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Title: Unraveling shock-induced chemistry using ultrafast lasers

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Unraveling Shock-Induced Chemistry Using Ultrafast Lasers

The exquisite time synchronicity between shock and diagnostics needed to unravel chemical events occurring in picoseconds has been achieved using a shaped ultrafast laser pulse to both drive the shocks and interrogate the sample via a multiplicity of optical diagnostics. The shaped laser drive pulse can produce well-controlled shock states of sub-ns duration with sub-10 ps risetimes, sufficient for investigation of fast reactions or phase transformations in a thin layer with picosecond time resolution. The shock state is characterized using ultrafast dynamic ellipsometry (UDE) in either planar or Gaussian spatial geometries, the latter allowing measurements of the equation of state of materials at a range of stresses in a single laser pulse. Time-resolved processes in materials are being interrogated using UDE, ultrafast infrared absorption, ultrafast UV/visible absorption, and femtosecond stimulated Raman spectroscopy. Using these tools we showed that chemistry in an energetic thin film starts only after an induction time of a few tens of ps, an observation that allows differentiation between proposed shock-induced reaction mechanisms. These tools are presently being applied to a variety of energetic and reactive sample systems, from nitromethane and carbon disulfide, to micro-engineered interfaces in tunable energetic mixtures. Recent results will be presented, and future trends outlined.

Unraveling Shock-Induced Chemistry Using Ultrafast Lasers

David Moore

with Shawn McGrane, Cindy Bolme, Dan Eakins, Margo Greenfield, Jason Scharff, Von Whitley, and others

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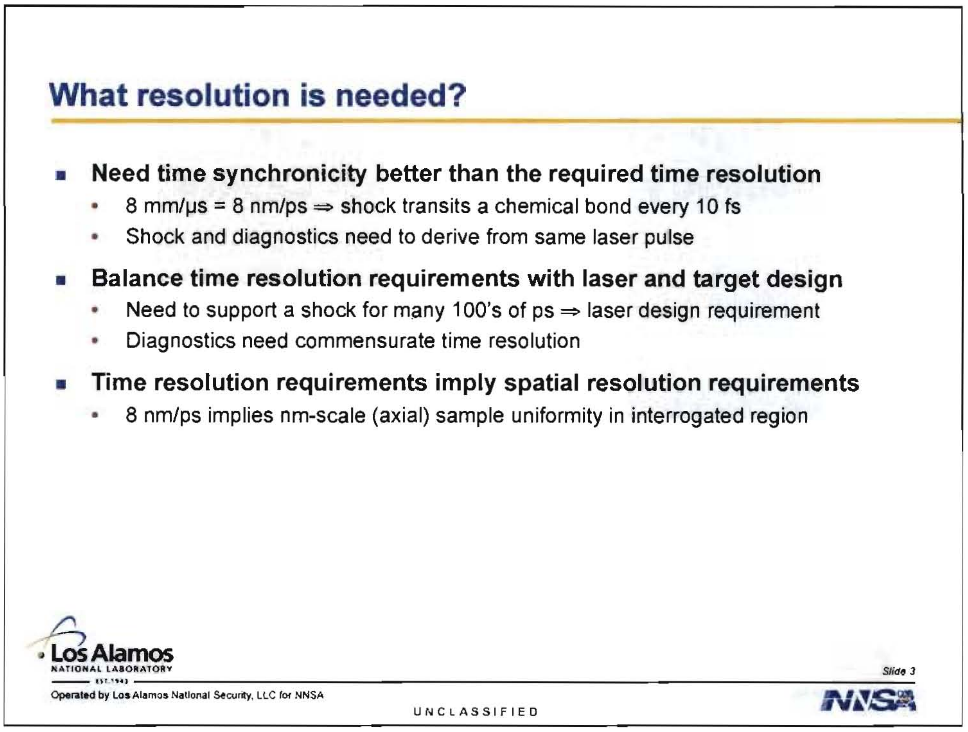
What questions are we trying to answer?

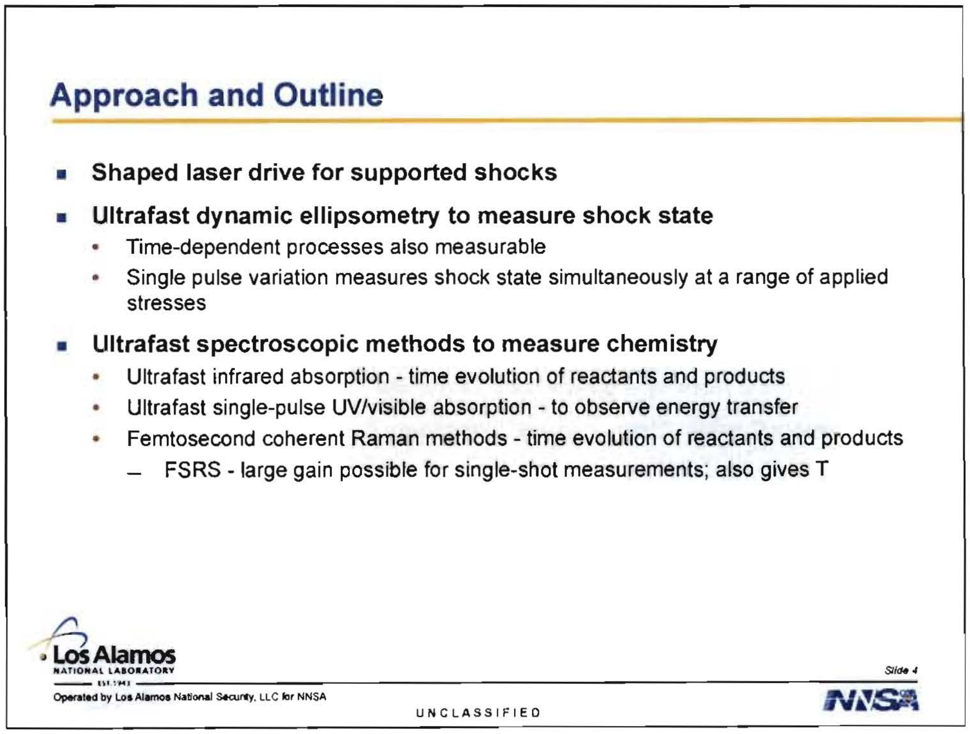
- **Is the initiating shock impulsive?**
- **What mechanism transfers shock energy into the reactive molecules?**
  - Are anharmonic interactions needed?
  - How quickly does transferred energy move within the excited molecules?
- **Are observed kinetics consistent with Arrhenius or transition state theory?**
  - Or does the shock wave provide something unique?
- **Is non-equilibrium "temperature" necessary?**

