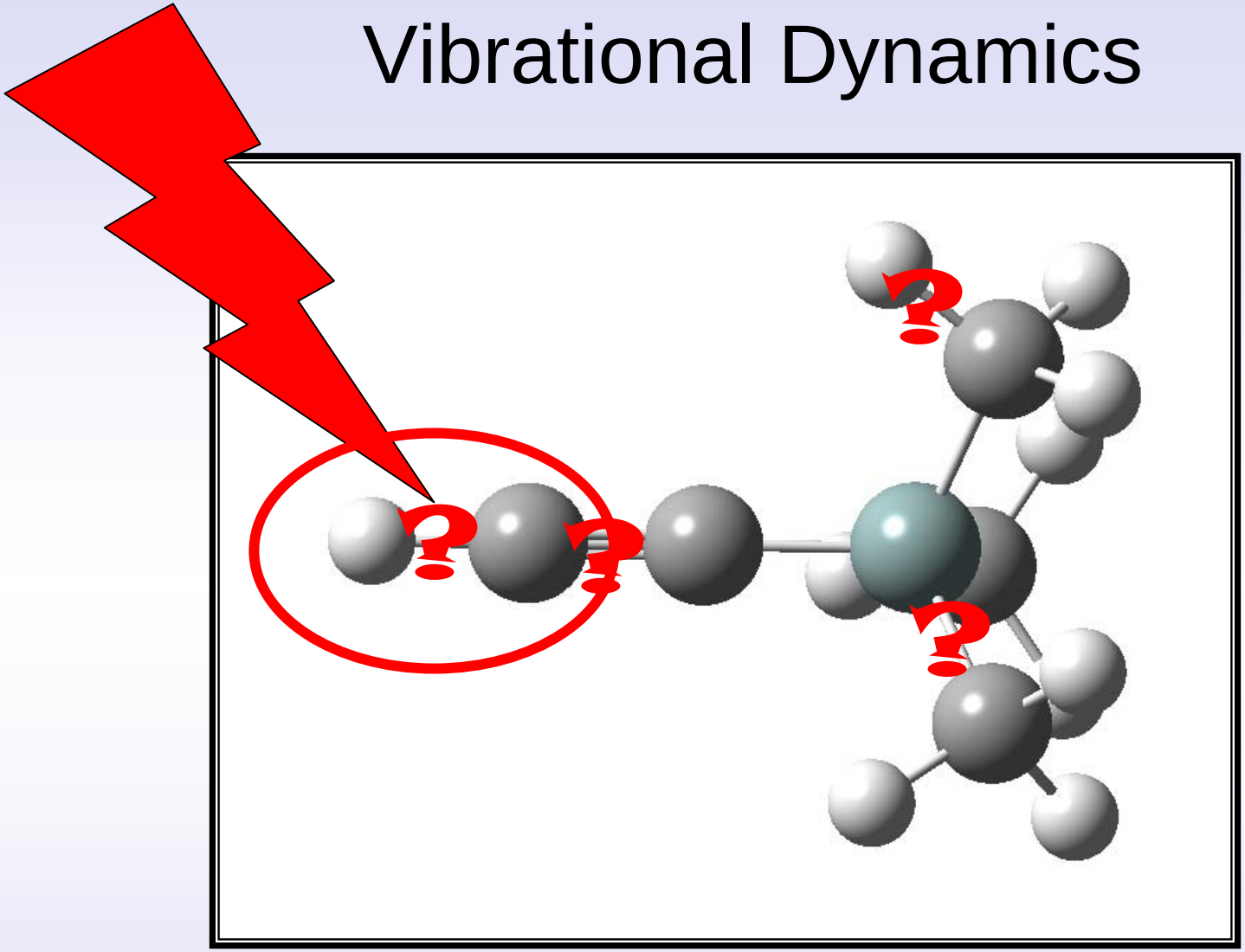
Ultrafast Vibrational Energy Flow in Molecules

A brief history of The Pate Lab and the FEL at JLAB

Pam Crum
Pate Lab
University of Virginia

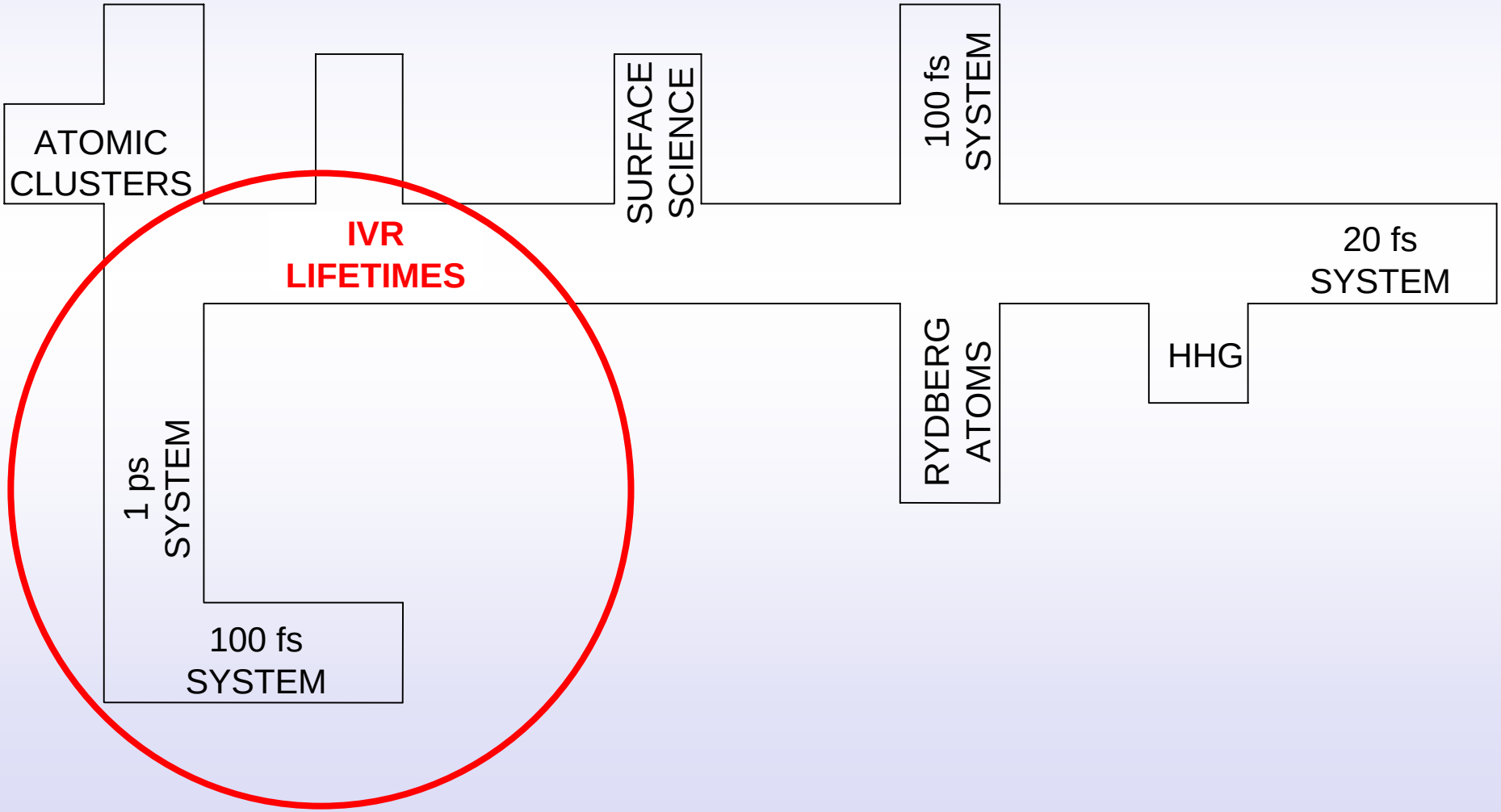
Vibrational Dynamics

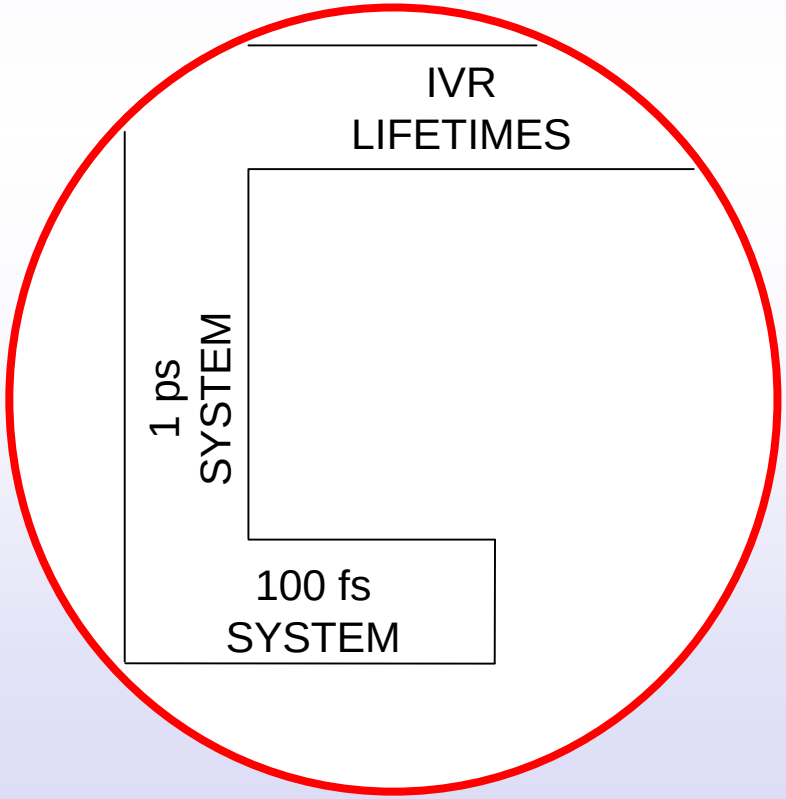


Understanding Dynamics Across a Wide Range of Environments

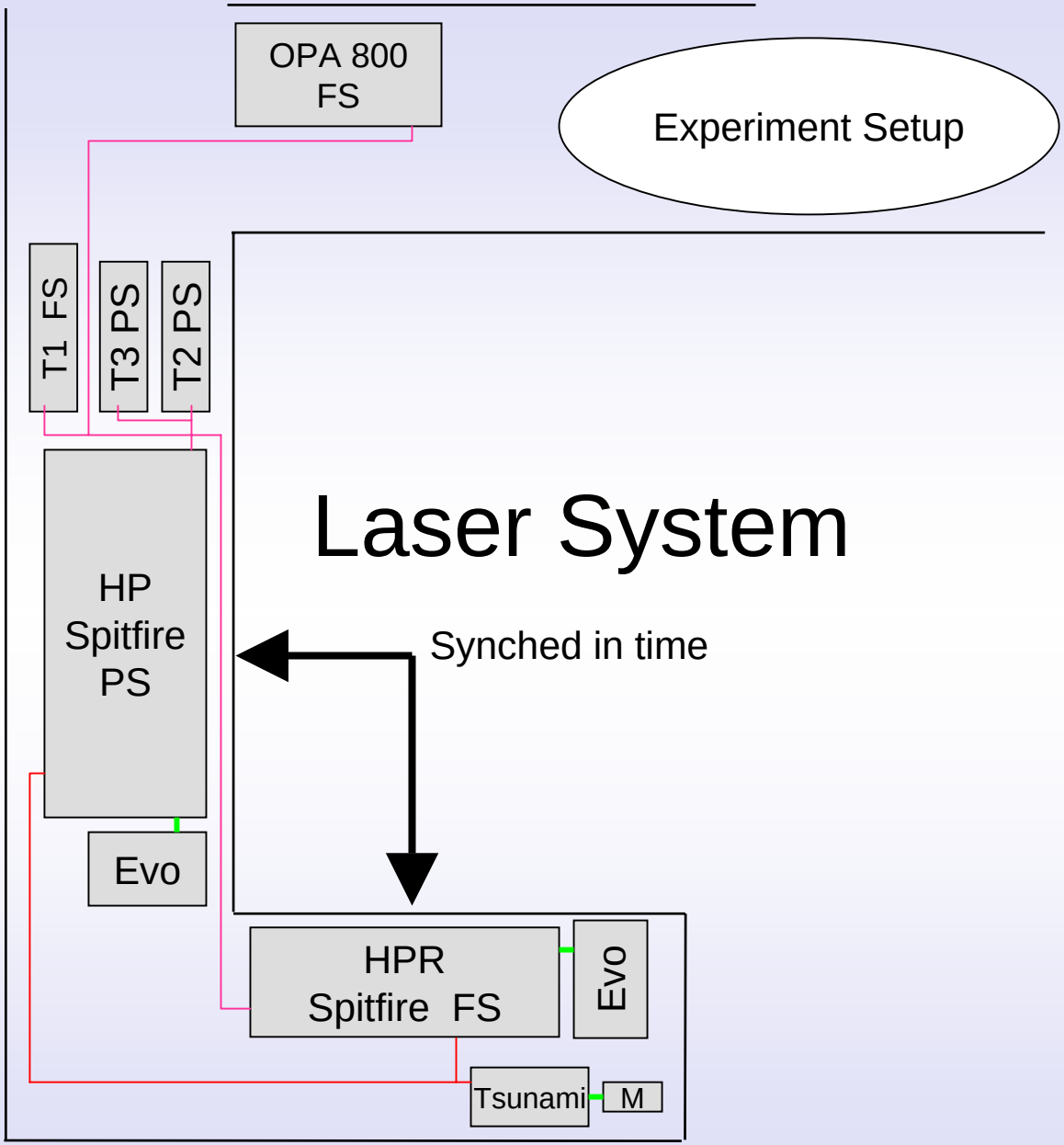
Ultracold	Room Temp.	Room Temp.
ISOLATED	**ISOLATED**	**SOLVATED**
Frequency Domain Free Jet Expansion	Time Domain Gas Phase	Time Domain Solution Phase

CAMOS Laser Facility Overview





Pate Lab Portion


OPA 800
FS
Experiment Setup
T1 FS
T3 PS
T2 PS
Laser System
HP
Spitfire
PS
Synched in time
Evo
HPR
Spitfire FS
Evo
Tsunami
M

