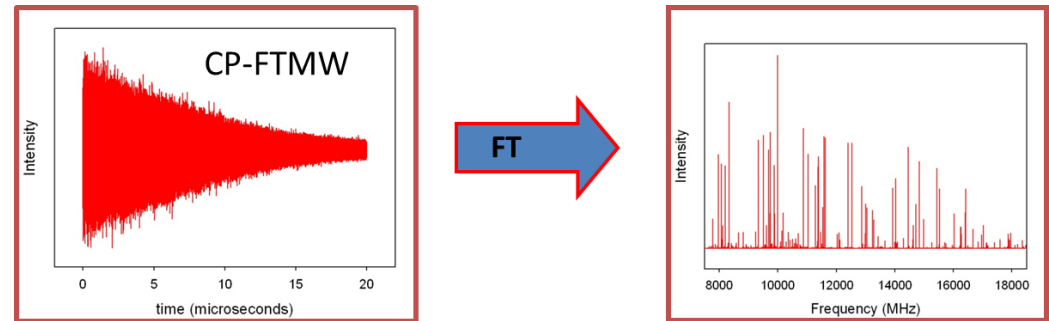
- 1) The spectrum is high-resolution

$$(1/T_2 \ll \text{Freq Range})$$

- 2) The available power is much higher than the power required for saturation

$$(P \gg P_{\text{sat}})$$

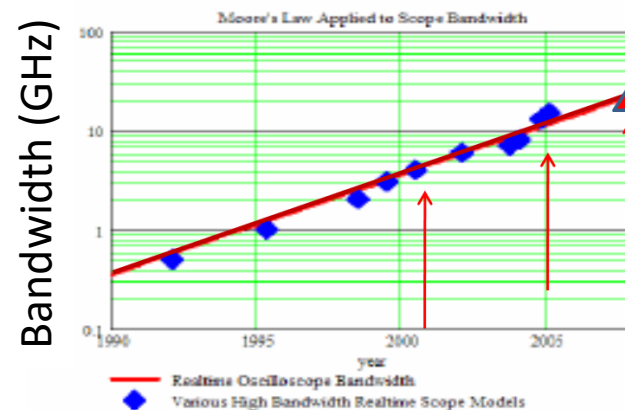
- 3) High-speed digital electronics are available



Free Induction Decay
(FID)

Fourier Transform

Moore's Law Applied to Scope Bandwidth



Agilent
160 Gs/s
63 GHz Bandwidth
April 2012

LeCroy Technical Brief, March 2005

Current AWG:
92 Gs/s, 36 GHz

Molecular Structure from Isotopic Substitution

Structure Information through Principal Moments of Inertia: $I = \sum_i M_i R_i^2$

Measure: A, B, C “normal species”
A, B, C singly substituted isotopomer

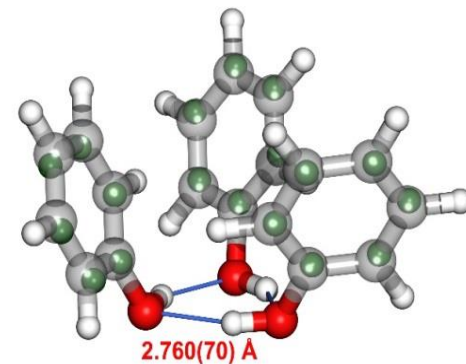
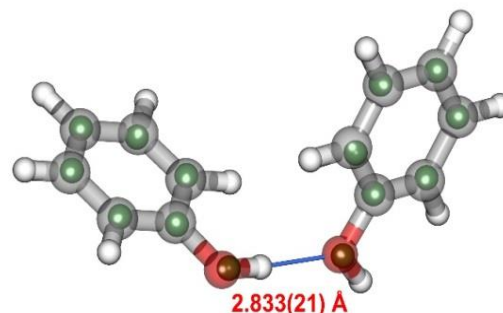


From : $\Delta I_a, \Delta I_b, \Delta I_c$
Obtain: $(|R_a|, |R_b|, |R_c|)$

J. Kraitchman, Am. J. Phys. 21, 17 (1953).

Kraitchman Analysis

- 1) Build up the molecular structure “atom-by-atom”
- 2) No model assumptions required (but guidance on sign is helpful)
- 3) A single answer for a single data set
- 4) Other methods for refinement

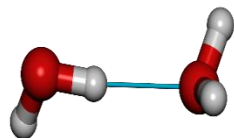


*Structures of Phenol Dimer and Trimer from
Isotopes in Natural Abundance*

Phys.Chem.Chem.Phys., 2013, 15, 11468
Alberto Lesarri, Valladolid

Rotationally Resolved Studies of Water Clusters

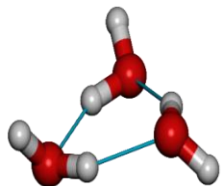
Microwave Spectroscopy



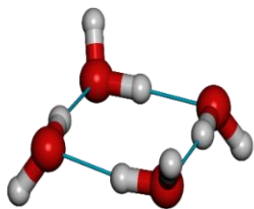
Dimer

Dyke, T. R., Muentert, J. S., *J. Chem. Phys.* **1974** 2929.

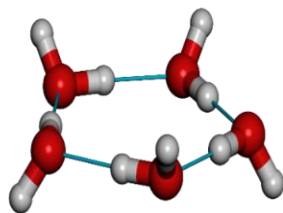
THz Spectroscopy



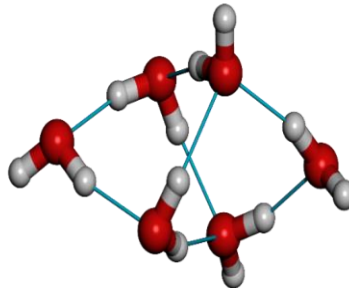
Trimer



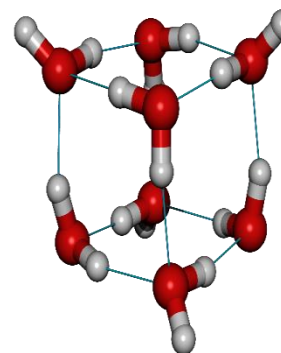
Tetramer



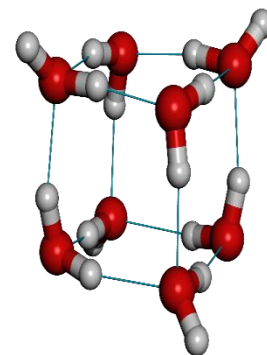
Pentamer



Hexamer "Cage"



Octamer D_{2d}



Octamer S_4

Liu, K.; Brown, et al. *Nature* **1996**, 381, 501.

N. Pugliano and R. J. Saykally, *Science* **1992** 257 1937.

Liu, K.; Brown, M.G.; Cruzan, J.D.; Saykally, R.J. *Science* **1996**, 271, 62.

K. Liu, J. D. Cruzan, R. J. Saykally, *Science* **1996** 271 929.

Cruzan, J.D..et al *Science* **1996**, 271 59.

Richardson, J. O. et al., J. Phys. Chem. A, Article ASAP (2013).

Low Frequency CP-FTMW Spectroscopy: 2-8 GHz

$T_{\text{rot}} < 10\text{K}$



Normal Water Spectrum:

3 Hexamers

2 Heptamers

5 Nonamers

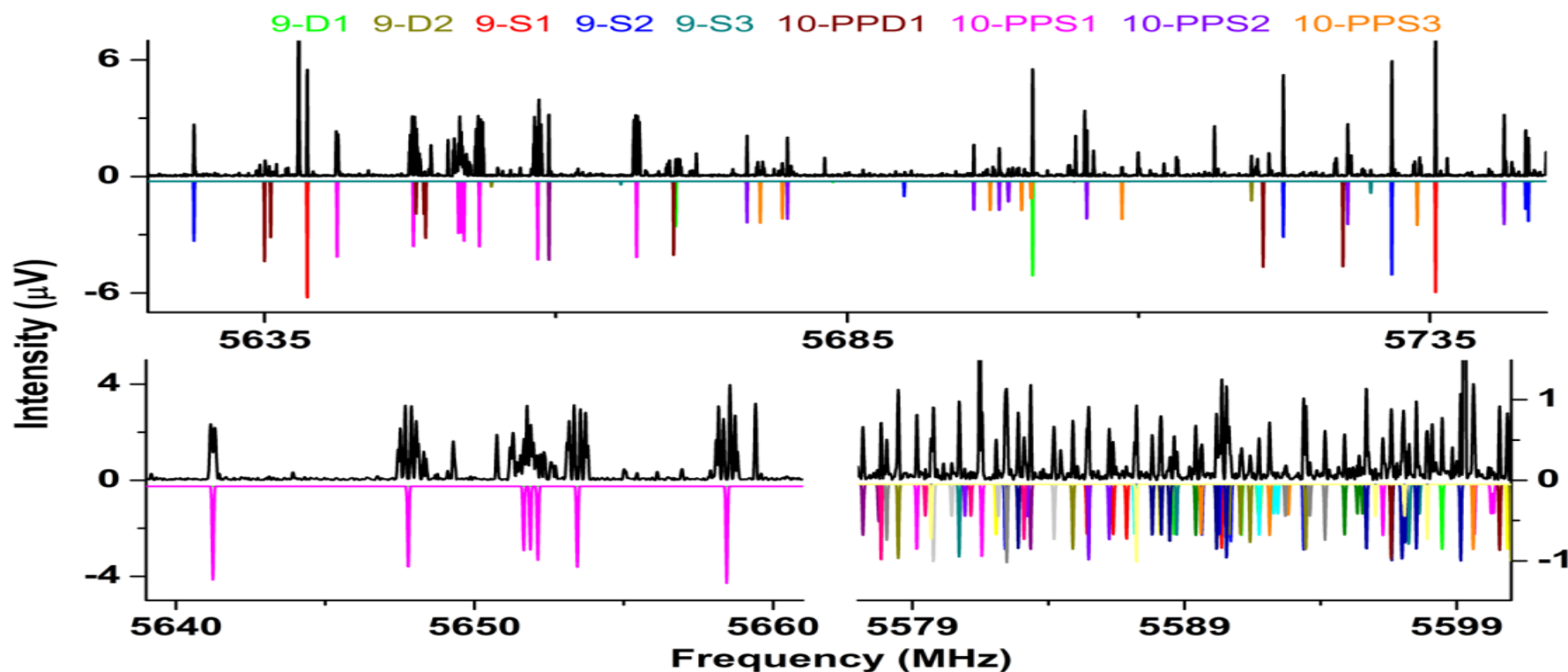
4 Decamers

7 Undecamers

2 Tridecamer

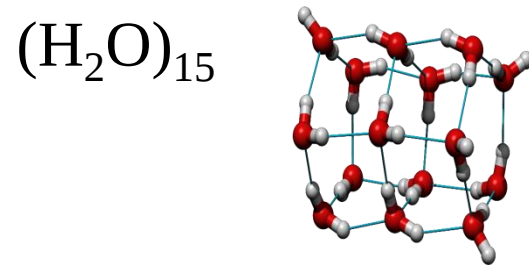
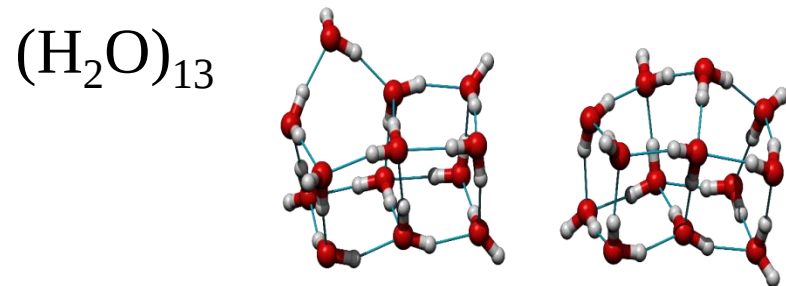
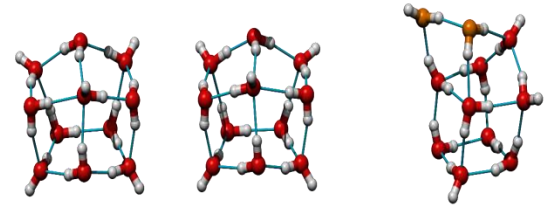
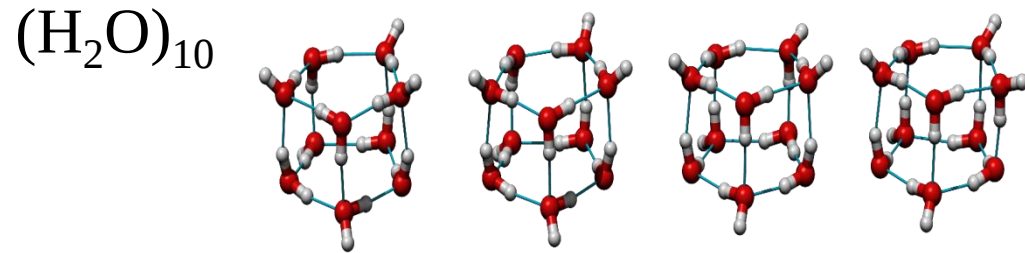
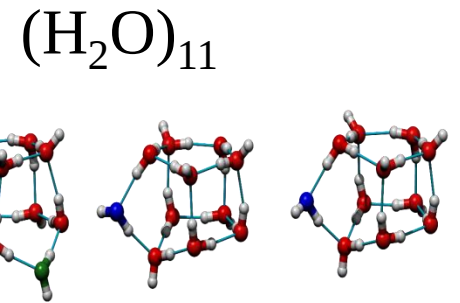
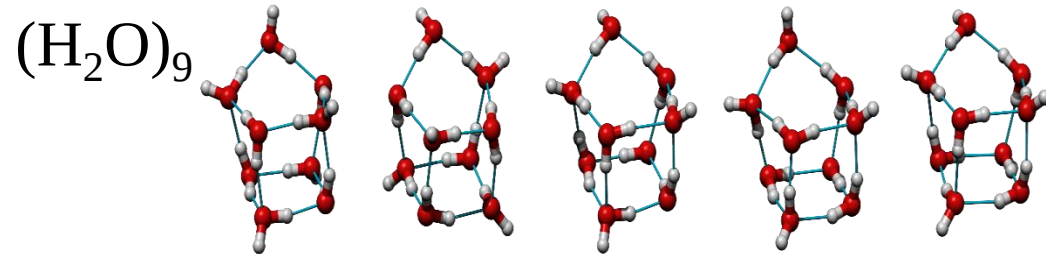
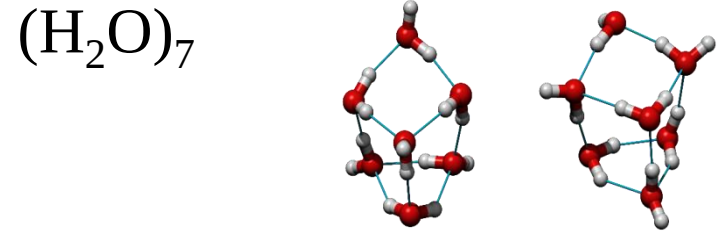
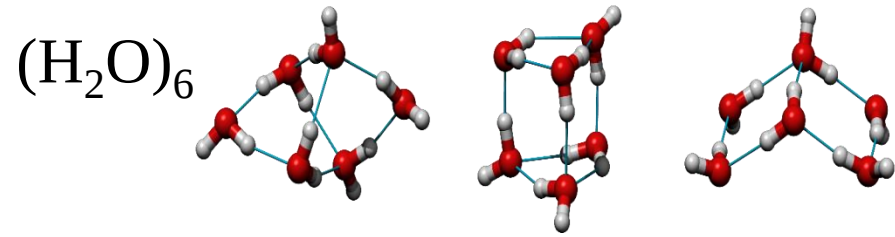
1 Pentadecamer

- 700 transitions (140 MHz of bandwidth)
- 1700 transitions at 3:1 signal-to-noise ratio or higher unassigned



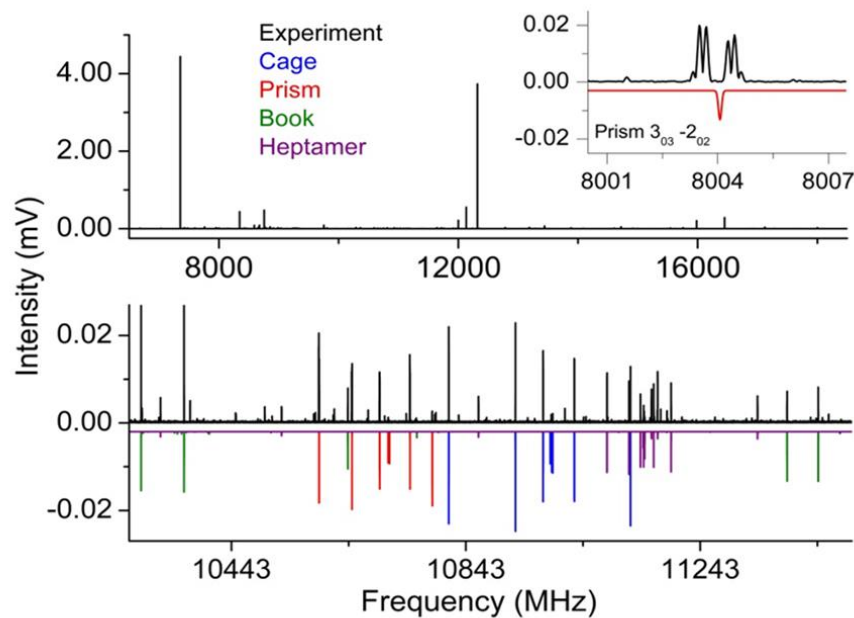
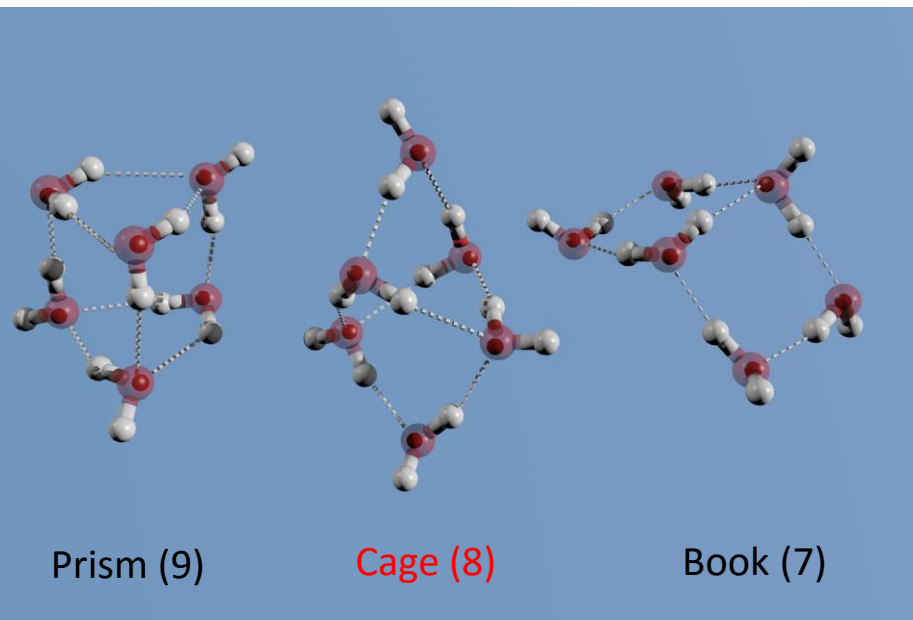
Isotope Spiking: $\sim 15\%$ H_2^{18}O