Our experiments are designed to obtain data at the time and length scales necessary to answer these questions



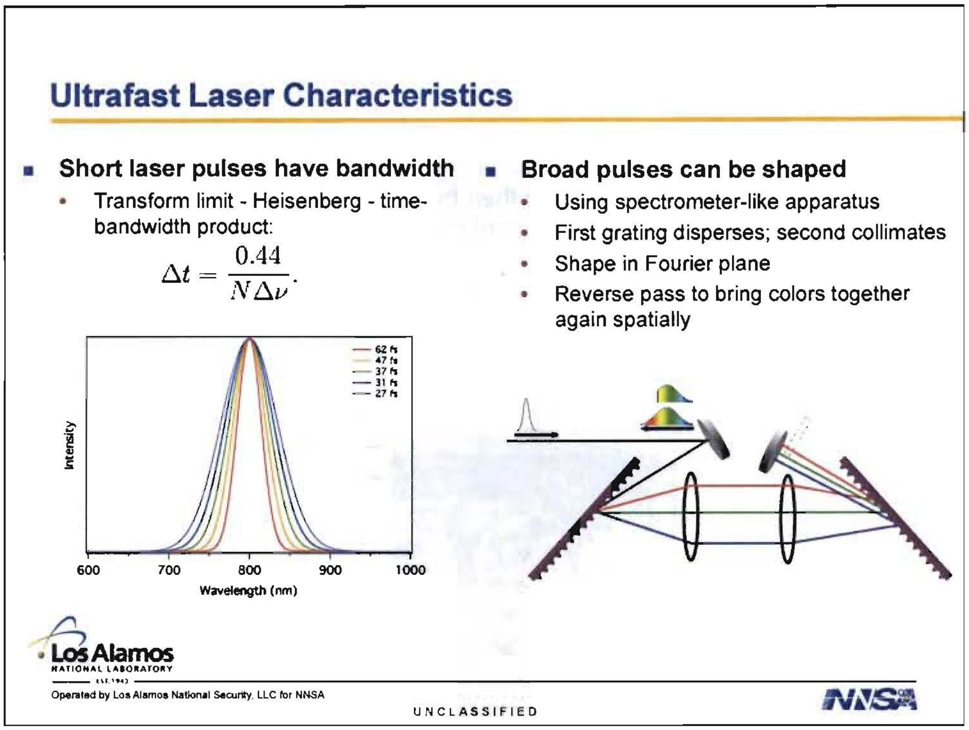
What resolution is needed?

- **Need time synchronicity better than the required time resolution**
  - 8 mm/μs = 8 nm/ps ⇒ shock transits a chemical bond every 10 fs
  - Shock and diagnostics need to derive from same laser pulse
- **Balance time resolution requirements with laser and target design**
  - Need to support a shock for many 100's of ps ⇒ laser design requirement
  - Diagnostics need commensurate time resolution
- **Time resolution requirements imply spatial resolution requirements**
  - 8 nm/ps implies nm-scale (axial) sample uniformity in interrogated region



Approach and Outline

- **Shaped laser drive for supported shocks**
- **Ultrafast dynamic ellipsometry to measure shock state**
  - Time-dependent processes also measurable
  - Single pulse variation measures shock state simultaneously at a range of applied stresses
- **Ultrafast spectroscopic methods to measure chemistry**
  - Ultrafast infrared absorption - time evolution of reactants and products
  - Ultrafast single-pulse UV/visible absorption - to observe energy transfer
  - Femtosecond coherent Raman methods - time evolution of reactants and products
    - FSRS - large gain possible for single-shot measurements; also gives T



Ultrafast Laser Characteristics

- **Short laser pulses have bandwidth**
  - Transform limit - Heisenberg - time-bandwidth product:

$$\Delta t = \frac{0.44}{N\Delta\nu}.$$

- **Broad pulses can be shaped**
  - Using spectrometer-like apparatus
  - First grating disperses; second collimates
  - Shape in Fourier plane
  - Reverse pass to bring colors together again spatially

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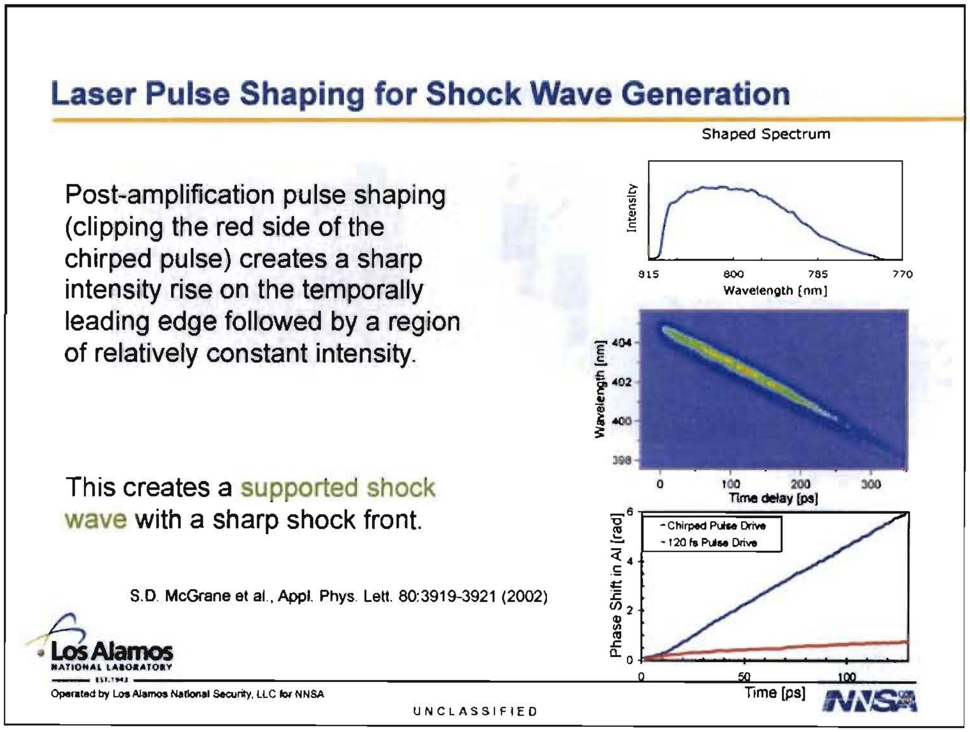

Laser Pulse Shaping for Shock Wave Generation

Post-amplification pulse shaping (clipping the red side of the chirped pulse) creates a sharp intensity rise on the temporally leading edge followed by a region of relatively constant intensity.