Vibrational Dynamics Processes

IVR

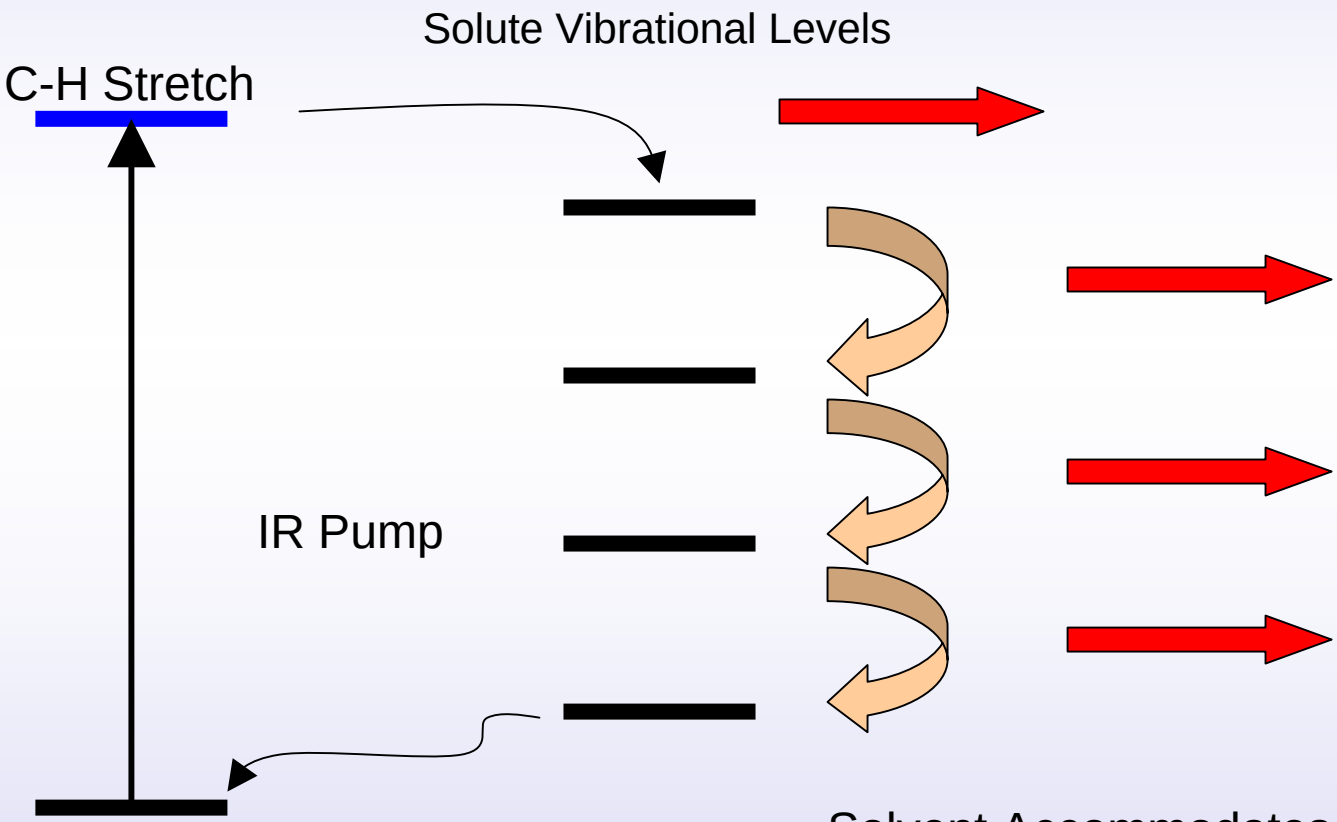
- Total amount of vibrational energy constant
- Threshold density of states ~10 states/cm^{-1}
- Only pathway for energy flow in isolated molecule
- Rate is molecule dependent

VER

- Energy removed from molecule
- Rate is solvent dependent

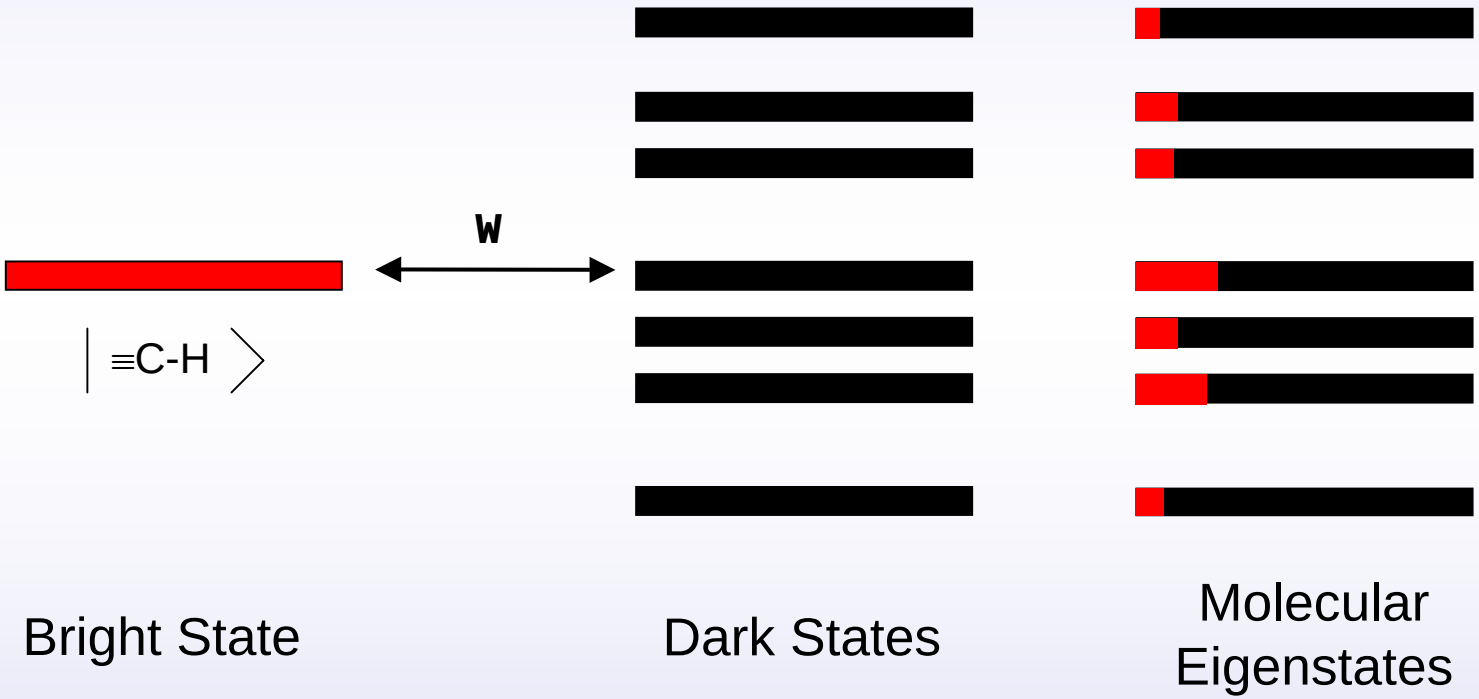
Vibrational Energy Relaxation (VER) of Polyatomic Molecules in Solution

(Solvent Assisted IVR)

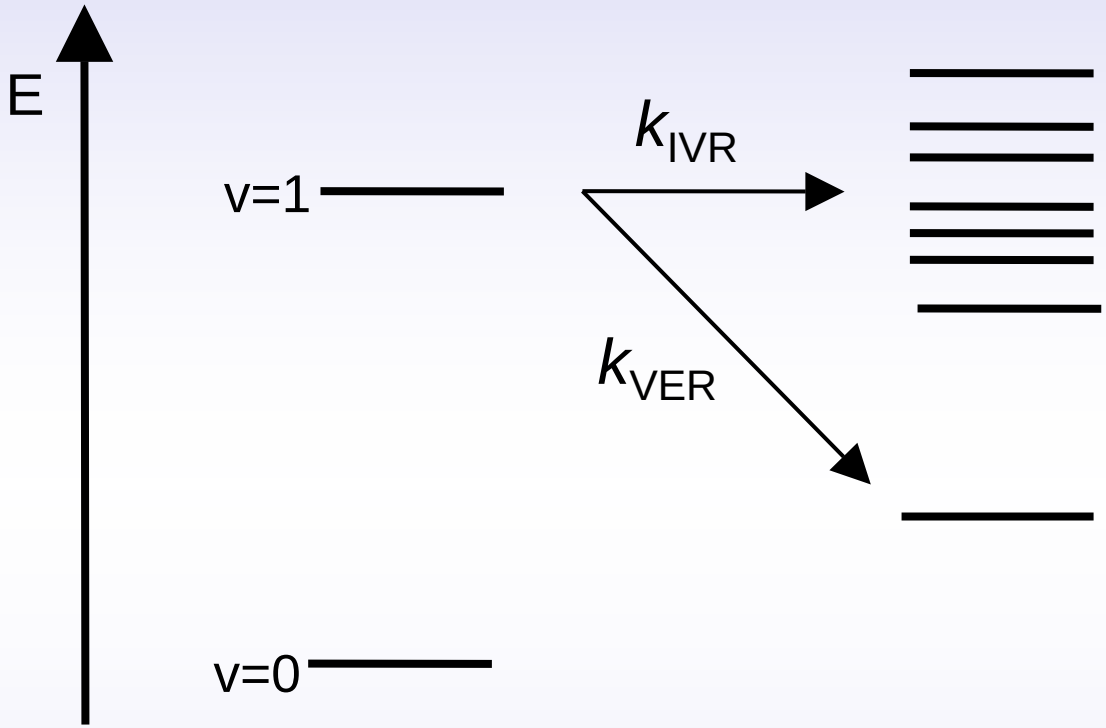


Solvent Accommodates Energy Difference at Each Step of the Relaxation “Cascade”

