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Title: Ultrafast Dynamic Ellipsometry and Spectroscopy of Laser Shocked Materials

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Ultrafast Dynamic Ellipsometry and Spectroscopy of Laser Shocked Materials

Ultrafast dynamic ellipsometry is used to measure the material motion and changes in the optical refractive index of laser shock compressed materials. This diagnostic has shown us that the ultrafast laser driven shocks are the same as shocks on longer timescales and larger length scales. We have added spectroscopic diagnostics of infrared absorption, ultra-violet – visible transient absorption, and femtosecond stimulated Raman scattering to begin probing the initiation chemistry that occurs in shock reactive materials. We have also used the femtosecond stimulated Raman scattering to measure the vibrational temperature of materials using the Stokes gain to anti-Stokes loss ratio.

Ultrafast Dynamic Ellipsometry and Spectroscopy of Laser Shocked Materials

Cindy Bolme, Shawn McGrane, Nhan Dang, Von Whitley, David Moore

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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

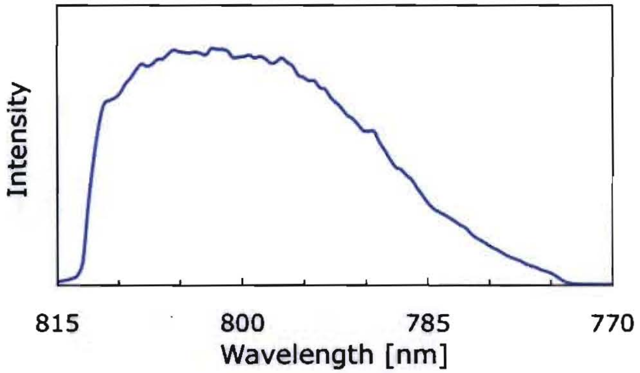
Approach and Outline

- **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**
  - IR absorption – to monitor specific vibrations
  - Ultrafast single-pulse UV/visible absorption - to observe energy transfer/electronic excitation
  - Femtosecond coherent Raman methods - time evolution of reactants and products & measure temperature

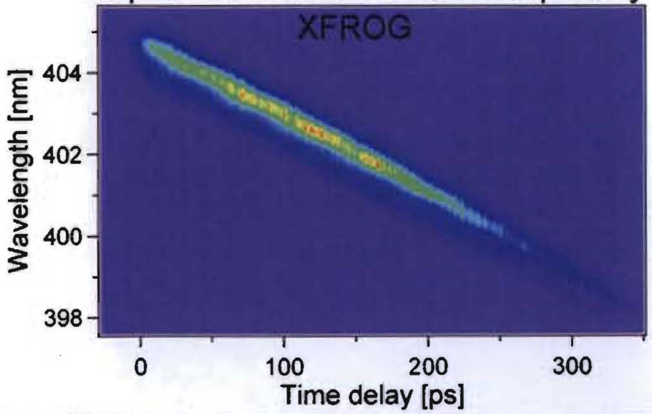
Laser Pulse Shaping for Shock Wave Generation & Laser Chirp for Single-Shot Acquisition

Post-amplification pulse shaping creates a sharp intensity rise on the temporally leading edge followed by a region of relatively constant intensity

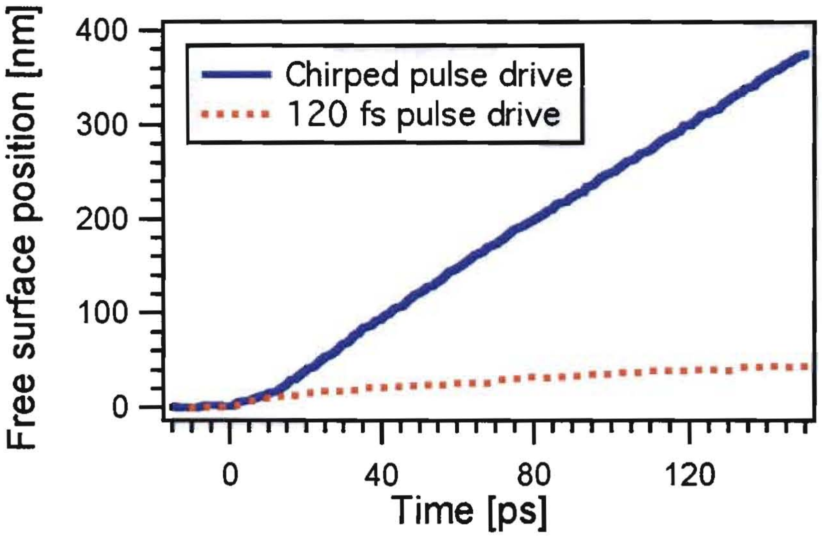
Shaped Spectrum



Pulse chirp is used to translate frequency into time



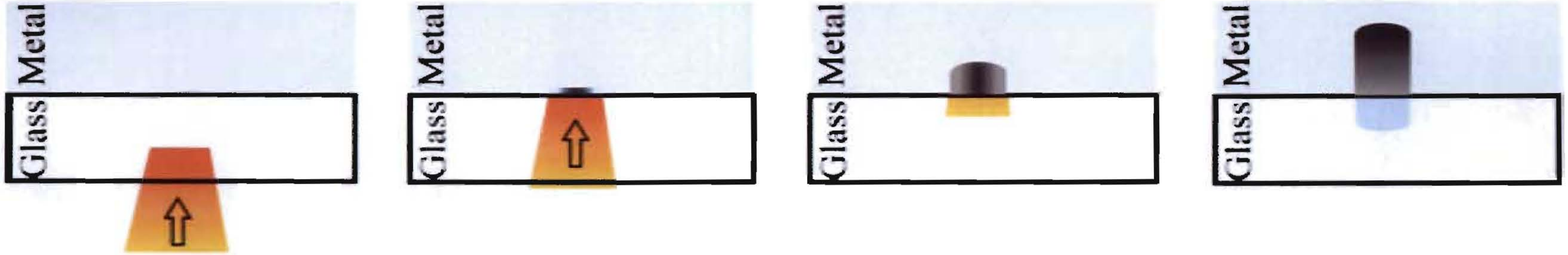
Temporal shaping creates a supported shock wave with a sharp shock front



