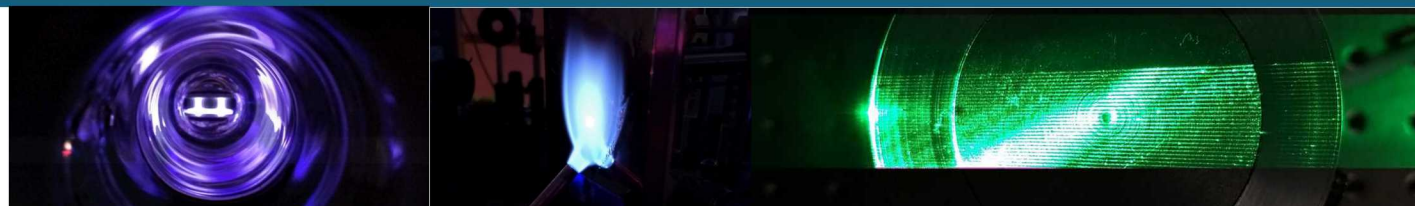


Transient Ro-Vibrational SFG of Physisorbed Molecules at a Metal Surface



PRESENTED BY

Benjamin M. Goldberg



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

My background: Nanosecond Pulse Plasma Discharges

Nanosecond pulse discharges represent a novel way to initiate chemistry

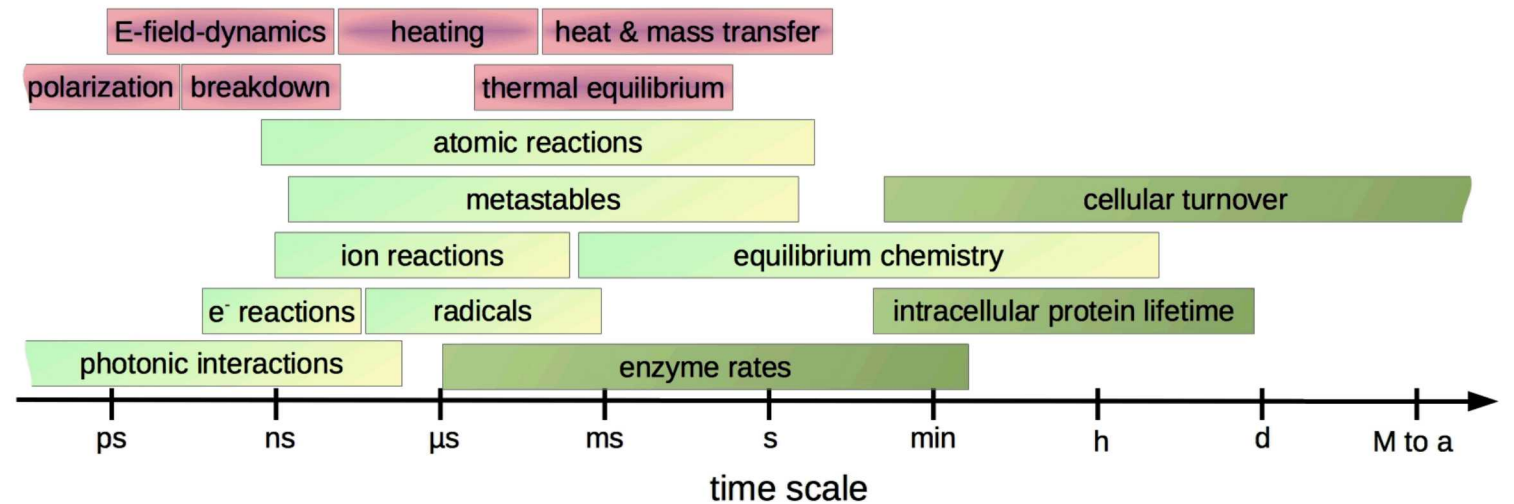
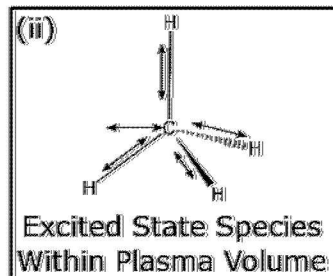
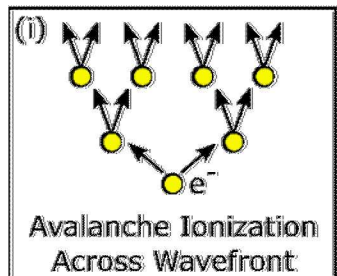
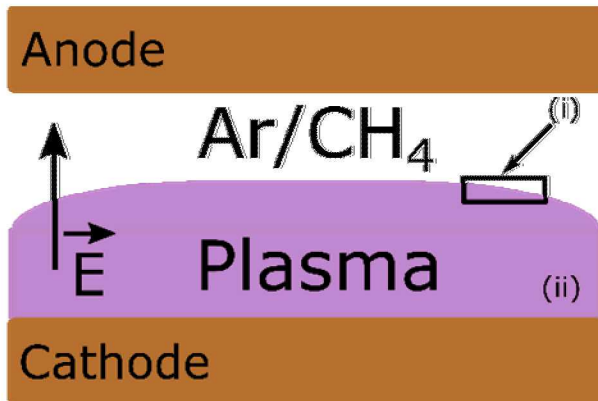
- When an electric field is present, charges in the gas are accelerated
- Energy transfer typically excites internal degrees of freedom

If electron energy is large enough, ionization occurs typically through electron impact

- Generates an electron avalanche (ionization wave)

Such discharges are known to be nonequilibrium

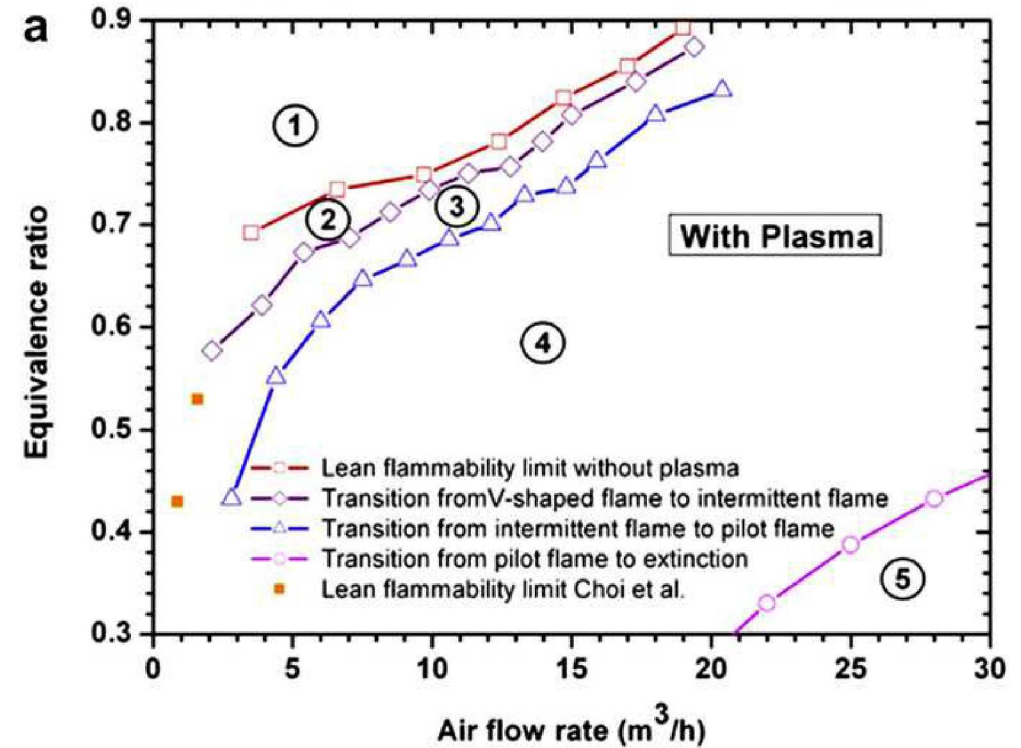
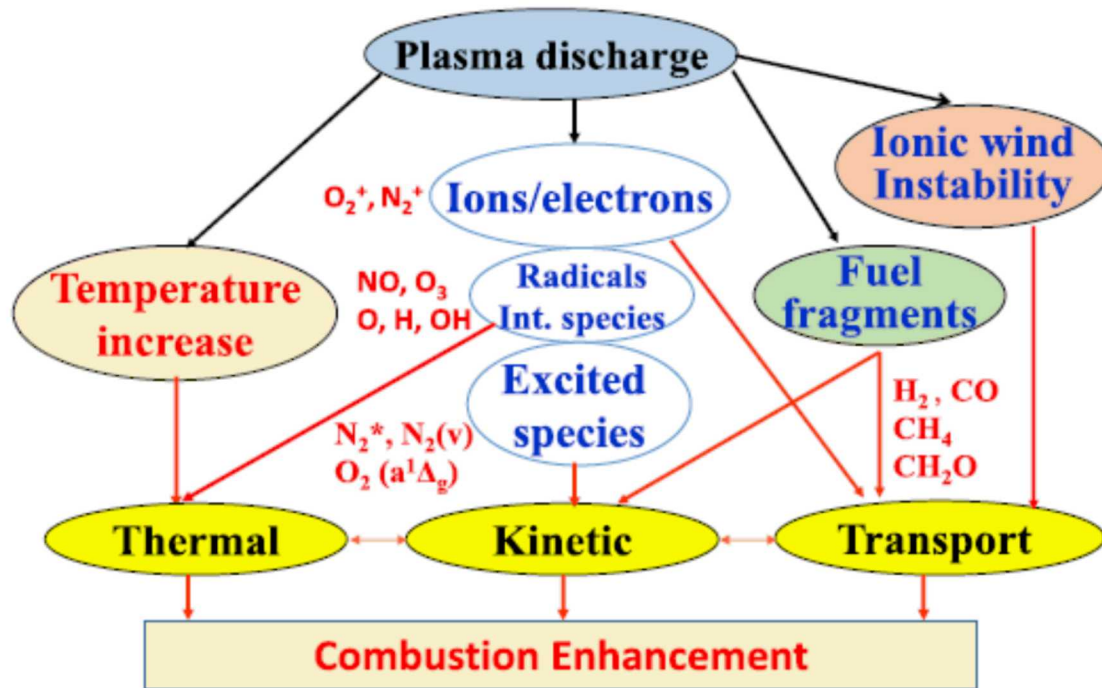
- i.e. - $T_{rot} \neq T_{vib} \neq T_{ele}$
- These can present a unique starting point for combustion applications



- In order to understand how we can use the plasma we must have an in depth understanding of fundamental plasma processes

Motivation: Plasma Assisted Combustion

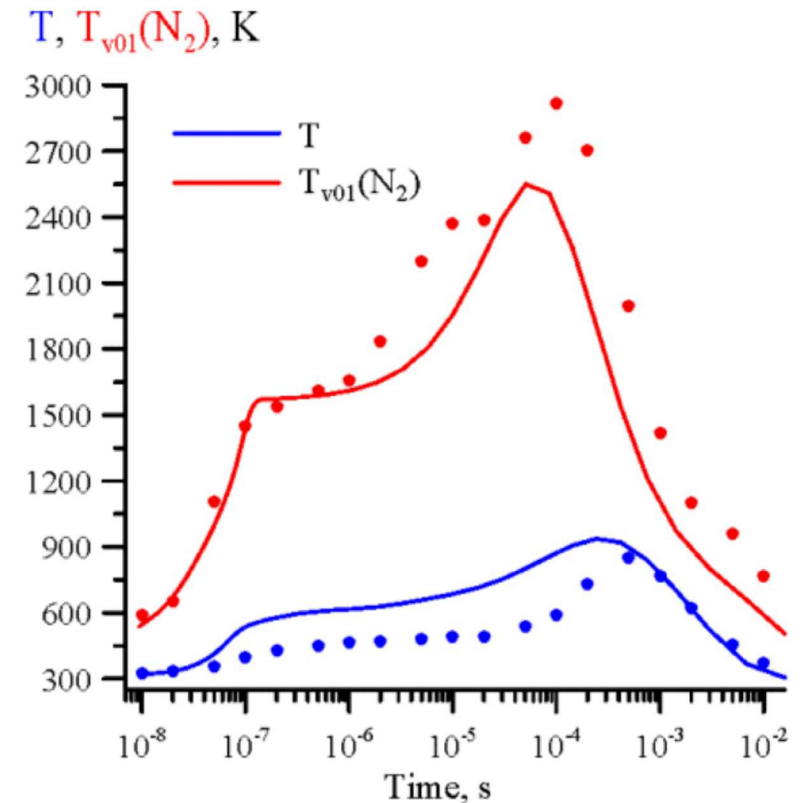
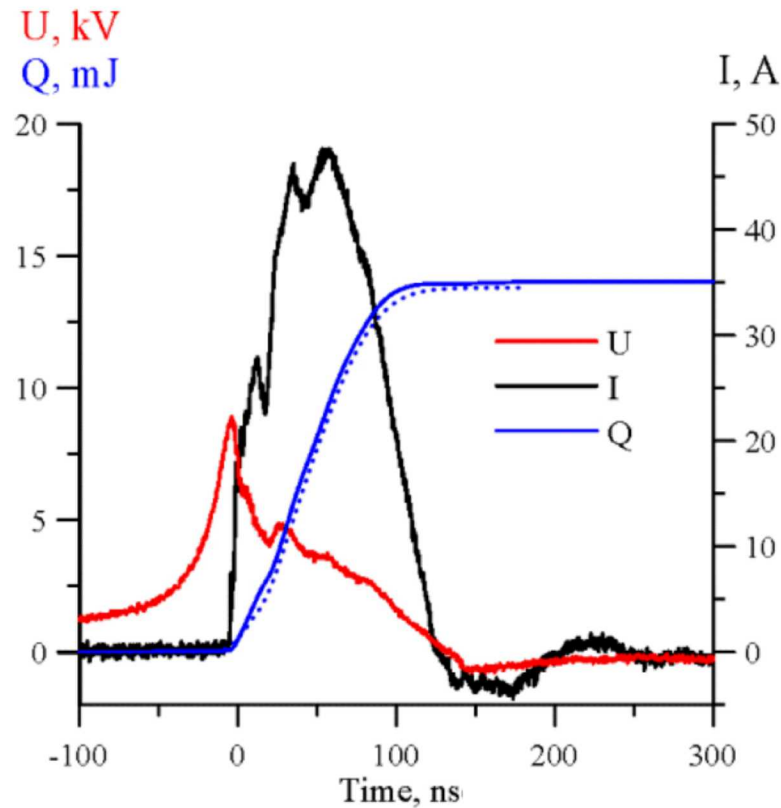
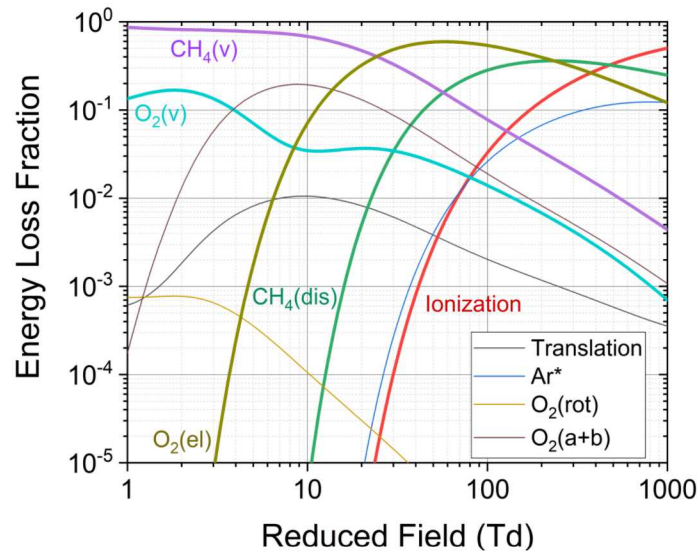
Excited species and radicals within discharges have been shown to enhance combustion processes



Energy Cascading to Vibrational Excitation

Electron energy loss is a function of E/N

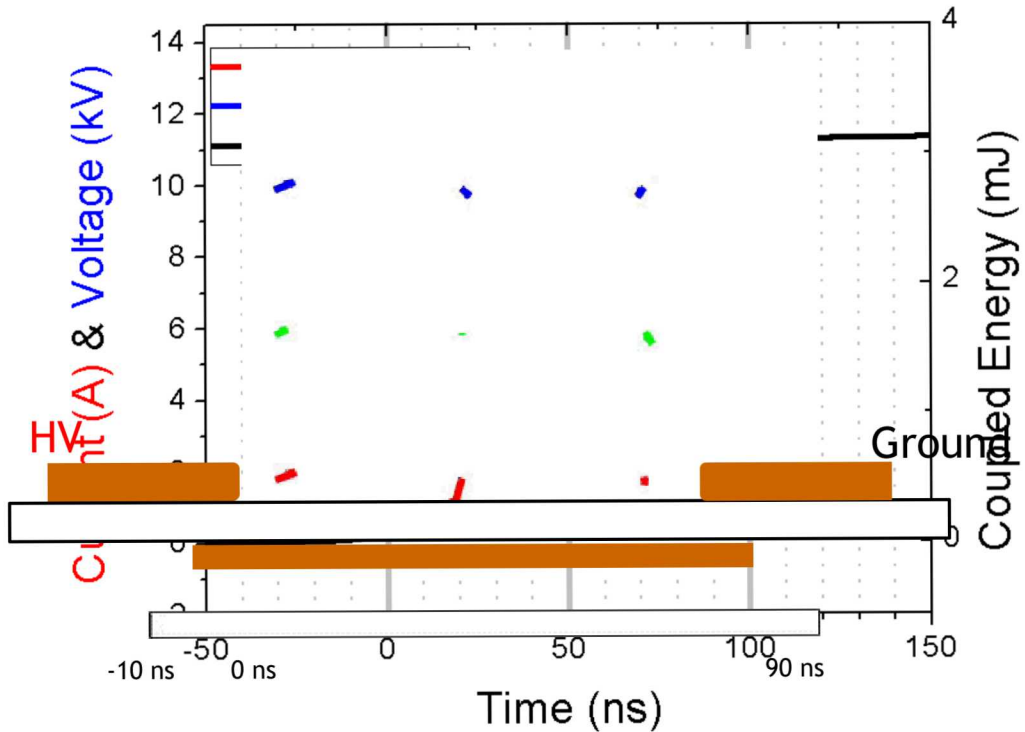
- Ratio of how much energy we give electrons collision frequency
- Ionization happens at ~ 100 Td, but vibrational pumping is optimized at $\sim 1-10$ Td