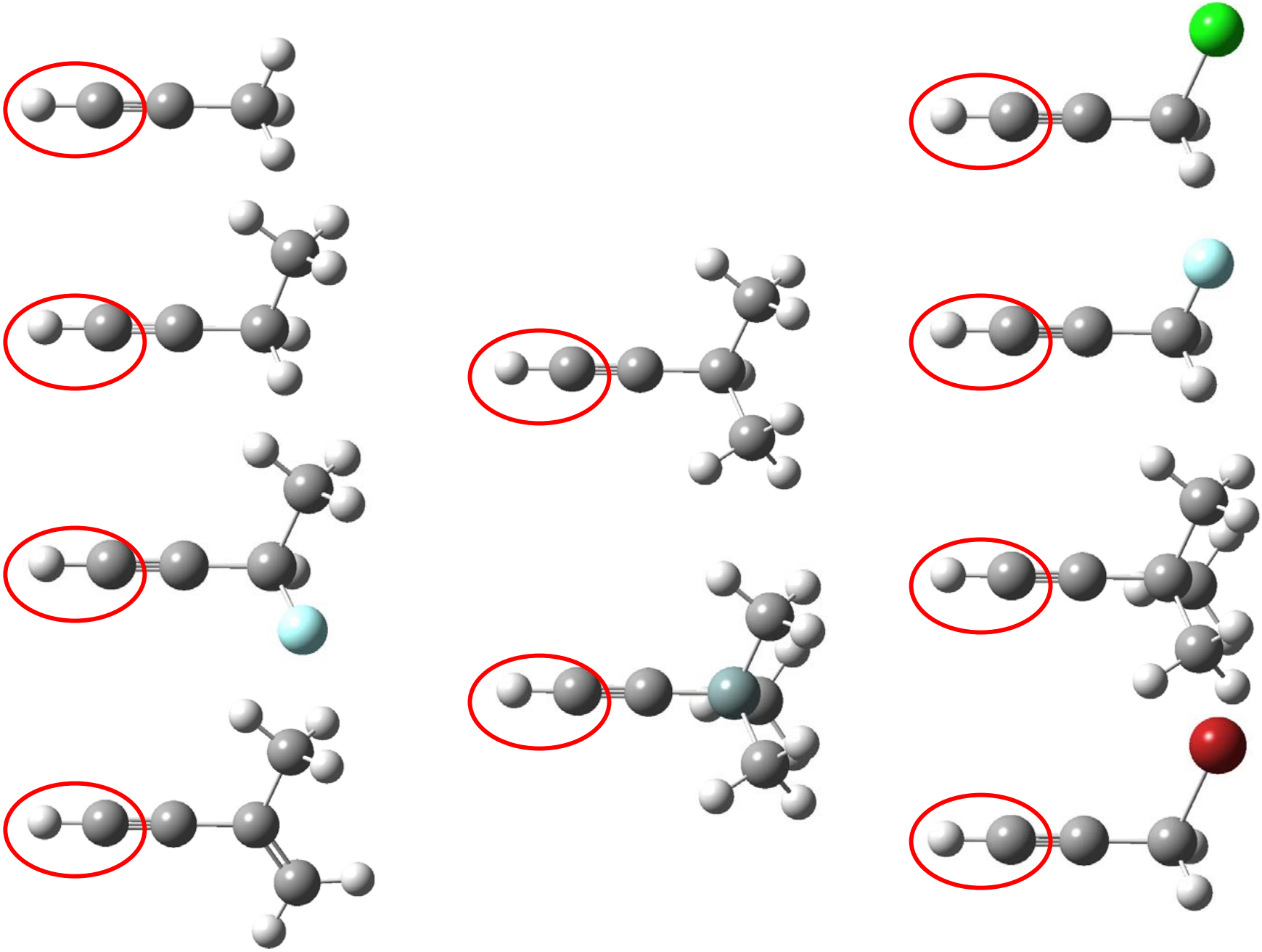
Standard Model of IVR



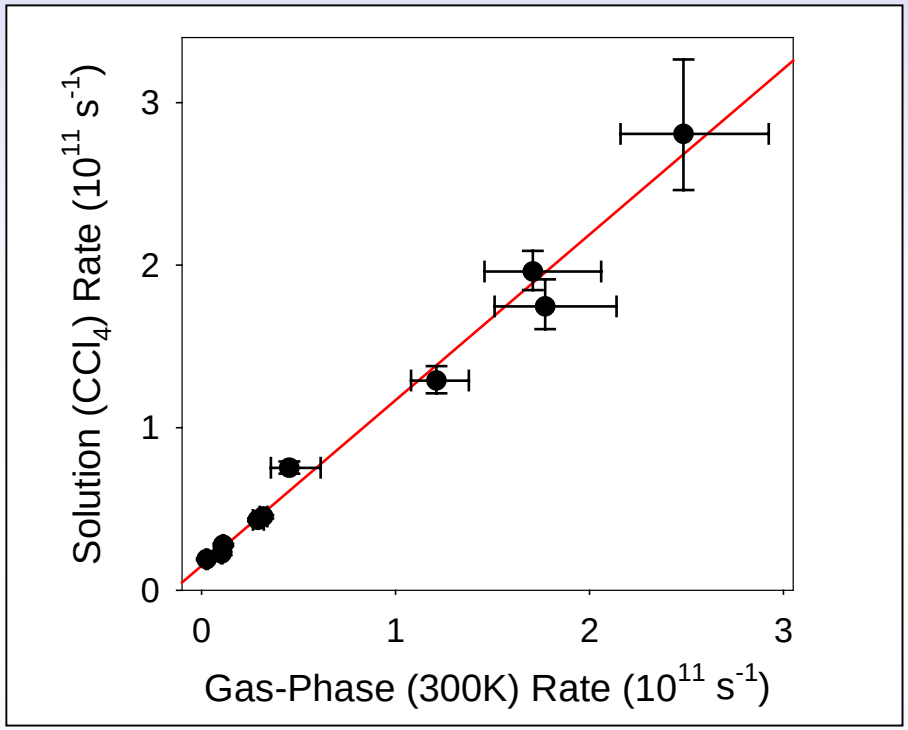
Vibrational Dynamics in Solution

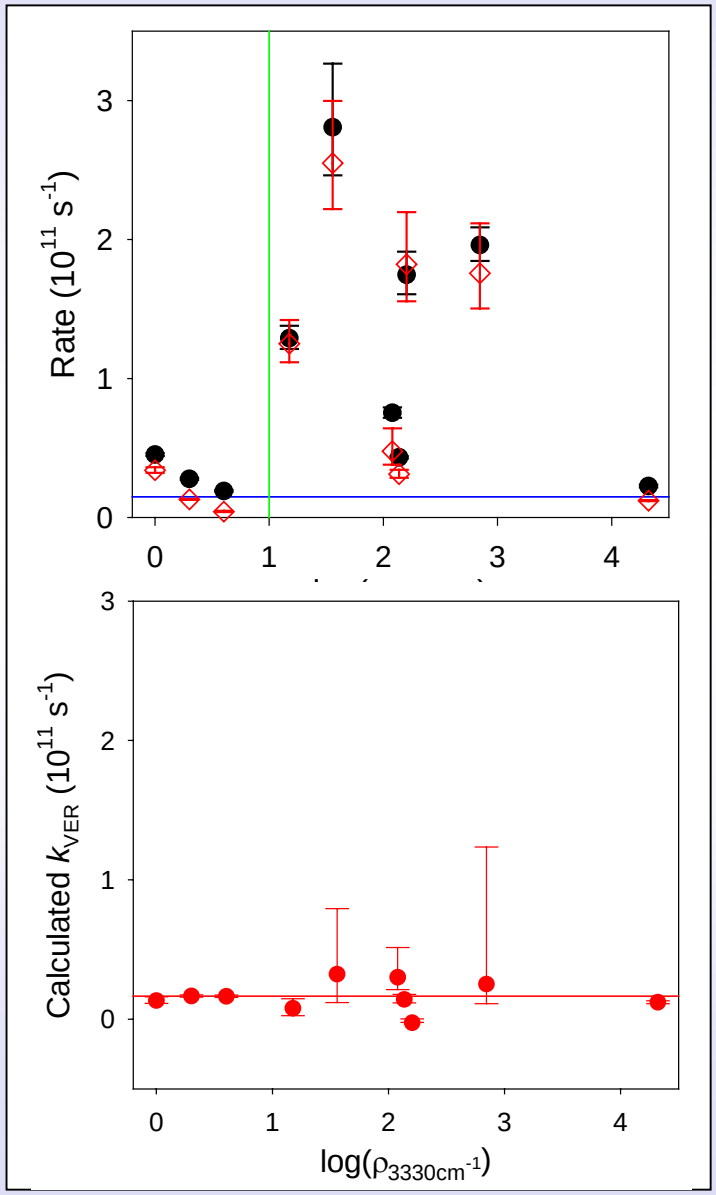


$$k_{TOT} = k_{IVR} + k_{VER}$$



Comparison of Solution Rate and Gas-Phase IVR Rate



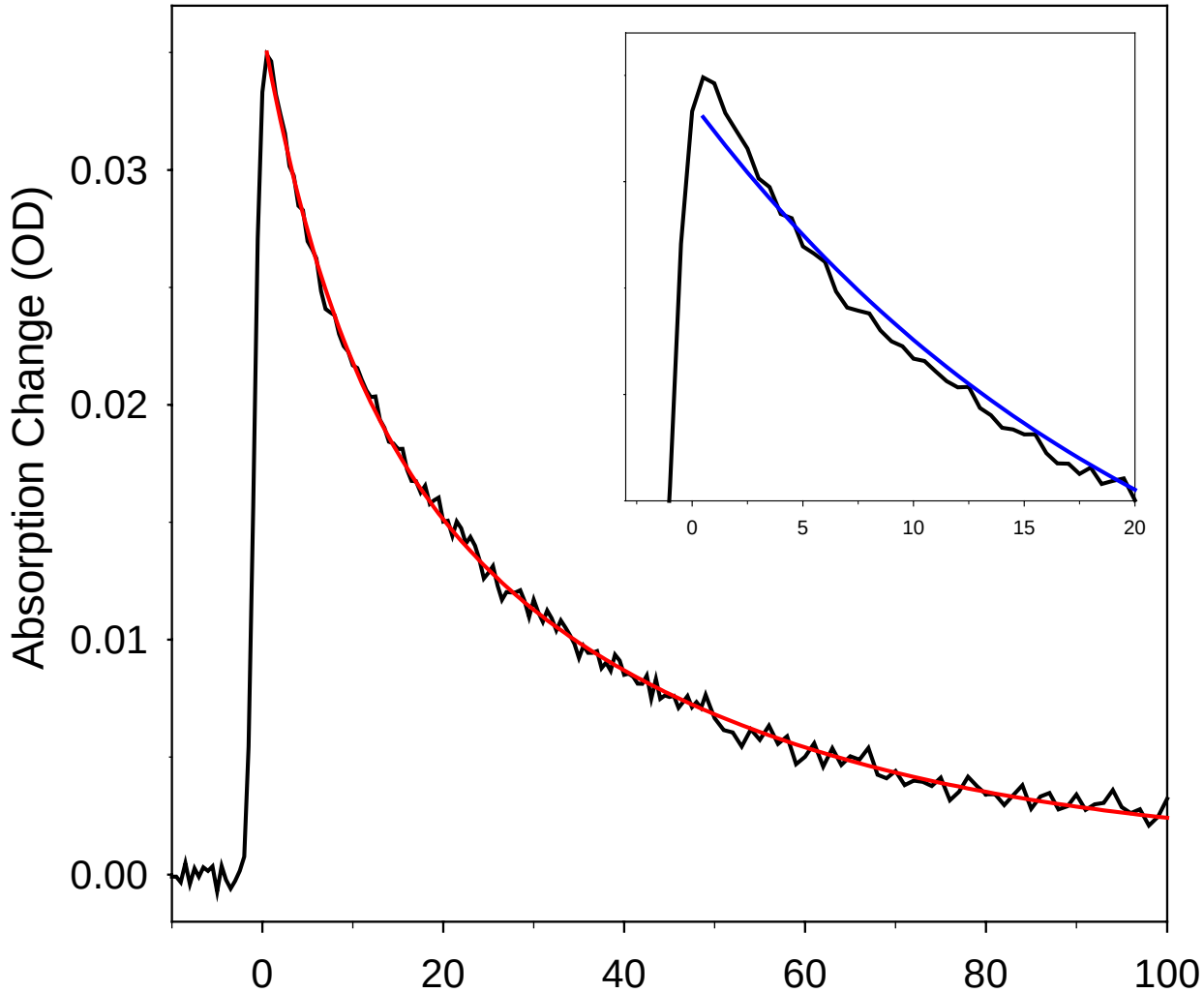


Acetylenic C-H Stretch
Fundamental Measurements

$$k_{TOT} = k_{IVR} + k_{VER}$$

Yoo, H.S. et al. *J. Phys. Chem A* **2004** *108*(8) 1348-1364
Yoo, H.S. et al. *J. Phys. Chem A* **2004** *108*(8) 1365-1379
Yoo, H.S. et al. *J. Phys. Chem A* **2004** *108*(8) 1380-1387

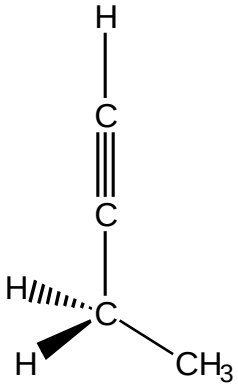
Biexponential Behavior in Room Temperature Gas-Phase Studies



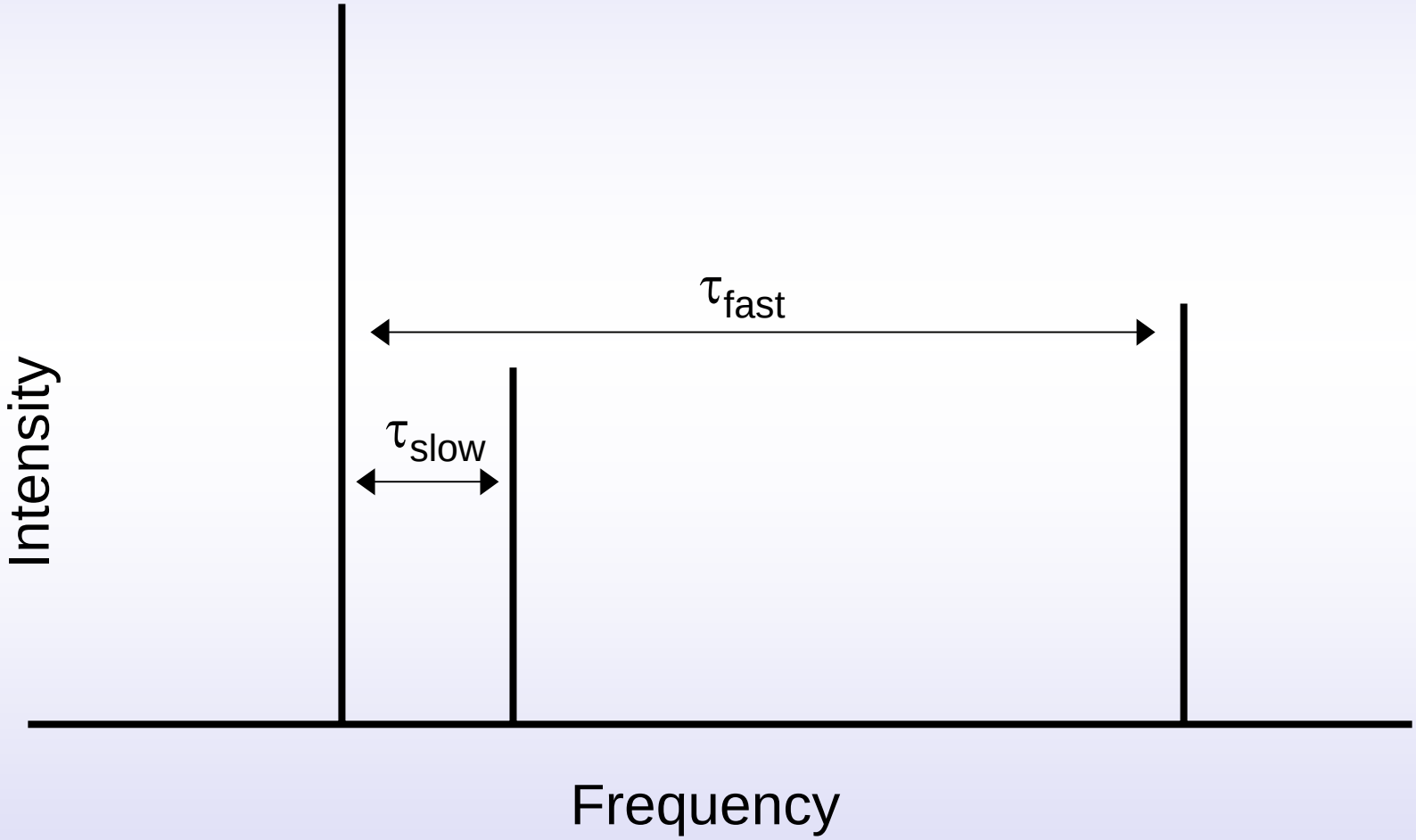
1-Butyne

τ_1 = 8 ps (A_1=0.0134)

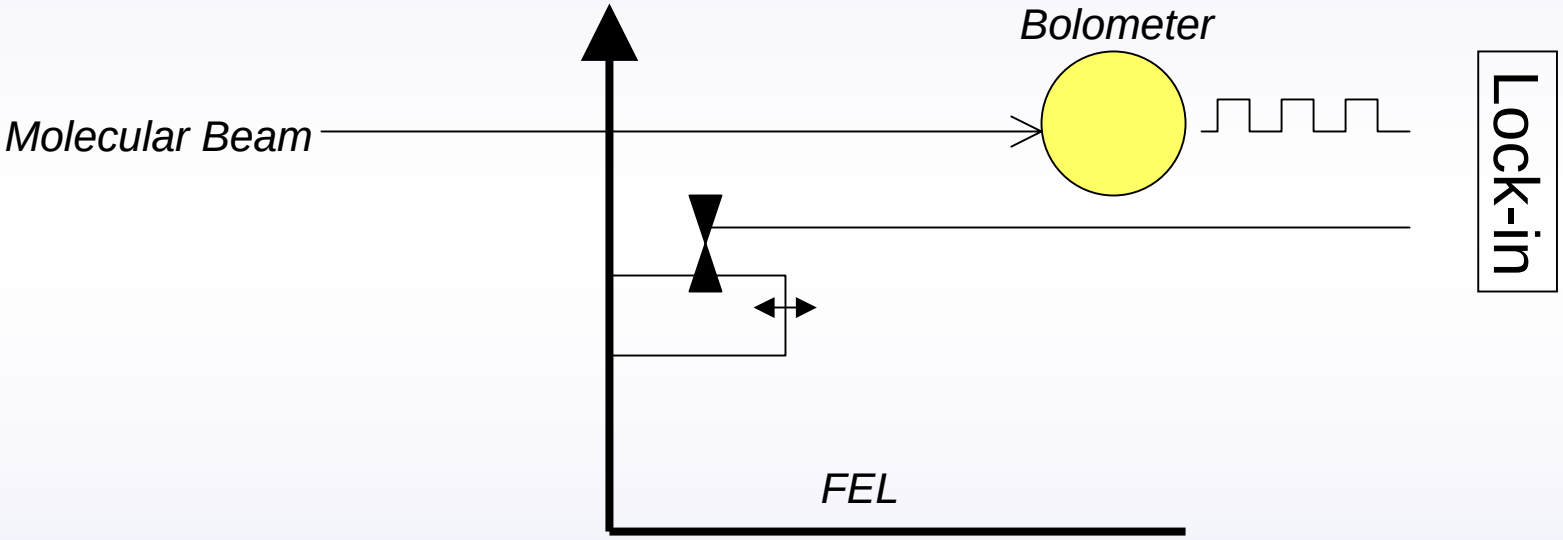
τ_2 = 40 ps (A_2=0.0227)



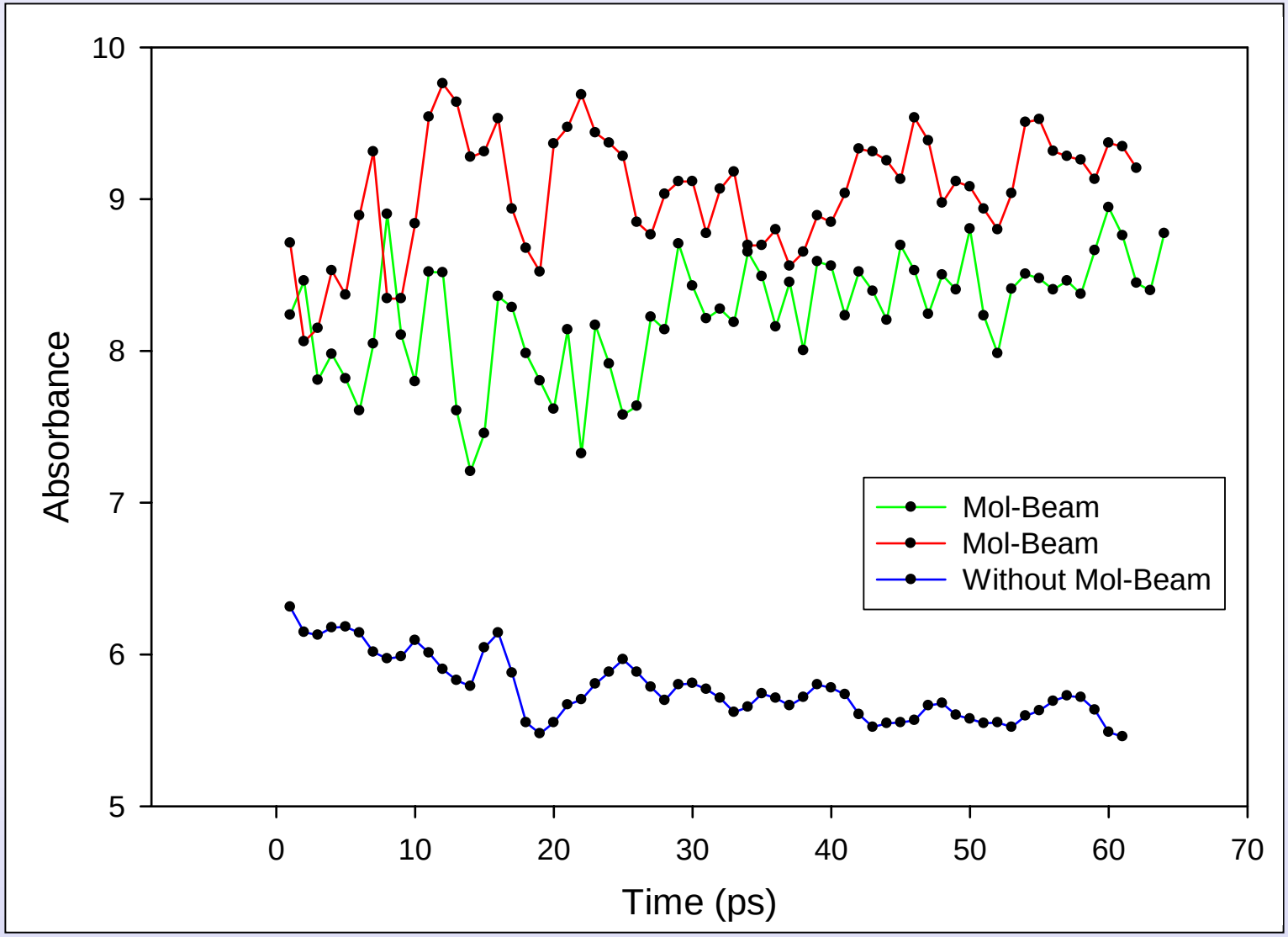
Importance of Spectral Wings to the Measurement of Fast Timescales