Generation of shock waves via frustrated laser ablation

Laser pulse was focused through a glass substrate on to the metal film

Laser energy absorbed in the metal creating a hot electron gas

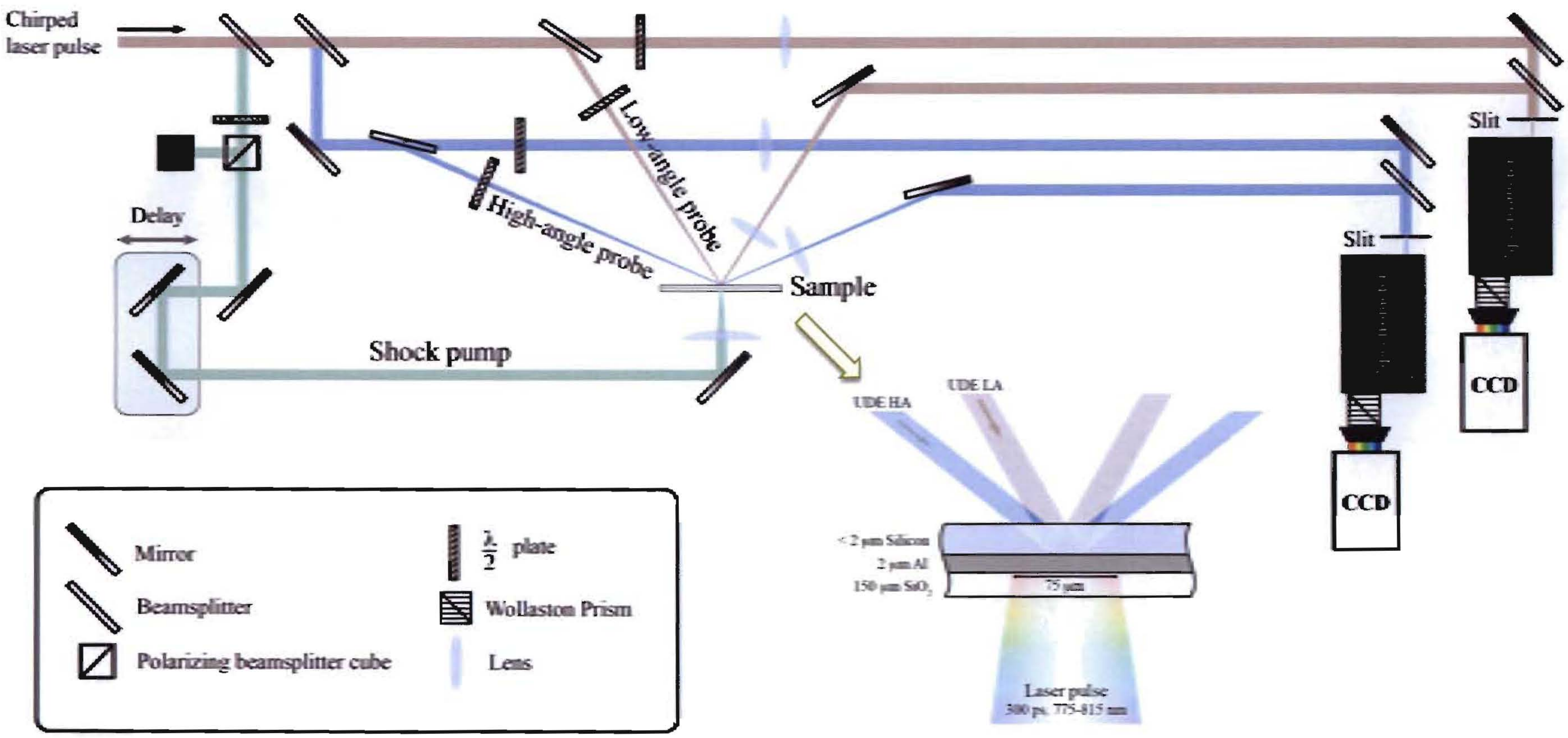


Energy transferred from the hot electrons to the metal lattice

Hot lattice expands to generate a shock wave

Laser-shock/UDE experimental schematic

Probes contain both s- and p-polarized light at each angle



Examples of interferograms recorded with our CCD cameras

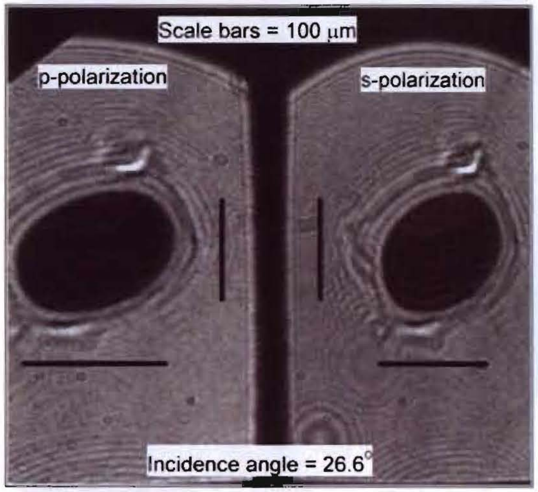
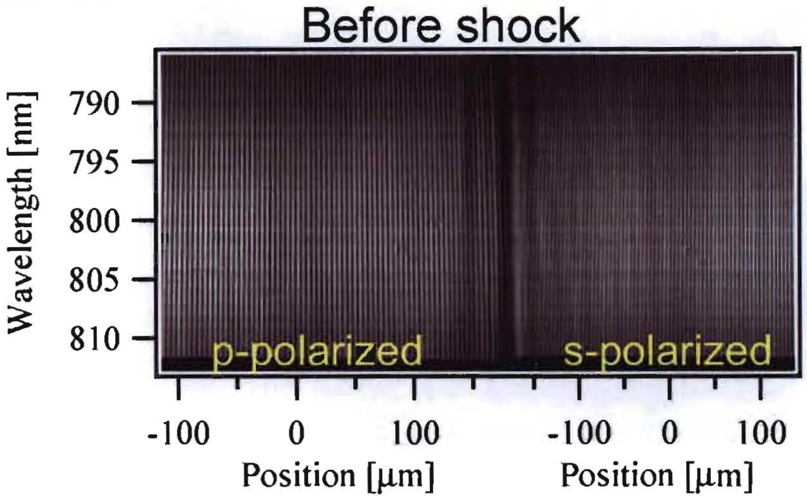
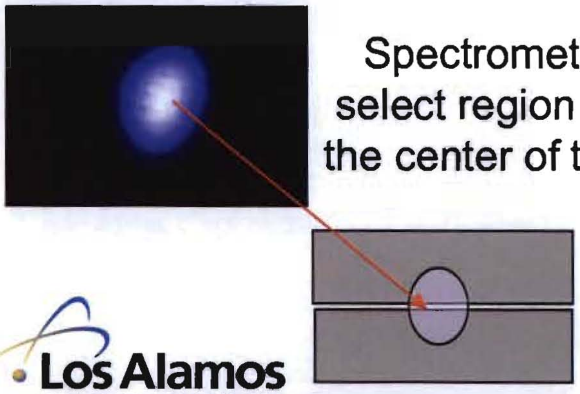
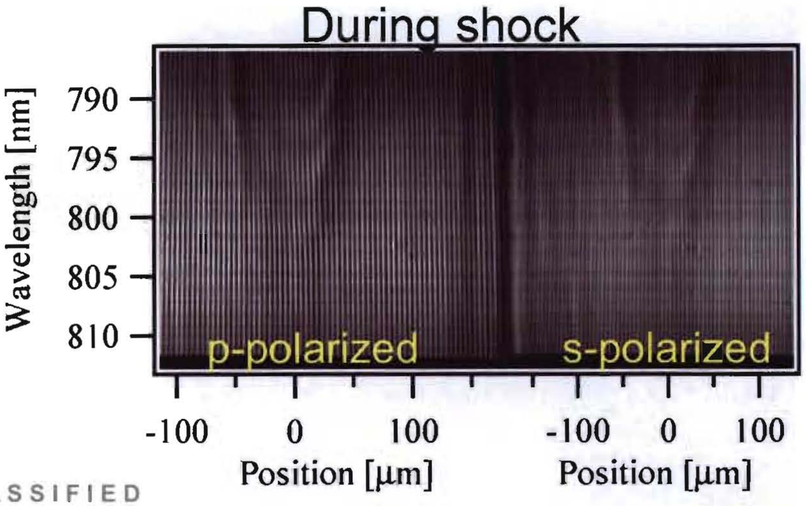