This creates a supported shock wave with a sharp shock front.

S.D. McGrane et al., Appl. Phys. Lett. 80:3919-3921 (2002)

Shaped Spectrum

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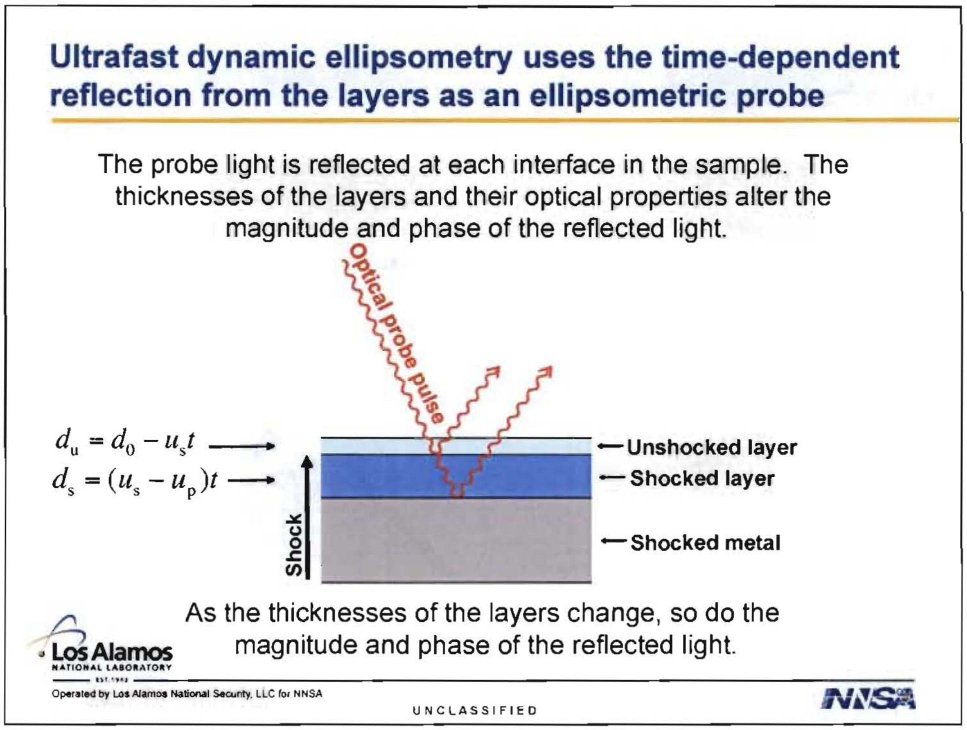


Ultrafast dynamic ellipsometry uses the time-dependent reflection from the layers as an ellipsometric probe

The probe light is reflected at each interface in the sample. The thicknesses of the layers and their optical properties alter the magnitude and phase of the reflected light.

$d_u = d_0 - u_s t$ →

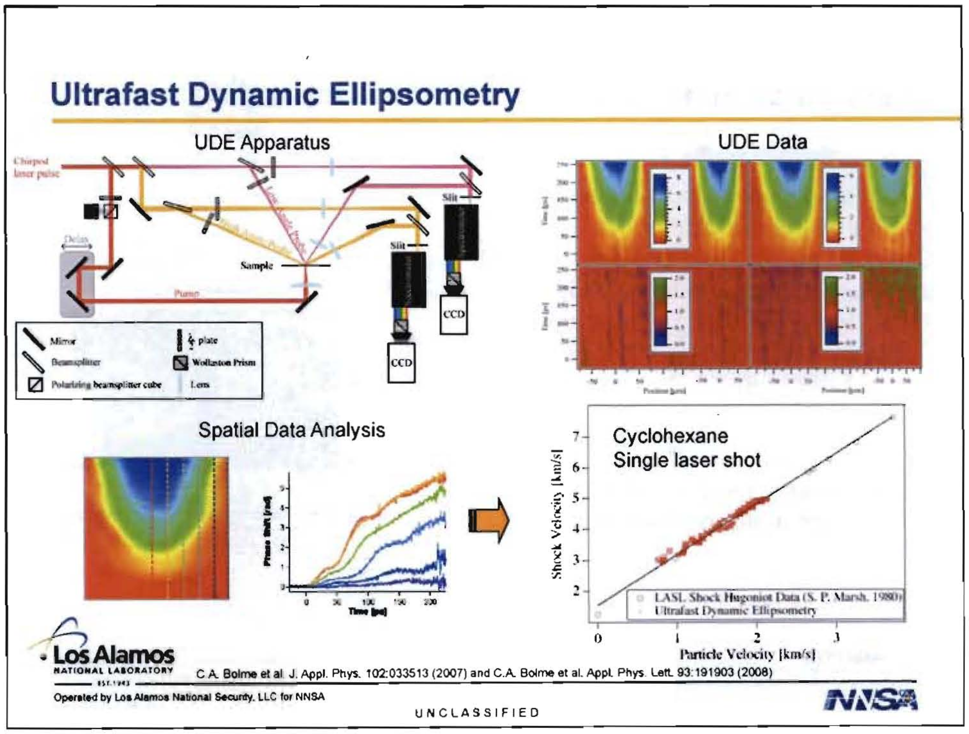
$d_s = (u_s - u_p)t$ →

← **Unshocked layer**

← **Shocked layer**

← **Shocked metal**

As the thicknesses of the layers change, so do the magnitude and phase of the reflected light.