Water Clusters Identified in a Single Measurement



Isomers of the Water Hexamer

Structure Parameter is O---O Bond Length: Correlates with H-bond strength and O-H stretch frequency



rms O...O bond length differences: ~0.01 Angstro

Structures of Cage, Prism, and Book Isomers of Water Hexamer from Broadband Rotational Spectroscopy

Cristóbal Pérez,¹ Matt T. Muckle,¹ Daniel P. Zaleski,¹ Nathan A. Seifert,¹ Berhane Temelso,² George C. Shields,^{2*} Zbigniew Kisiel,^{3*} Brooks H. Pate^{1*}

Science **336**, 897 (2012)

JCTC
Journal of Chemical Theory and Computation

ARTICLE

pubs.acs.org/JCTC

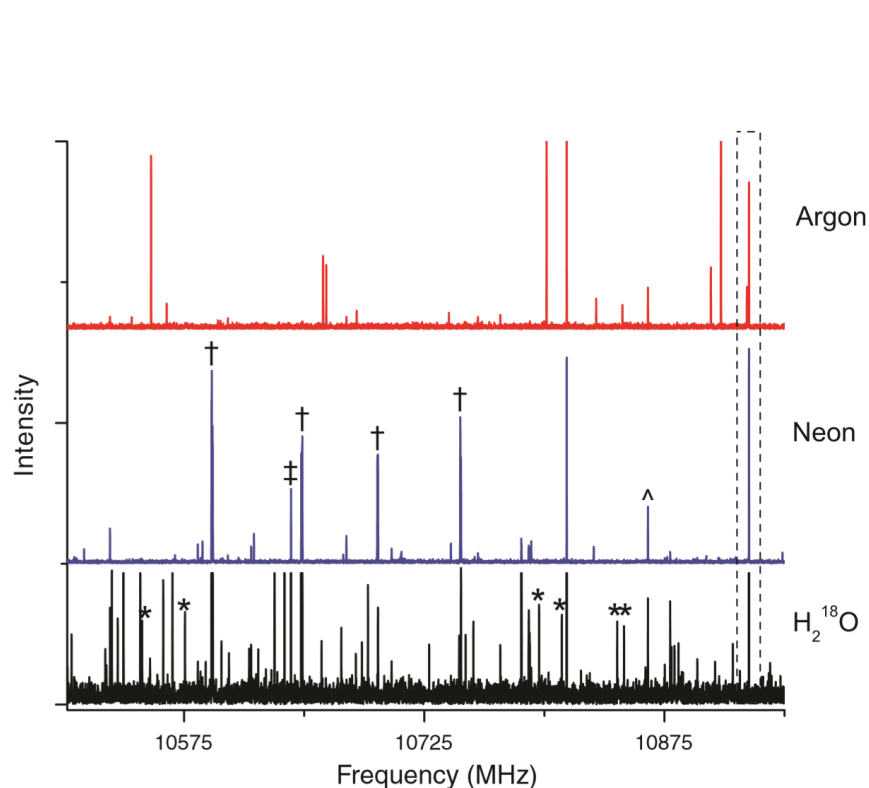
The Role of Anharmonicity in Hydrogen-Bonded Systems: The Case of Water Clusters

Berhane Temelso and George C. Shields*

Dean's Office, College of Arts and Sciences, Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837, United States

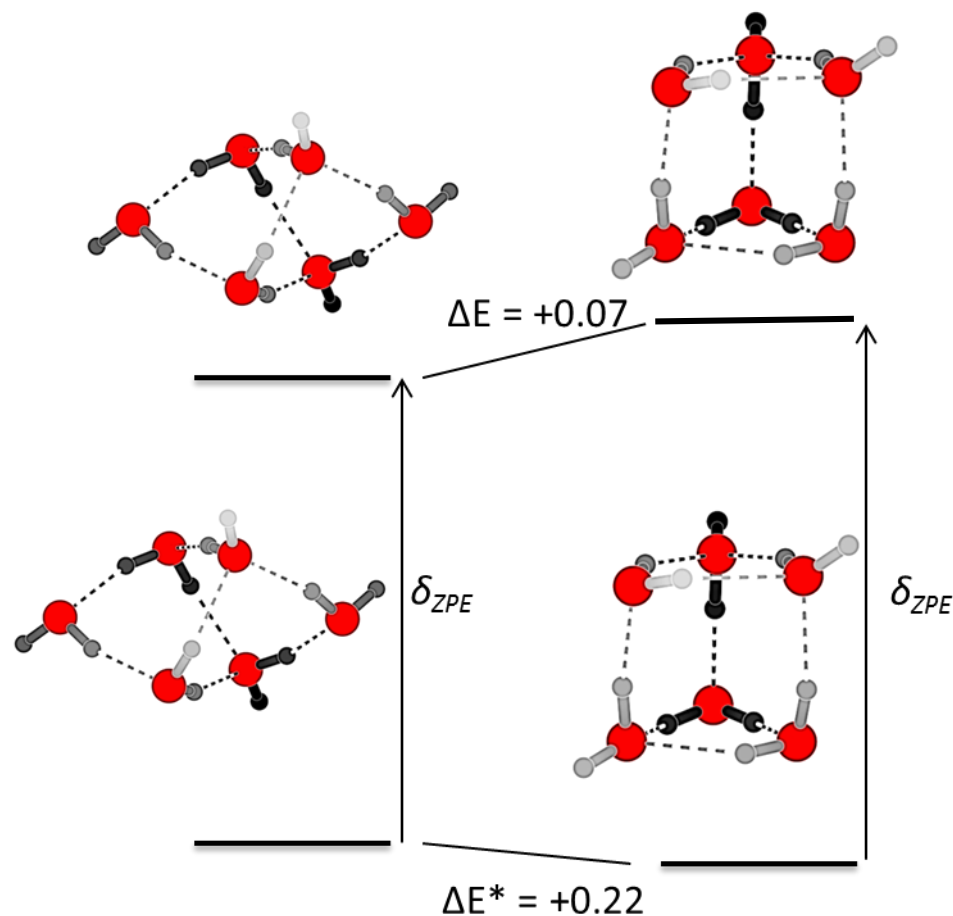
[dx.doi.org/10.1021/ct2003308](https://doi.org/10.1021/ct2003308) | *J. Chem. Theory Comput.* 2011, 7, 2804–2817

Lowest Energy Structural Isomer of the Water Hexamer



Only the cage isomer is observed in an argon expansion (200:1).

Transitions for the prism (†) and book (‡) isomers are present in neon.