Image of the holes created by the shock



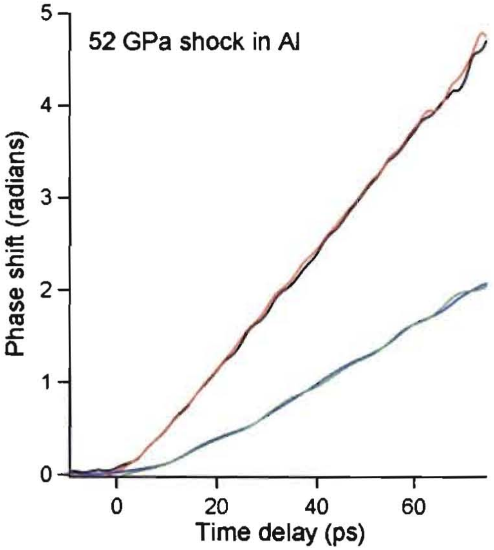


Spectrometer slits select region through the center of the holes

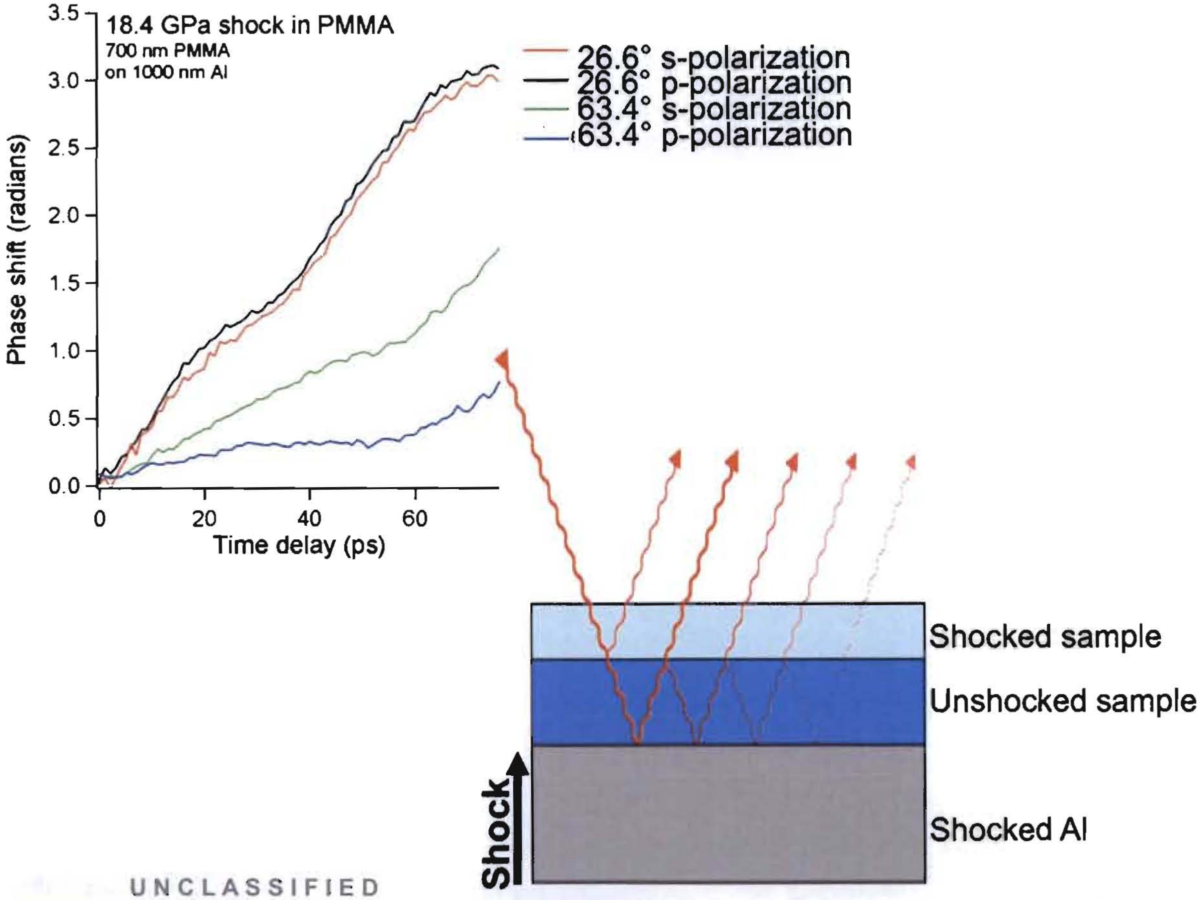


UDE data from Al and PMMA/Al

In Al, the phase shift as a function of time measures the free surface velocity



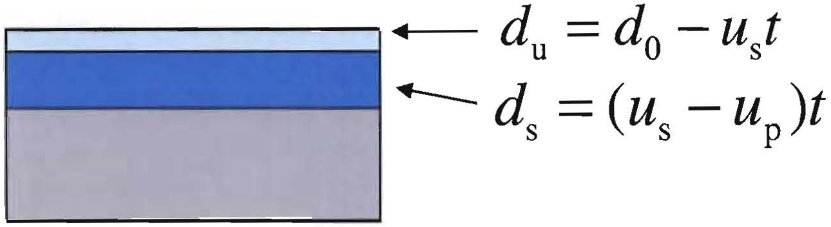
In PMMA, the oscillations result from interference of the probe light from the multiple time-dependant layers



Analysis of shocked dielectrics data

Levenberg-Marquardt algorithm for least squares fit.

Fit uses the thin film equations to calculate the reflectivity and phase. After the initial acceleration, layer thicknesses change linearly as a function of time.

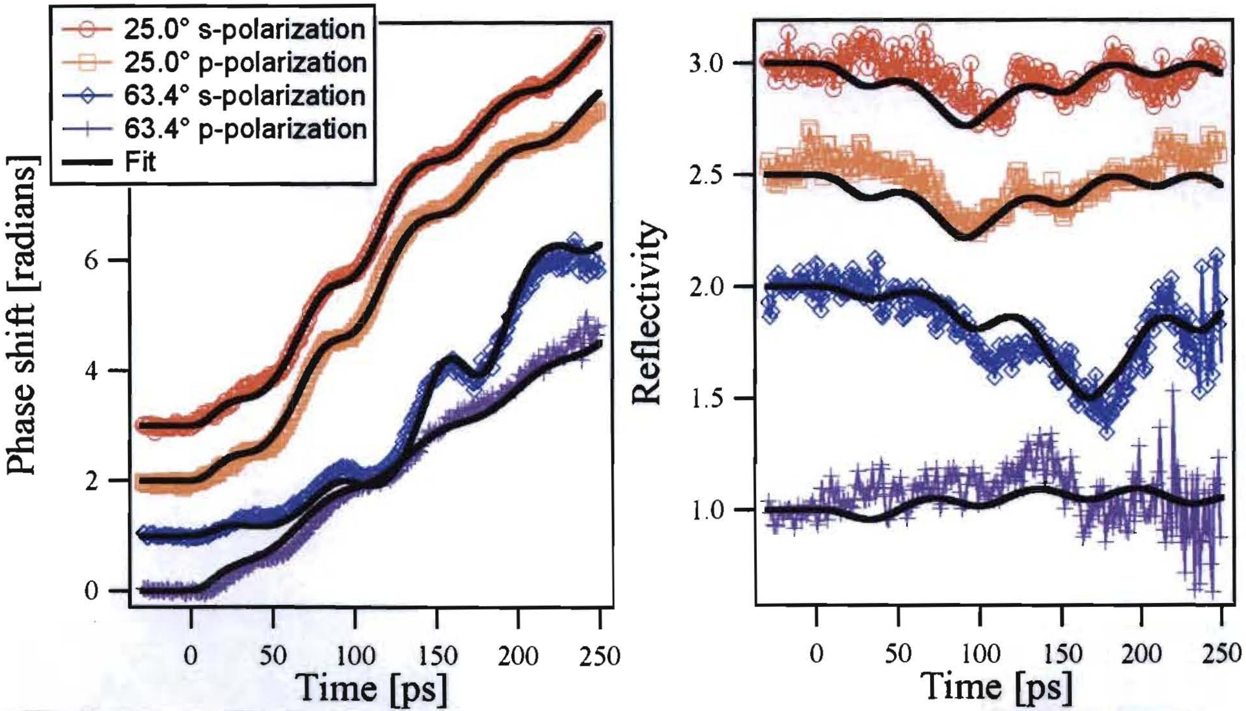


$d_u = d_0 - u_s t$

$d_s = (u_s - u_p)t$

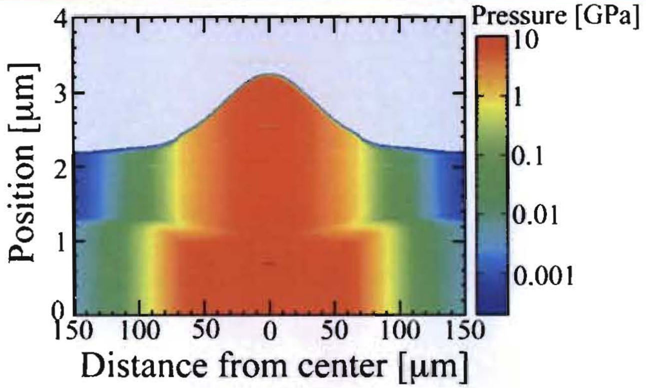
Assumptions in the analysis:

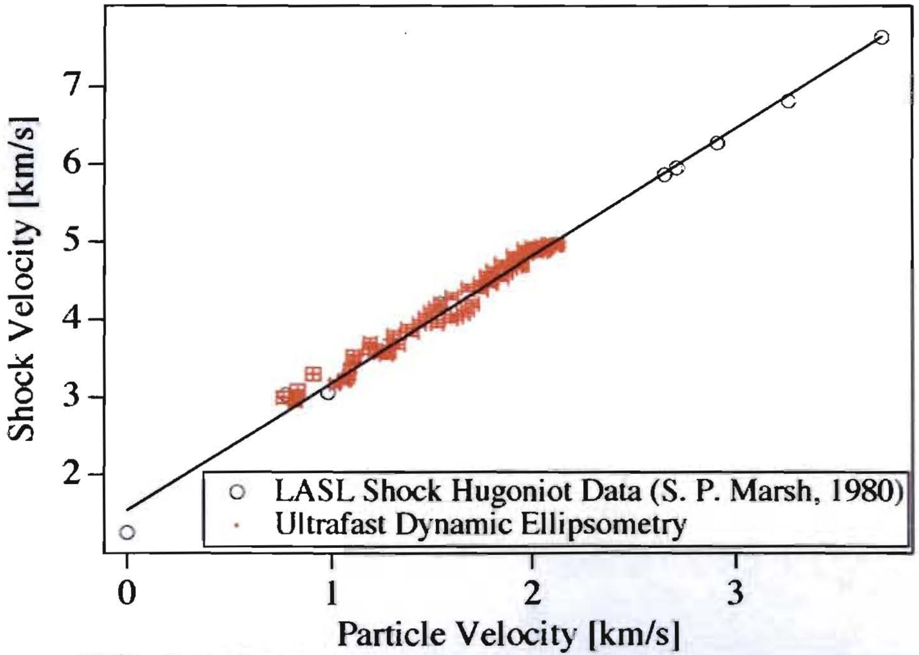
- Constant pressure
- Constant shocked refractive index
- Negligible variation in refractive index of Al



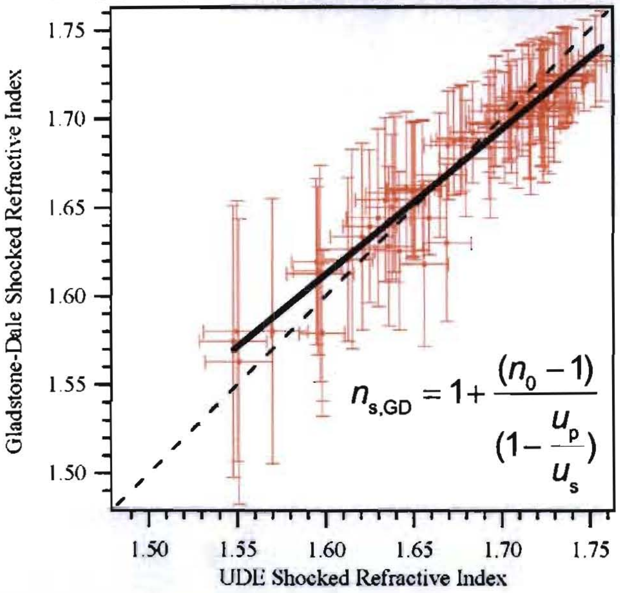
Single Shot Cyclohexane Hugoniot

Hugoniot data collected from 1 laser shot using the intensity distribution of the drive laser





Gladstone-Dale shocked refractive index:

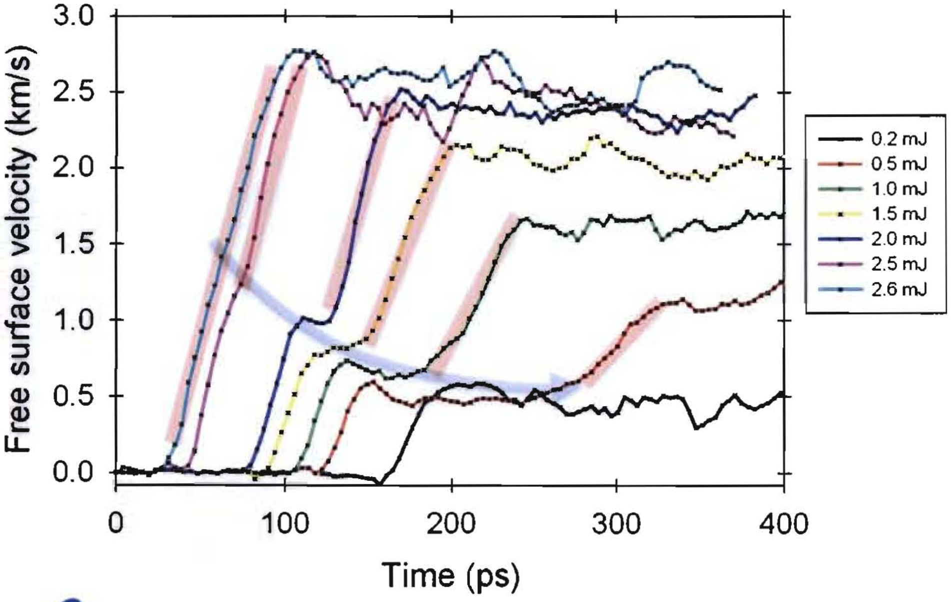


C. A. Bolme, *et al.*, Appl. Phys. Lett., **93,** 191903 (2008).

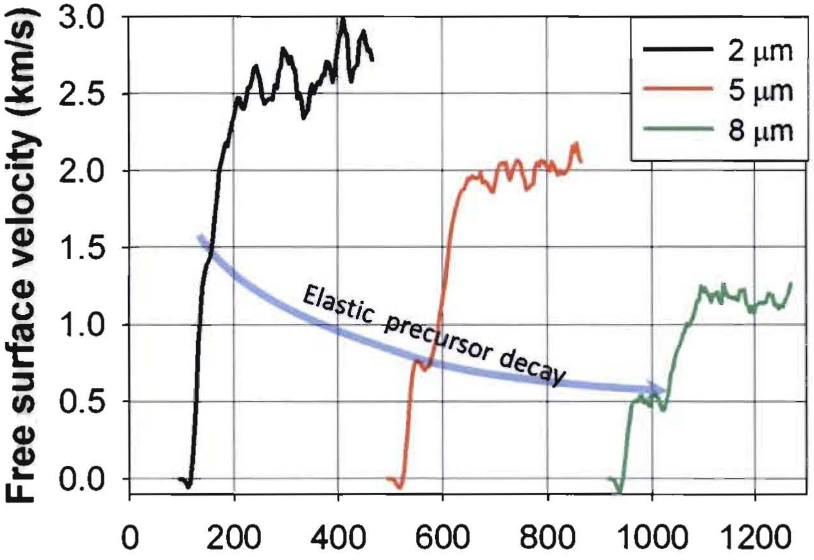
Standard shock physics occurs at nm/ps scales