V-T relaxation rates are known to be slow, so this represents an available pool of energy to help lower reaction barriers

We can control radical production by controlling the electric field

Example Measurement: Surface Ionization Wave

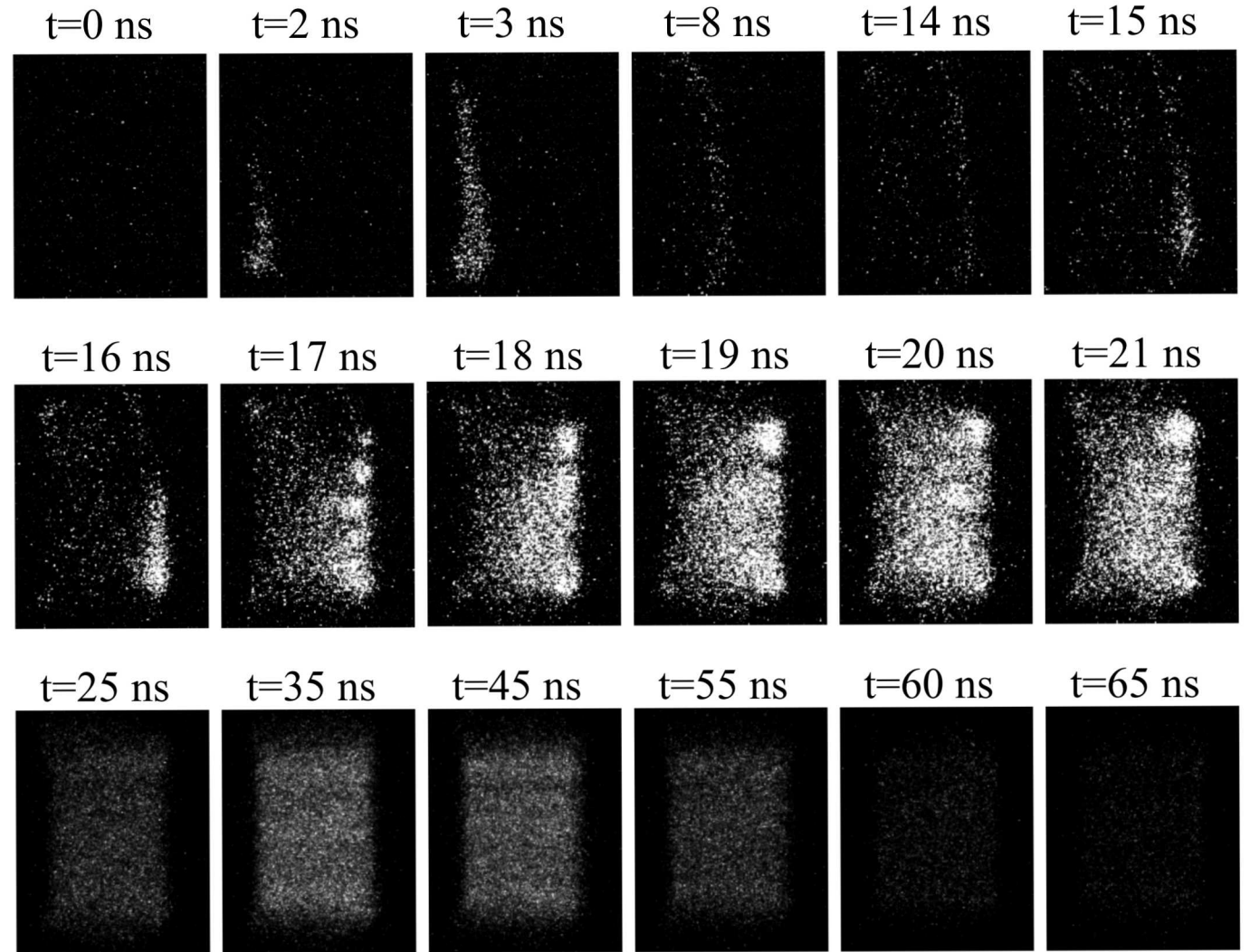


ICCD images taken with a 1ns gate

Upon reaching ground, reverse wave can be seen

- Quasi DC discharge established

Ionization wave speed of $\sim 1\text{mm/ns}$



My Background: E-Field Induced Second Harmonic (E-FISH)

For SHG, define second order polarization to be: $\mathbf{P}^{(2)}(t) = \chi^{(2)} \epsilon_0 \mathbf{E}^2(t)$

Assuming an oscillating electromagnetic field of frequency ω :

$$\circ E(t) = E_0 e^{-i\omega t} + E_0^* e^{+i\omega t}$$

$$\Rightarrow P^{(2)}(t) = (2\epsilon_0 \chi^{(2)} E^* E) + 2\epsilon_0 \chi^{(2)} (E_0^2 e^{-2i\omega t} + c.c.)$$

E-FISH is described as a third order nonlinear process:

$$\circ P^{(2\omega)} = \frac{3}{2} N \chi^{(3)}(-2\omega, 0, \omega, \omega) E_{Ext} E_{Pump} E_{Pump}$$

$$\circ \Rightarrow I^{(2\omega)} = A \cdot N^2 (E_{Ext})^2 (I_{Pump})^2$$

Benefits of E-FISH Method:

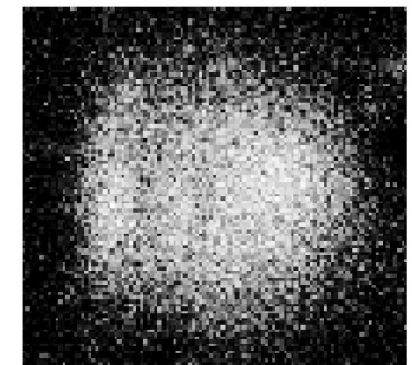
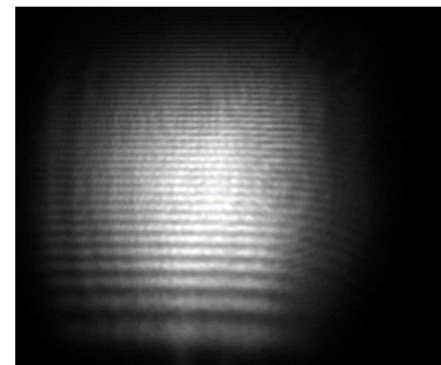
- Signal scales as N^2
- Signal scales as E^2
- Time resolution determined by pump beam duration
- Spatial resolution determined by beam focusing parameters
- Non-resonant method works in any species and gas mixtures

- \mathbf{P} : Induced polarization
- χ : Electric Susceptibility
- ϵ_0 : Permittivity of vacuum
- \mathbf{E} : Electric Field

- $P^{(2\omega)}$: Induced polarization at 2ω
- N : Number Density
- $\chi^{(3)}$: Nonlinear Susceptibility (species dependent)
- E_{Ext} : Electric Field to be measured
- E_{Pump} : Electric field of incident laser

800 nm

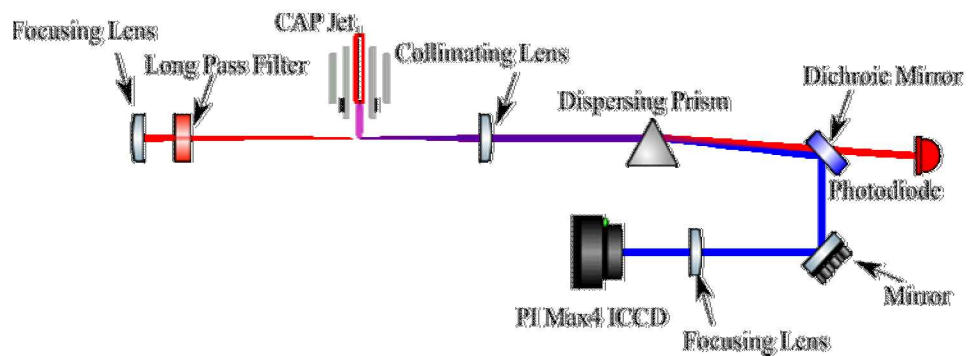
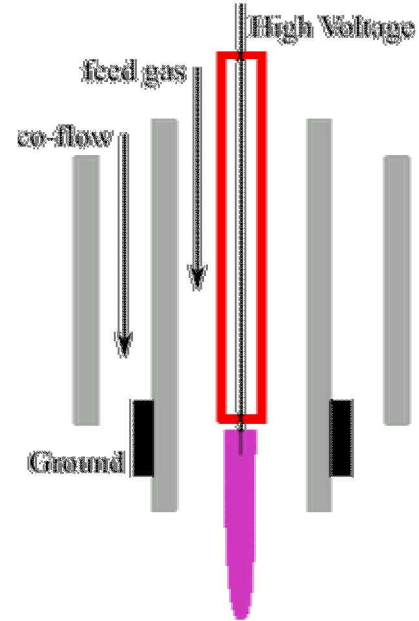
400 nm



Example Measurements: Cold Atmospheric Plasma Jet (CAP)

Individual laser shots collected and analyzed in a post processing routine

- Time bins of 500 ps used
- ~100 shots per bin



Example Measurements: Cold Atmospheric Plasma Jet (CAP)

Individual laser shots collected and analyzed in a post processing routine

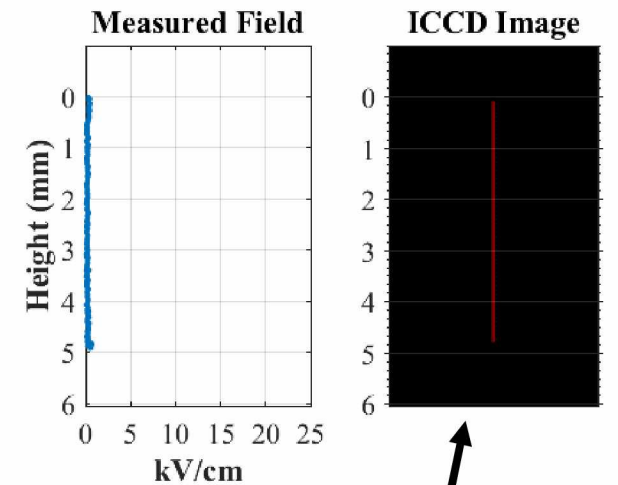
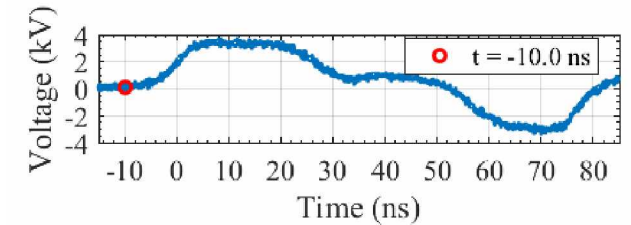
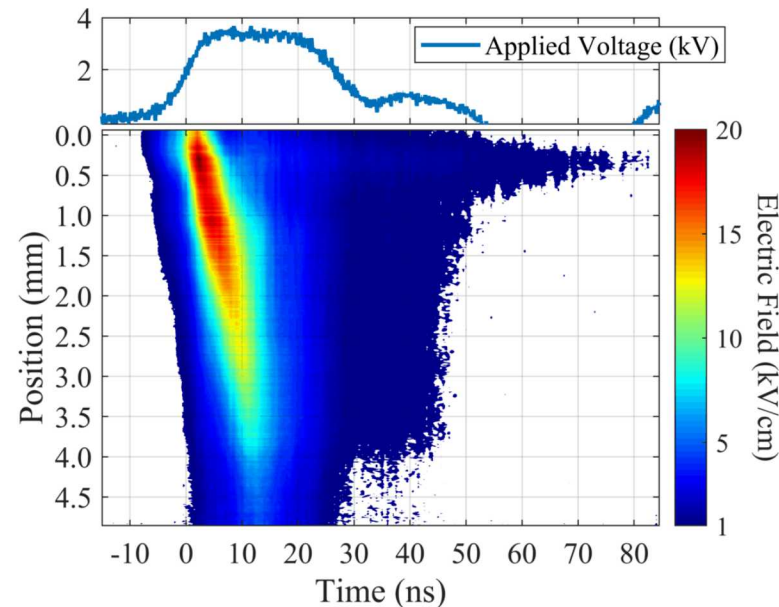
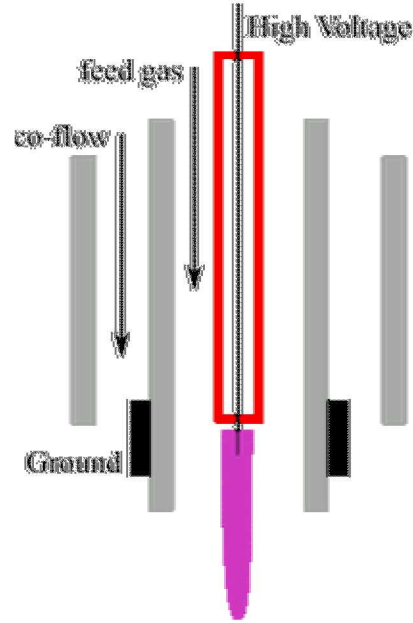
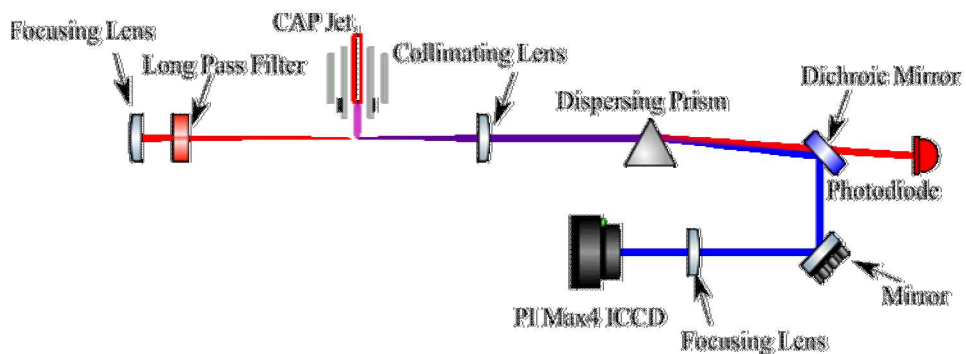
- Time bins of 500 ps used
- ~100 shots per bin

Ionization wave propagation clearly visible

- Wave speed ~ 0.3 mm/ns, consistent with ICCD images

Peak field ~ 20 kV/cm, much lower than expected

- Likely due to spatial sensitivity as plasma filaments move



- 3 ns gate with 1 ns time steps
- Averages represent 16 images
 - Red line represents laser probe

Current Work: SFG for Surface Adsorbates

SFG is forbidden in isotropic media

- At interfaces, symmetry is fundamentally broken, allowing for SFG signal

$\chi_{Res,NR}^{(2)}$ = Resonant and Nonresonant Susceptibility

a_j = Strength of Vibrational Mode, Γ_j = Relaxation time

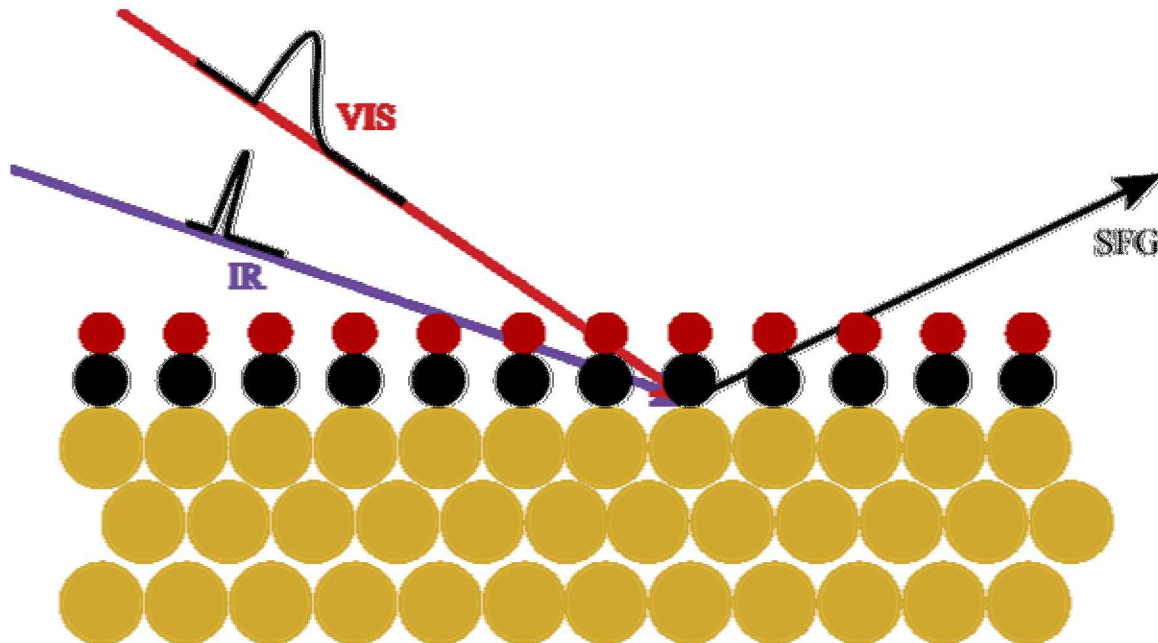
ω_v = Resonance Frequency, ω_{IR} = IR Frequency

$$I_{SFG} \propto \left| \chi_{Nr}^{(2)} + \chi_{Res,j}^{(2)} \right|^2$$

$$\chi_{Res,j}^{(2)} = \frac{a_j}{(\omega_j - \omega_{IR} - i\Gamma_j)}$$

$$I_{SFG} \propto \left| \chi_{Nr}^{(2)} + \frac{a_j}{(\omega_j - \omega_{IR} - i\Gamma_j)} \right|^2$$