* kcal/mol: CCSD(T)~MP2+ Δ MP2_CCSDt
Anharmonic VPT2/MP2/CBS+ + Δ MP2_CCSDt

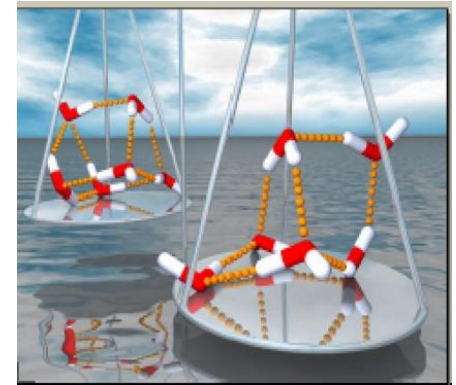
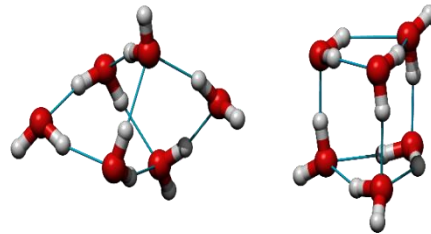
D₂O Hexamers: Energy order

FRONTIERS ARTICLE

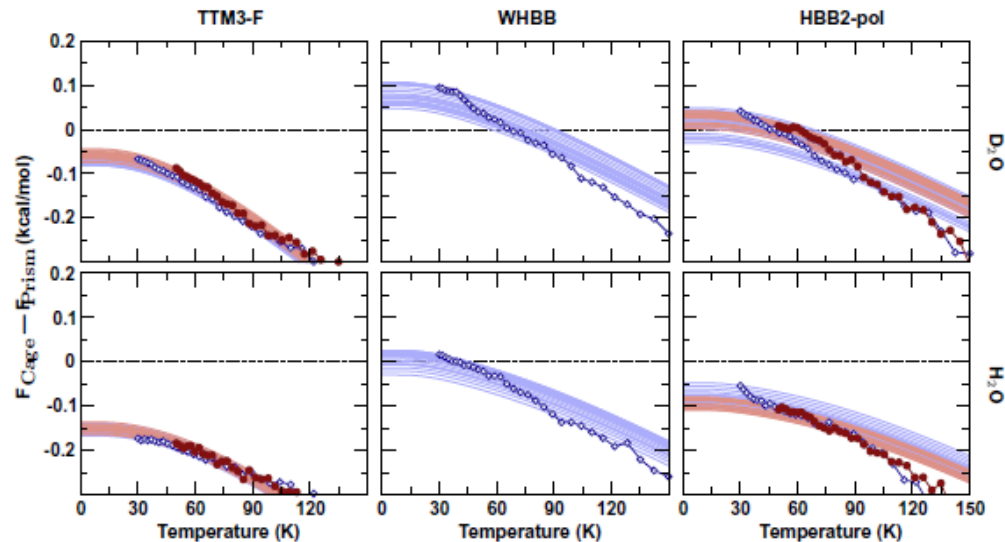
The curious case of the water hexamer: Cage vs. Prism

Volodymyr Babin, Francesco Paesani *

Chemical Physics Letters 580 (2013) 1–8

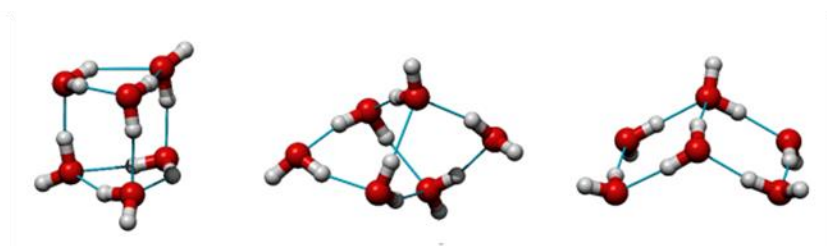
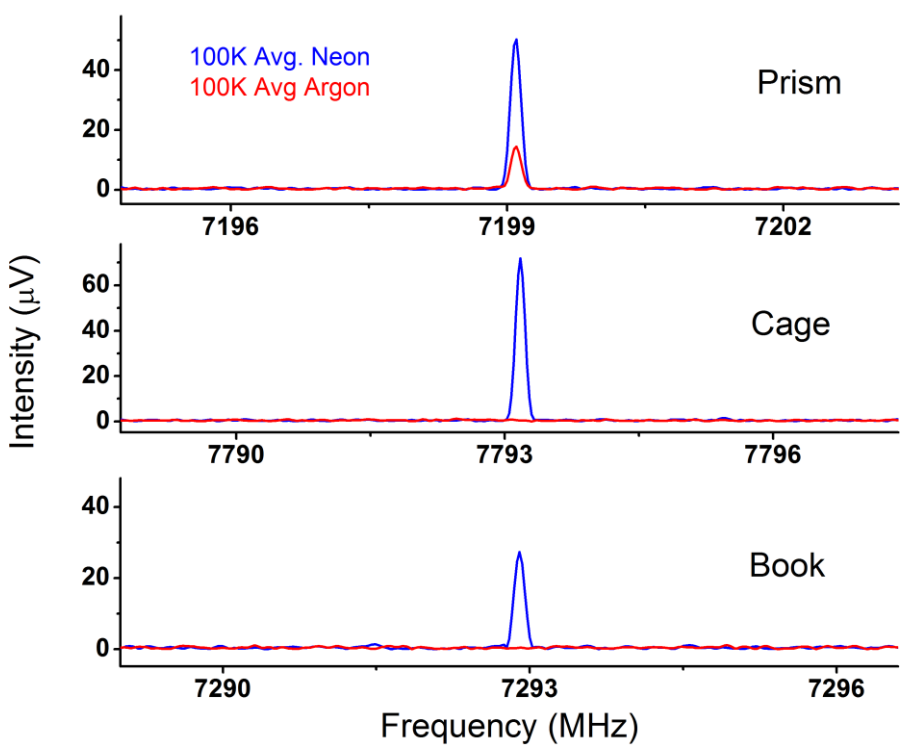
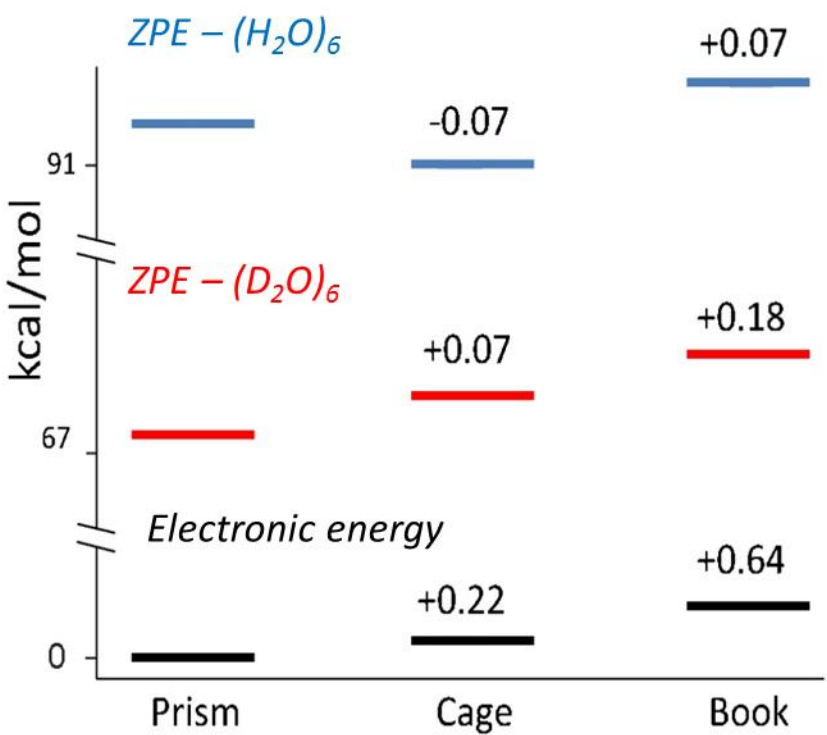


Replica Exchange Path Integral MD



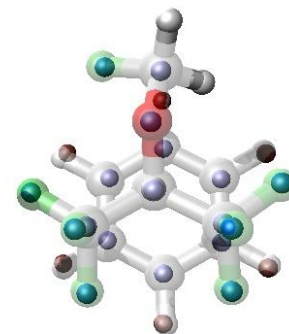
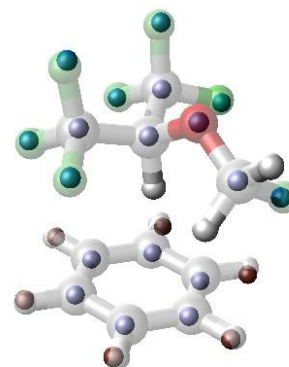
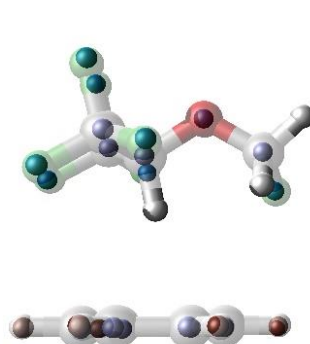
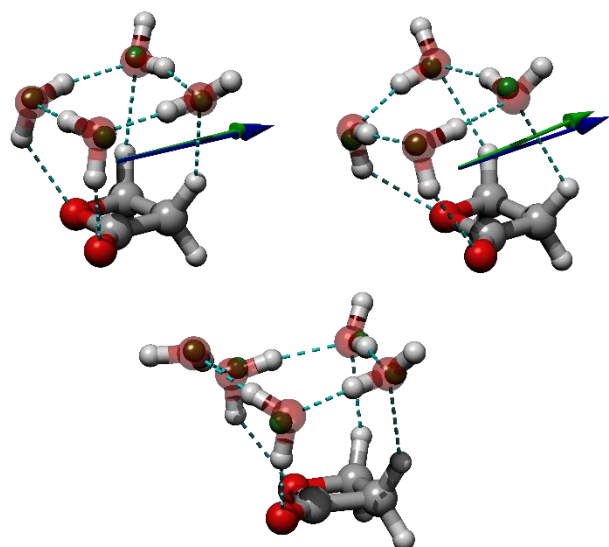
Proceeding with extreme caution, it can be concluded from Figure 5 that the ground state of the water hexamer predicted by the HBB2-pol model is likely “prism” for the deuterated (D₂O)₆ cluster and “cage” for the hydrogenated (H₂O)₆ cluster.