Elastic/plastic wave separation in aluminum analogous to bulk experiments at longer length and time scales

Effect of drive energy on 8 μm Al

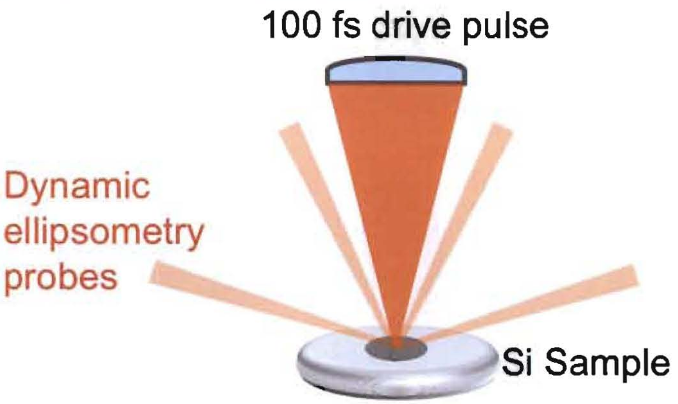


Effect of run distance

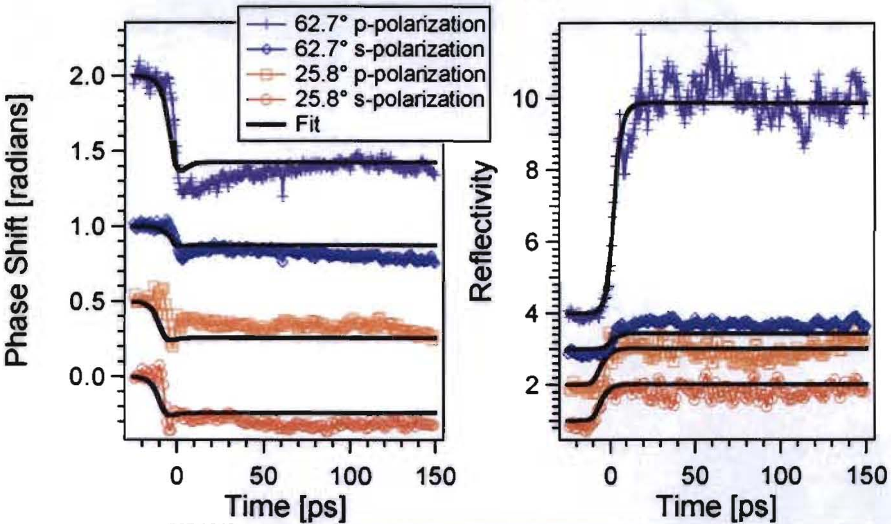


V. H. Whitley, *et al.*, J. Appl. Phys. **109**, 013505 (2011)

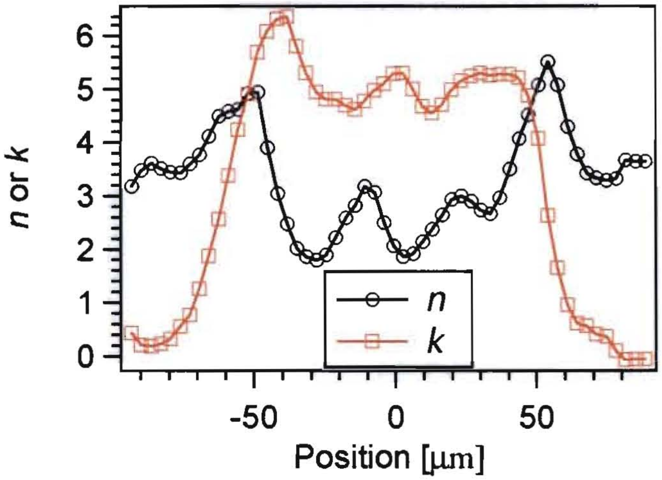
Laser-induced phase transition: Melting of Si(111)



All 8 sets of data at each spatial position are fit for a transition to a final complex refractive index



Si refractive index shows the material is solid on the sides of the pulse and liquid in the center



$$\tilde{n}_{\text{solid}} = 3.57 + i0.006$$

$$\tilde{n}_{\text{liquid}} \approx 3.3 + i5.6$$

C. A. Bolme, *et al.*, SPIE Vol. 7005 (2008)

Competing hypotheses of explosive initiation

- **The thermal equilibrium hypothesis:**

- all excitations and chemistry can be described by a single temperature.

- *Predictions: No electronic excitations are expected. Vibrations will be populated according to the Boltzmann distribution.*

- **The multiphonon up-pumping hypothesis**:

- the delocalized shock wave preferentially excites low frequency phonons which must drive chemistry by anharmonic energy transfer to high frequency vibrations.

- *Predictions: No electronic excitations are expected. Vibrational excitations will be athermal and time dependent.*

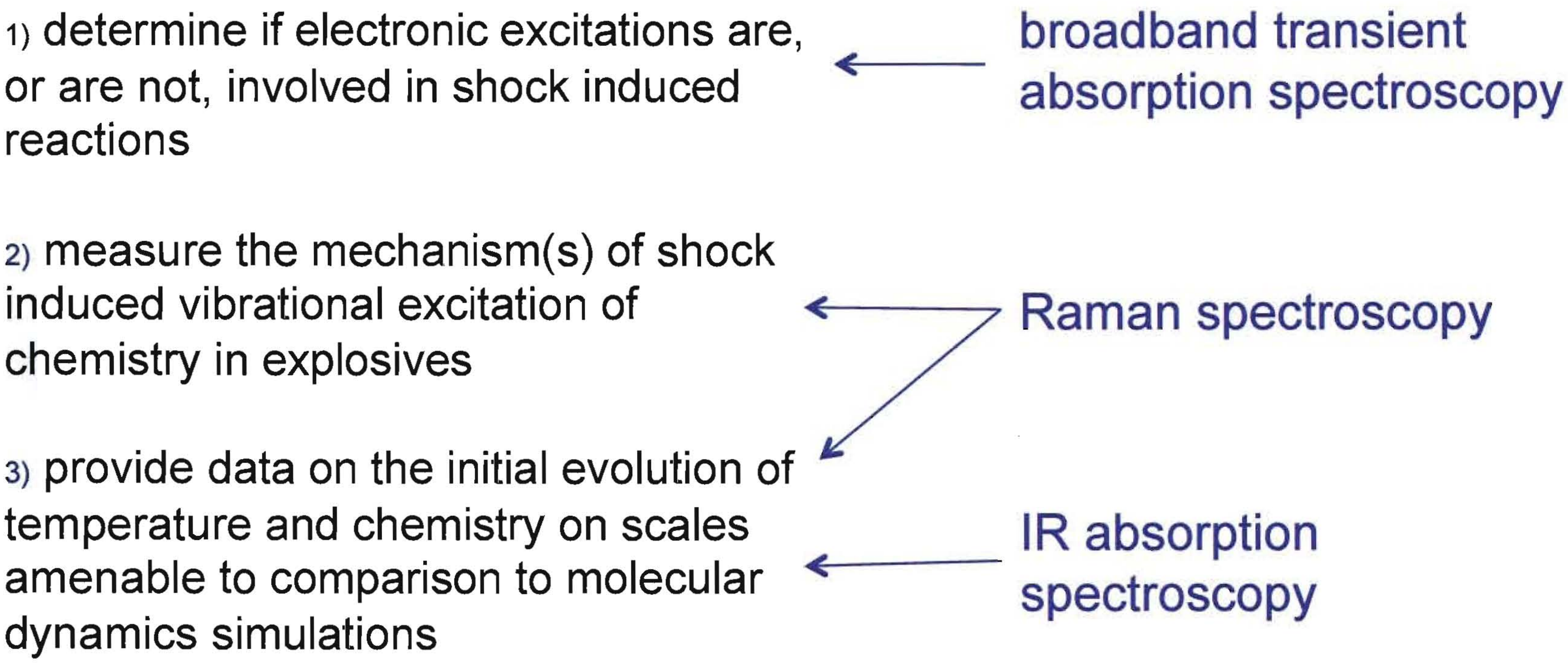
- **The mechanochemistry (or shock discontinuity zone) hypothesis**:

- molecular impacts directly excite the molecules. Bonds are compressed and bent, nuclear configuration changes rapidly, electronic energy levels shift, and chemistry is essentially dissimilar to chemistry under nonshock conditions.