Ultrafast Dynamic Ellipsometry

UDE Apparatus

UDE Data

Spatial Data Analysis

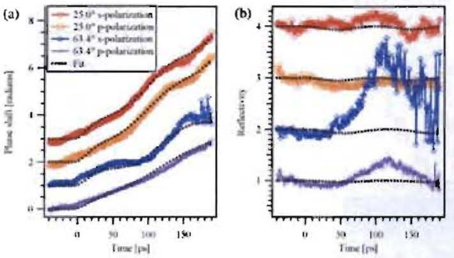
Cyclohexane
Single laser shot

C.A. Bolme et al. J. Appl. Phys. 102:033513 (2007) and C.A. Bolme et al. Appl. Phys. Lett. 93:191903 (2008)

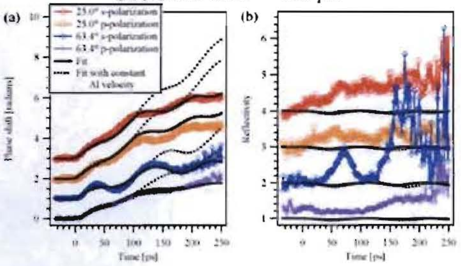
Ultrafast dynamic ellipsometry suggests that reaction begins within 100 ps of shock front in nitromethane

At 7.9 GPa, the Al interface behind the nitromethane appears to decrease in velocity ~100 ps after shock arrival

7.0 GPa, no reaction apparent



7.9 GPa, interface velocity decrease after ~ 100 ps



The shocked refractive index of nitromethane showed Gladstone-Dale behavior for both the "normal" and "abnormal" shots

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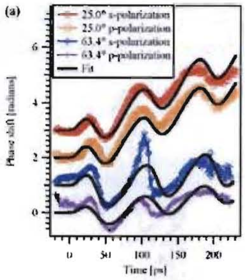
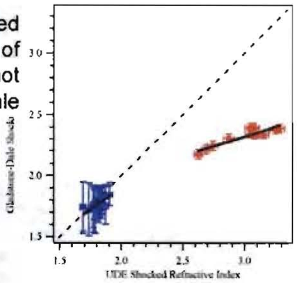
UDE data for shocked liquid CS_2

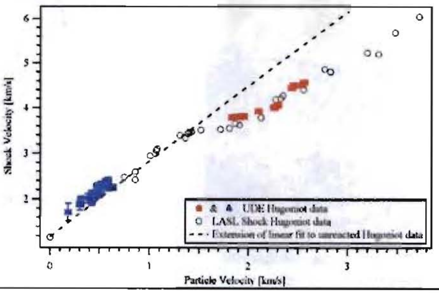
The strong oscillations result from a large change in shocked CS_2 refractive index



The shocked refractive index of CS_2 is clearly not Gladstone-Dale



Hugoniot above cusp similar to that obtained at longer time scales



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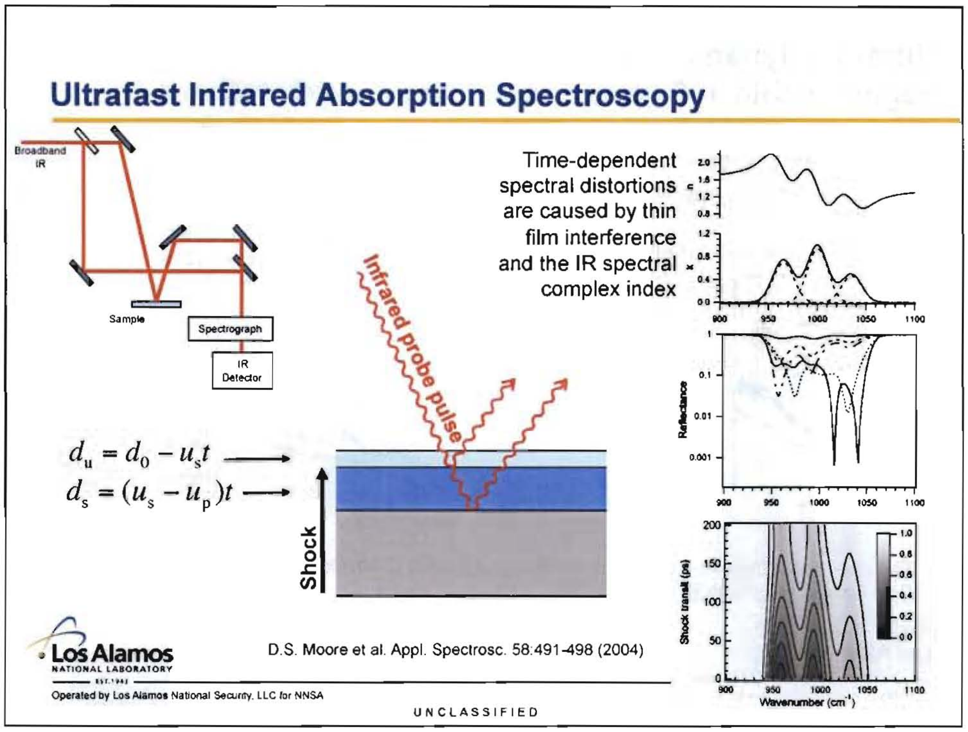

Ultrafast Infrared Absorption Spectroscopy

Time-dependent spectral distortions are caused by thin film interference and the IR spectral complex index

$$d_u = d_0 - u_s t \longrightarrow$$
$$d_s = (u_s - u_p)t \longrightarrow$$

D.S. Moore et al. Appl. Spectrosc. 58:491-498 (2004)