Lowest Energy Structural Isomer of the D₂O Hexamer



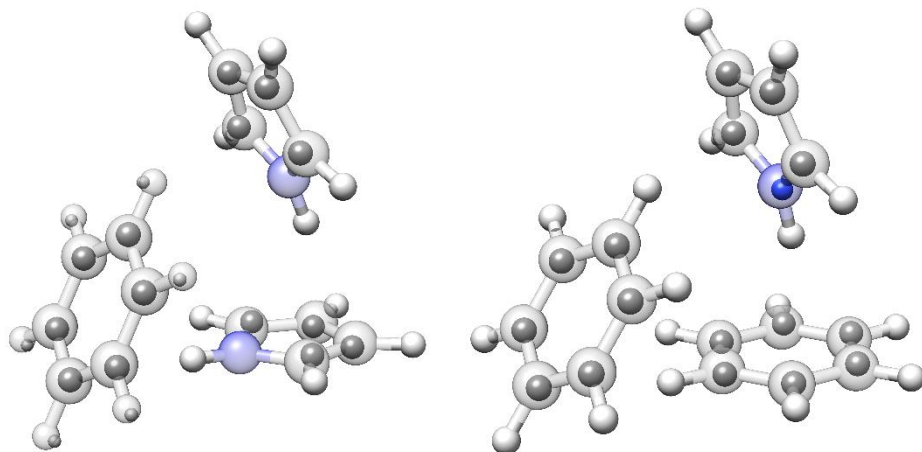
CCSD(T)~MP2+ΔMP2_CCSDt Anharmonic
VPT2/MP2/CBS+ +ΔMP2_CCSDt

Modern Quantum Chemistry is Really Good at Calculating Molecular Structure



Seifert, N. A.; Zaleski, D. P.; Pérez, C.; Neill, J. L.; Pate, B. H.; Vallejo-López, M.; Lesarri, A.; Cocinero, E. J.; Castaño, F.; Kleiner, I., "Probing the C-H... π Weak Hydrogen Bond in Anesthetic Binding: The Sevoflurane-Benzene Cluster", *Angewandte Chemie Int. Ed.* **53**, 3210-3213 (2014).

Cristóbal Pérez, Justin L. Neill, Matthew T. Muckle, Daniel P. Zaleski, Isabel Peña, Juan C. Lopez, Jose L. Alonso, and Brooks H. Pate, "Water-Water and Water-Solute Interactions in Microsolvated organic complexes", *Angewandte Chemie Int. Ed.* **54**, 979-982 (2015).



Simon Lobsiger

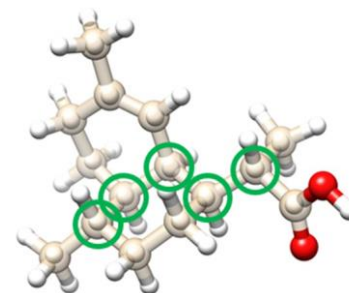


Luca Evangelisti, Cristobal Perez, Nathan A. Seifert, Brooks H. Pate, M. Dehghany, N. Moazzen-Ahmadi, and A.R.W. McKellar, "Theory vs. Experiment for Molecular Clusters: Spectra of OCS Trimers and Tetramers", *J. Chem. Phys.* **142**, 104309 (2015).

Chiral Analysis for Molecules with Multiple Chiral Centers in Pharmaceutical Manufacturing

1) Quantitative Analysis of Diastereomers

Resolution for molecules with multiple chiral centers (2^{N-1})



Dihydroartemisinin Acid

2) Absolute Configuration

Determination of left-handed or right-handed form

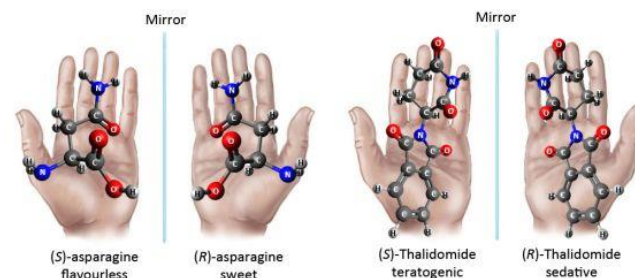
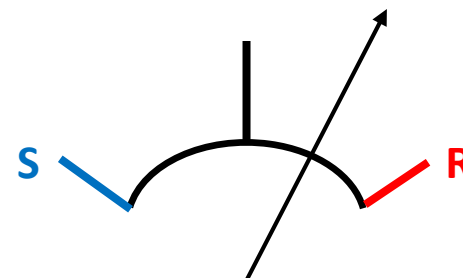


Image Credit:
http://doktori.bme.hu/bme_palyazat/2013/honlap/Bagi_Peter_en.htm

3) Enantiomeric Excess Measurements

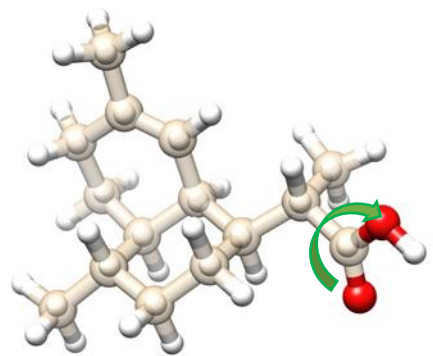
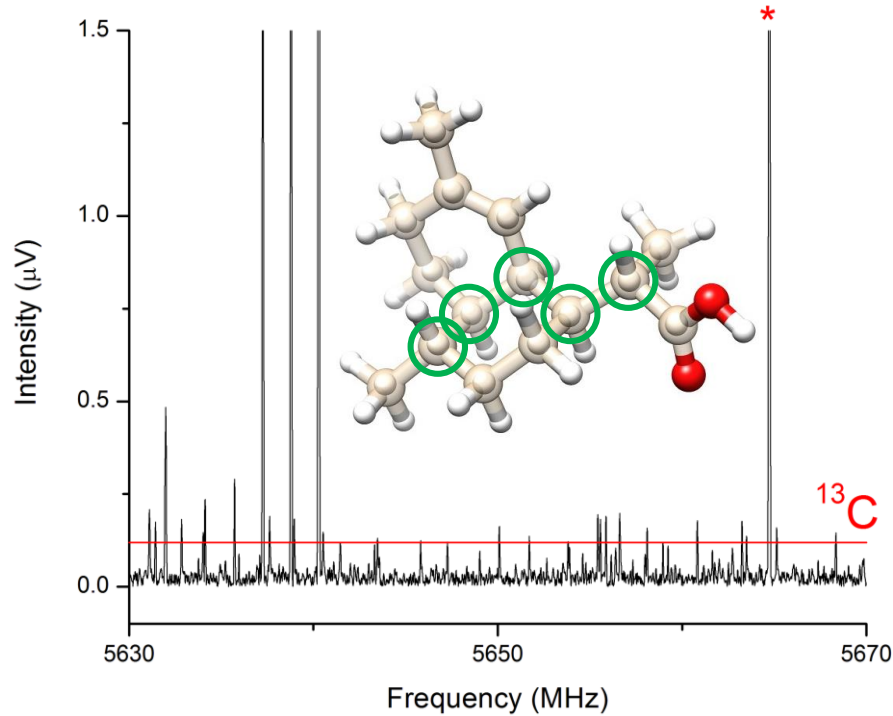
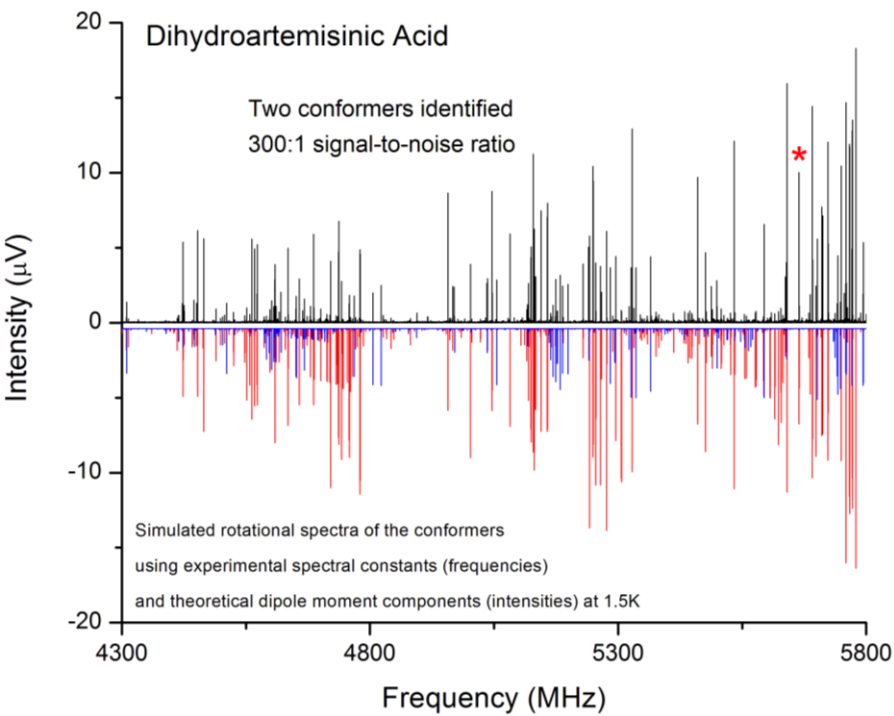
Internal calibration for accurate, linear ee measurement