- *Predictions: Electronic excitations or distortions of the electronic structure as well as vibrational excitations can be athermal, and are expected to occur directly following the shock front. Chemistry is unique to shock conditions and should vary with molecular structure and orientation.*

Investigating explosive initiation

We seek to:



1) determine if electronic excitations are, or are not, involved in shock induced reactions

2) measure the mechanism(s) of shock induced vibrational excitation of chemistry in explosives

3) provide data on the initial evolution of temperature and chemistry on scales amenable to comparison to molecular dynamics simulations

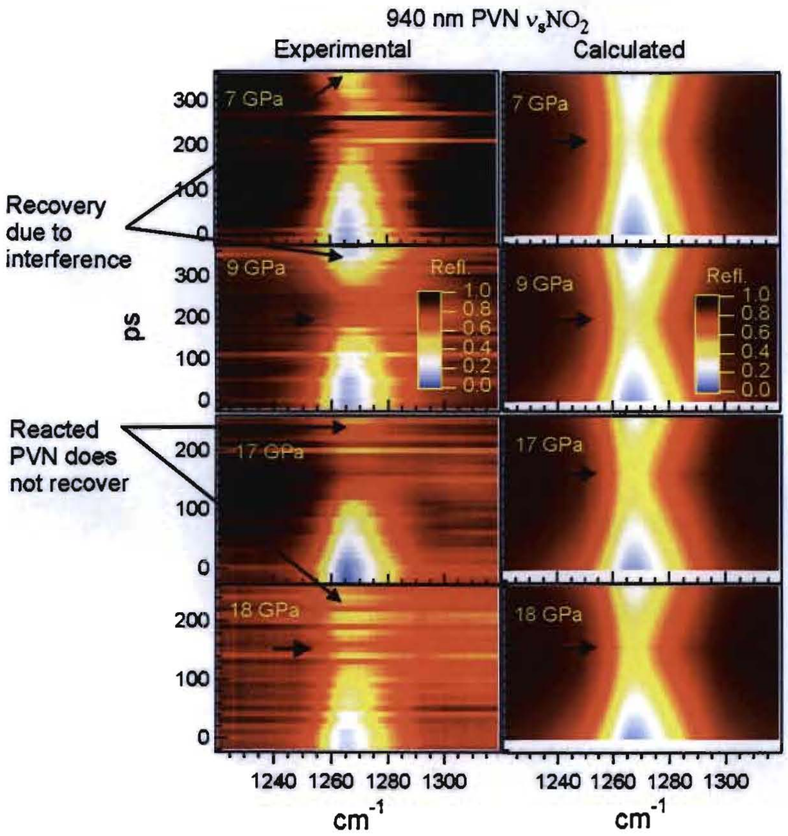
broadband transient absorption spectroscopy

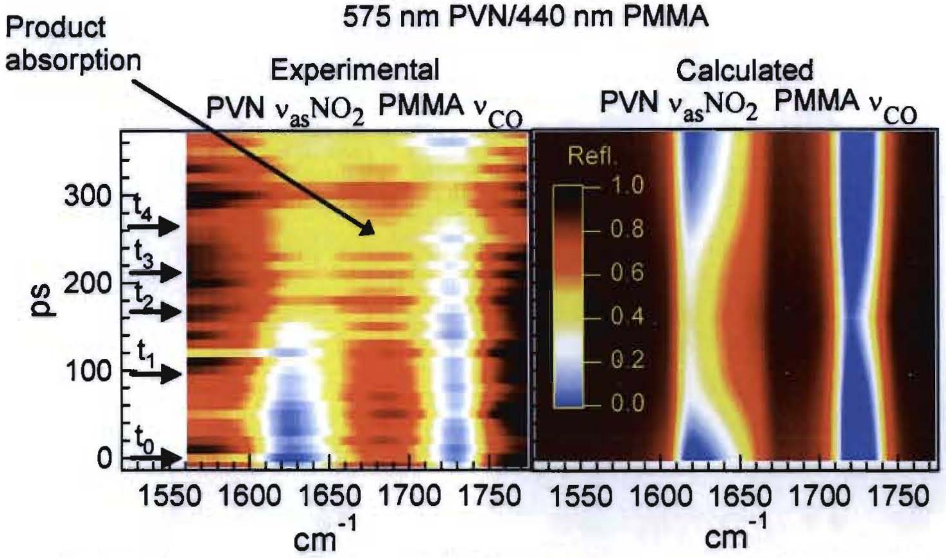
Raman spectroscopy

IR absorption spectroscopy

Completing these goals will help to identify the proper theoretical treatment of shock induced initiation at the molecular level

We have observed shock induced chemistry in poly(vinyl-nitrate) by transient IR absorption





S. D. McGrane, D. S. Moore, D. J. Funk, J. Phys. Chem. A, 108, 9342 (2004)

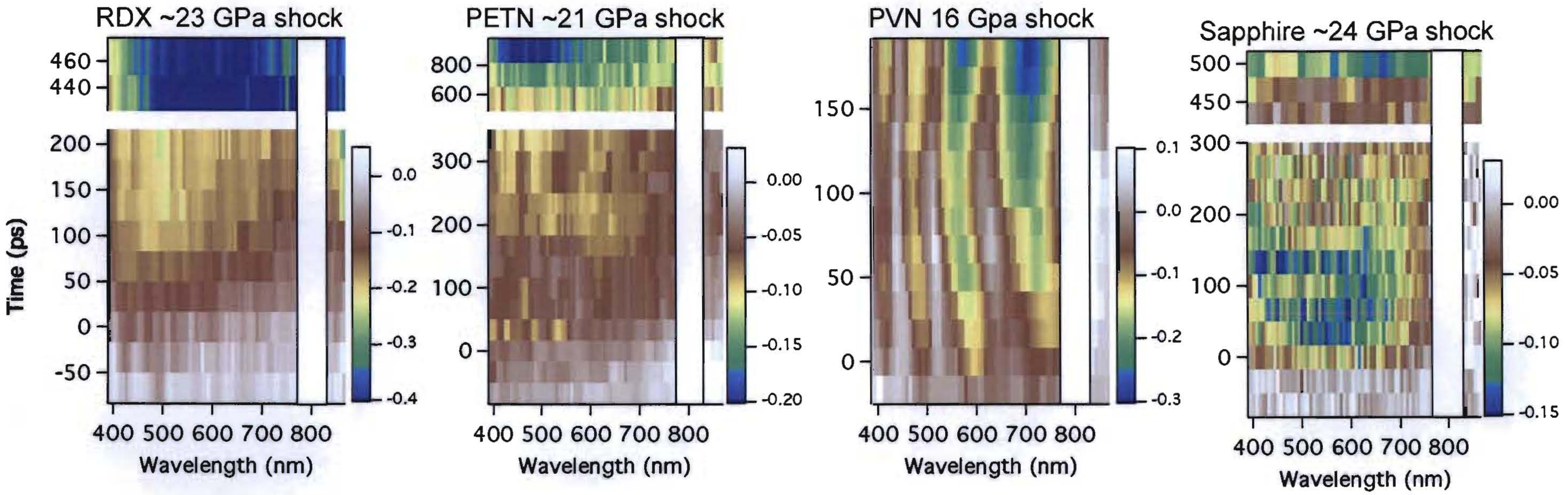
IR directly monitors breaking and making of bonds

Reaction required 10s of ps

However, spectral range was limited and species were not definitively identified

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

Transient absorption comparisons


RDX ~23 GPa shock

PETN ~21 GPa shock

PVN 16 Gpa shock

Sapphire ~24 GPa shock

Observations

RDX/PETN - absorptions grow with time (chemical reactions? band gap shifts?)