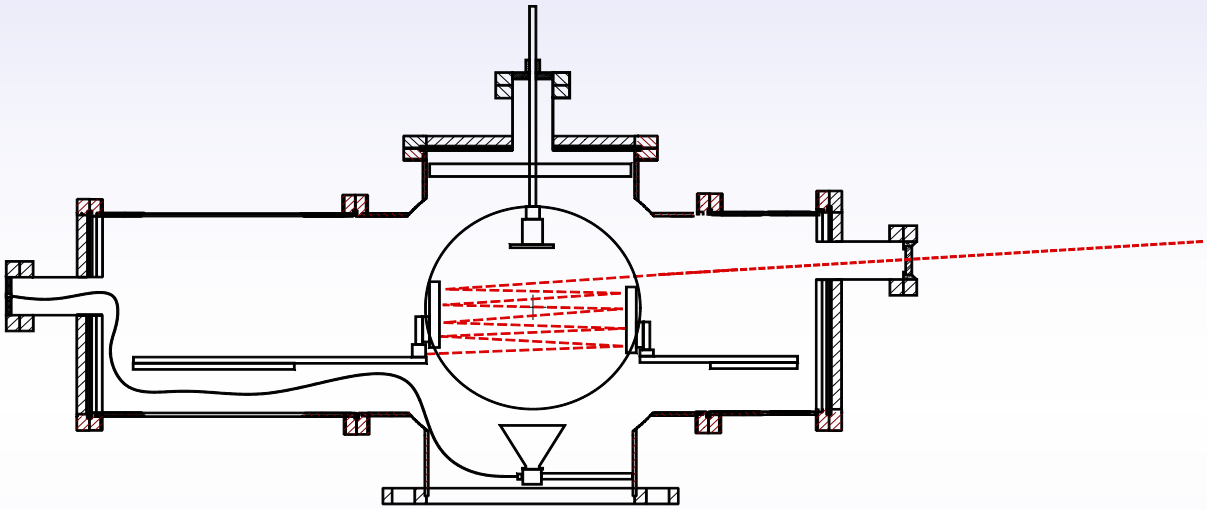
Off to the FEL at JLAB



Molecular Beam Data on Propyne Using the FEL



In The Meantime…
IR-FTMW Technique Development

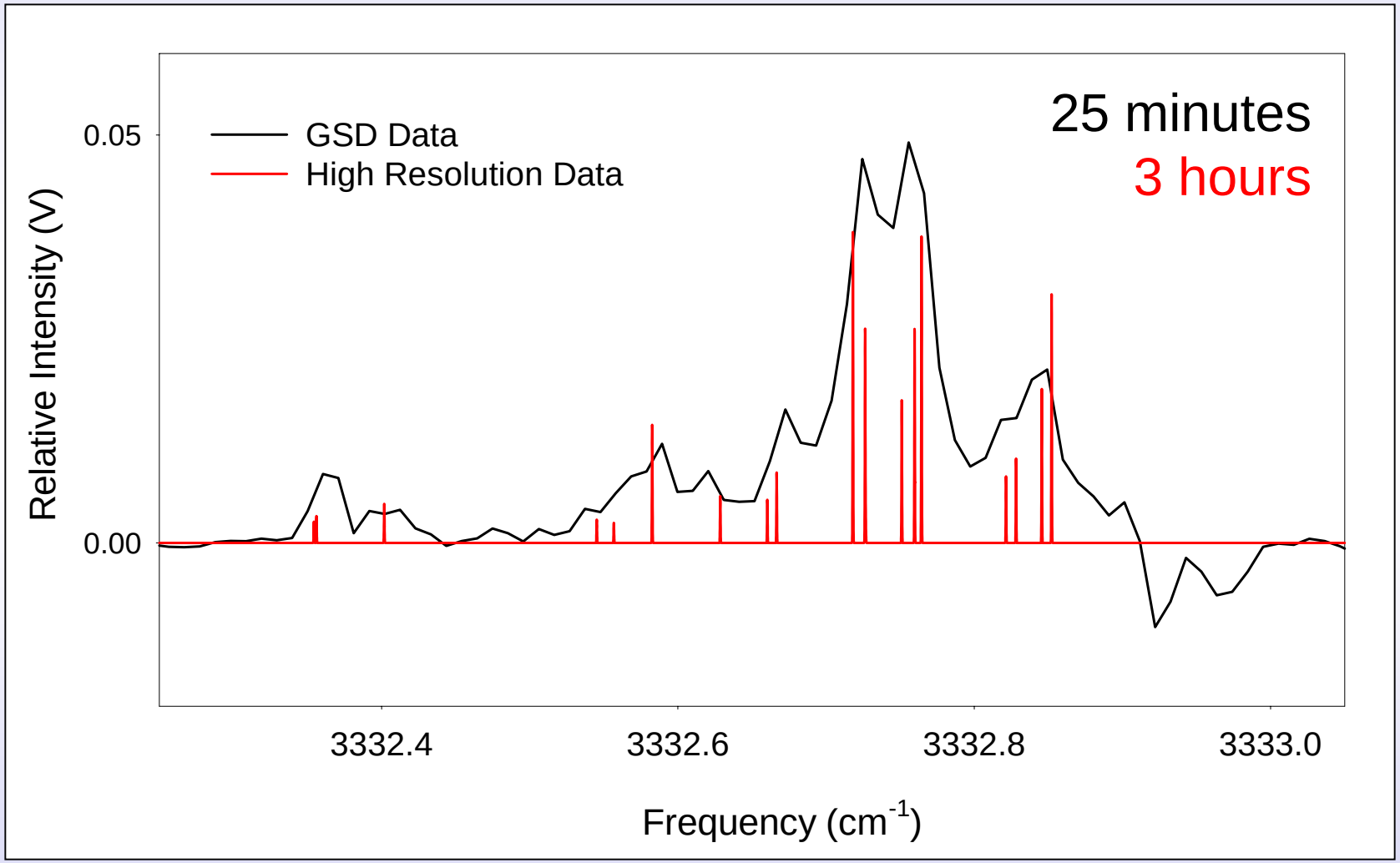


Ultracold Molecules in Free Jet Expansion

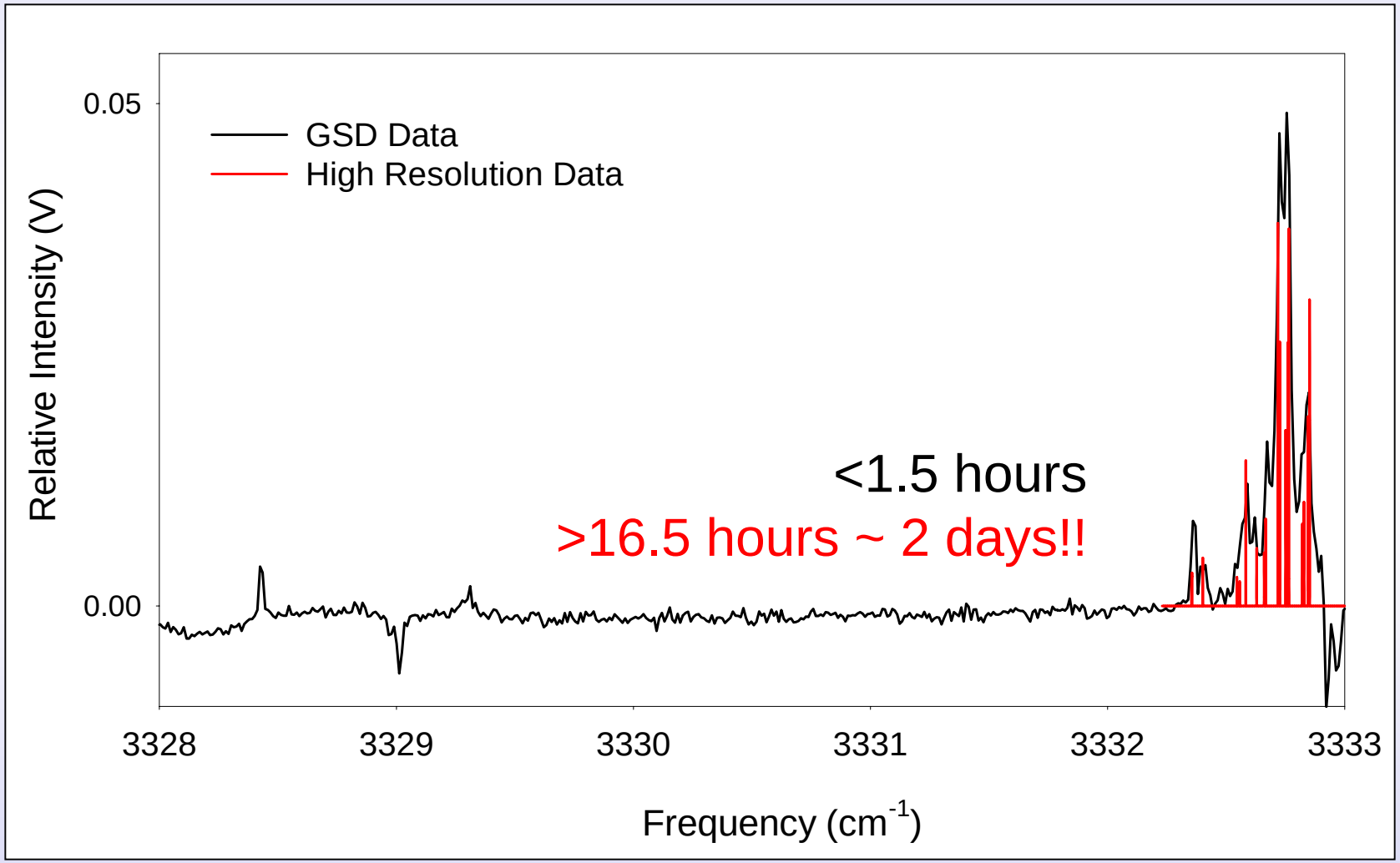
Fabry-Perot Cavity

Multipass IR

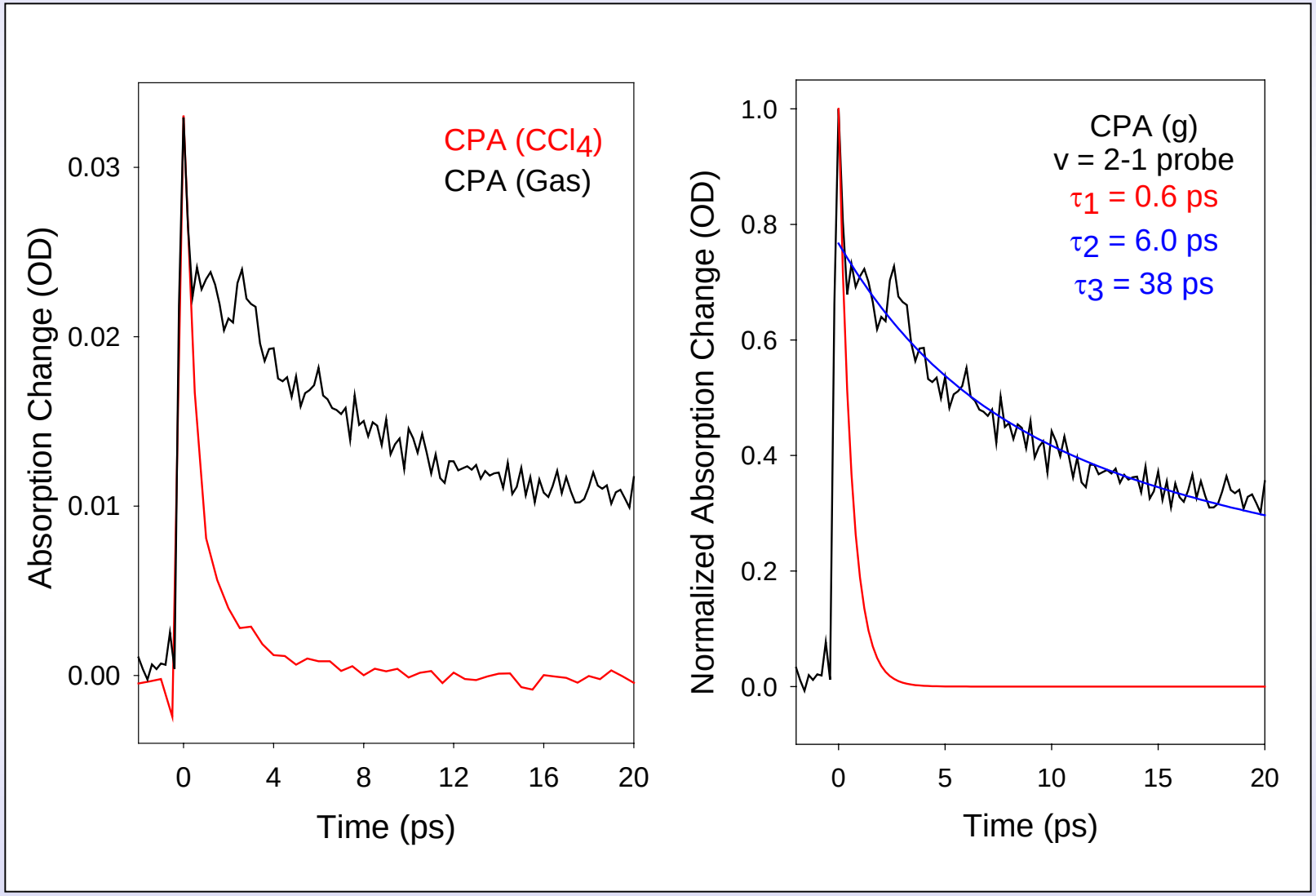
P(1) of 1-butyne



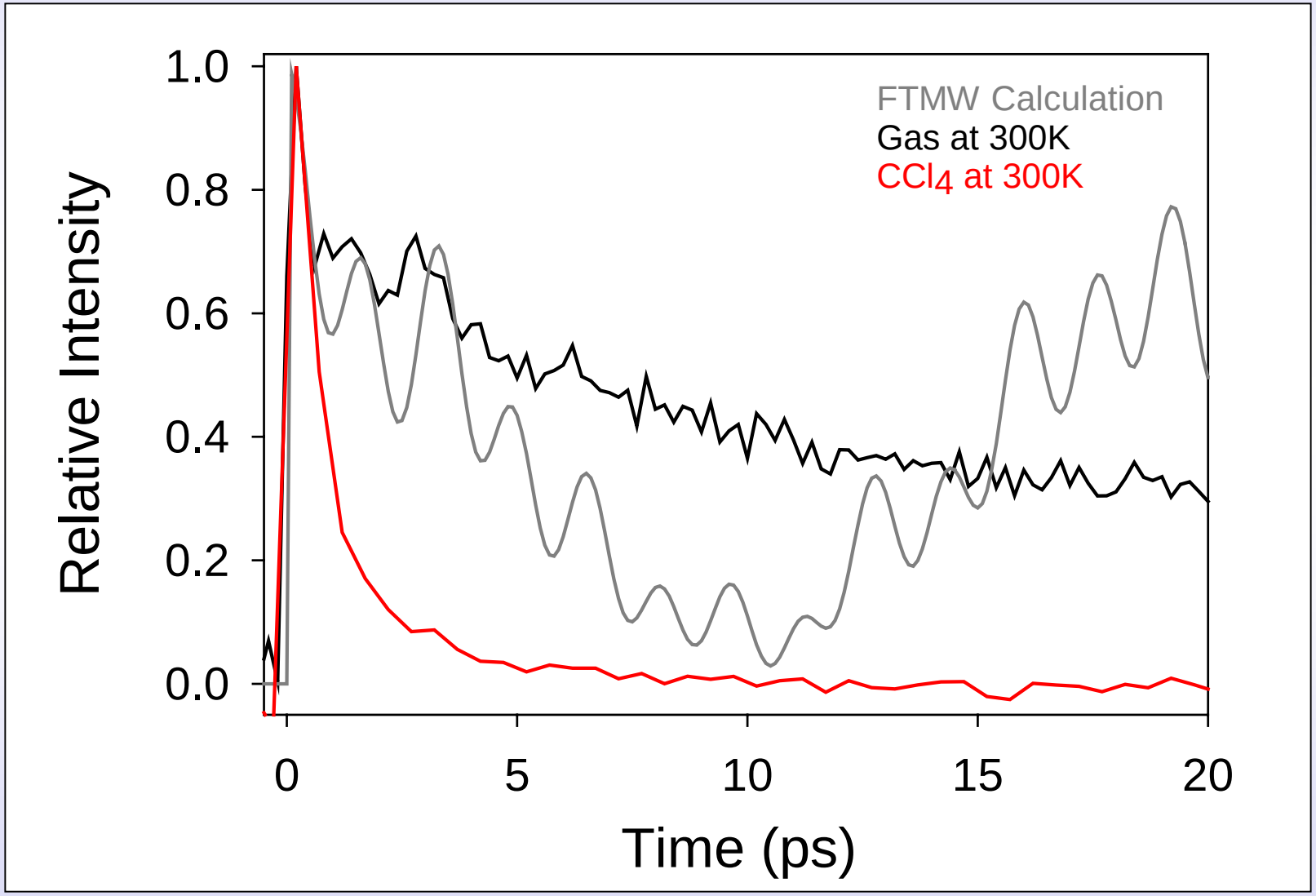
P(1) of 1-butyne… longer scan