Dihydroartemisinin Acid

(with Frank Gupton, VCU)

Stereochemistry of Chiral Centers Confirmed by Structure Determination



Conformer 1	Theory	Expt	% Error	Conformer 2	Theory	Expt	% Error
A	708.5	717.52100(8)	+1.3	A	706.2	715.1335(5)	+1.3
B	311.8	311.49420(5)	-0.1	B	313.3	312.8604(2)	-0.1
C	252.2	254.83759(6)	+1.0	C	255.7	258.6302(2)	+1.0

Theory: HF/6-311++g(d,p)

d3 (Grimme): <0.5% error on constants

Physical Principles for FT-MRR Analysis of Enantiomers

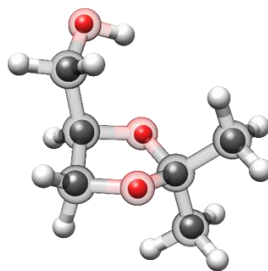
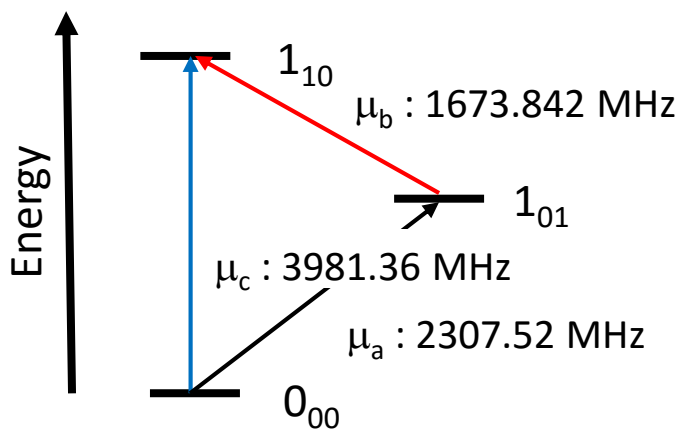


D. Patterson, M. Schnell, and J.M. Doyle, *Nature* **497**, 475- 478 (2013).

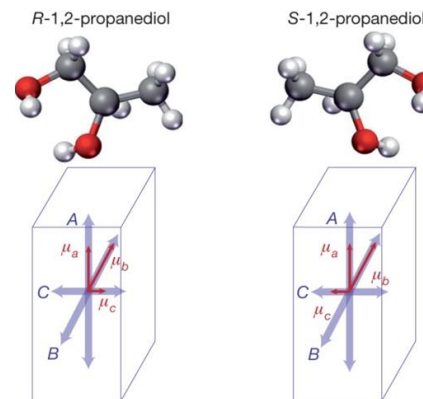
D. Patterson and J.M. Doyle, *Phys. Rev. Lett.* **111**, 023008 (2013).

J.U. Grabow, *Angew. Chem.* **52**, 11698 (2013).

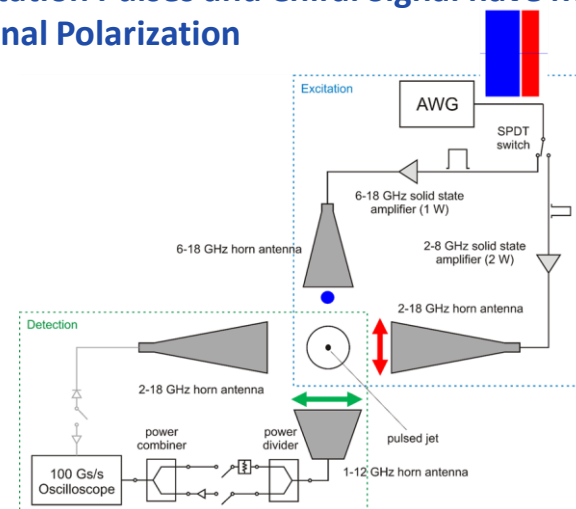
V.A Shubert, D. Schmitz, D. Patterson, J.M Doyle, and M. Schnell, *Angew. Chem.* **52**, (2013).



The Sign of the Product of the Dipole Moment Vector Components is Unique to an Enantiomer

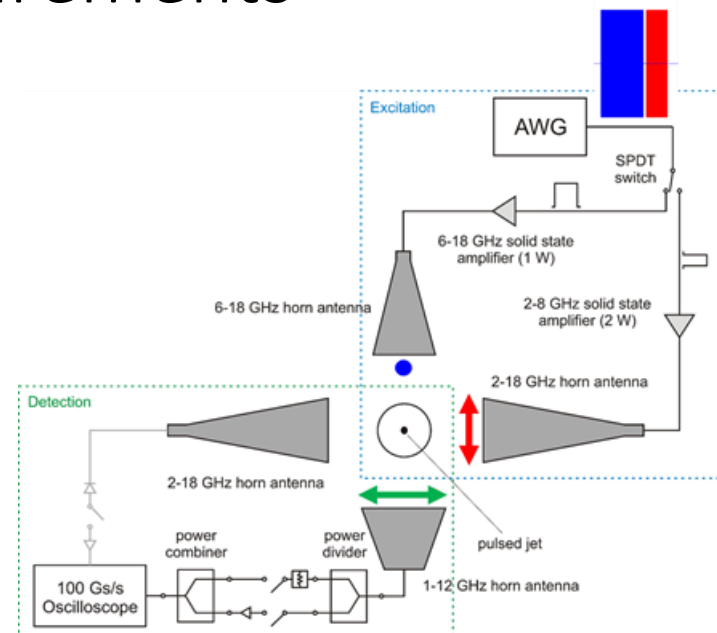
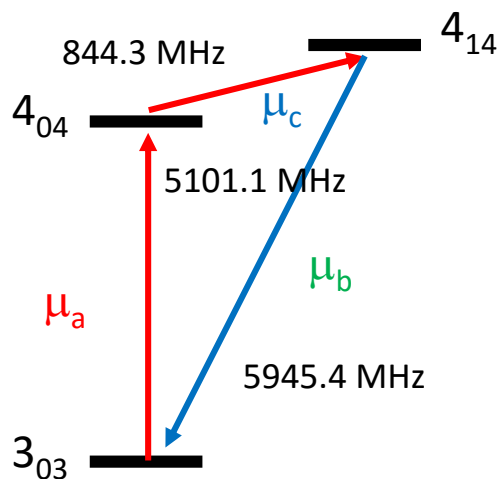


The Excitation Pulses and Chiral Signal have Mutual Orthogonal Polarization

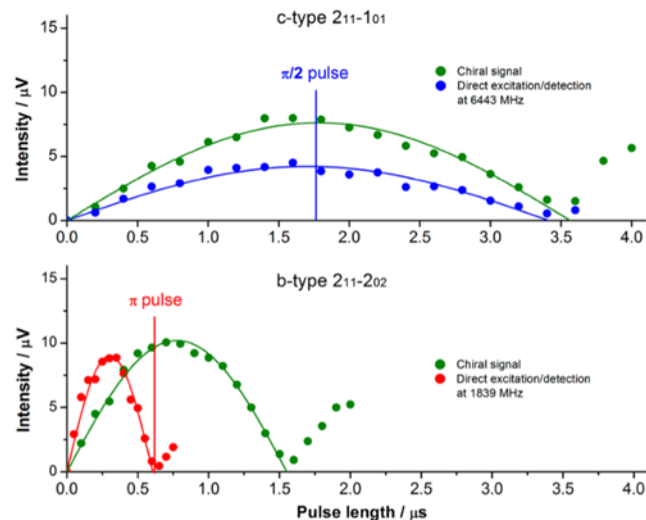


Simon Lobsiger, Cristobal Perez, Luca Evangelisti, Kevin K. Lehmann, Brooks H. Pate, "Molecular Structure and Chirality Detection by Fourier Transform Microwave Spectroscopy", *J. Phys. Chem. Lett.* **6**, 196-200 (2015).