Resonant enhancement occurs when $\omega_{IR} = \omega_j$



Key benefits for SFG:

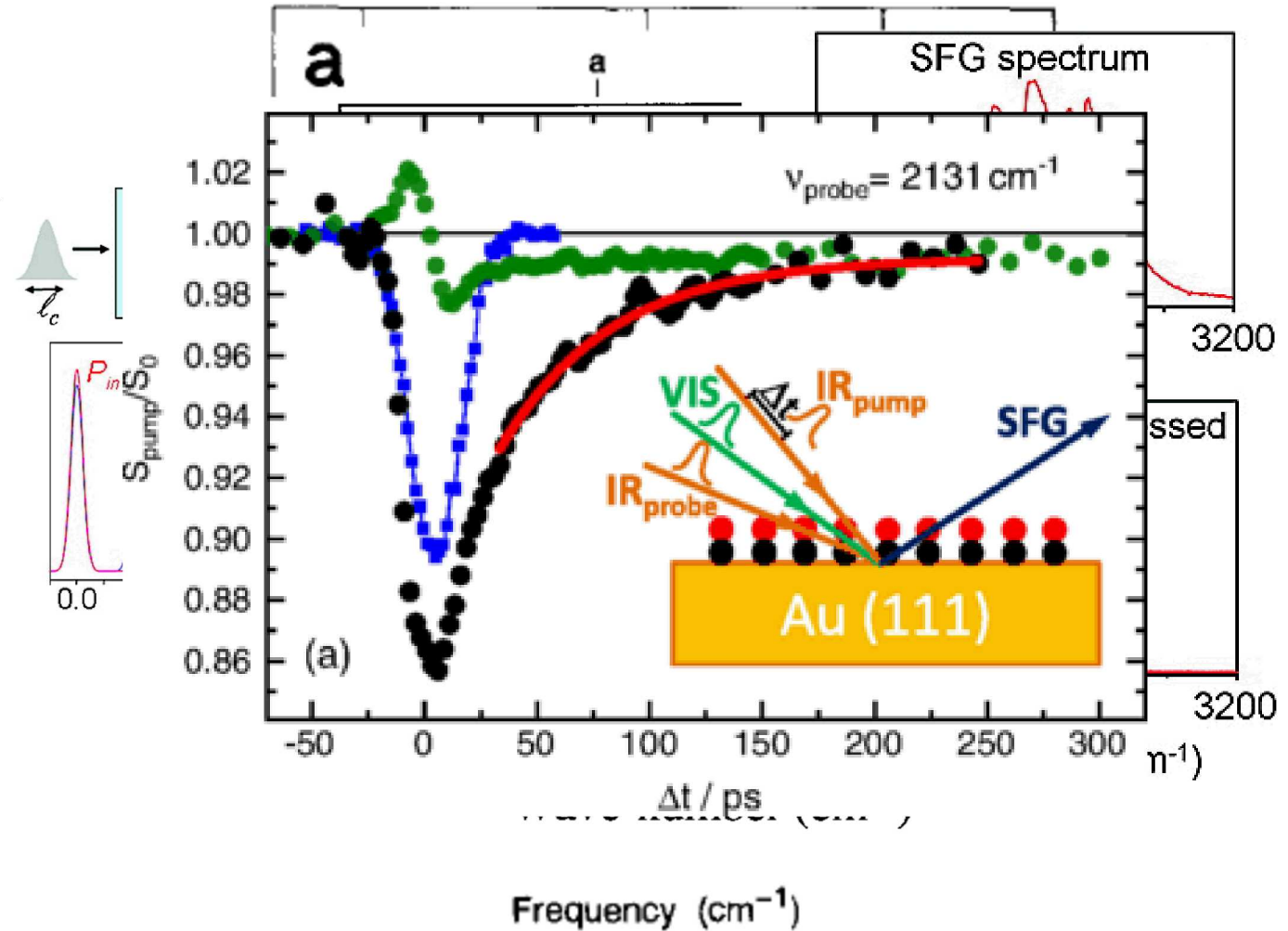
- Signal only occurs at the interface
- Coherent measurement method

Limitations to SFG:

- Input intensity limited by surface damage threshold
- Signal levels are typically low and difficult to detect

Brief Lit Review of Relevant SFG

1. SFG first recorded in 1987 by Shen et al.
 - Theoretical background described in 1962, but experiments had to wait for high power lasers
2. Broadband fs lasers first used for SFG, significantly reducing collection times
 - Broadband IR source theoretically allows for single shot measurement capability
3. Etalon first used to generate phase locked, asymmetric ps pulses
 - Efficient non-resonant background suppression as well perfectly phase locked measurements
4. Most recently, SFG has been used to measure long adsorption lifetimes for CO physisorbed onto Au (111) surfaces
 - Measured **extremely** long lifetimes



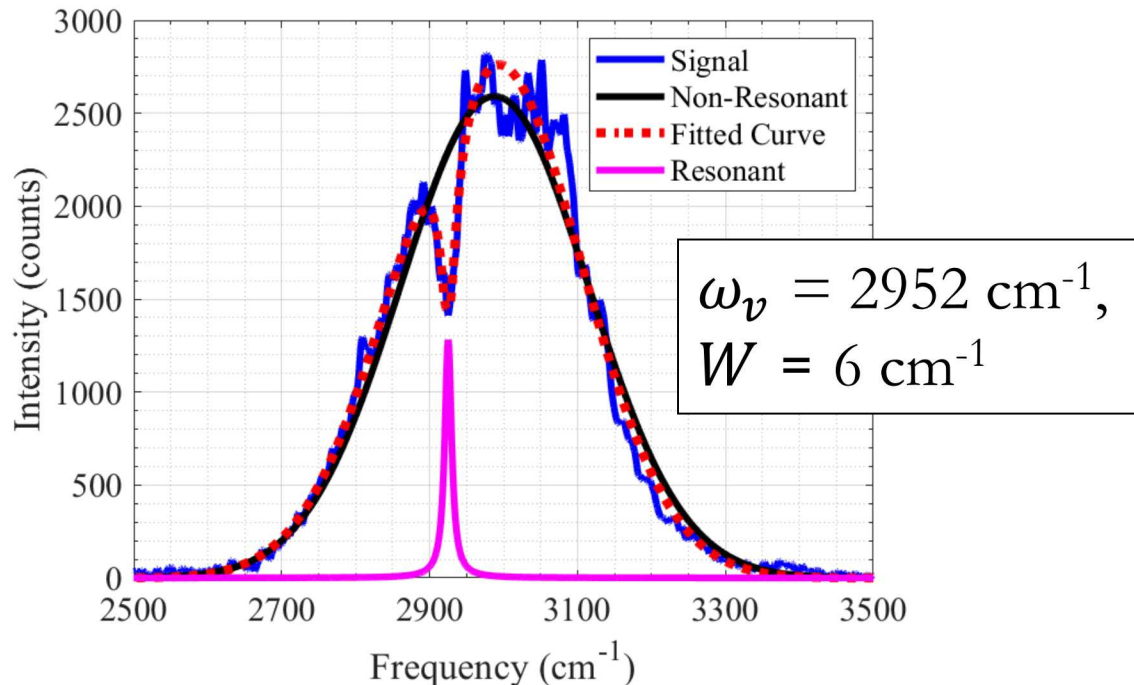
1. J.H., Hunt et al., Chem. Phys. Lett. **133**, (1987)
2. L. J. Richter et al., Optics Lett. **23**, (1998)

3. A. Lagutchev et al., J. Phys. Chem. C **111**, (2007)
4. S. Kumar et al., Phys. Rev. Lett. **123**, (2019)

Understanding an SFG Spectrum

First step: Generate SFG Spectrum

- Assume Gaussian lineshape for non-resonant
- Assume Lorentzian lineshape for resonant
- Solve with least squares fitting routine



$$I_{SF} \propto \left| \chi_{Res}^{(2)} e^{i\delta} + \chi_{NR}^{(2)} e^{i\varepsilon} \right|^2 = \left| \chi_{Res}^{(2)} \right|^2 + \left| \chi_{NR}^{(2)} \right|^2 + 2 \left| \chi_{Res}^{(2)} \right| \left| \chi_{NR}^{(2)} \right| \cos[\varepsilon - \delta]$$

$$\left| \chi_{Res}^{(2)} \right| = \sqrt{\frac{HW^2}{(\omega_{\nu} - \omega_{IR} + W^2)}}$$

$$I_{SF} \propto \frac{HW^2}{(\omega_{\nu} - \omega_{IR} + W^2)} + \left| \chi_{NR}^{(2)} \right|^2 + 2 \sqrt{\frac{HW^2}{(\omega_{\nu} - \omega_{IR} + W^2)}} \times \left| \chi_{NR}^{(2)} \right| \cos \left[\varepsilon - \arctan \left(\frac{-W}{\omega_{\nu} - \omega_{IR}} \right) \right]$$

$\chi_{Res, NR}^{(2)}$ = Resonant and Nonresonant Susceptibility

δ, ε = phase of resonant and nonresonant components

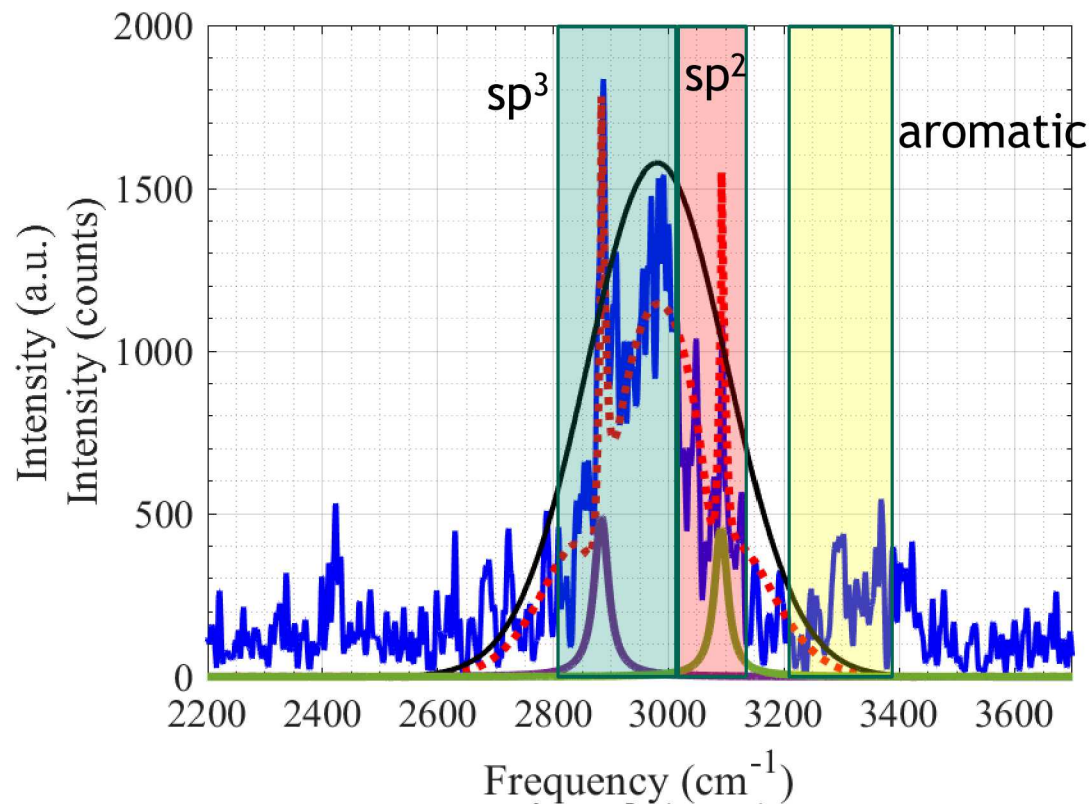
H = Lorentzian height, W = Lorentzian FWHM

ω_{ν} = Resonance Frequency, ω_{IR} = IR Frequency

Example Results – Head on Quench, Rich Flame

Flame-wall interactions induce quenching, leading to incomplete combustion emission

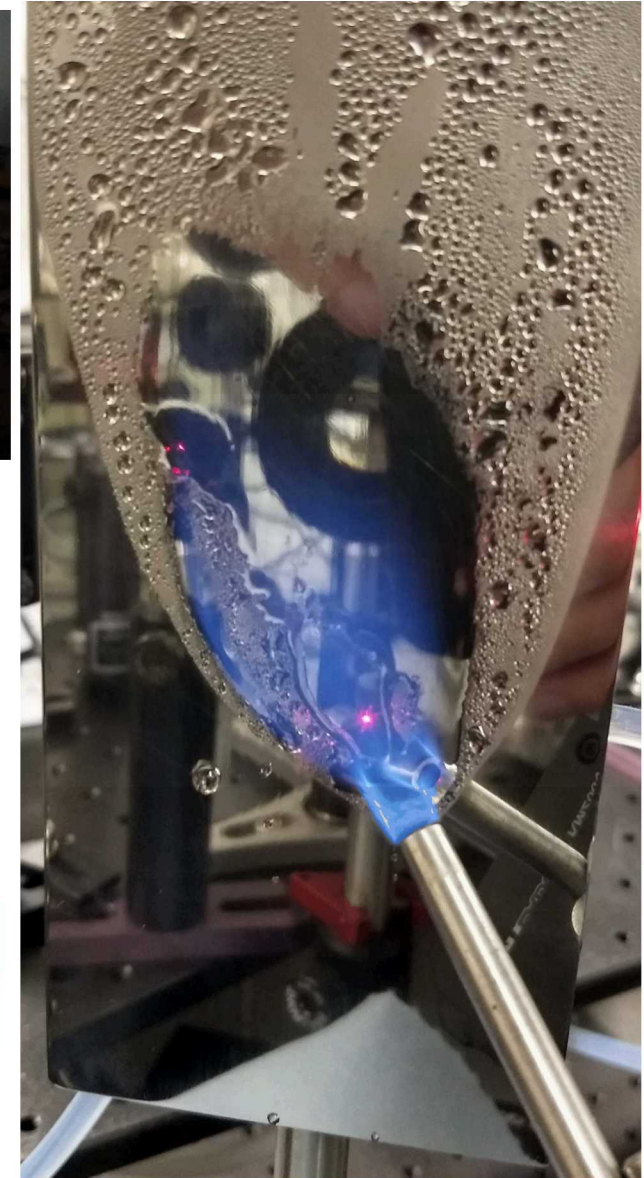
SFG can be a powerful tool to monitor species adsorbing to the wall during quench



See qualitative CH stretch signatures

Can try to use fitting routine for more quantitative results

ω_ν (cm ⁻¹)	FWHM (cm ⁻¹)
2883	15
3091	14



Recent Results Looking at Physisorption

Langmuir-Hinshelwood is one of the leading theories understanding catalysis on metals

- In LH theory, molecules adsorb onto the surface and instantly thermalize
- Chemical reactions then take place with a second adsorbed species

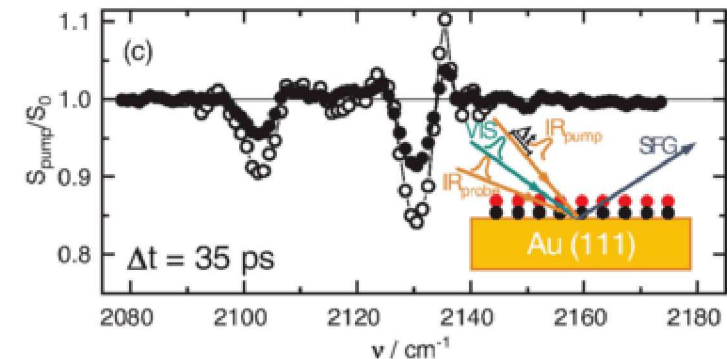
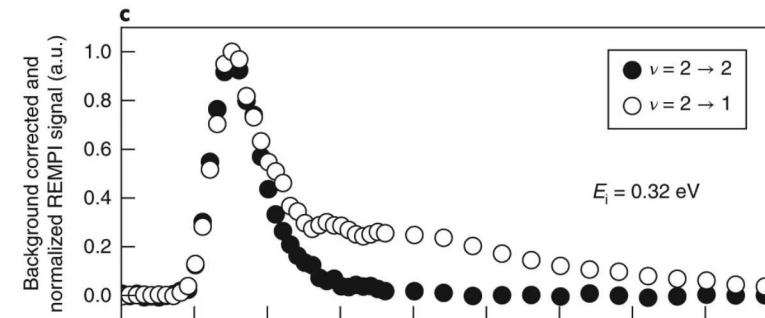
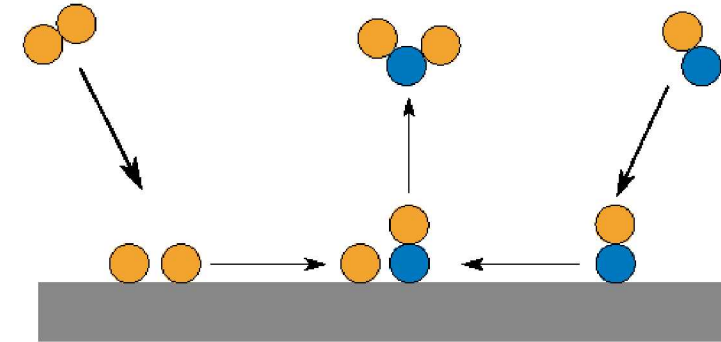
Recent results from 2018 demonstrated for the first time that vibrationally excited molecules can adsorb to a surface and desorb vibrationally hot