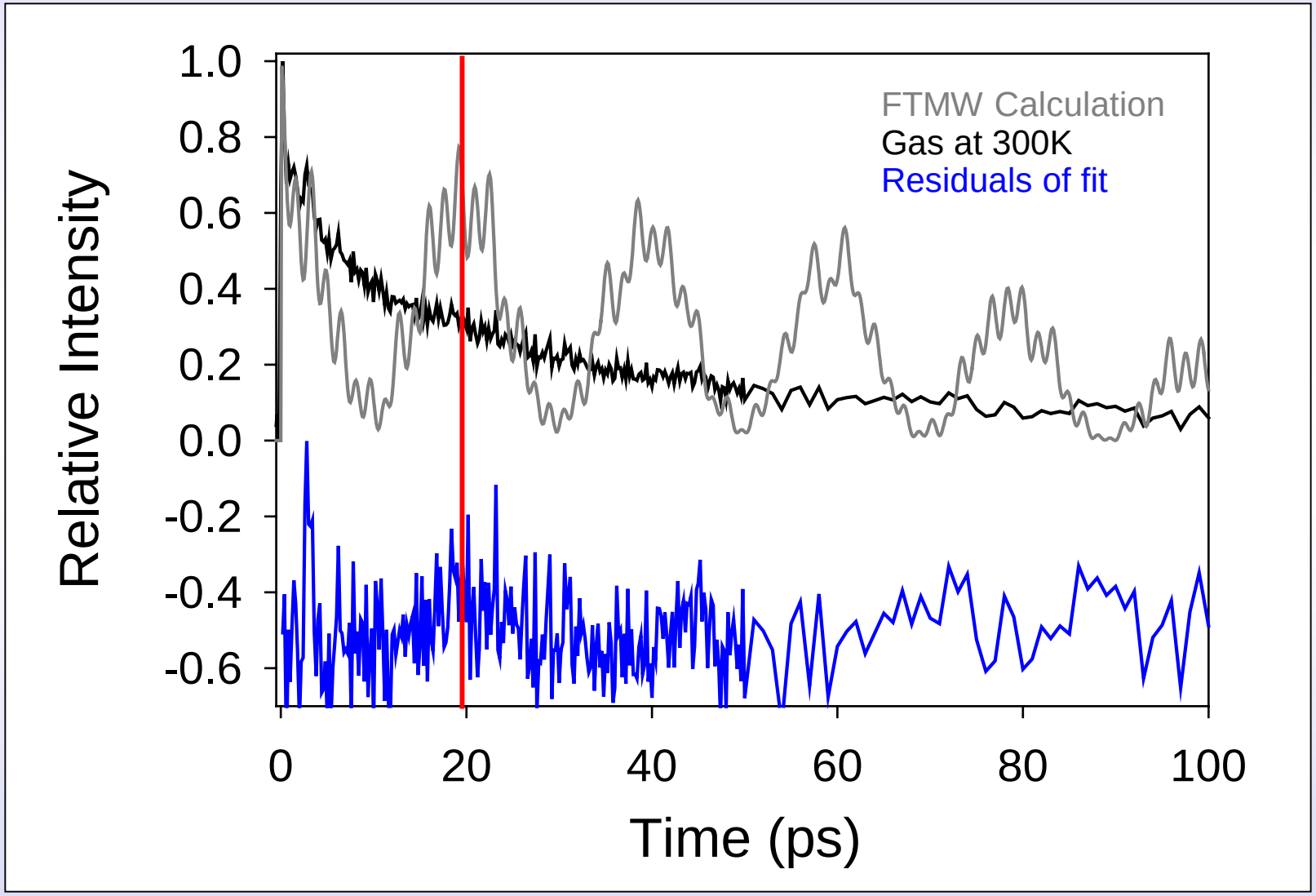
CPA: Time Domain Results



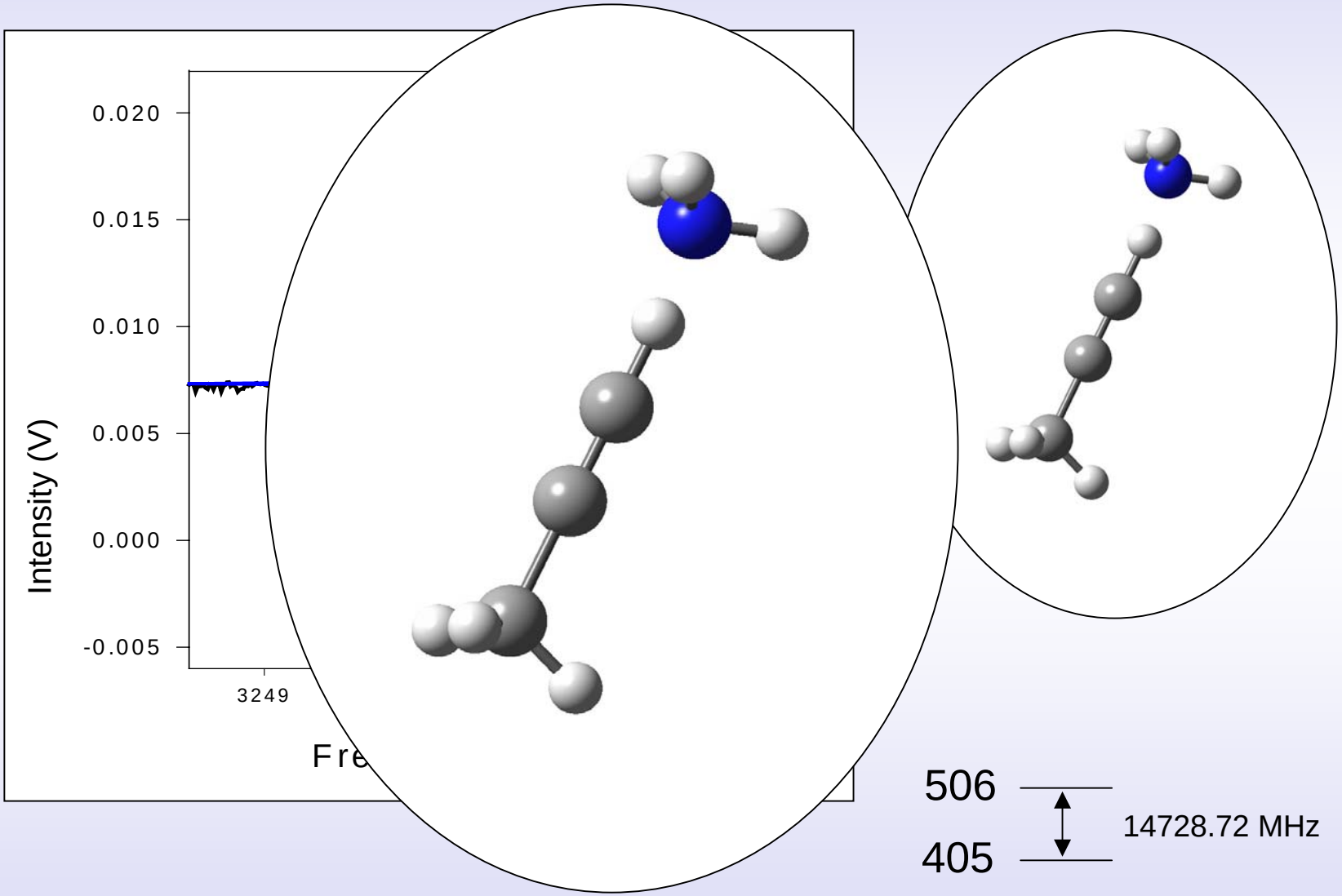
CPA Time and Frequency Domain Agreement



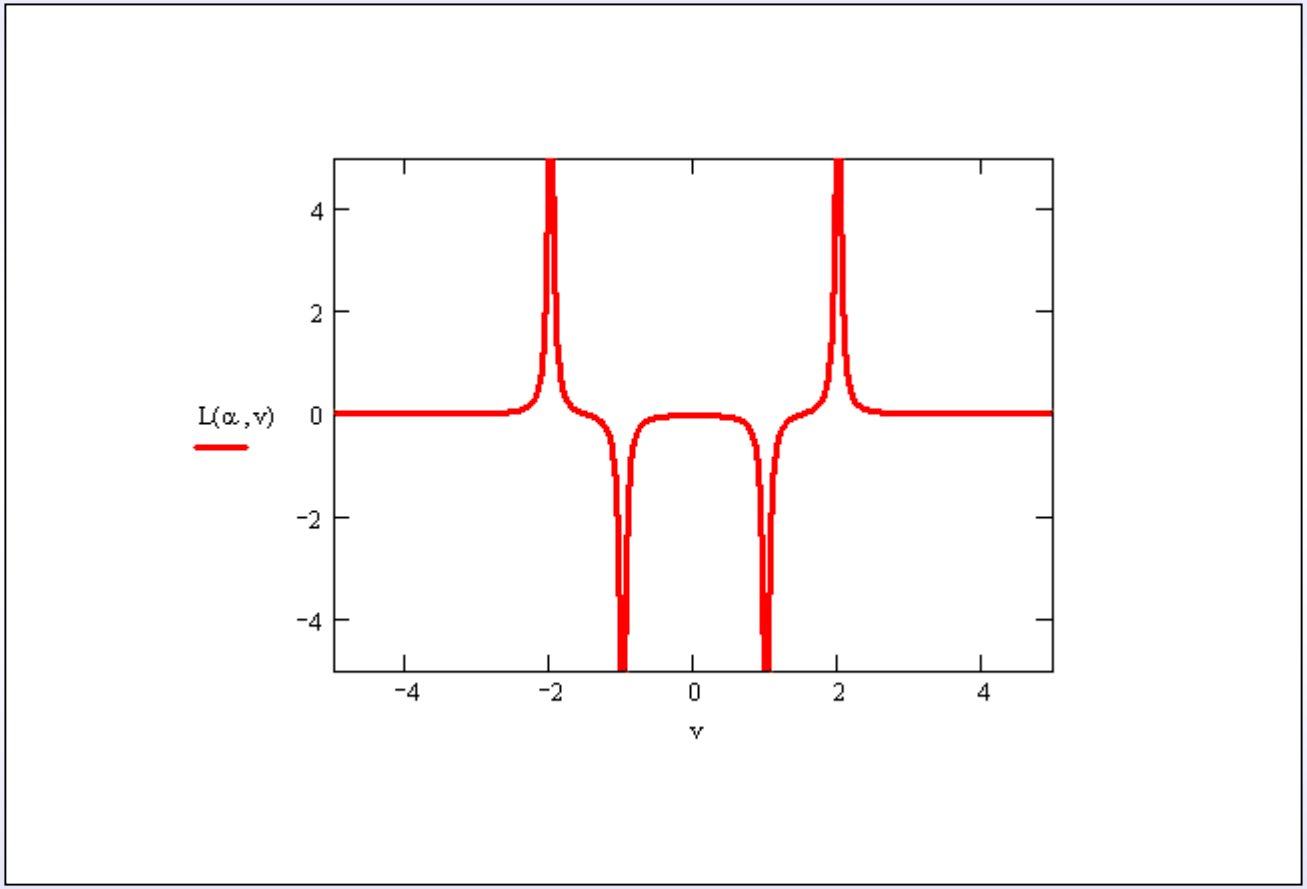
Oscillation Agreement



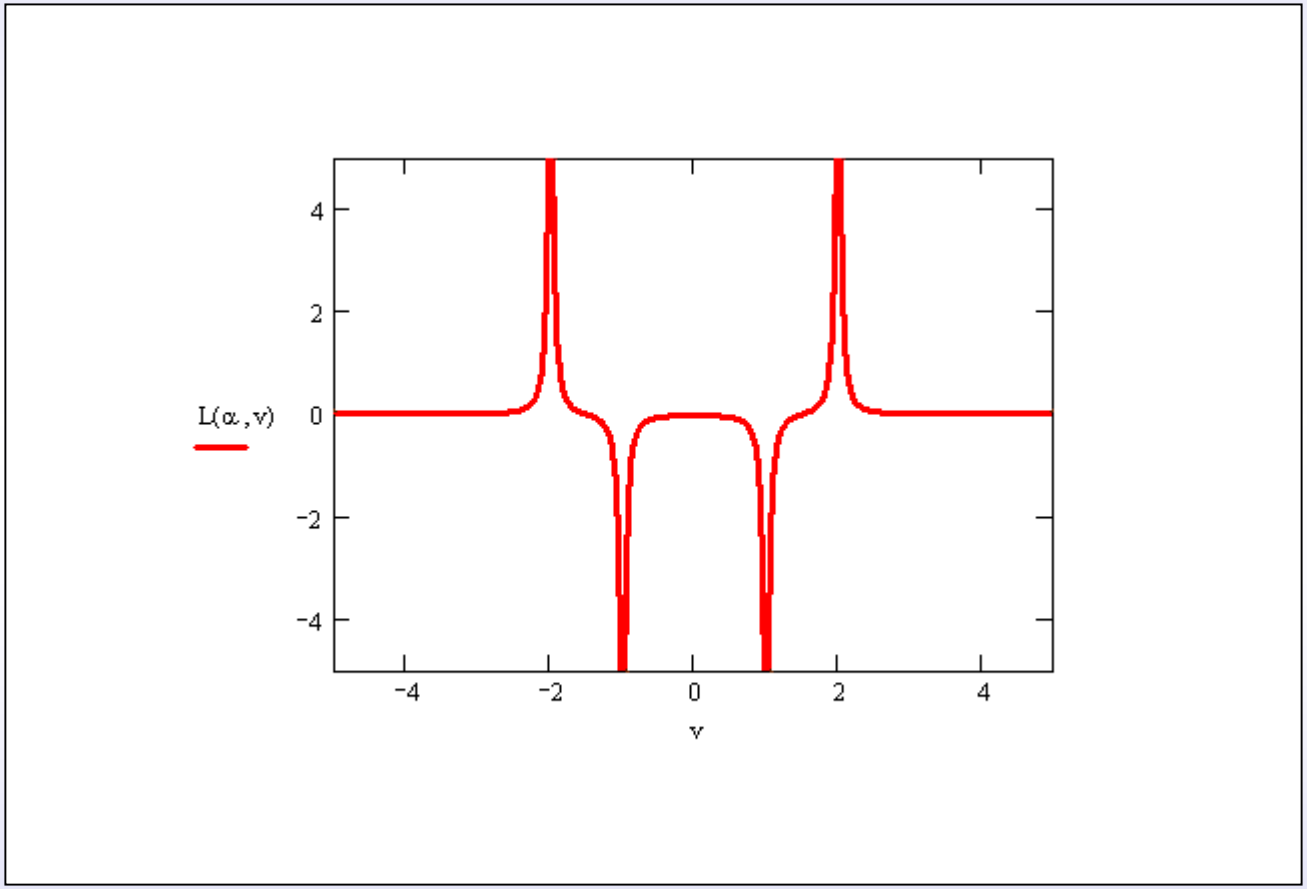
IR-FTMW of NH_3-$HCCCH_3$ Complex



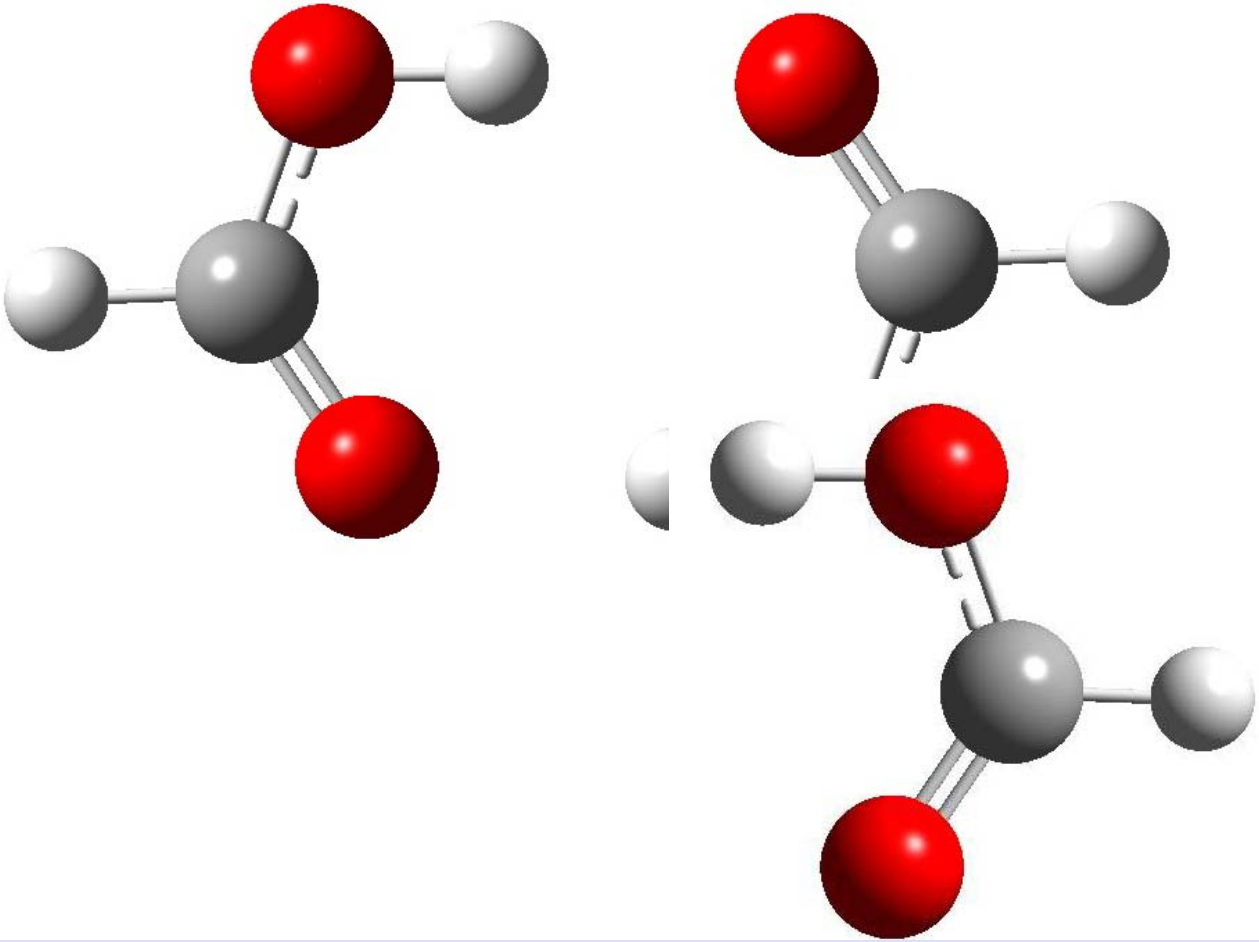
Limitations of Current FTMW Technique



Limitations of Current FTMW Technique

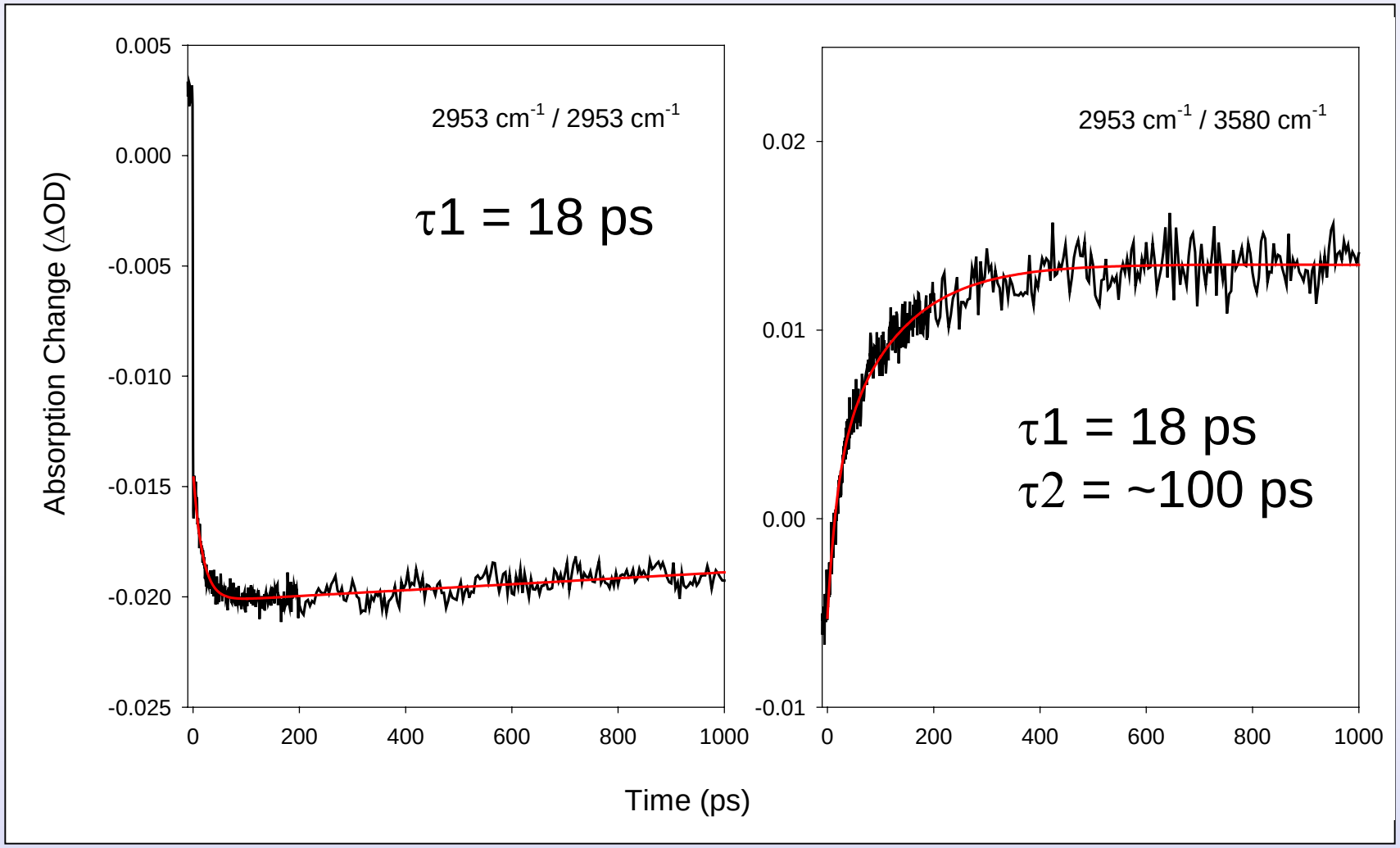