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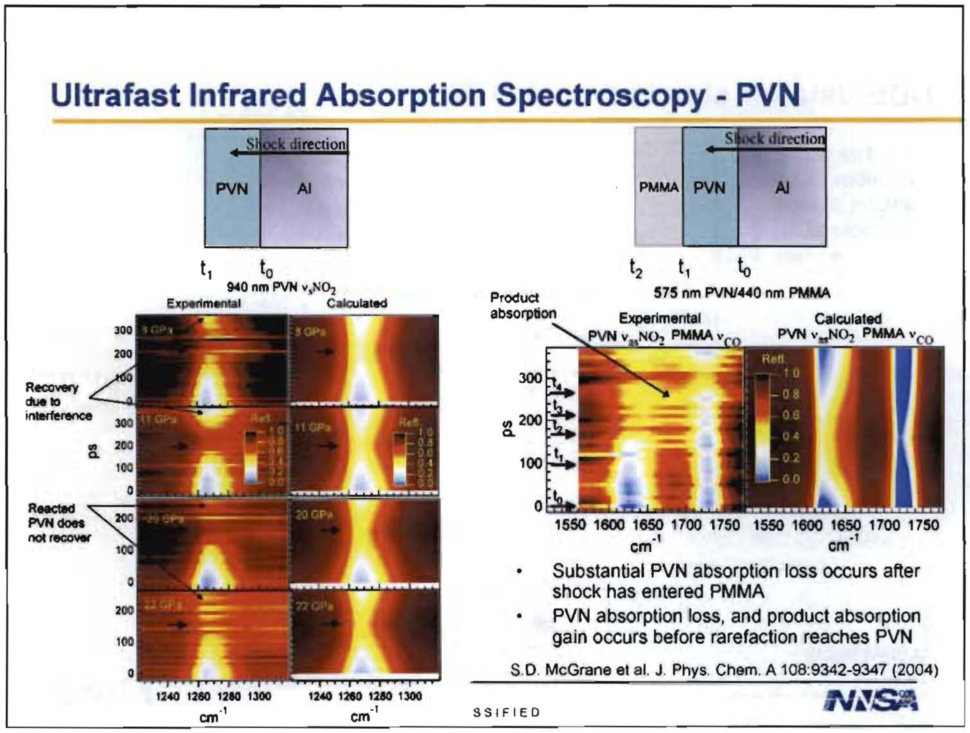

Ultrafast Infrared Absorption Spectroscopy - PVN

- Substantial PVN absorption loss occurs after shock has entered PMMA
- PVN absorption loss, and product absorption gain occurs before rarefaction reaches PVN

S.D. McGrane et al. J. Phys. Chem. A 108:9342-9347 (2004)

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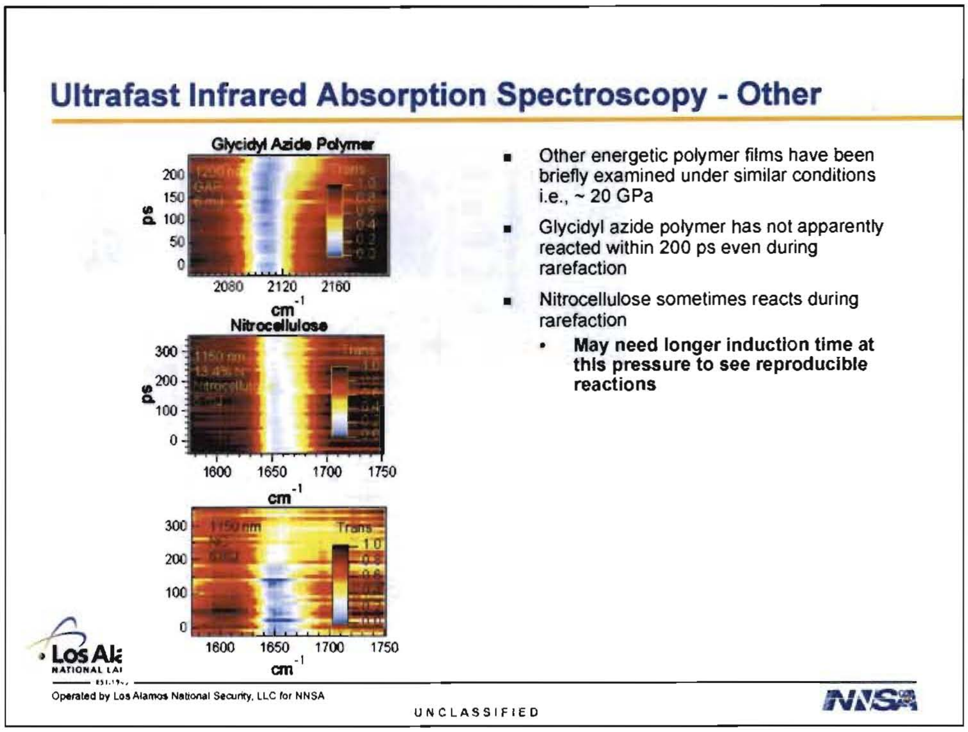

Ultrafast Infrared Absorption Spectroscopy - Other

- Other energetic polymer films have been briefly examined under similar conditions i.e., ~ 20 GPa
- Glycidyl azide polymer has not apparently reacted within 200 ps even during rarefaction
- Nitrocellulose sometimes reacts during rarefaction
  - **May need longer induction time at this pressure to see reproducible reactions**

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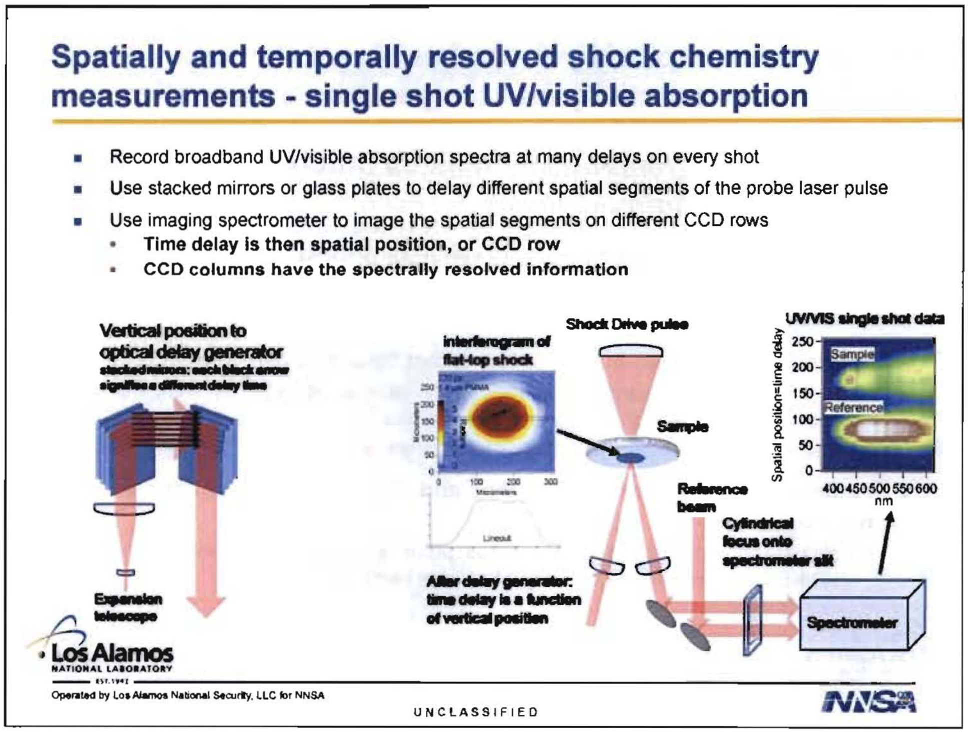