- **P. R. Shirhatti et al., Nature Chemistry 10, (2018)**

These results have since been backed up and verified in a 2019 paper looking at vibrational lifetimes of physisorbed molecules at metal surfaces

- **S. Kumar et al., PRL 123, (2019)**

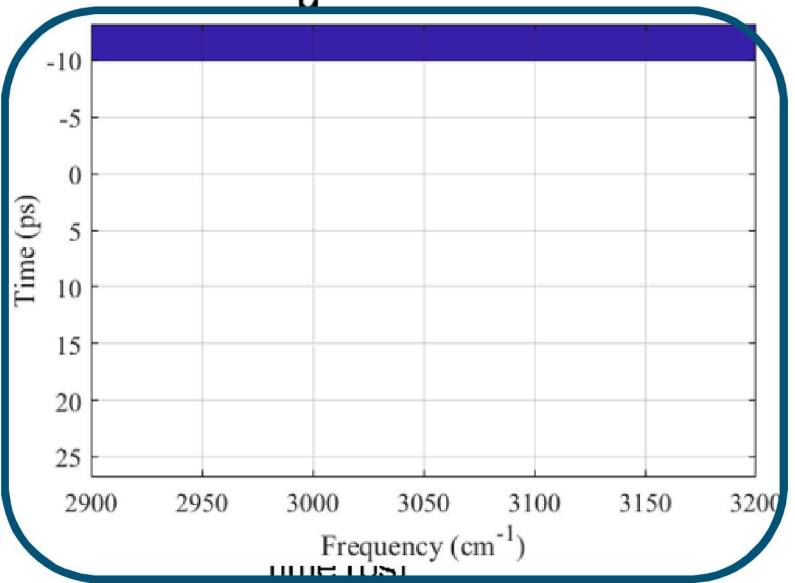
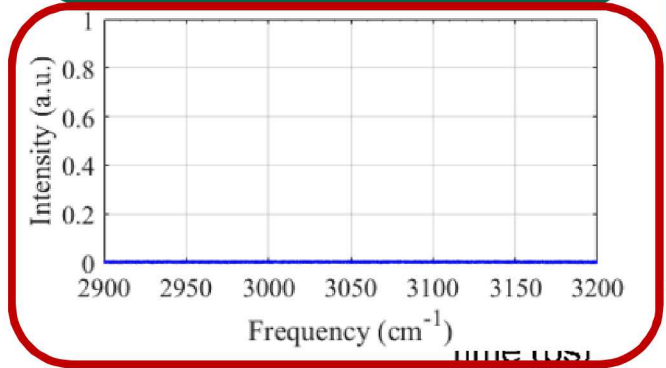
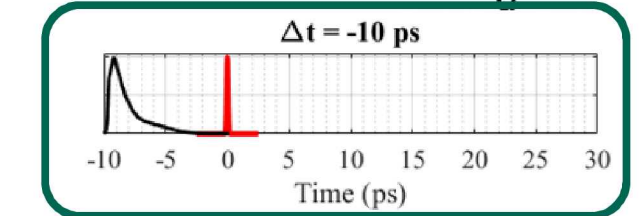
This could have huge implications for our understanding of catalysis!



SFG Experimental Schematic

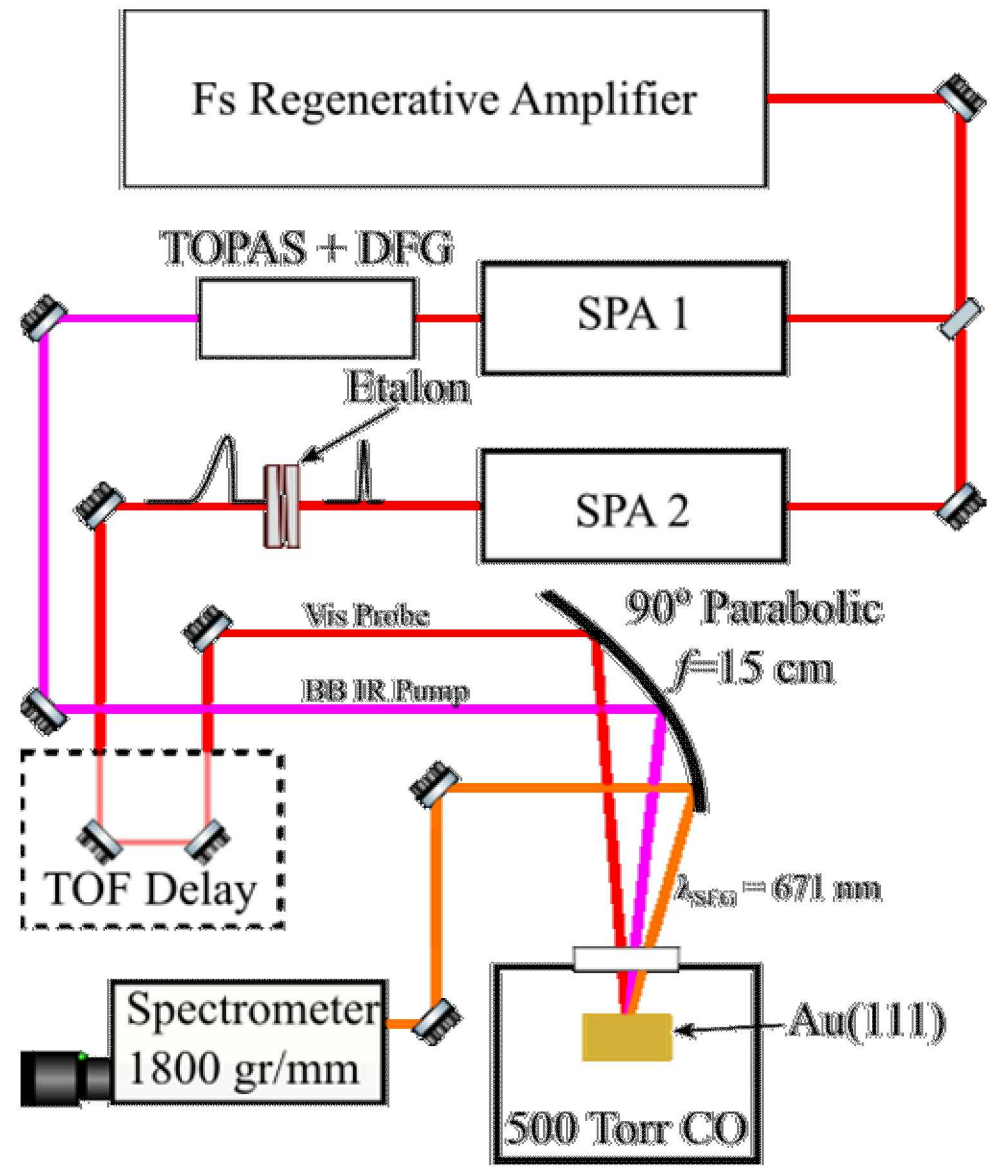
Coherent Legend Elite TiSaph Laser
 Etalon used to generate narrow band up-conversion pulse

Ps Probe and Fs Excitation



Spectrum at Each Time Step

Spectral Trace in Time

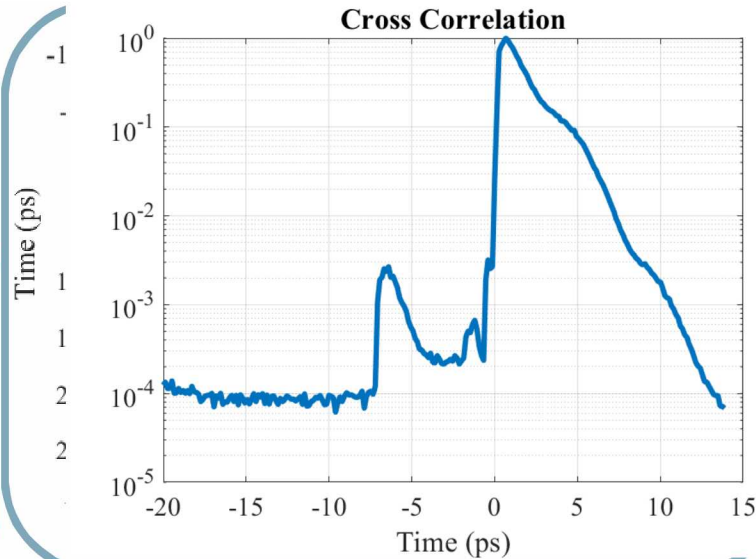
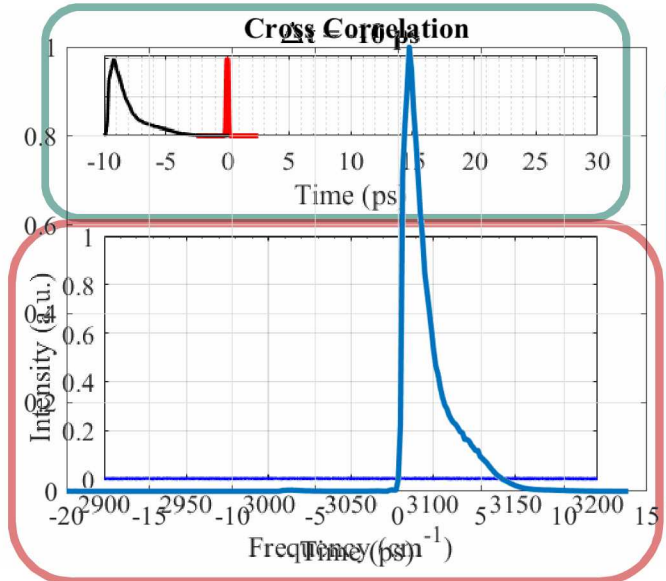


SFG Experimental Schematic

Coherent Legend Elite TiSaph Laser

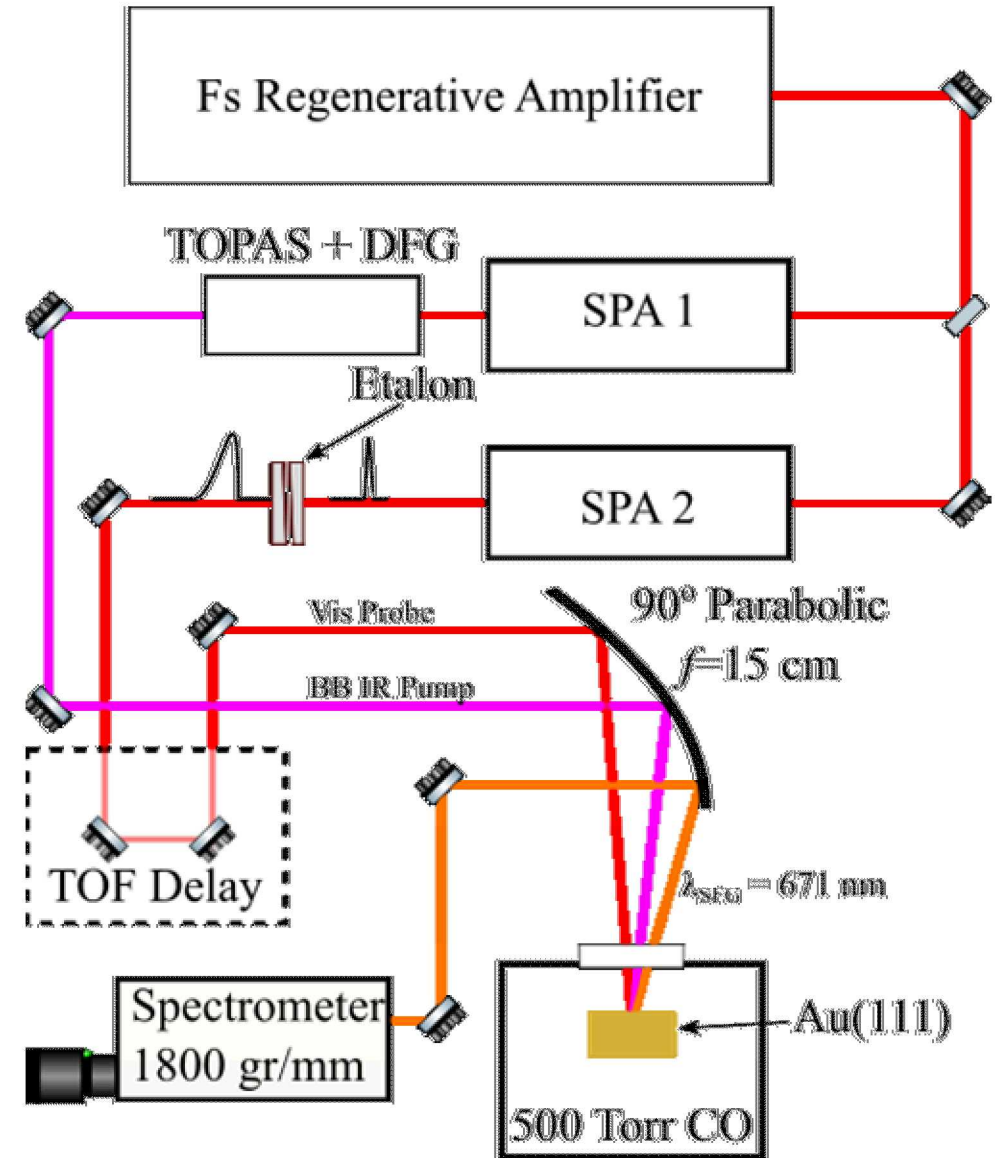
Etalon used to generate narrow band up-conversion pulse