Acid Dimers



Trifluoroacetic Acid:

Evidence for Cracking Open the Gas Phase Dimer



Back to the FEL?

- Upgrades!
  - give more energy/pulse
    - can’t beat it with our tabletop lasers
- Issues and problems
  - Out of commission equipment
  - Practical problems seen in the past…

Acknowledgements

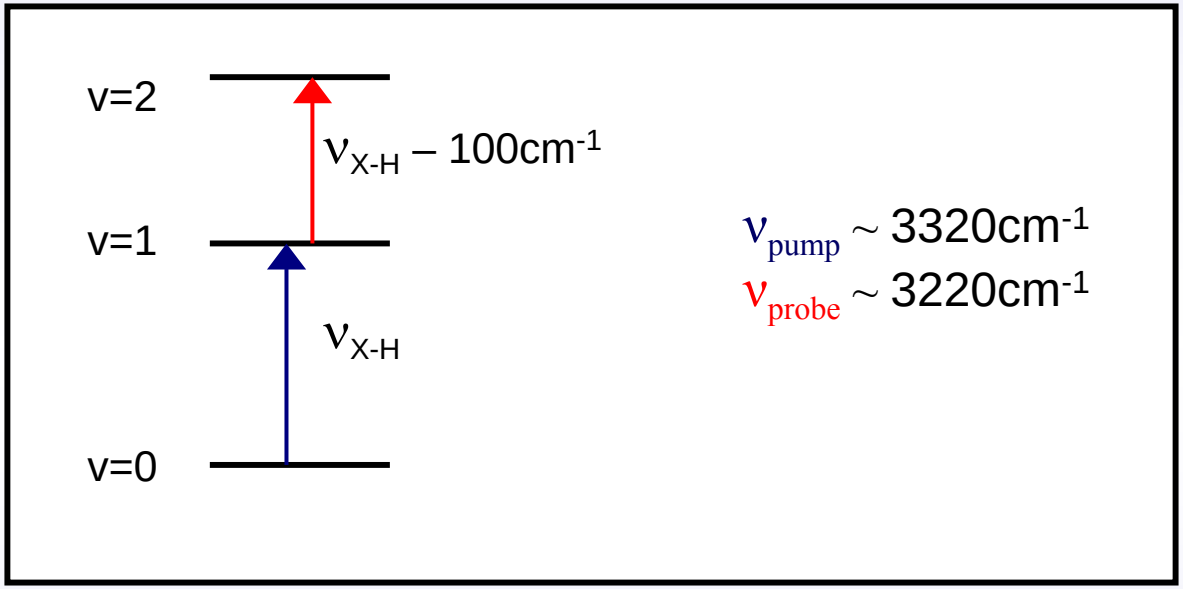
Pate Lab

NSF

SELIM

JLAB

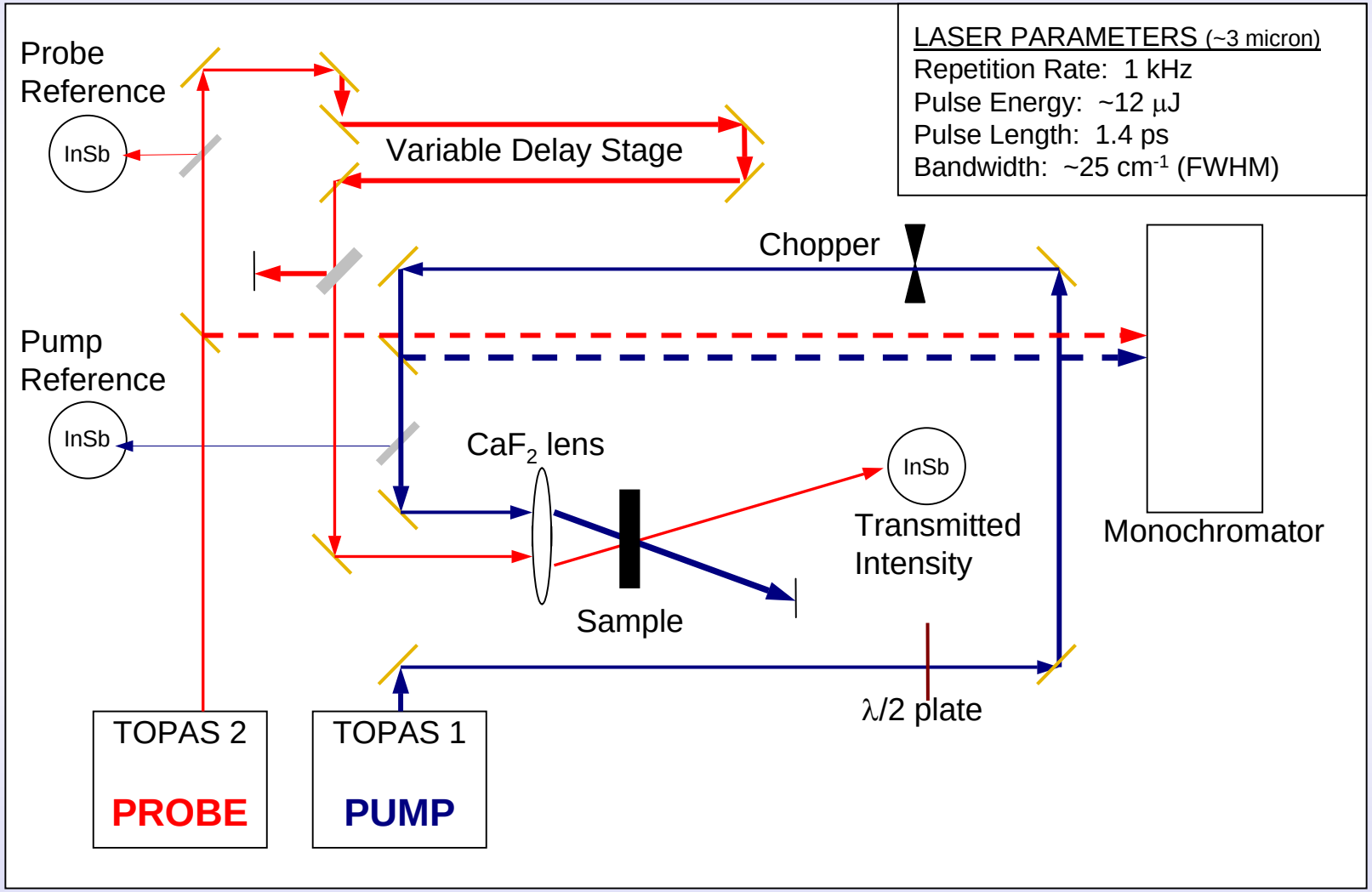
Transient Absorption Spectroscopy
Pump – Probe Scheme