Spatially and temporally resolved shock chemistry measurements - single shot UV/visible absorption

- Record broadband UV/visible absorption spectra at many delays on every shot
- Use stacked mirrors or glass plates to delay different spatial segments of the probe laser pulse
- Use imaging spectrometer to image the spatial segments on different CCD rows
  - **Time delay is then spatial position, or CCD row**
  - **CCD columns have the spectrally resolved information**

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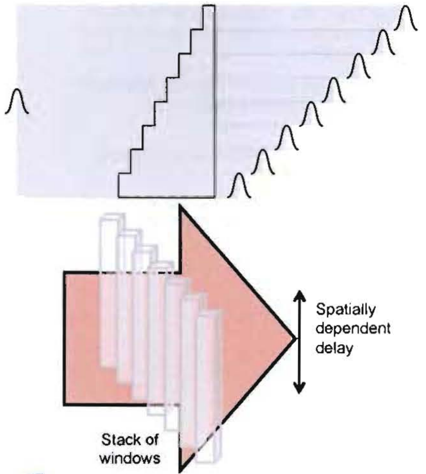
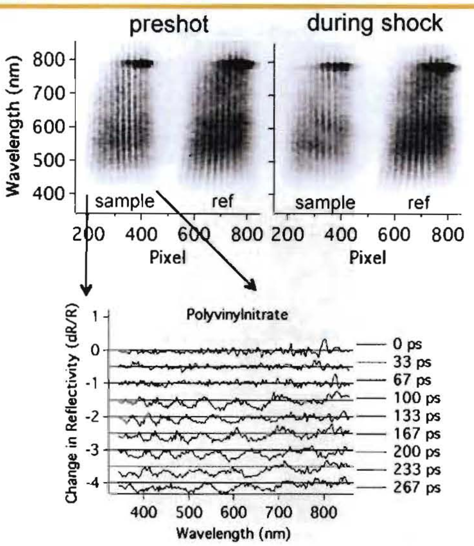
Single shot UV/visible absorption results

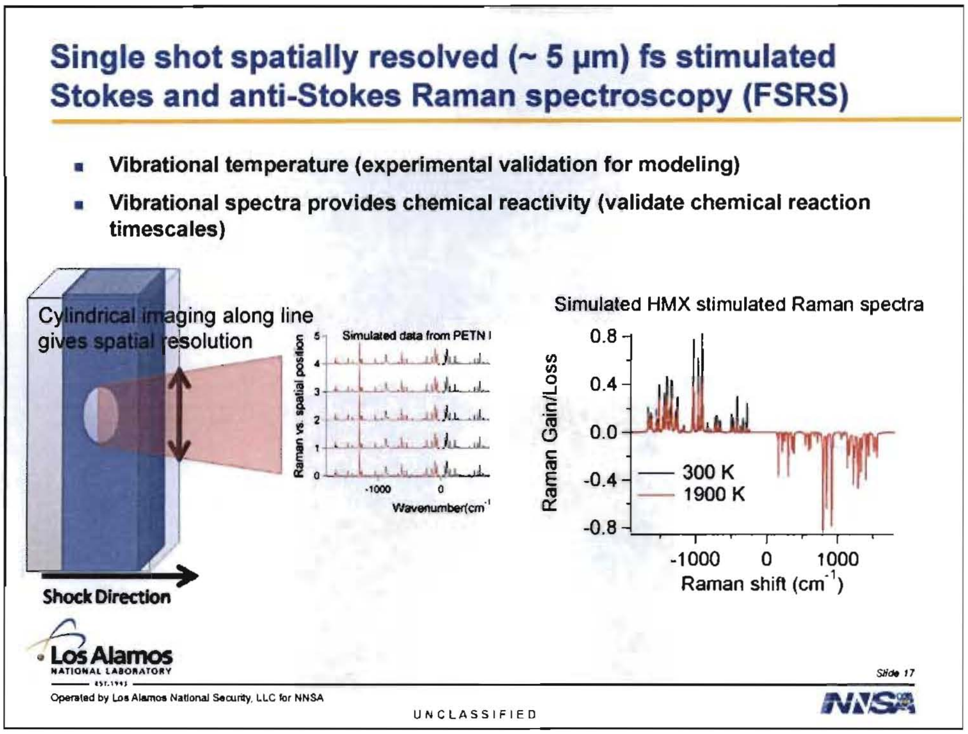




We have been exploring several coherent Raman techniques for reactivity and temperature diagnostics

Difficult measurement- but tells us much of what we want to know *directly*

- **Femtosecond stimulated Raman Scattering (FSRS)**
  - Raman efficiency ~10^{-8} , FSRS efficiency ~10^{-2}
  - Temperature is from ratio of Anti-Stokes loss to Stokes gain
- **Femtosecond Raman-induced Kerr Effect Spectroscopy (FRIKES)**
  - No background and same line shapes as spontaneous Raman scattering, but spectrum intensity is limited by intensity of probe
  - Shock-induced birefringence may distort Raman spectrum
- **Femtosecond Coherent Anti-Stokes and Stokes Raman scattering (CARS/CSRS)**
  - No background, no birefringence issues, probe requires less bandwidth than FRIKES or FSRS, but pump must have large bandwidth