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Spectrum at Each Time Step

Spectral Trace in Time

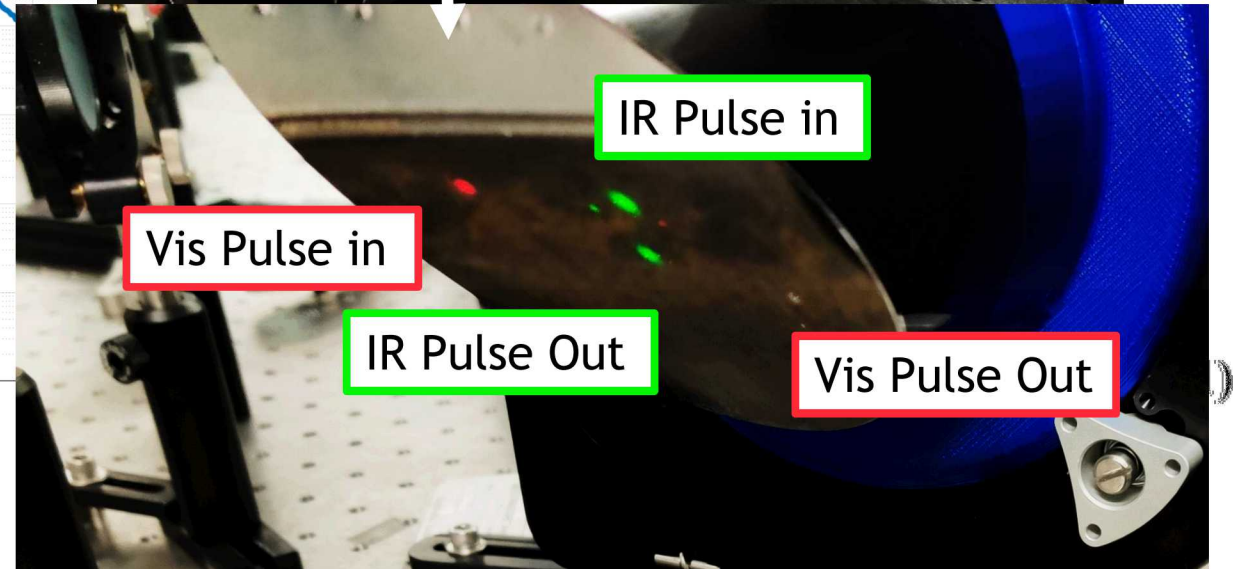
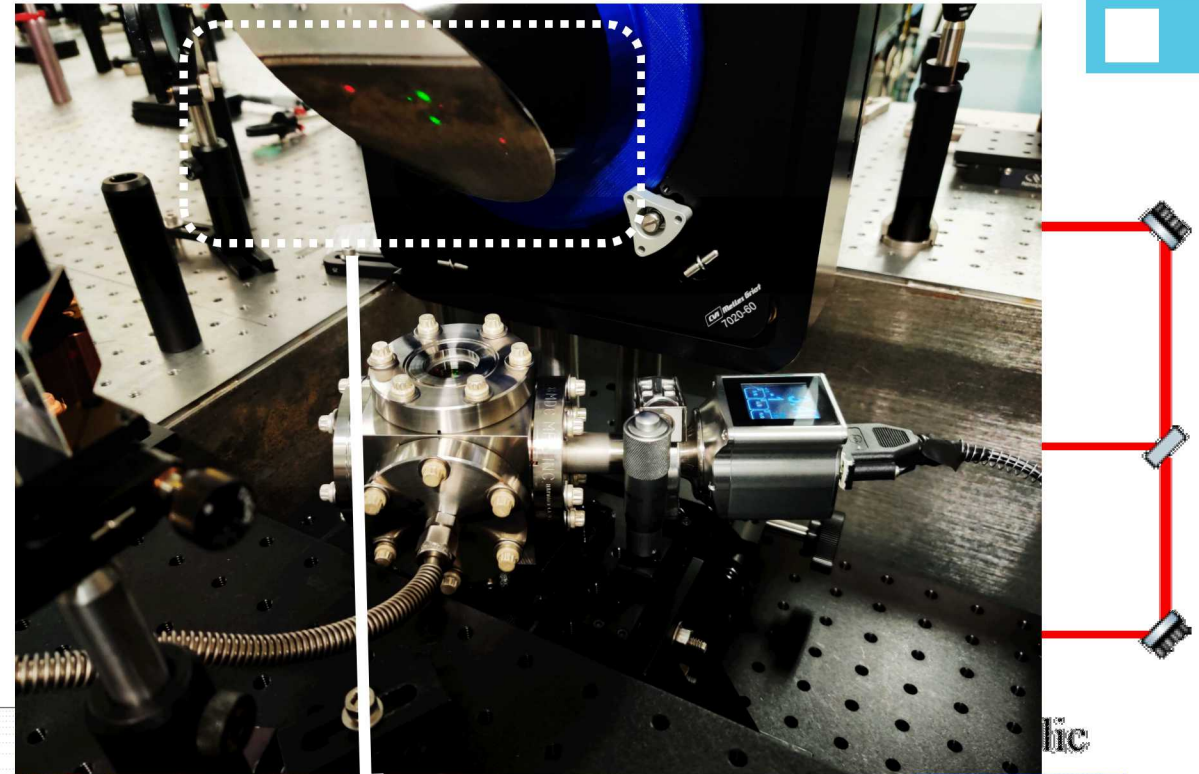
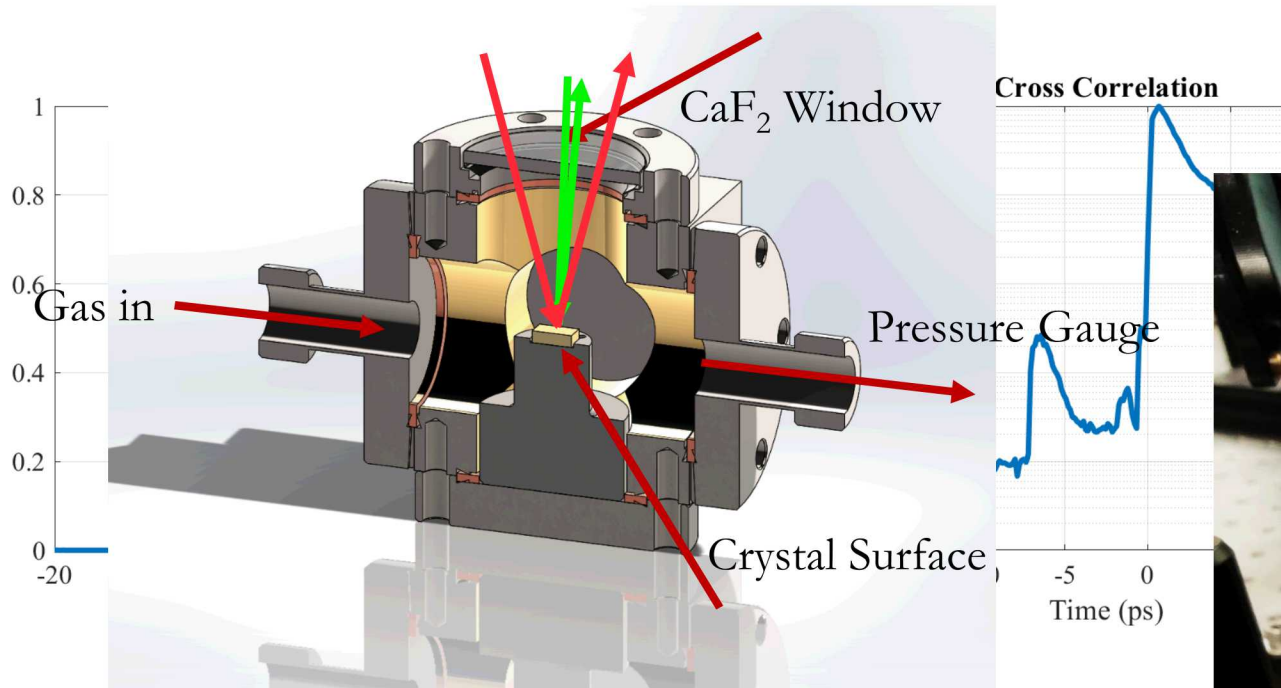


SFG Experimental Schematic

Coherent Legend Elite TiSaph Laser

Etalon used to generate narrow band up-conversion pulse

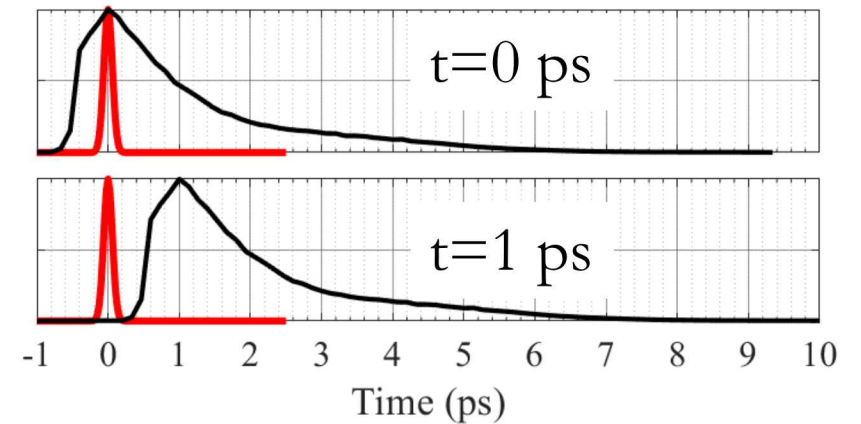
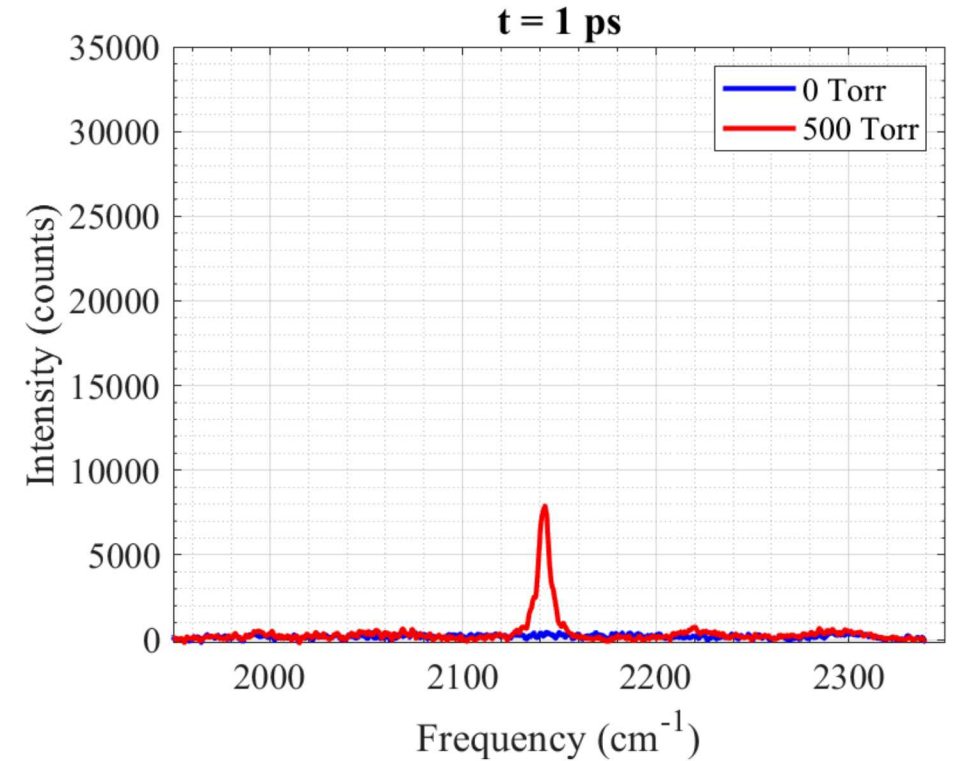
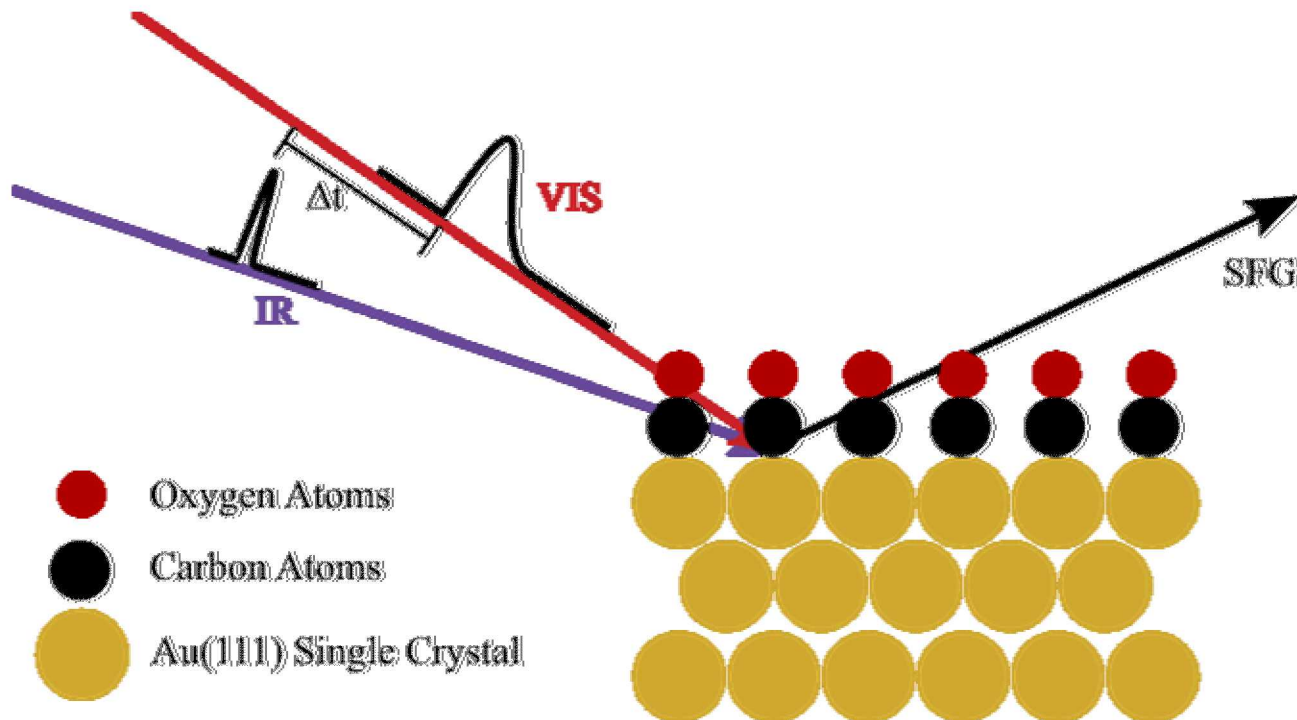
4" parabolic mirror used for focusing/signal collection



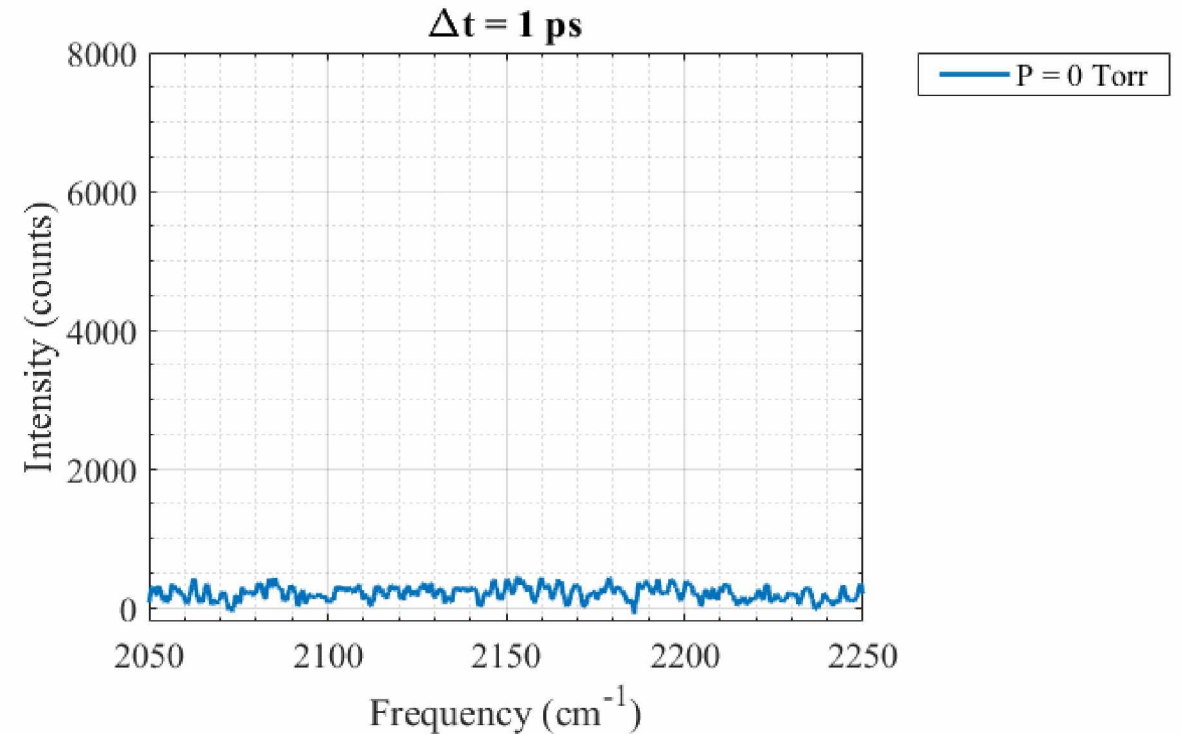
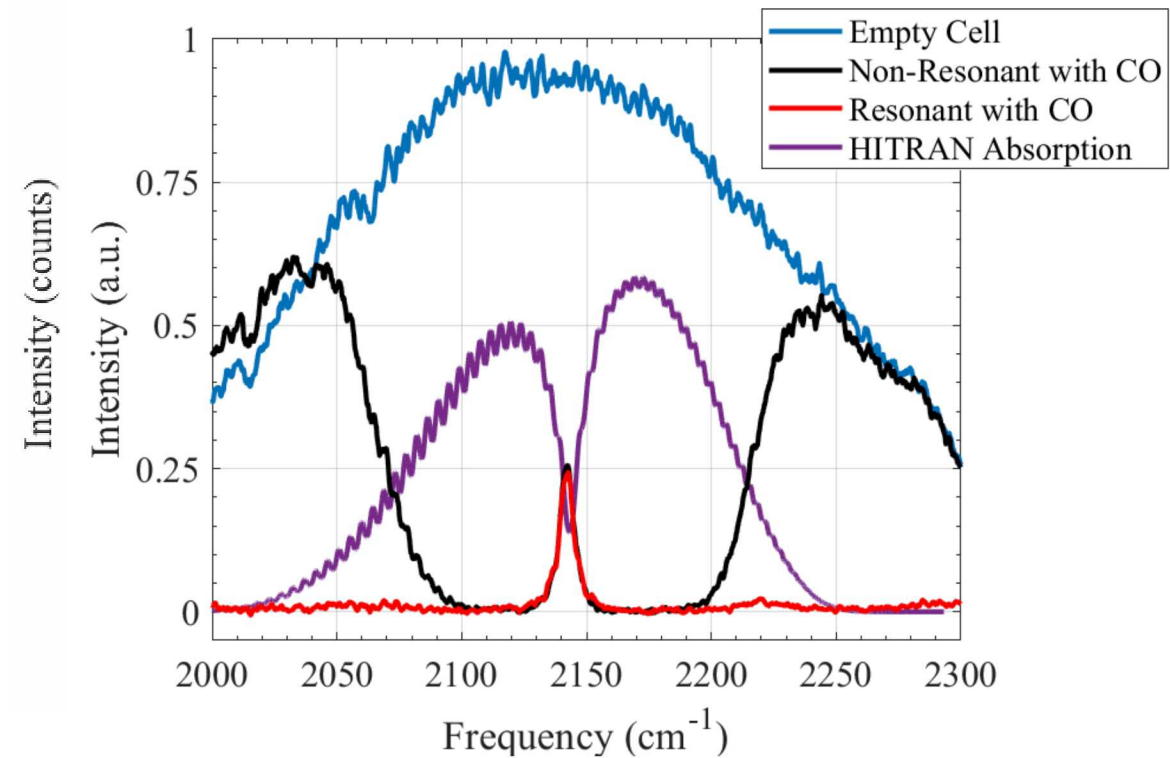
Initial Tests with CO