PVN – at <100 ps, shift due to thin film interference

at >100 ps, expansion and absorption likely originating in chemical reaction after an induction period (as seen in infrared absorption)

Vibrational spectroscopy needed to confirm that absorption are due to chemical products

Data 3x3 median filtered

CARS=Coherent anti-Stokes Raman scattering

RIKES=Raman-induced Kerr Effect Spectroscopy

SRS=Stimulated Raman scattering

For T measurement, SRS is a special type of coherent Raman

- Bose-Einstein phonon number

$$n(\omega) = 1/(\exp(\hbar\omega/kT) - 1)$$

- Spontaneous Raman

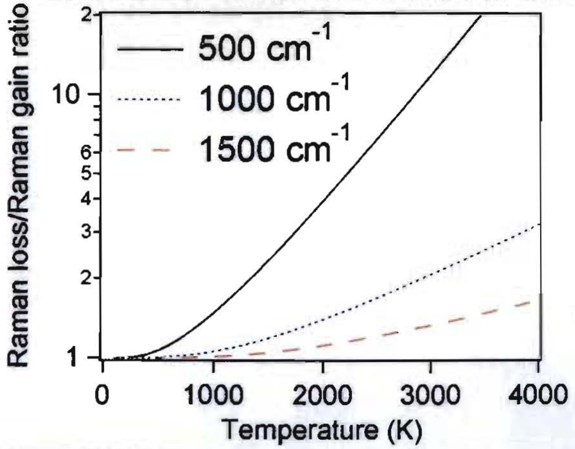
$$I_S^{spon} \propto n(\omega) + 1$$

$$I_{aS}^{spon} \propto n(\omega)$$

$$I_{AS}^{spon} / I_S^{spon} \propto \exp(-\hbar\omega/kT)$$

- *Ratio is a function of T*

- Stimulated Raman anti-Stokes to Stokes ratio



- Third order coherent Raman

$$\mathrm{Im}(\chi_S^{(3)}) \propto -1/(n(\omega)+1) = \exp(-\hbar\omega/kT) - 1$$

$$\chi_{AS}^{(3)}(\omega_{AS}) = \chi_S^{(3)}(\omega_S)^{\dagger}$$

$$\mathrm{Im}(\chi_{AS}^{(3)}) = -\mathrm{Im}(\chi_S^{(3)}(\omega_S))$$

$$I_{CARS} \propto (-\mathrm{Im}(\chi_S^{(3)}))^2$$

$$I_{CSRS} \propto (\mathrm{Im}(\chi_S^{(3)}))^2$$

$$I_{CARS} / I_{CSRS} = 1$$

$$I_{OHD-RIKES}^{AS} \propto -\mathrm{Im}(\chi_S^{(3)})$$

$$I_{OHD-RIKES}^{S} \propto \mathrm{Im}(\chi_S^{(3)})$$

$$I_{OHD-RIKES}^{AS} / I_{OHD-RIKES}^{S} = -1$$

- *CARS or RIKES Ratio is NOT a function of T*

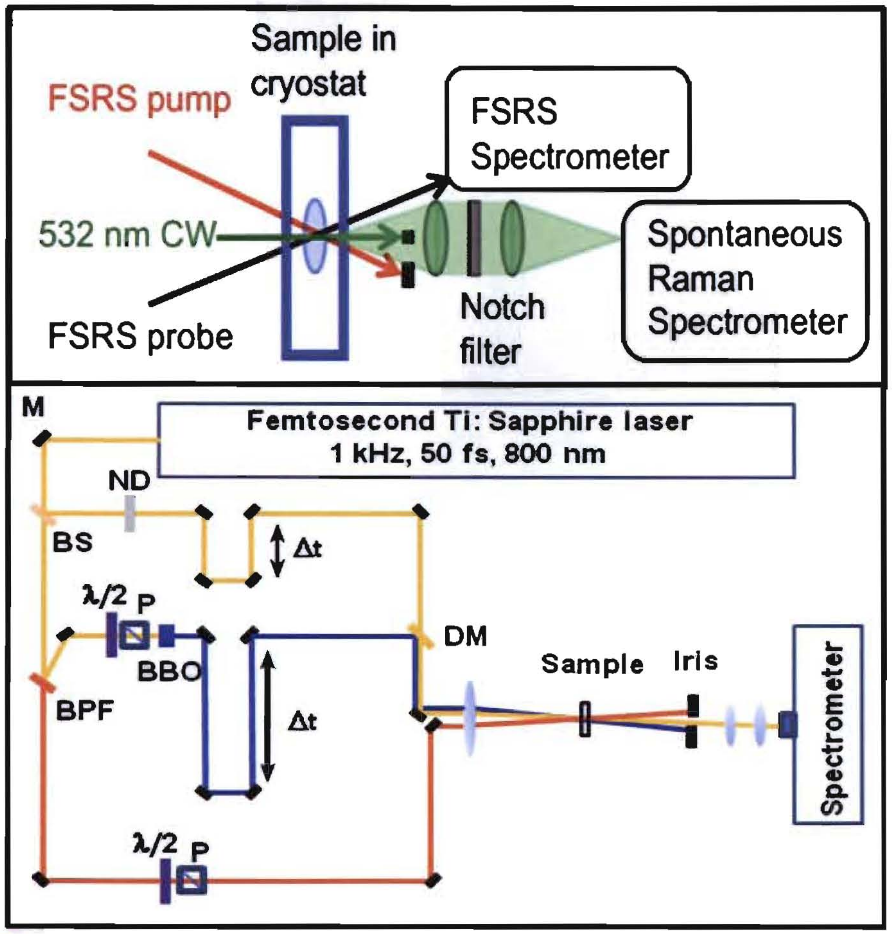
$$I_{SRS}^{S} \propto I_{probe} \exp(-\mathrm{Im}(\chi_S^{(3)}) I_{pump} C_S)$$

$$I_{SRS}^{AS} \propto I_{probe} \exp(\mathrm{Im}(\chi_S^{(3)}) I_{pump} C_{AS})$$

$$I_{SRS}^{AS} / I_{SRS}^{S} = \exp(\mathrm{Im}(\chi_S^{(3)}) I_{pump} C_{AS}) / \exp(-\mathrm{Im}(\chi_S^{(3)}) I_{pump} C_S)$$

- *FSRS ratio is a function of T because susceptibility is in the exponent*

Spontaneous and Stimulated Raman Temperature Measurements



Femtosecond stimulated Raman scattering (FSRS)