$$\Delta OD = \ln \frac{T}{T_0} = Ae^{-\frac{t_d}{\tau}}$$

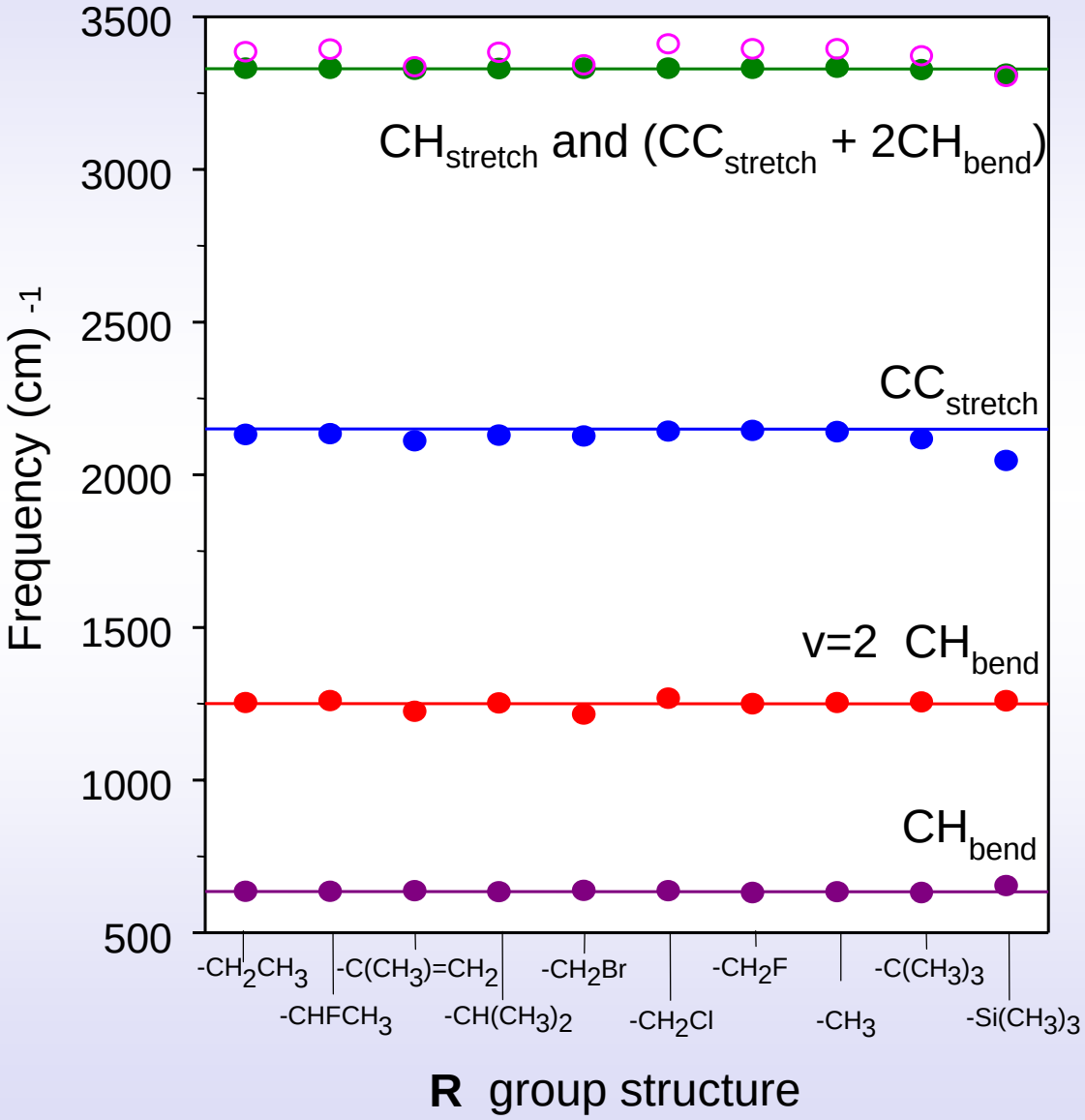
T: transmission of probe in presence of pump
T_0: transmission of probe in absence of pump
A: maximum signal
t_d: variable optical delay time
τ: vibrational lifetime

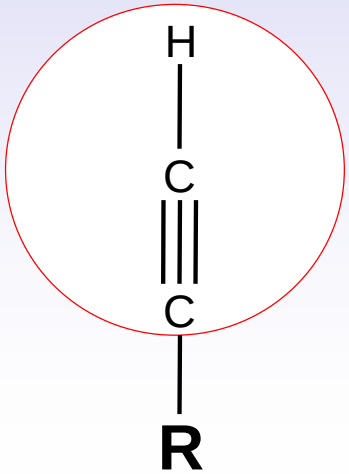
Experiment Setup:
Transient Absorption Spectroscopy



Acetylenic Compounds:

Possibility of Constant Intermolecular Rate



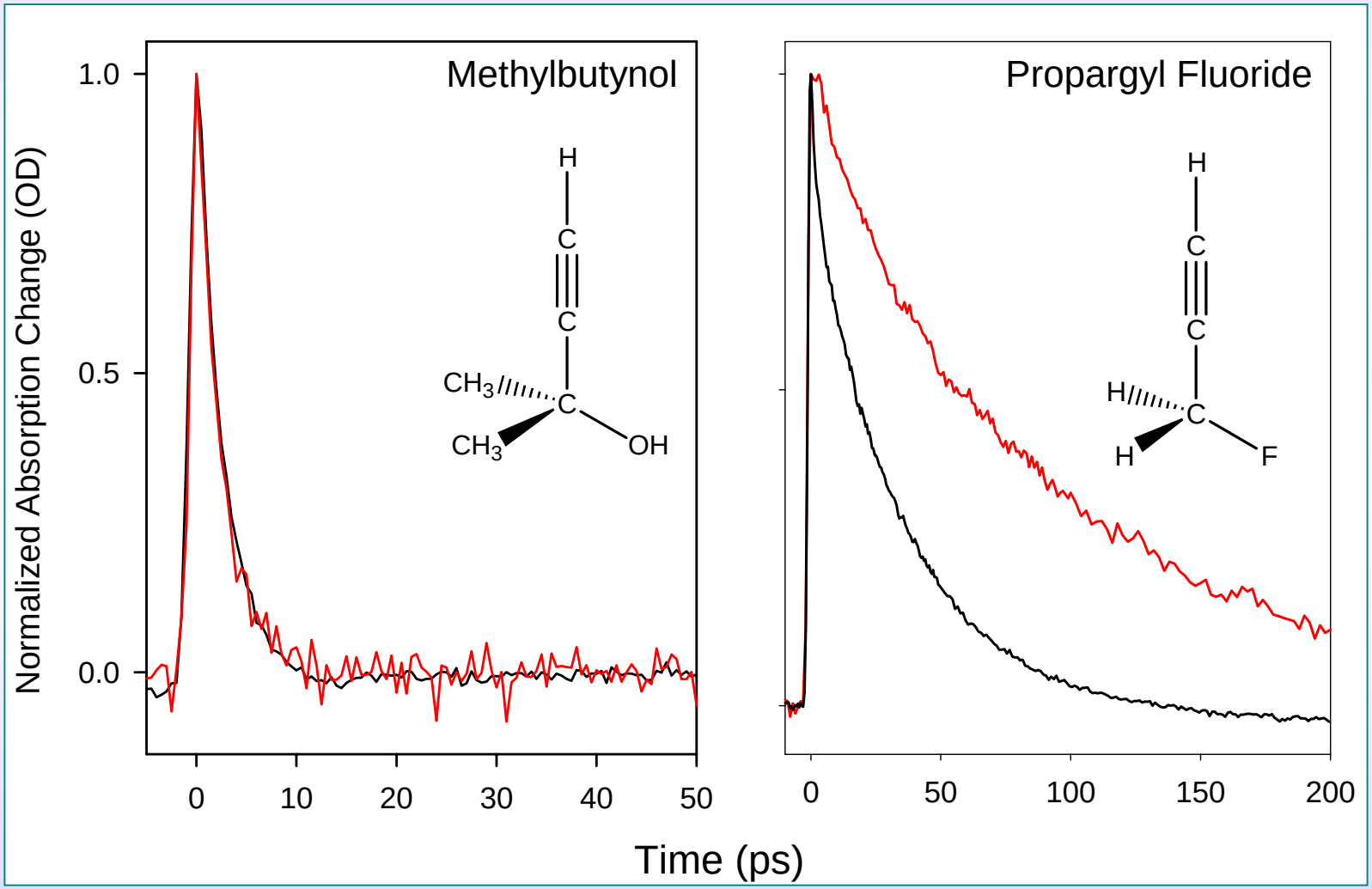


Acetylenic CH stretch is a local mode oscillator with motion dominated by the terminal H-atom.

This atom extends approximately 3A from the R group.

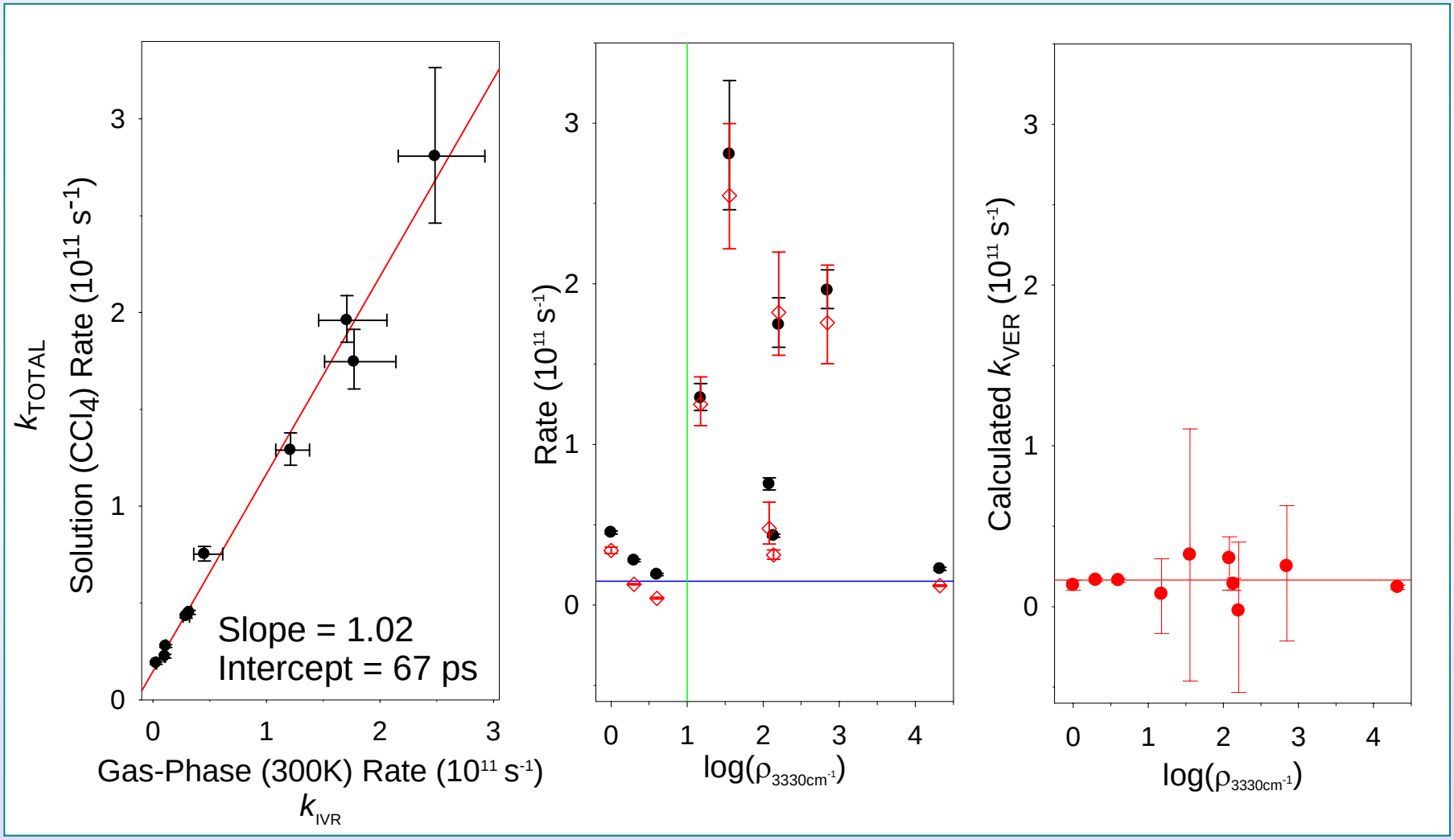
Gas Phase vs Solution Phase:

$$k_{TOT} = k_{IVR} + k_{VER}$$



Comparison of Solution Rate and Gas-Phase IVR Rate

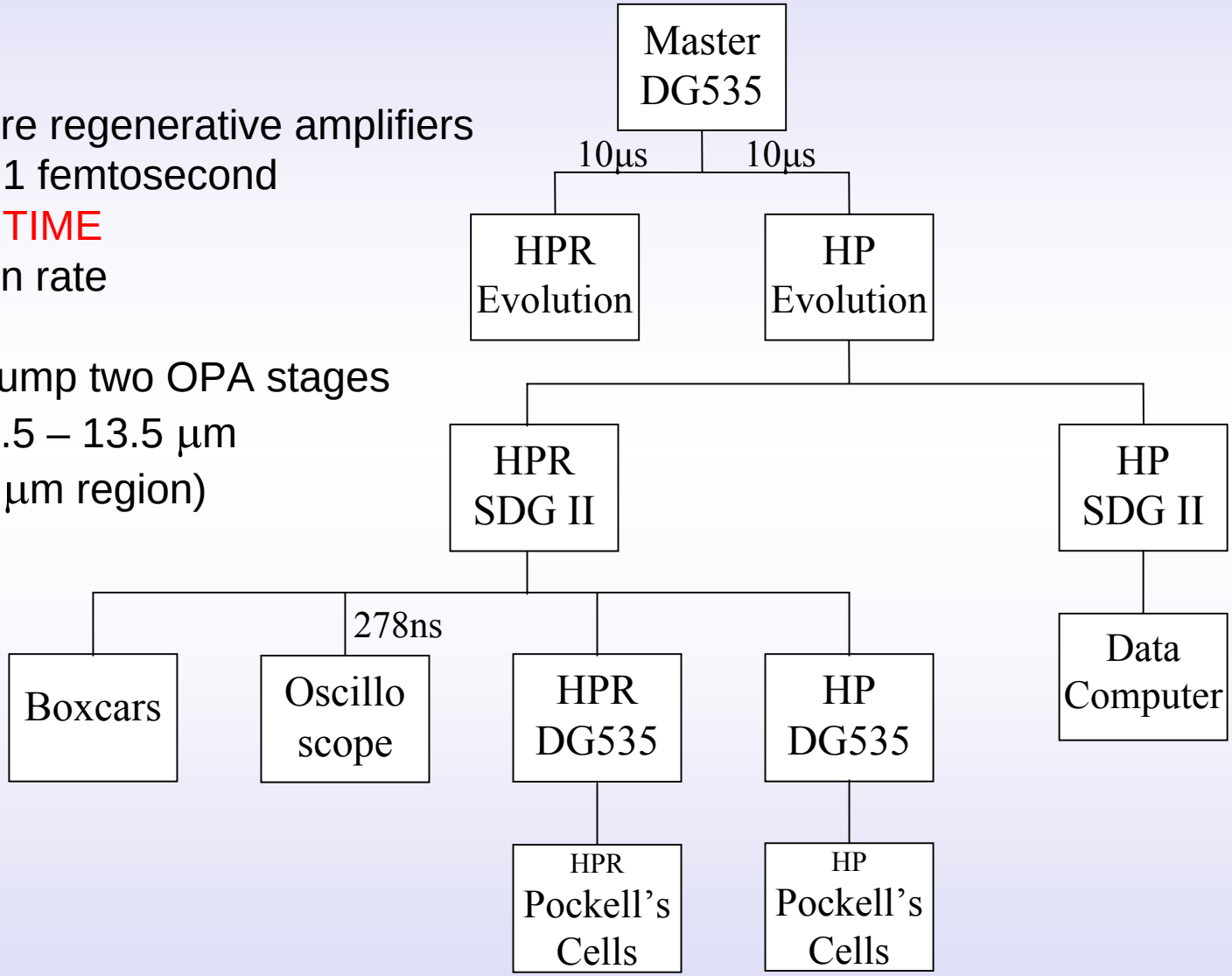
$$k_{TOT} = k_{IVR} + k_{VER}$$



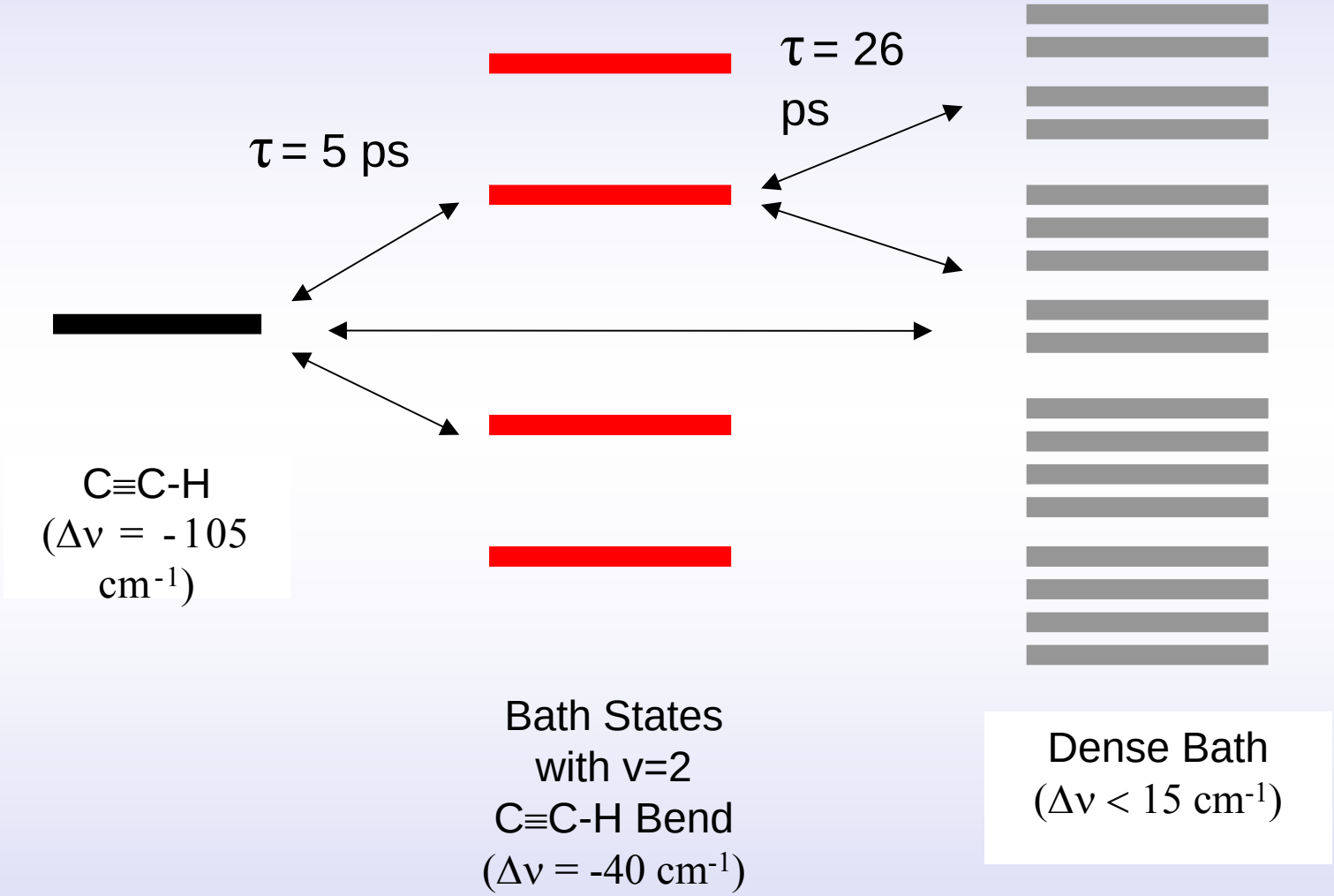
Time Synching Triggering Scheme

Two Ti:Sapphire regenerative amplifiers
1 picosecond, 1 femtosecond
SYNCHED IN TIME
1 kHz repetition rate

Each split to pump two OPA stages
tunable from 2.5 – 13.5 μm
(~10 μJ in 3 μm region)

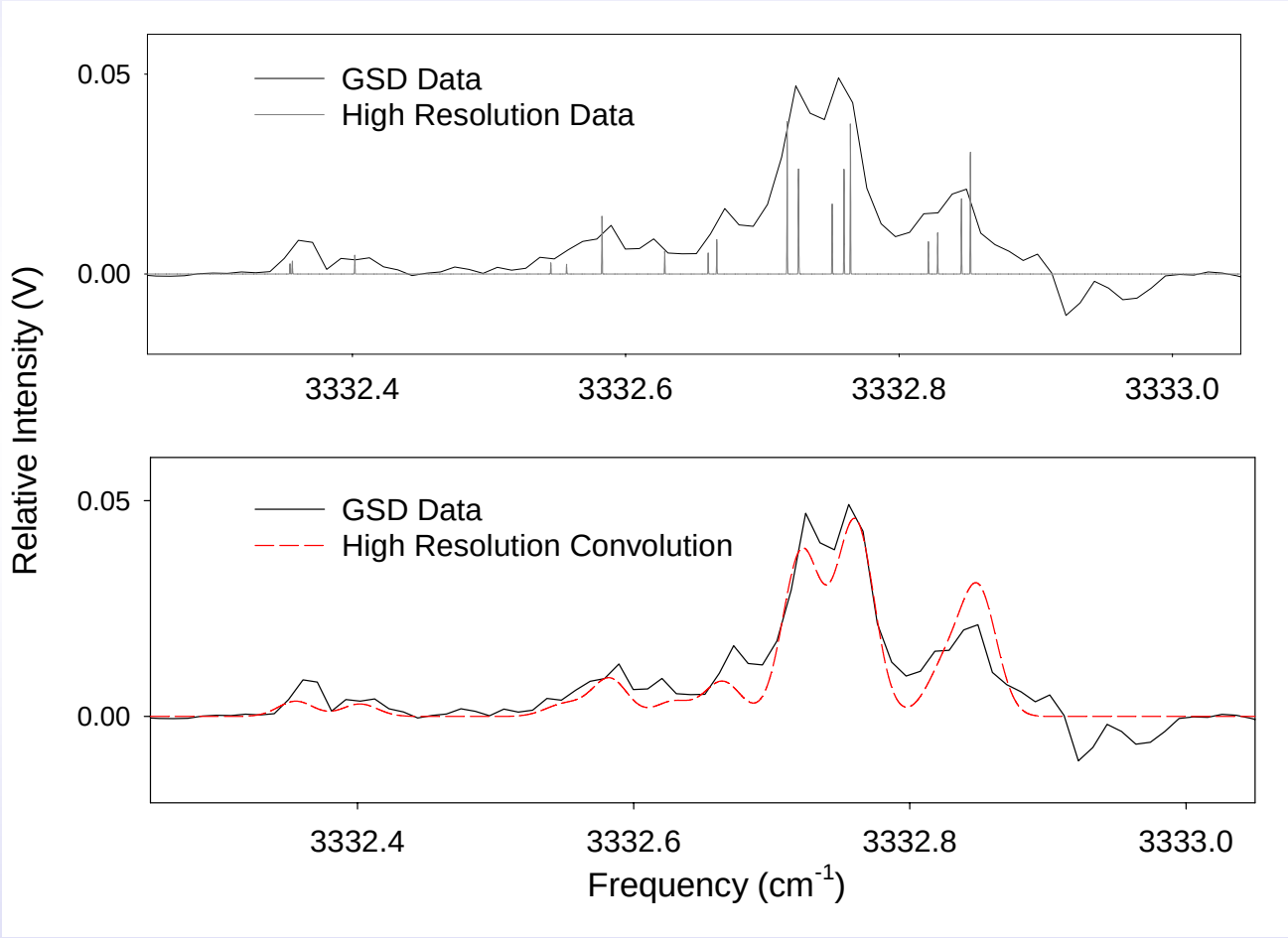


Tier Model Dynamics for Terminal Acetylenes



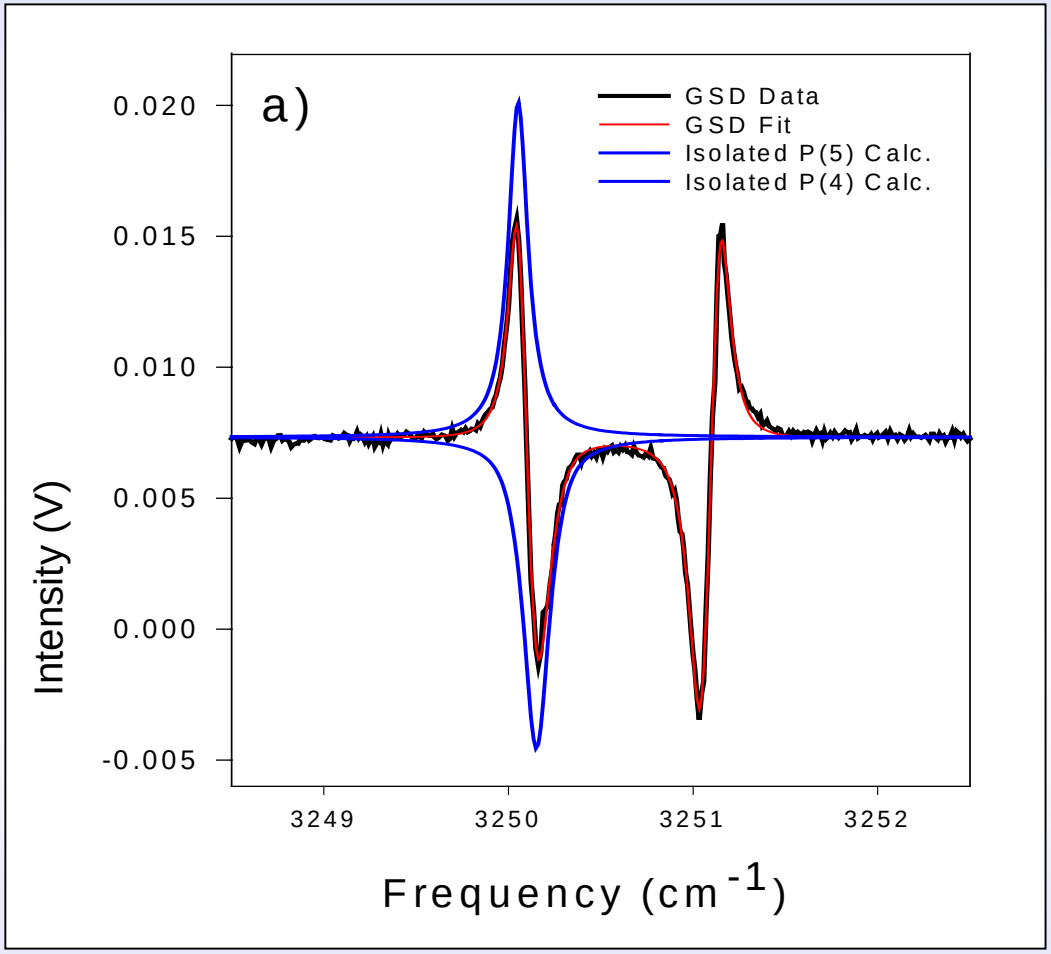
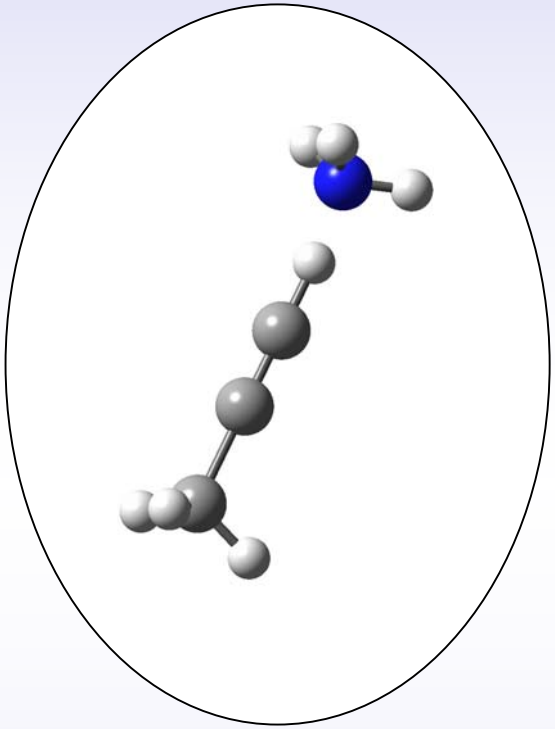
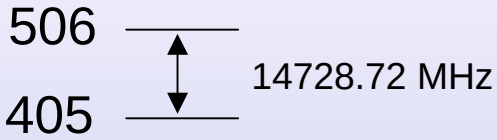
Yoo, H.S. et al. *J. Phys. Chem A* **2004** *108*(8) 1365-1379

Comparison: GSD to MB



SCAN RATES

FTMW: 0.001 cm^{-1}/s

MB: 0.3 cm^{-1}/s

IR-FTMW of NH_3-$HCCCH_3$ Complex