At $t=0$ (ps and fs pulses coincident), non-resonant background is superimposed with CO absorption

When probe pulse is translated 1 ps, the non-resonant background has died completely, leaving only the resonant contribution



CO Signal Scaling with Pressure

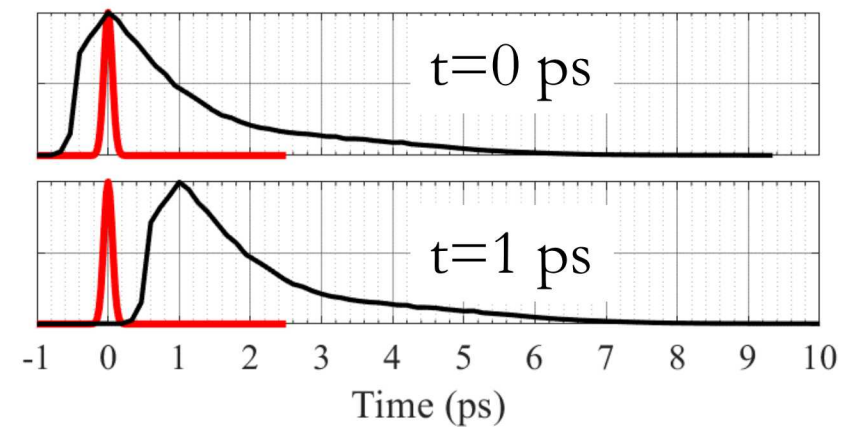


From nonresonant, absorption increases with pressure

- NR is convolution between absorption and possible out of phase SFG

$$I_{SF} \propto \left| \left| \chi_{Res}^{(2)} \right| e^{i\delta} + \left| \chi_{NR}^{(2)} \right| e^{i\epsilon} \right|^2$$

Resonant component maximized at ~500 Torr

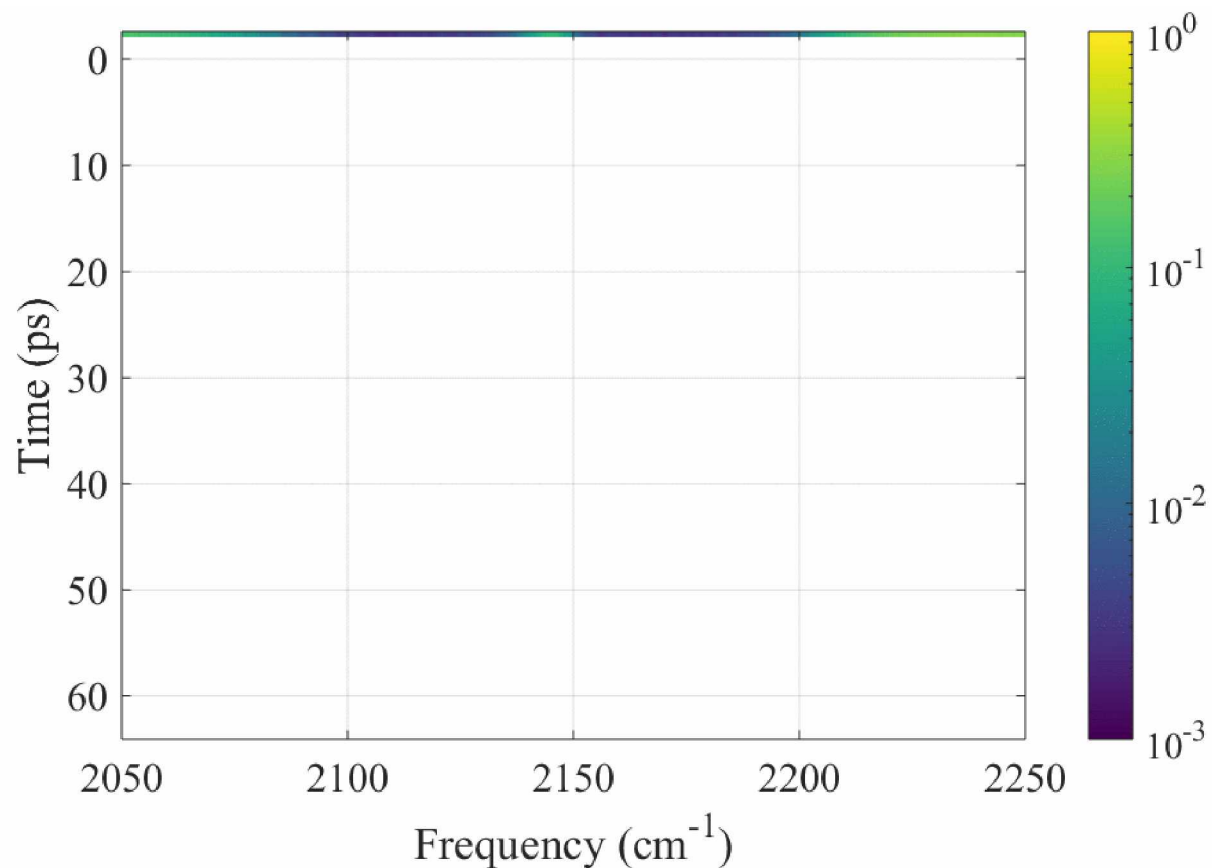
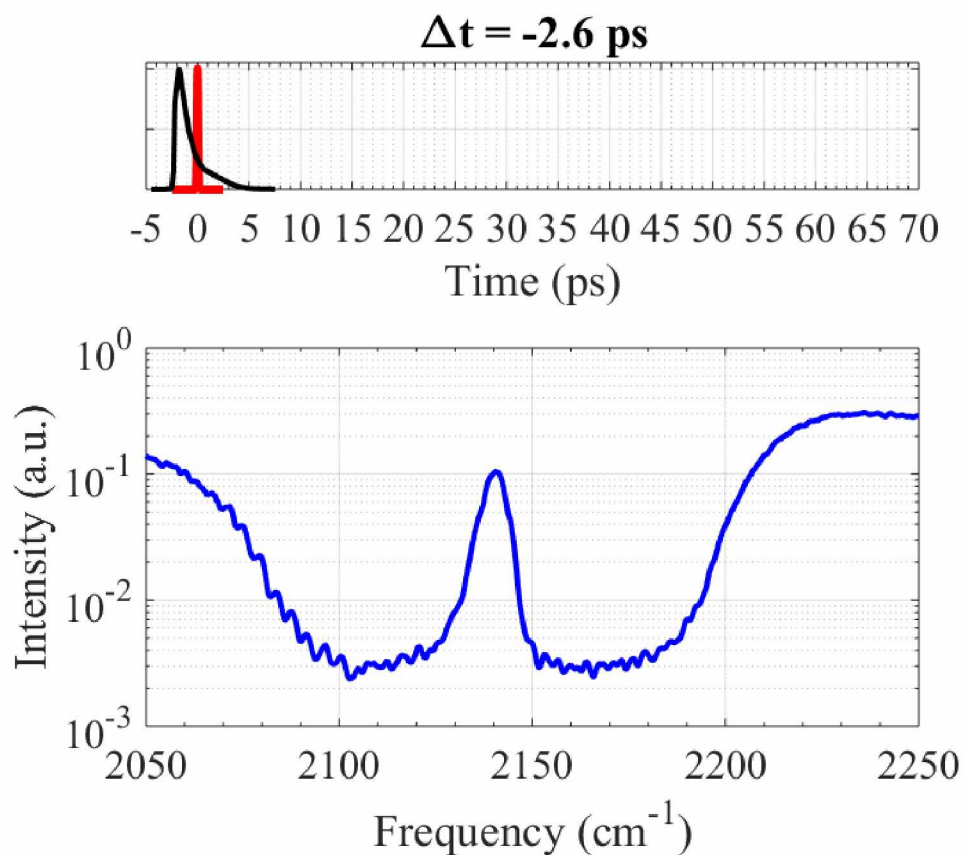


500 Torr CO – Coherence Decay Scan

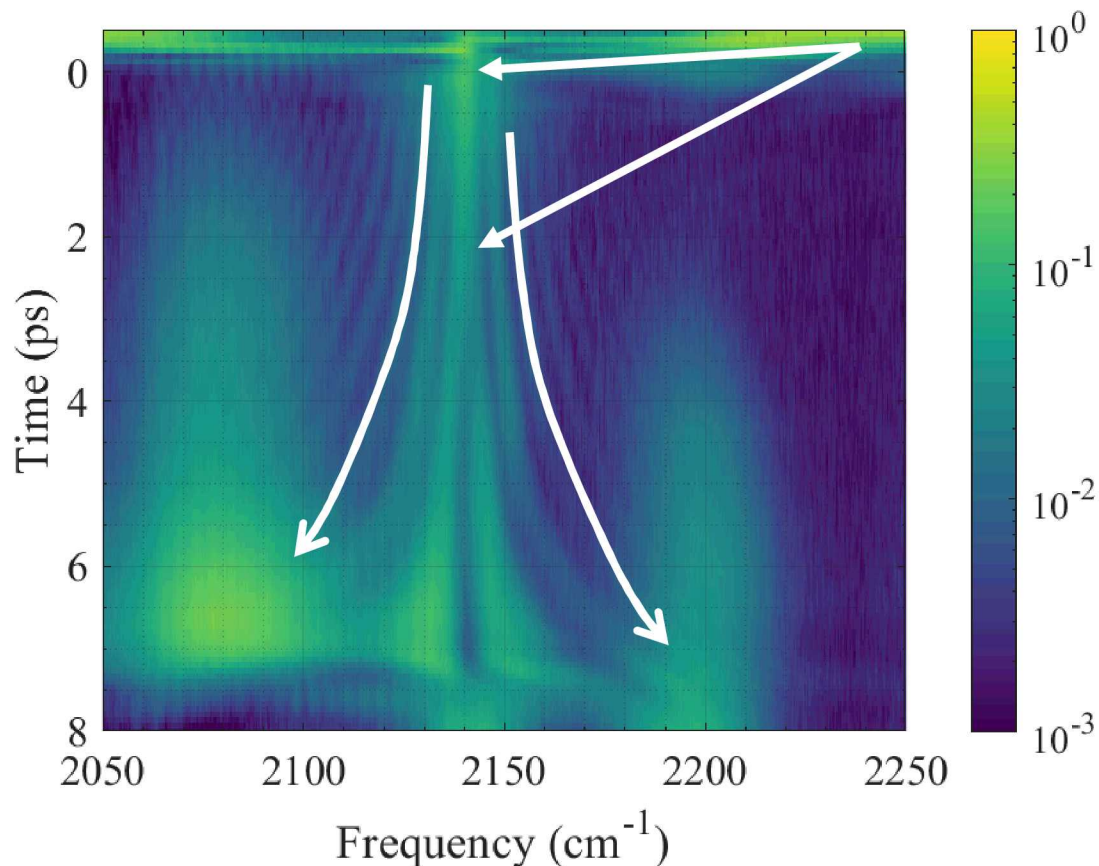
67 fs per step

- 2s CCD gate per image
- 16 images per time step

Total scan times of $\sim 2\text{-}3$ hours



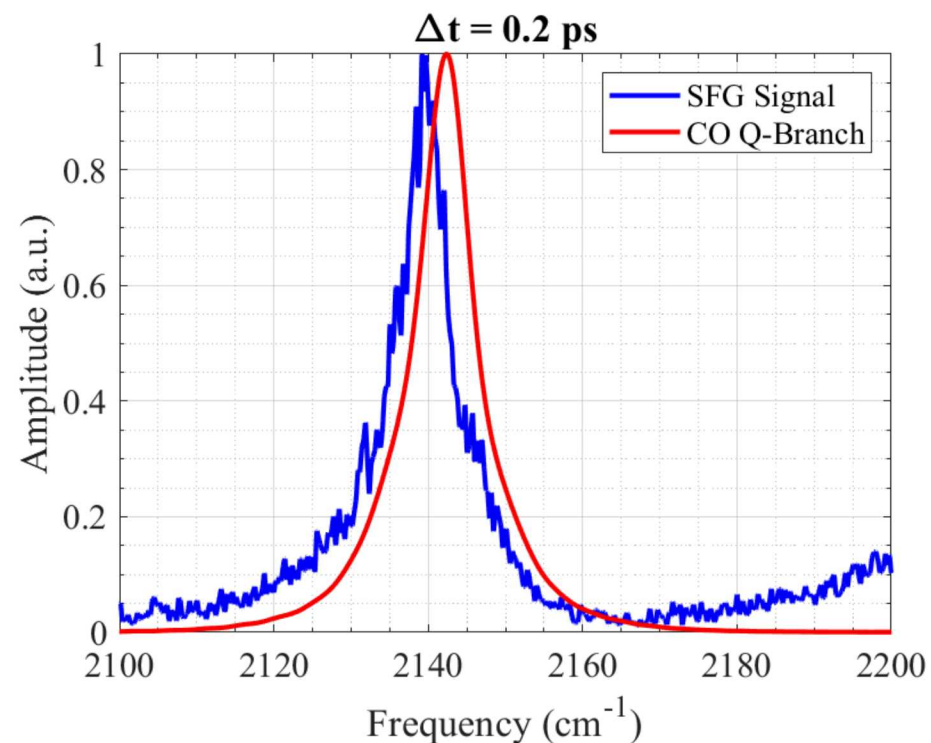
500 Torr CO – Coherence Decay Scan



For the first time ever, rotational energy states clearly visible in SFG

Initial decay dominated by redshifted Q-Branch transitions

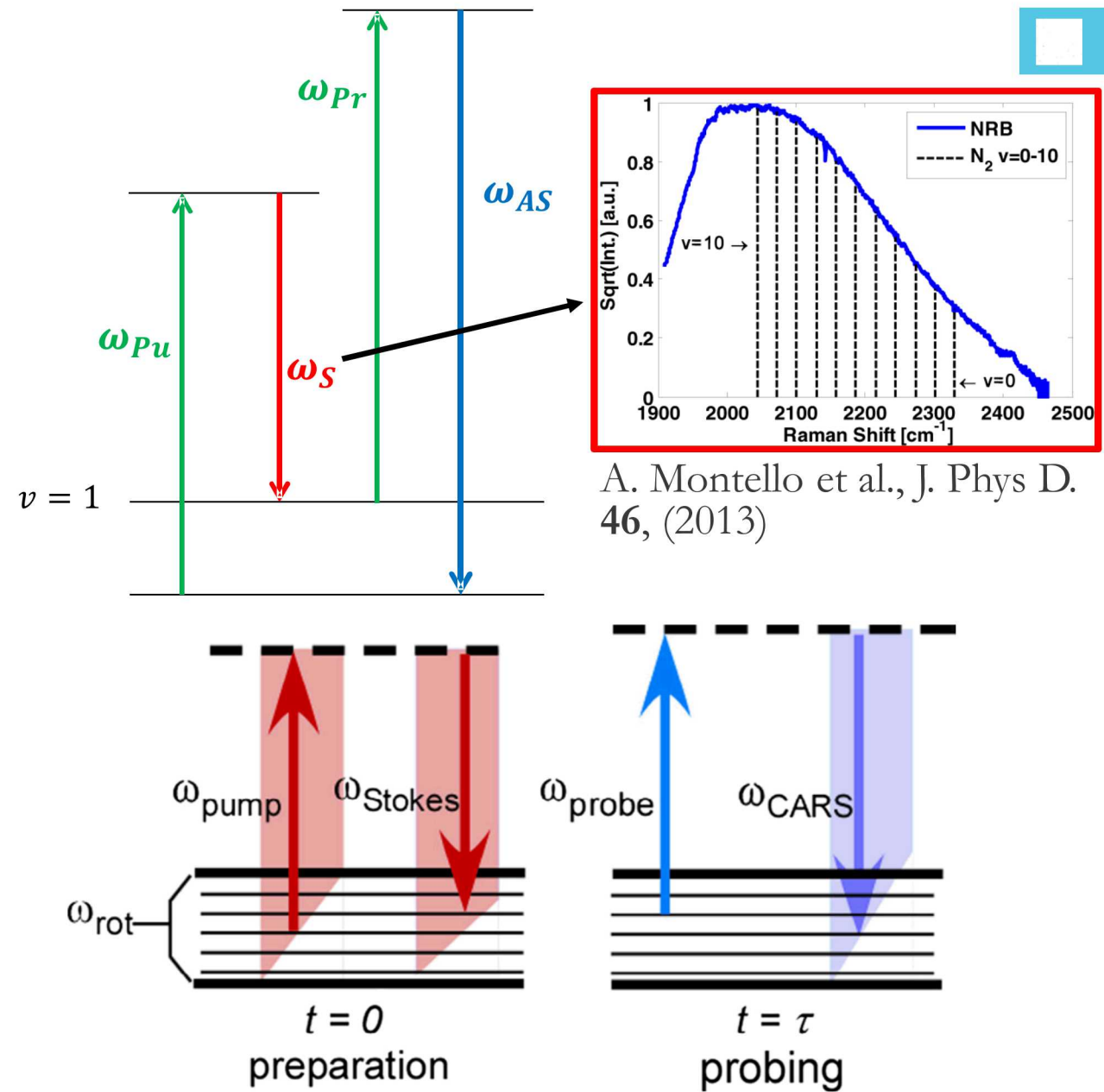
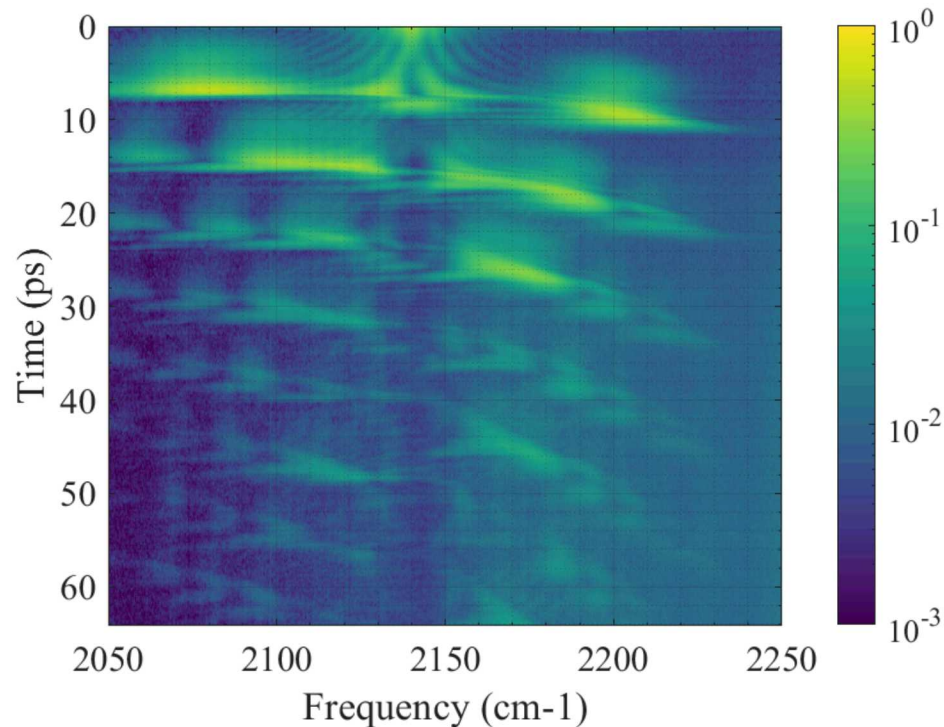
$$I_{SFG} \propto \left| \chi_{Nr}^{(2)} + \frac{a_j}{(\omega_j - \omega_{IR} - i\Gamma_j)} \right|^2$$