Three Wave Mixing Measurements



Optimal Pulse Sequence: $\pi/2 - \pi$



$\pi/2$ – Pulse: Converts population to coherence

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}|3_{03}\rangle \pm \frac{1}{\sqrt{2}}e^{-i\left(\frac{E_{404}-E_{303}}{h}t\right)}|4_{04}\rangle$$

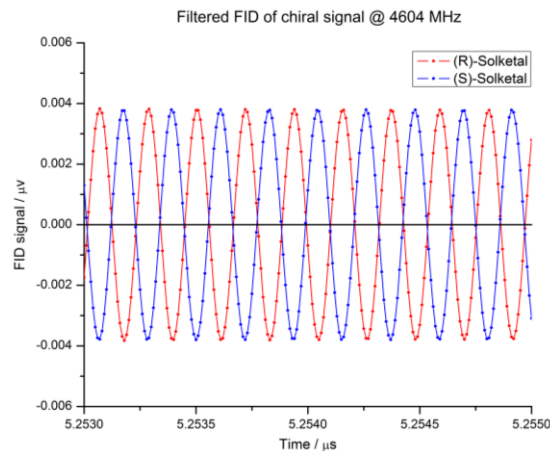
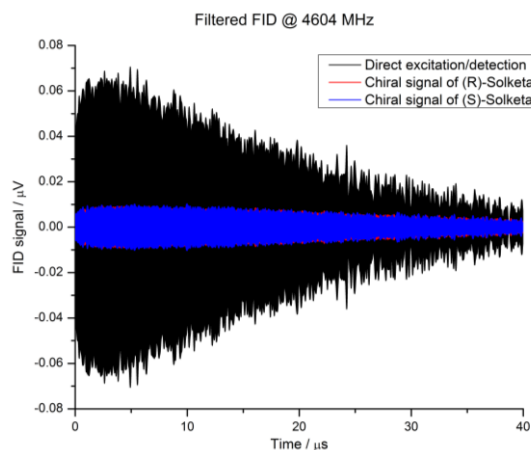
π -Pulse: Transfers coherence

$$|\psi'(t)\rangle = \frac{1}{\sqrt{2}}|3_{03}\rangle \pm \frac{1}{\sqrt{2}}e^{-i\left(\frac{E_{414}-E_{303}}{h}t+\phi_{\pi}\right)}|4_{14}\rangle$$

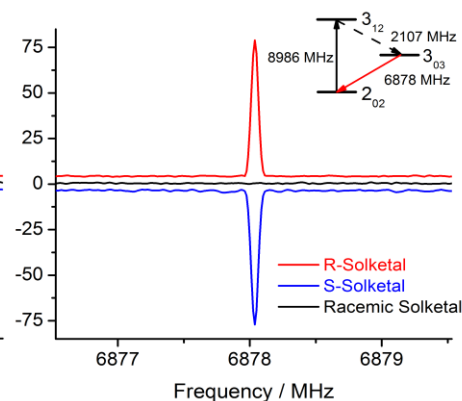
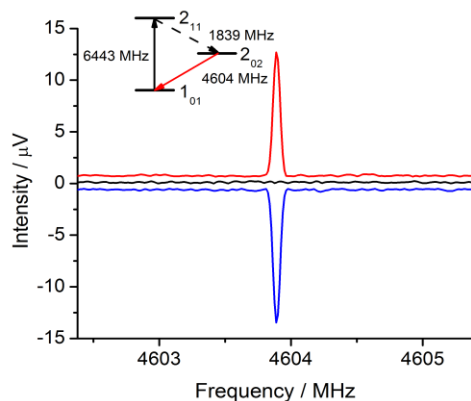
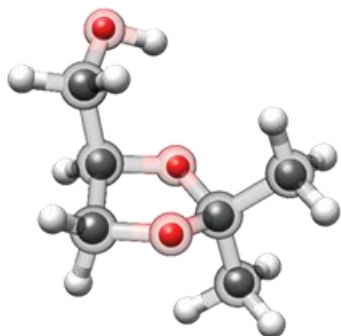
M_J -dependence to the transition moment makes terminology only approximate

Features of Microwave Three Wave Mixing Spectroscopy

- 1) The chiral signal has an amplitude comparable to regular rotational transitions.
- 2) The chiral signal is background free.
- 3) The chiral signal is triply resonant and compatible with complex sample mixtures.

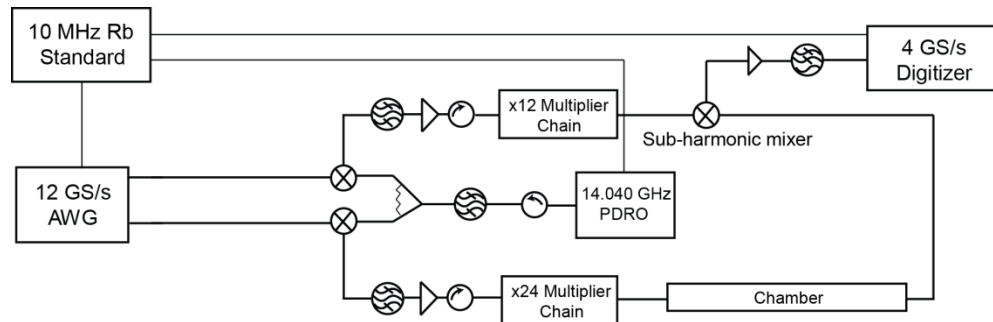


Actual digitized data points are shown along with sine wave fit.



Simon Lobsiger, Cristobal Perez, Luca Evangelisti, Kevin K. Lehmann, Brooks H. Pate, "Molecular Structure and Chirality Detection by Fourier Transform Microwave Spectroscopy", J. Phys. Chem. Lett. 6, 196-200 (2015).

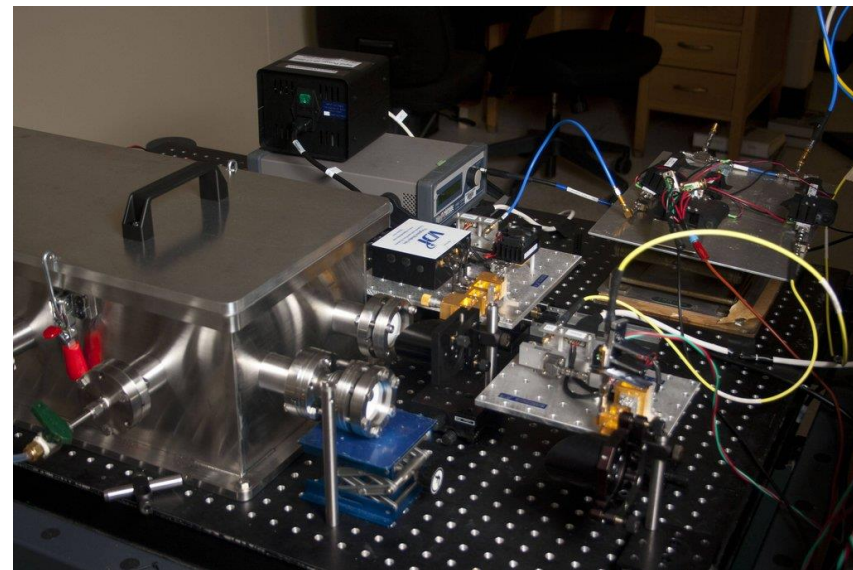
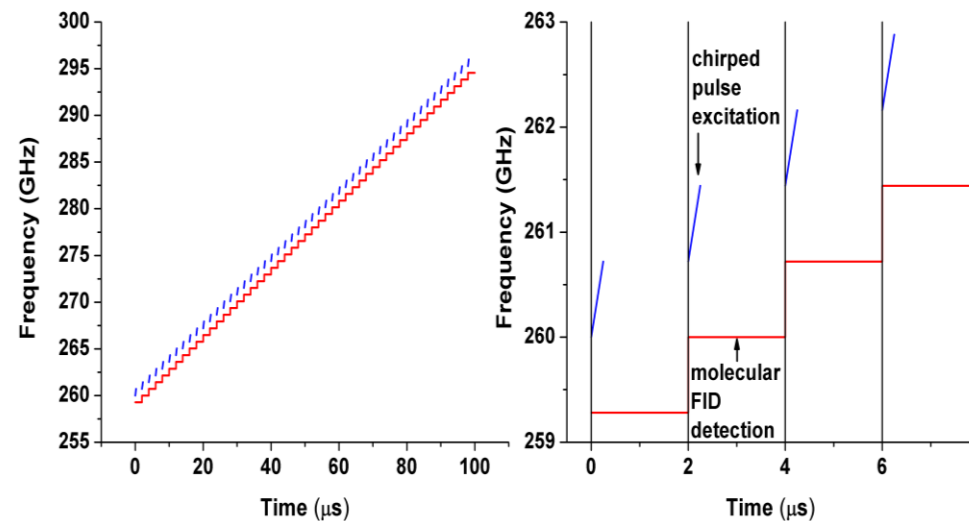
Segmented Chirped-Pulse Fourier Transform Spectroscopy