Single shot spatially resolved (~ 5 μm) fs stimulated Stokes and anti-Stokes Raman spectroscopy (FSRS)

- **Vibrational temperature (experimental validation for modeling)**
- **Vibrational spectra provides chemical reactivity (validate chemical reaction timescales)**

Cylindrical imaging along line gives spatial resolution

Simulated HMX stimulated Raman spectra

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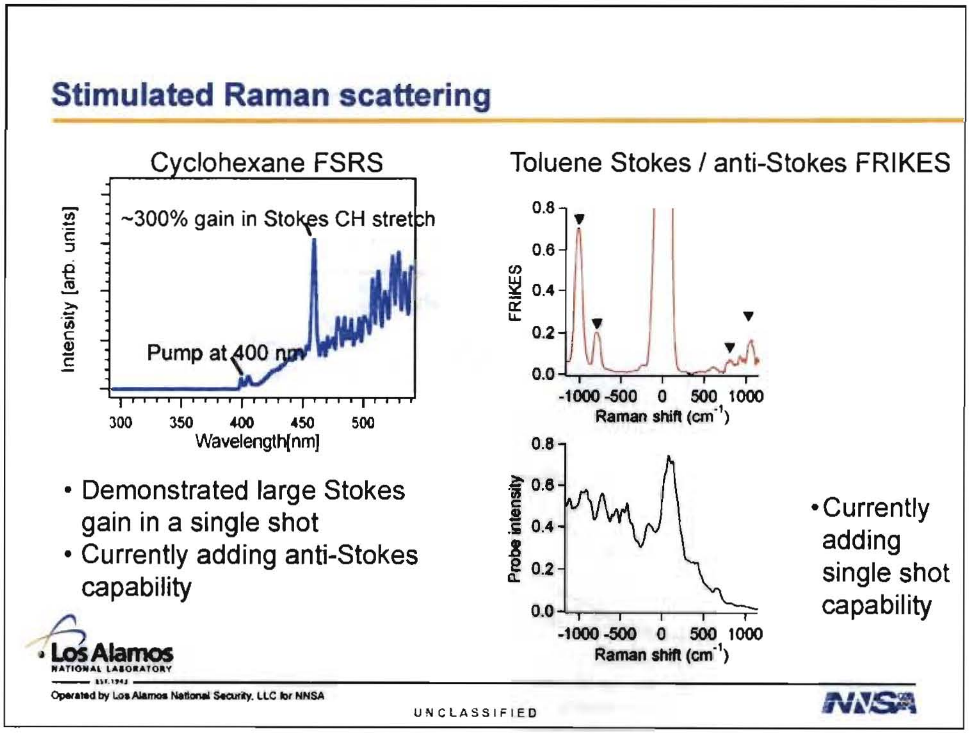

Stimulated Raman scattering

Cyclohexane FSRS

- Demonstrated large Stokes gain in a single shot
- Currently adding anti-Stokes capability

Toluene Stokes / anti-Stokes FRIKES

- Currently adding single shot capability

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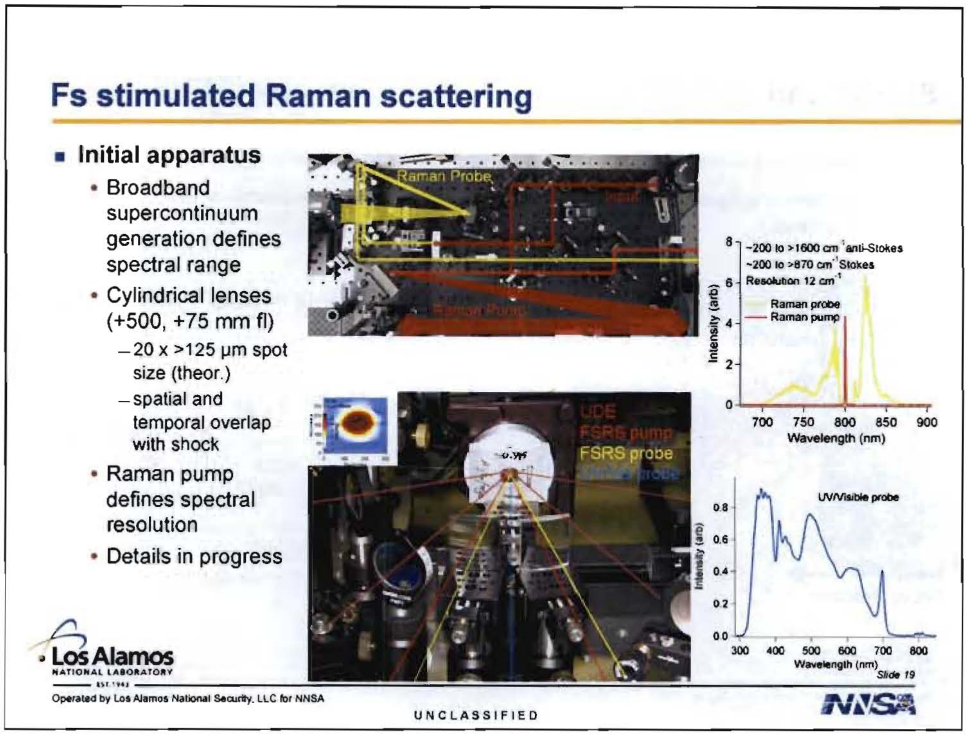

Fs stimulated Raman scattering

- **Initial apparatus**
  - Broadband supercontinuum generation defines spectral range
  - Cylindrical lenses (+500, +75 mm fl)
    - 20 x >125 µm spot size (theor.)
    - spatial and temporal overlap with shock
  - Raman pump defines spectral resolution
  - Details in progress