Comparison to Hybrid CARS

Similar rephasing is often seen in hybrid CARS experiments

- Standard CARS – Narrow Pump/Probe & Broadband Stokes
- Hybrid CARS – fs Pump/Stokes & ps Probe beams

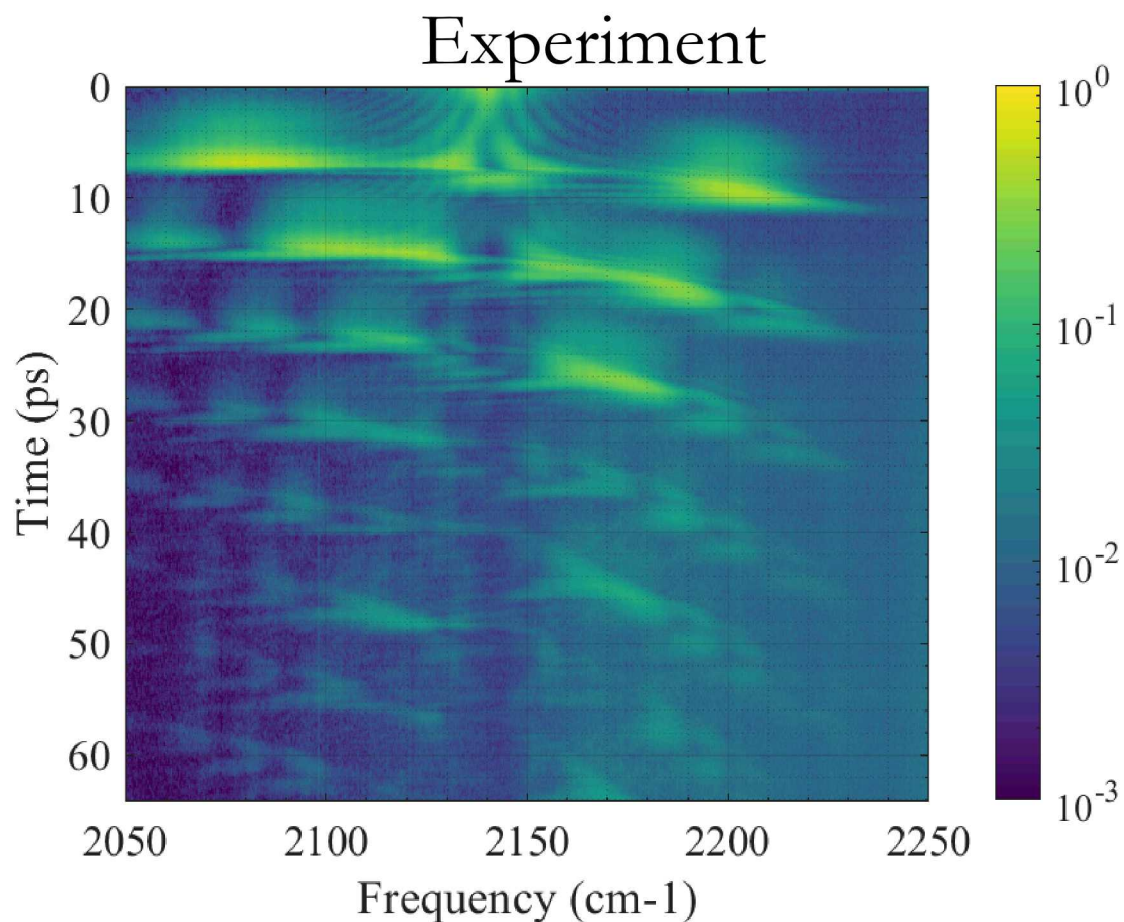


A. Montello et al., J. Phys D. **46**, (2013)

Comparison to hybrid CARS Model

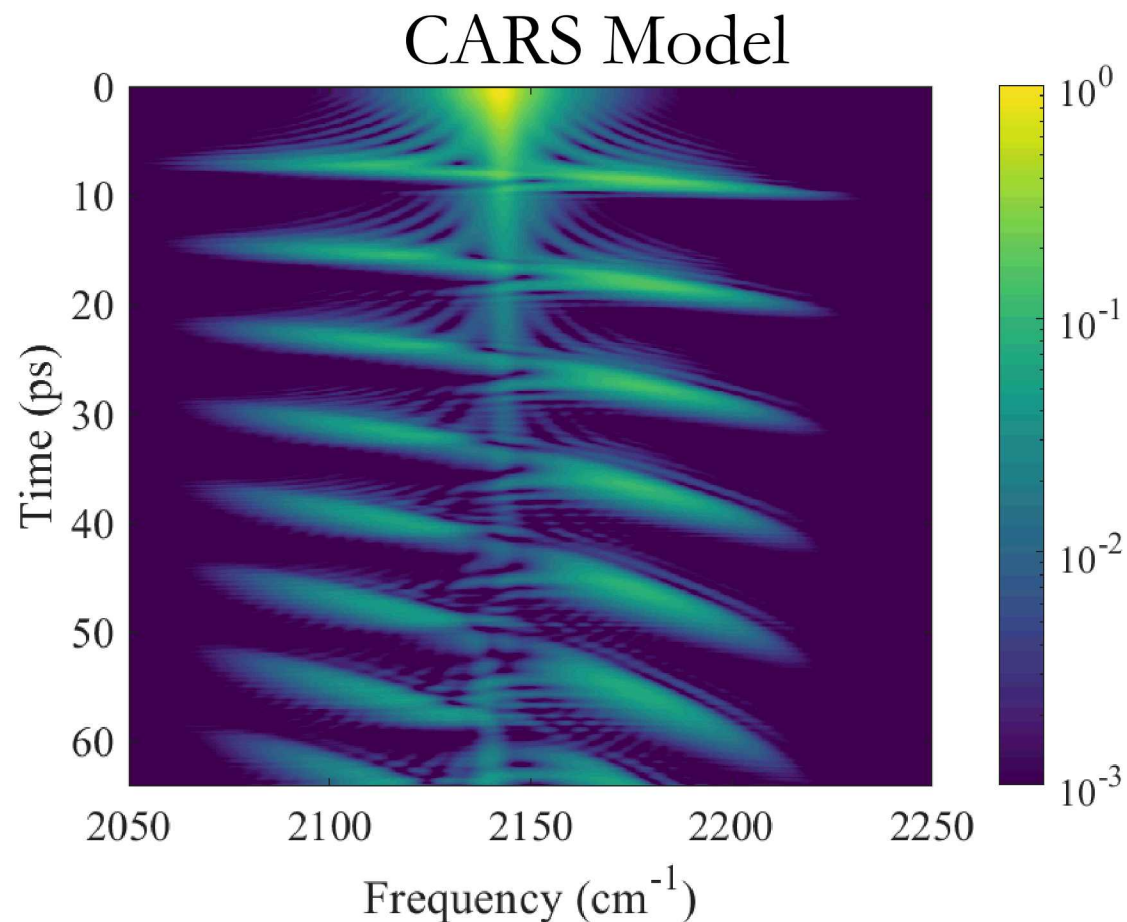
Similarities:

- Frequency of rephasing
- Fanning out of rotational states
- Twisting towards $\Delta J = +1$

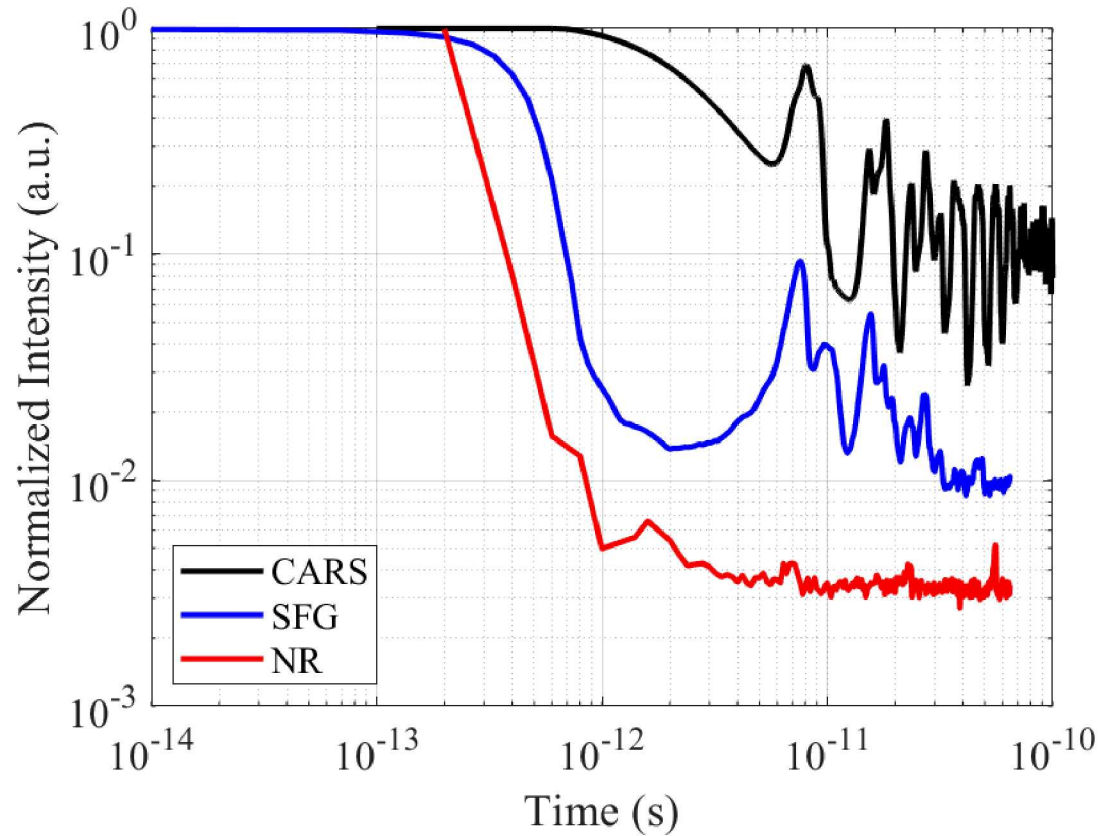


Differences:

- Strong, persistent Q-Branch
- Higher order vibrational modes
- Longer coherence decay times



Coherence Decay Time



Nonresonant decay nearly instantaneous

- Indicative of probe pulse fast rising edge

SFG shows separate decays:

- Initial Q-Branch SFG decay, $\tau_{fast} \approx 0.4 \text{ ps}$
- Possible indication of chemisorbed state
- On the limit of our detection response
- Slow P- & R-Branch decay, $\tau_{slow} \approx 32 \text{ ps}$
- Clear indication of physisorbed state
- Consistent with similar results monitoring CO on Au(111)

CARS decay significantly longer

- Total decay time is $\sim 1 \text{ ns}$
- Dephasing is due to collisions

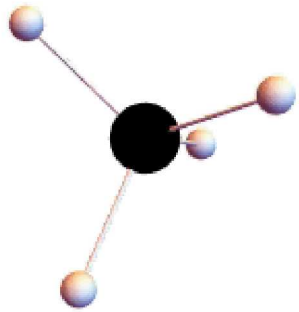
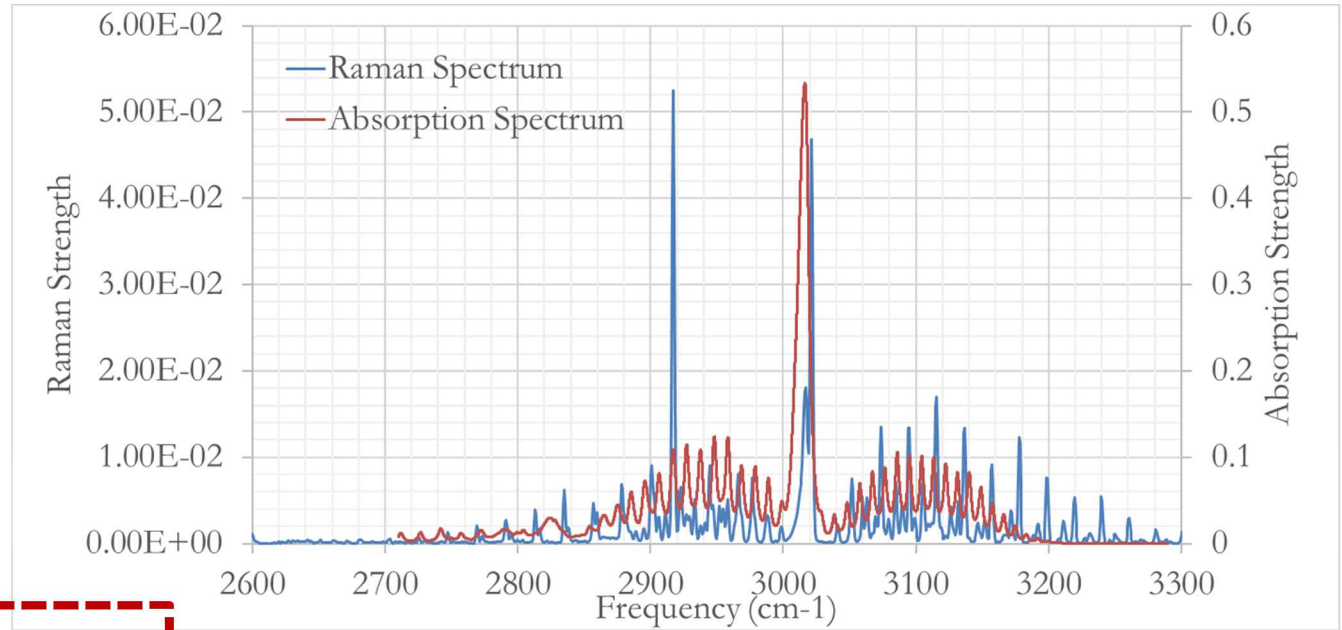
Is this effect ubiquitous? CH_4 could be another molecule with long physisorption lifetime

Bending Modes of Methane

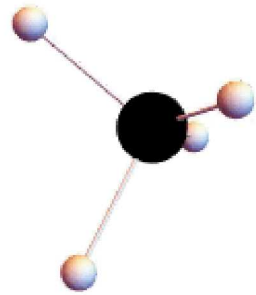
Spherical top molecule with 4 distinct vibrational modes

- ν_3 & ν_4 IR active

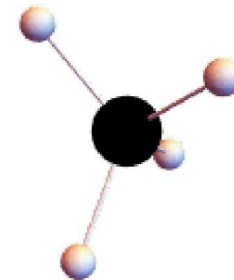
$$\chi_{Res,j}^{(2)} = \frac{a_j}{(\omega_j - \omega_{IR} - i\Gamma_j)}$$



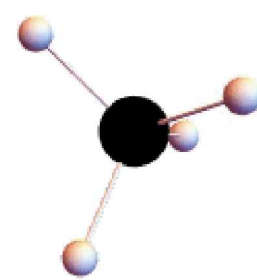
ν_1 , Symmetric Stretch
Raman active 2916 cm^{-1}