AWG Output of 2.0-3.5 GHz
Linearly Addresses the
Frequency Range
260 – 295 GHz

LO Shifting Reduces Required
Detection Bandwidth

Output Power: 30-40 mW



Separate AWG Channels Generate Chirp
Segments (Blue) and Local Oscillator (LO)
Frequency (Blue) with Phase Reproducibility

Applications of mm-wave Chirped Pulse Fourier Transform Rotational Spectroscopy

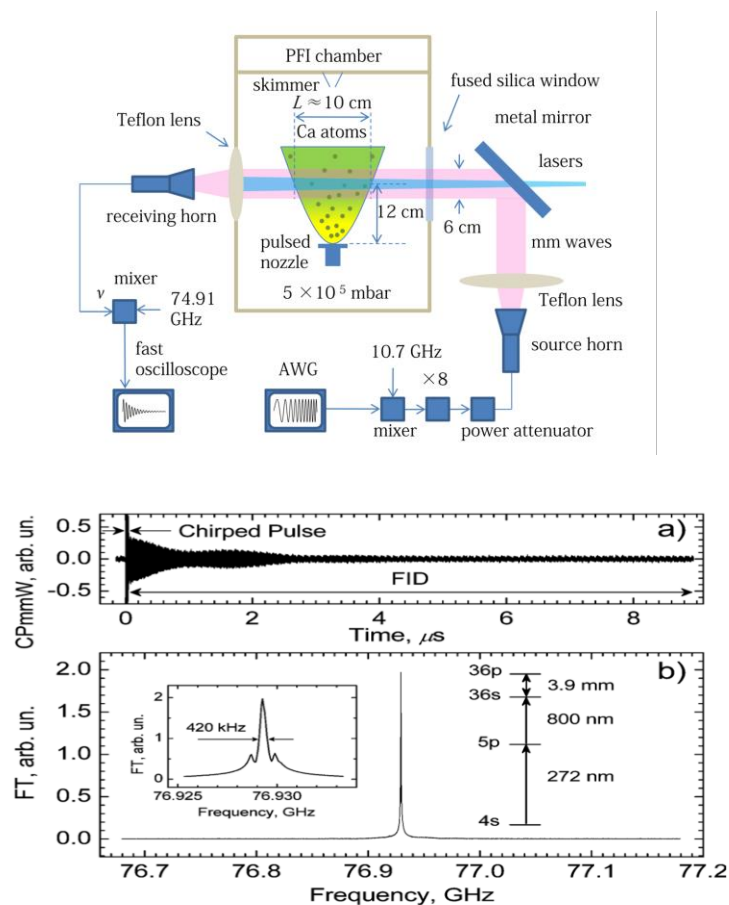
PRL 107, 143001 (2011)

PHYSICAL REVIEW LETTERS

week ending
30 SEPTEMBER 2011

Chirped-Pulse Millimeter-Wave Spectroscopy of Rydberg-Rydberg Transitions

Kirill Prozument, Anthony P. Colombo, Yan Zhou, G. Barratt Park, Vladimir S. Petrović,*
Stephen L. Coy, and Robert W. Field†



Chirped-pulse millimeter-wave spectroscopy for dynamics and kinetics studies of pyrolysis reactions

Kirill Prozument,^{*ab} G. Barratt Park,^a Rachel G. Shaver,^a AnGayle K. Vasiliou,^c James M. Oldham,^b Donald E. David,^d John S. Muentert,^e John F. Stanton,^f Arthur G. Suits,^b G. Barney Ellison^d and Robert W. Field^{*a}

PCCP Perspectives DOI: 10.1039/c3cp55352c

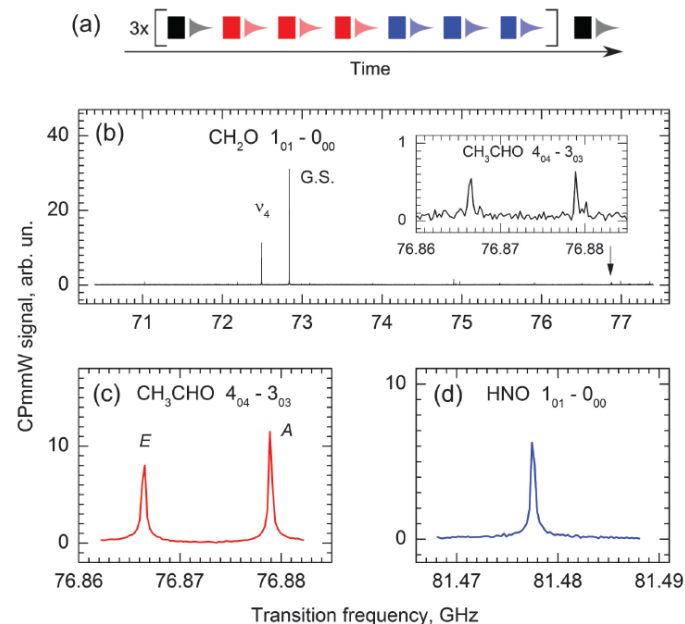
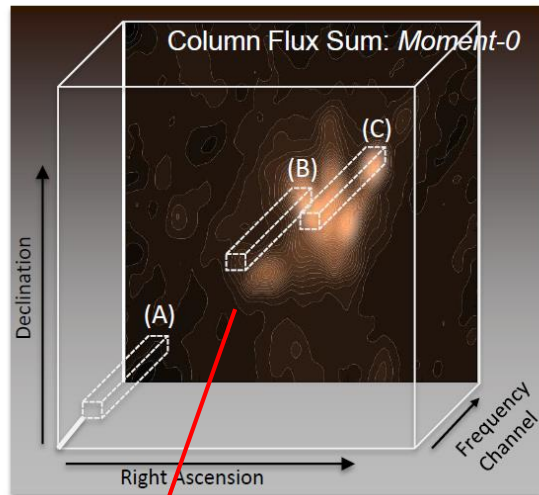


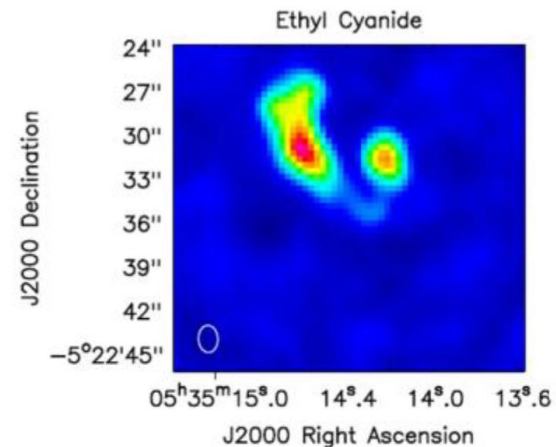
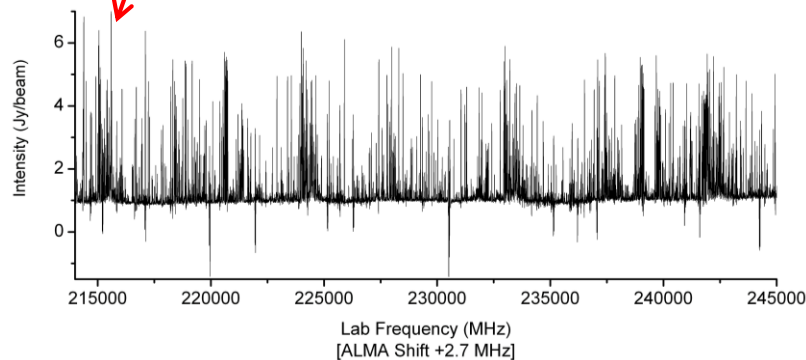
Fig. 3 CPmmW spectroscopy of CH₃CHO, H₂CO, and HNO products of CH₃CH₂ONO pyrolysis using the multi-chirp approach. (a) Example of a

Interferometric Observations in Radio Astronomy



The **Data Cube** contains the high spectral resolution mm-wave spectrum (frequency channel) for each “pixel” in the spatially-resolved image.

The mm-wave rotational spectrum contains the molecular rotational spectroscopy signatures of the molecules in the interstellar environment.



The **high spectral resolution** and broadband frequency coverage permit the analysis of the chemical composition in spatially localized regions

A **high spatial resolution** image of the column density of each molecule can be created after analysis of the frequency-resolved spectrum

214 – 246 GHz, 500 kHz resolution (77Kpt), 17 GB Data Structure, 75 minutes of observation

Conclusions

- Broadband techniques have significantly improved the measurement speed, measurement sensitivity, and molecular size range for molecular rotational spectroscopy.
- New theoretical advances in molecular rotational spectroscopy include dynamical rotational spectroscopy of highly excited molecules and three wave mixing spectroscopy for chiral analysis.
- These advances have led to new applications of rotational spectroscopy in chemical dynamics and kinetics, analytical chemistry, and pharmaceutical manufacturing.