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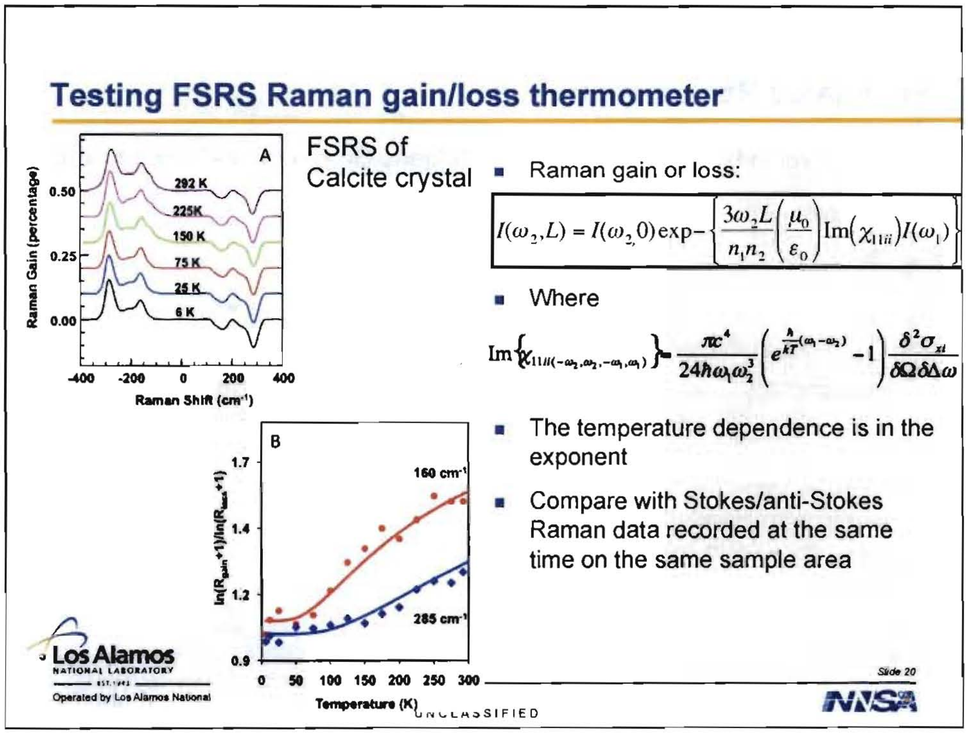

Testing FSRS Raman gain/loss thermometer

FSRS of Calcite crystal

- Raman gain or loss:

$$\boxed{I(\omega_2,L) = I(\omega_2,0)\exp-\left\{\frac{3\omega_2 L}{n_1 n_2}\left(\frac{\mu_0}{\varepsilon_0}\right)\mathrm{Im}\left(\chi_{11ii}\right)I(\omega_1)\right\}}$$

- Where

$$\mathrm{Im}\left\{\chi_{11ll(-\omega_2,\omega_2,-\omega_1,\omega_1)}\right\} = \frac{\pi c^4}{24\hbar\omega_1\omega_2^3}\left(e^{\frac{\hbar}{kT}(\omega_1-\omega_2)}-1\right)\frac{\delta^2\sigma_{xl}}{\delta\Omega\delta\Delta\omega}$$

- The temperature dependence is in the exponent
- Compare with Stokes/anti-Stokes Raman data recorded at the same time on the same sample area

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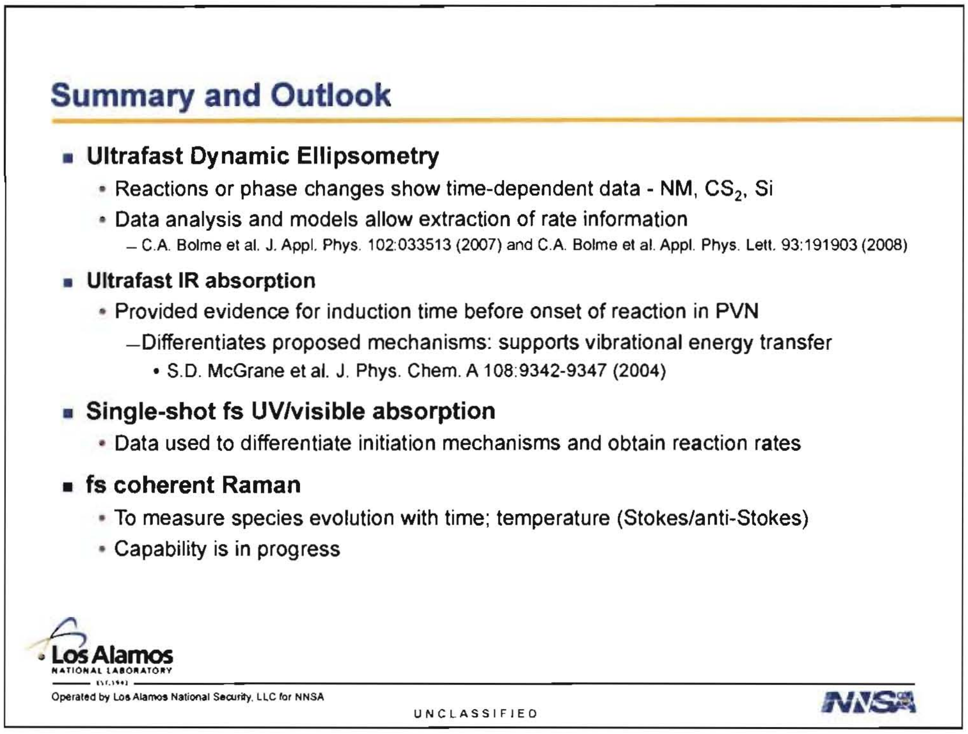

Summary and Outlook

- **Ultrafast Dynamic Ellipsometry**
  - Reactions or phase changes show time-dependent data - NM, CS_2, Si
  - Data analysis and models allow extraction of rate information
    - C.A. Bolme et al. J. Appl. Phys. 102:033513 (2007) and C.A. Bolme et al. Appl. Phys. Lett. 93:191903 (2008)
- **Ultrafast IR absorption**
  - Provided evidence for induction time before onset of reaction in PVN
    - Differentiates proposed mechanisms: supports vibrational energy transfer
      - S.D. McGrane et al. J. Phys. Chem. A 108:9342-9347 (2004)
- **Single-shot fs UV/visible absorption**
  - Data used to differentiate initiation mechanisms and obtain reaction rates
- **fs coherent Raman**
  - To measure species evolution with time; temperature (Stokes/anti-Stokes)
  - Capability is in progress

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