ν_3 , Stretching
IR active at 3019 cm^{-1}
triply degenerate



ν_2 , Bending
Raman active 1534 cm^{-1}
doubly degenerate



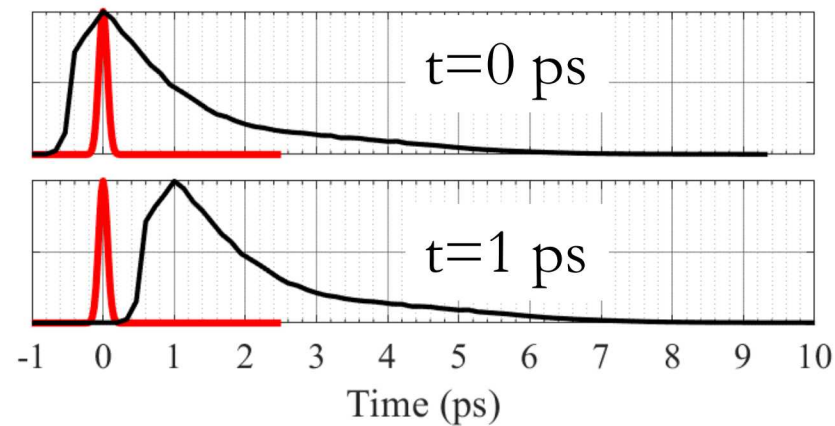
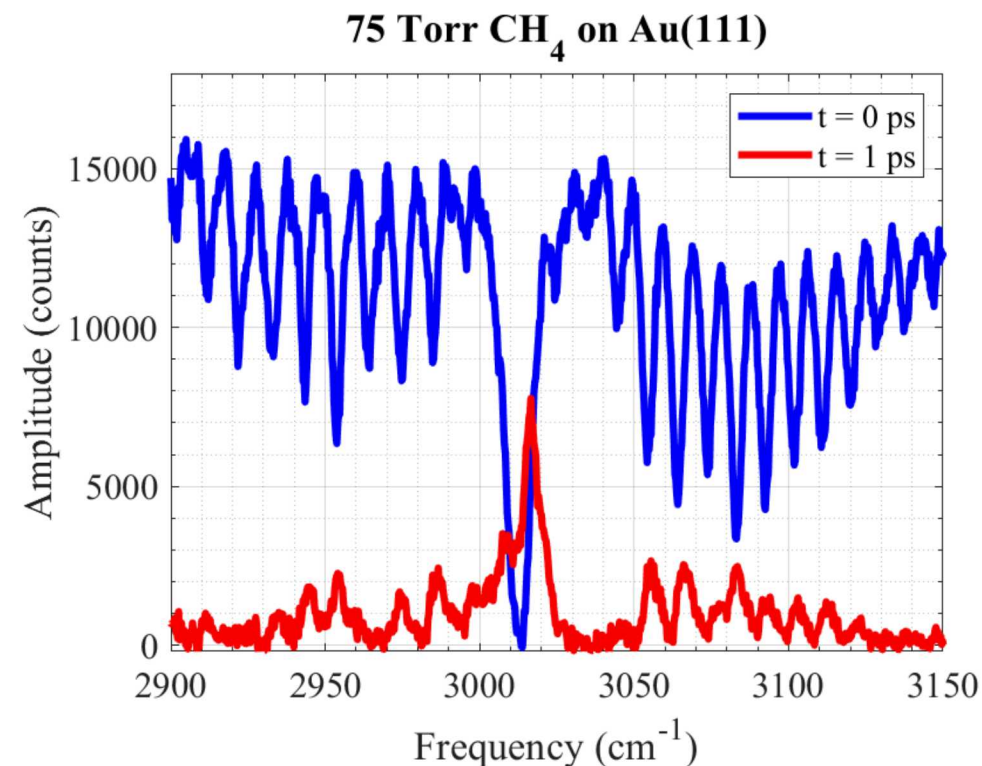
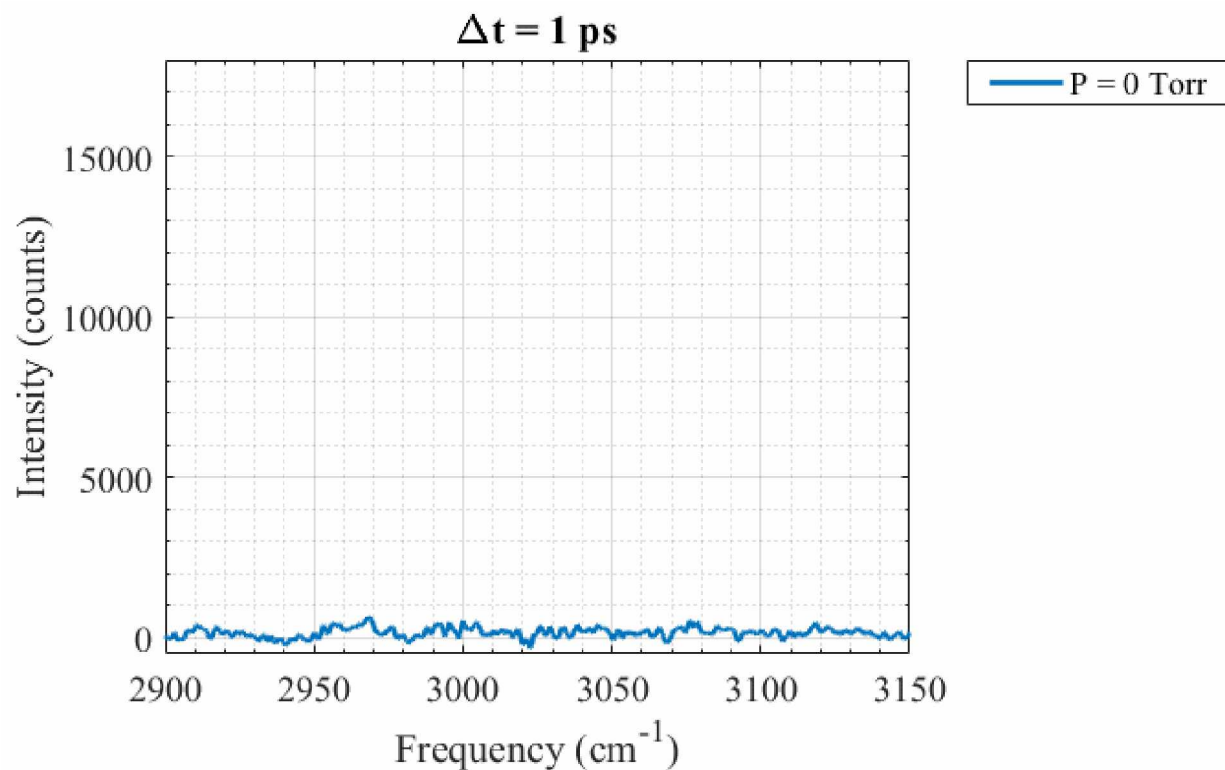
ν_4 , Bending
IR active 1306 cm^{-1}
triply degenerate

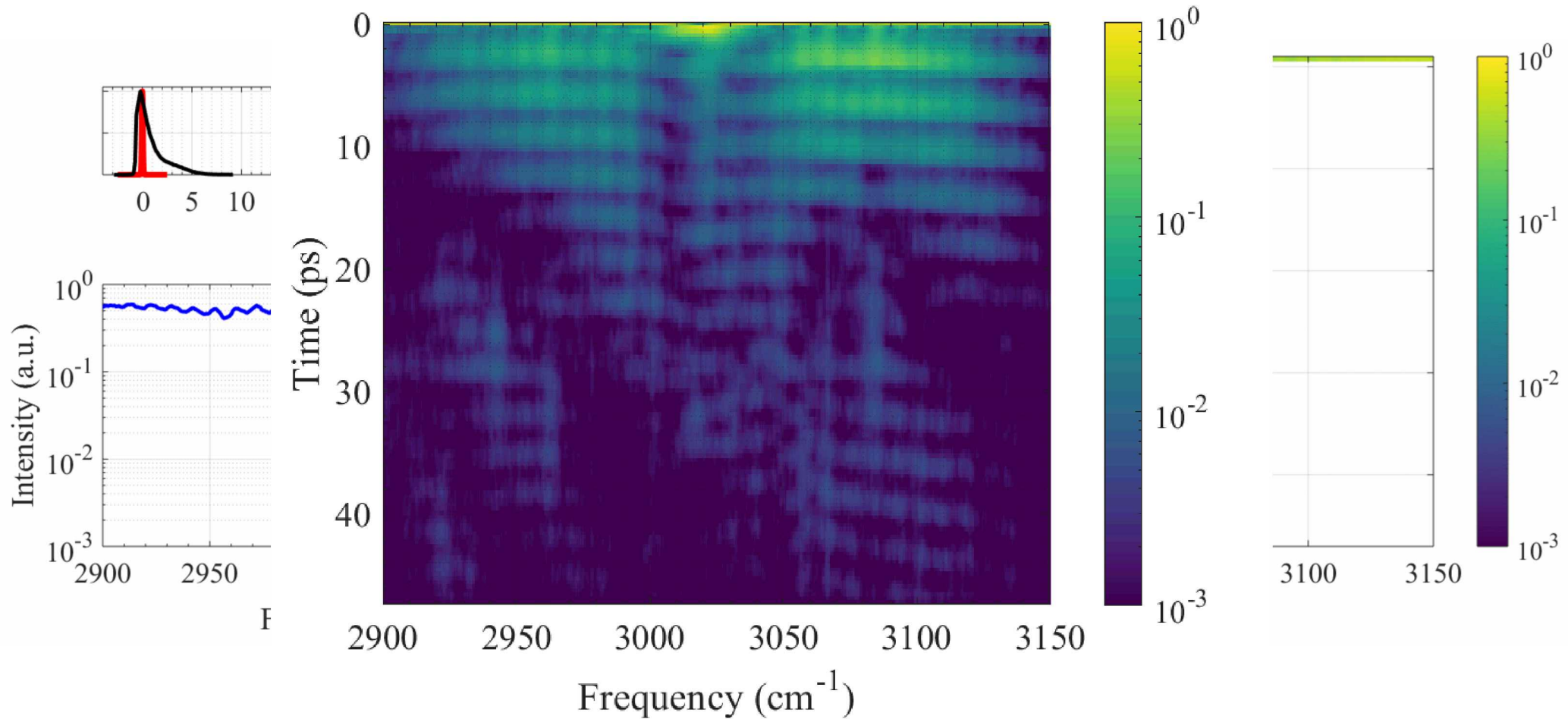
Initial Tests with CH₄

Ro-vibrational spectrum seen in both resonant and non-resonant spectra

Energy levels match up almost perfectly with gas phase measurements

Optimum pressure is ~ 75 Torr



Time Scans with 75 Torr CH₄

Next steps will be to build methane into the CARS model...

Conclusions

Nonequilibrium plasma discharges represent a unique and controllable way to input energy into a system

- Control is provided through the electric field

SFG has been used to observe physisorbed molecules on a Au(111) surface

- Physisorbed molecules are an important way to couple energy into the wall from the gas phase
- Long coherence lifetimes indicate long residence times

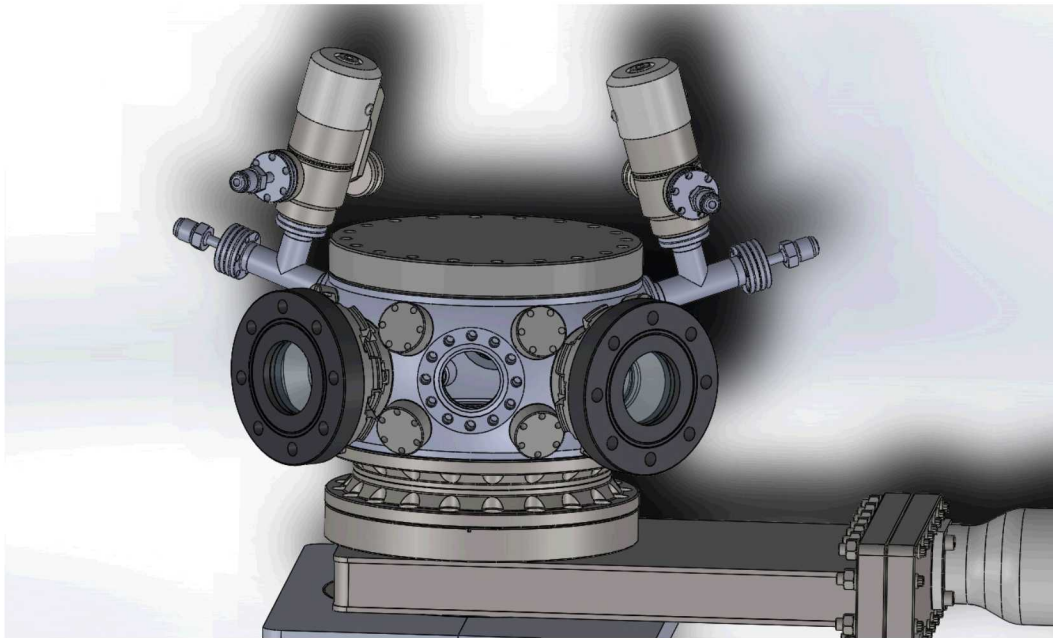
For the first time ever, the entire ro-vibrational manifold has been measured using SFG

Future Work

A new chamber has been designed and ordered to better understand the coupling to the surface

- This compact chamber should have similar capabilities as many surface science chambers currently in use
- First efforts will be to measure T1 residence time of physisorbed molecules on crystal the surfaces at different temperatures and pressures

Currently discussing theoretical basis for some of the interesting observations we see



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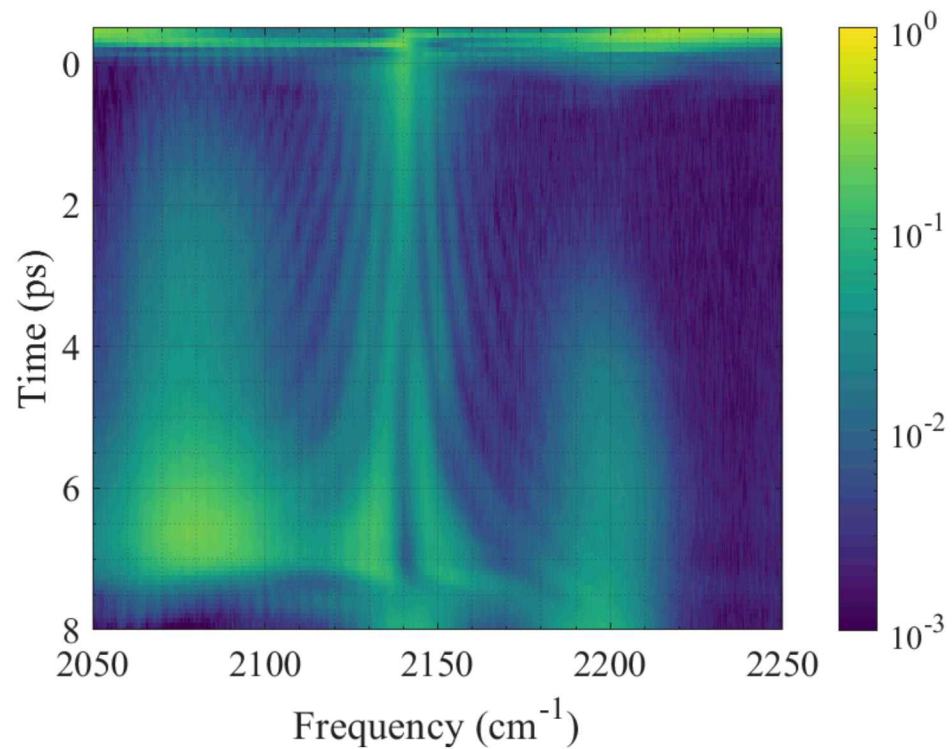
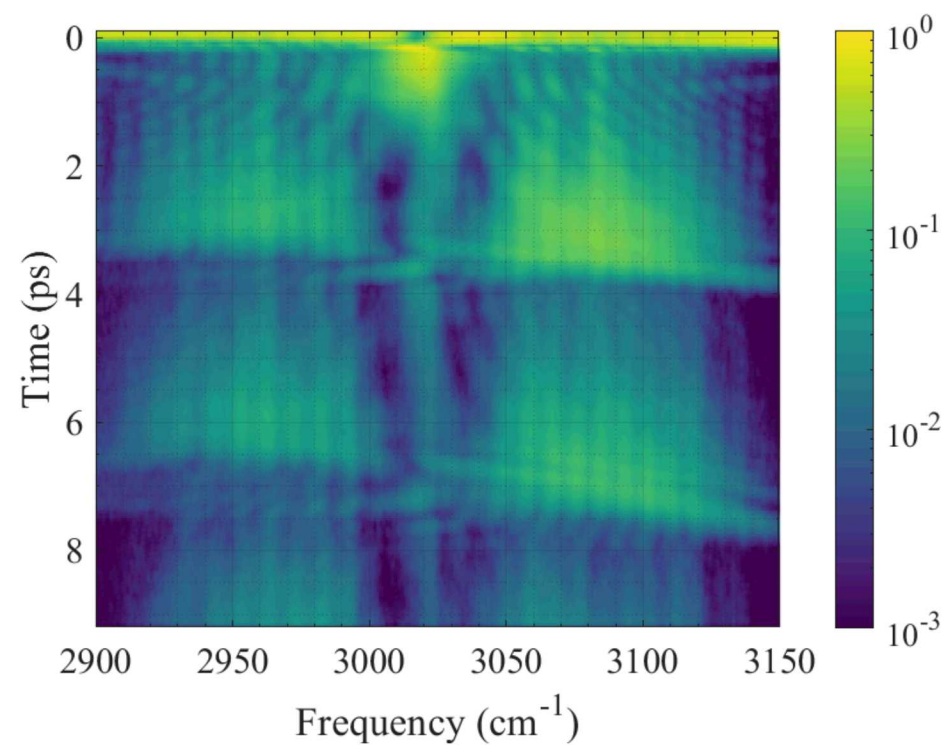


Thank you for your attention

Questions?

CO and CH₄ Comparison

500 Torr CO

75 Torr CH₄

Spectra With and Without CO