The intensity of the Raman gain ($\omega_{pump} > \omega_{probe}$) or loss ($\omega_{pump} < \omega_{probe}$) is:

$$I(\omega_{probe}, L) = I(\omega_{probe} 0) \exp - \left\{ \frac{3\omega_{probe} L}{n_{pump} n_{probe}} \left(\frac{\mu_0}{\varepsilon_0} \right) \mathrm{Im}\left(\chi_{11ii} \right) I(\omega_{pump}) \right\}$$

$$\mathrm{Im}\left\{ \chi_{11ii(-\omega_{probe}, \omega_{probe}, -\omega_{pump}, \omega_{pump})} \right\} =$$

Where: $$\frac{\pi c^4}{24\hbar \omega_{pump} \omega^3_{probe}} \left(e^{\frac{\hbar}{kT}(\omega_{pump} - \omega_{probe})} - 1 \right) \frac{\delta^2 \sigma_{xi}}{\delta\Omega \delta\Delta\omega}$$

which has a T dependence

FSRS is several orders of magnitude higher efficiency that spontaneous Raman and can have sub-ps time resolution

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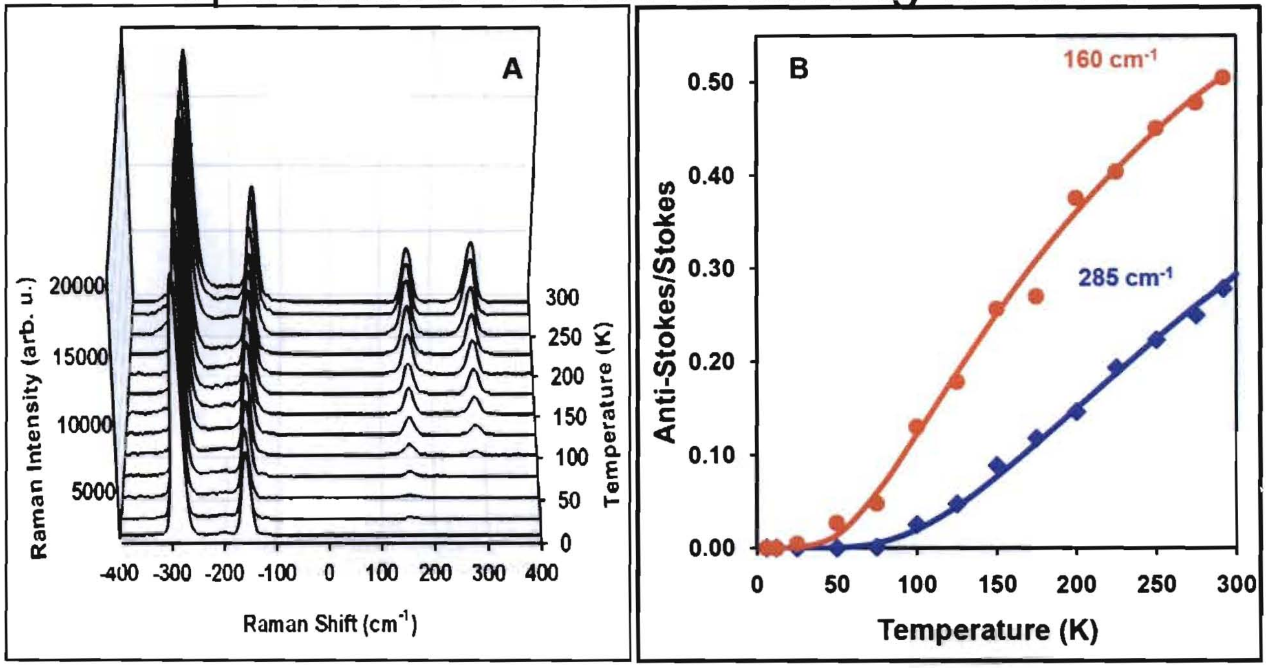
An anti-Stokes/Stokes ratio avoids the need for high spectral resolution

Spontaneous Raman scattering of calcite

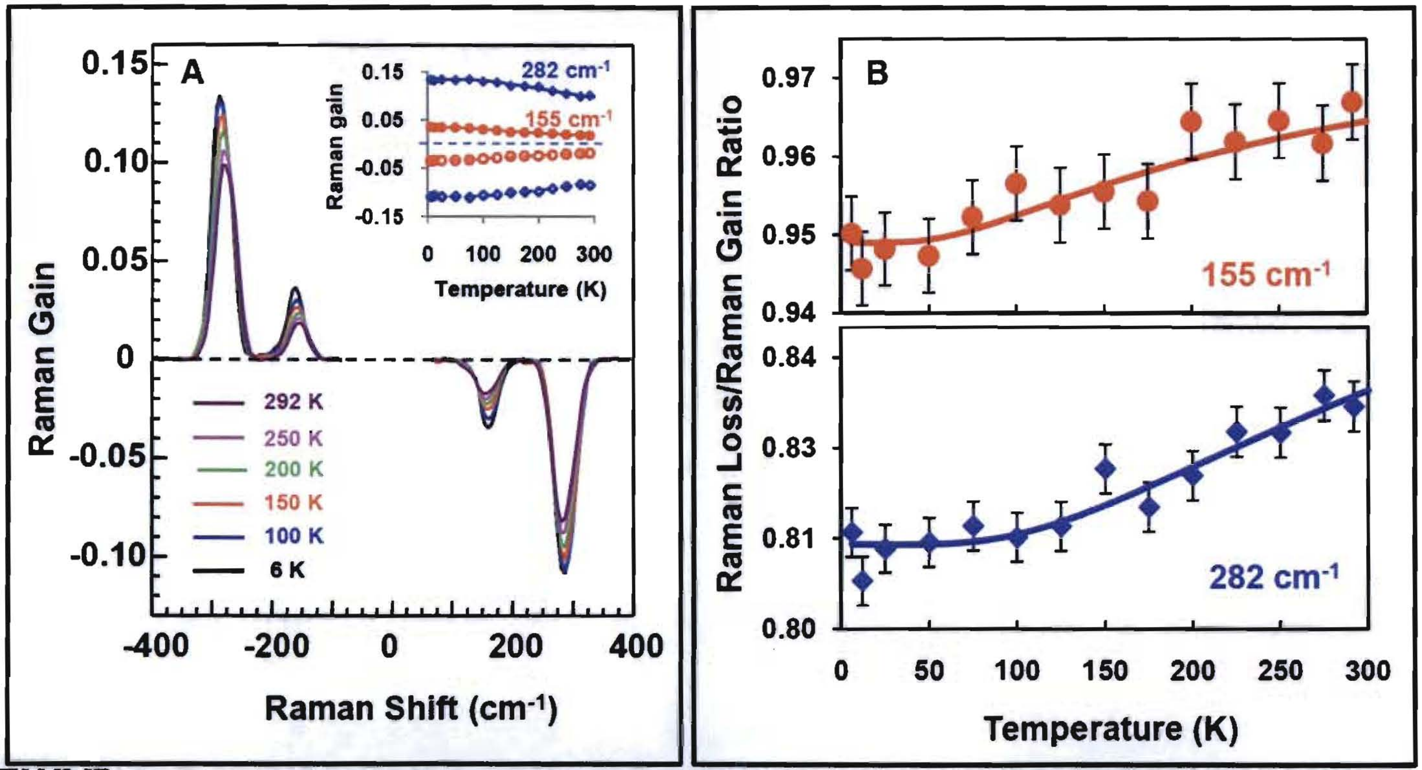


Spontaneous Raman Stokes/anti-Stokes ratios have been used often, can be time resolved with pulsed lasers, but suffer from the low efficiency of spontaneous Raman, ~ 10^{-8}.

$$\boxed{\frac{I_{AS}}{I_s} = \frac{\nu_{AS}^4}{\nu_S^4} \exp\left[\frac{-hc(\nu_0 - \nu_s)}{kT}\right]}$$

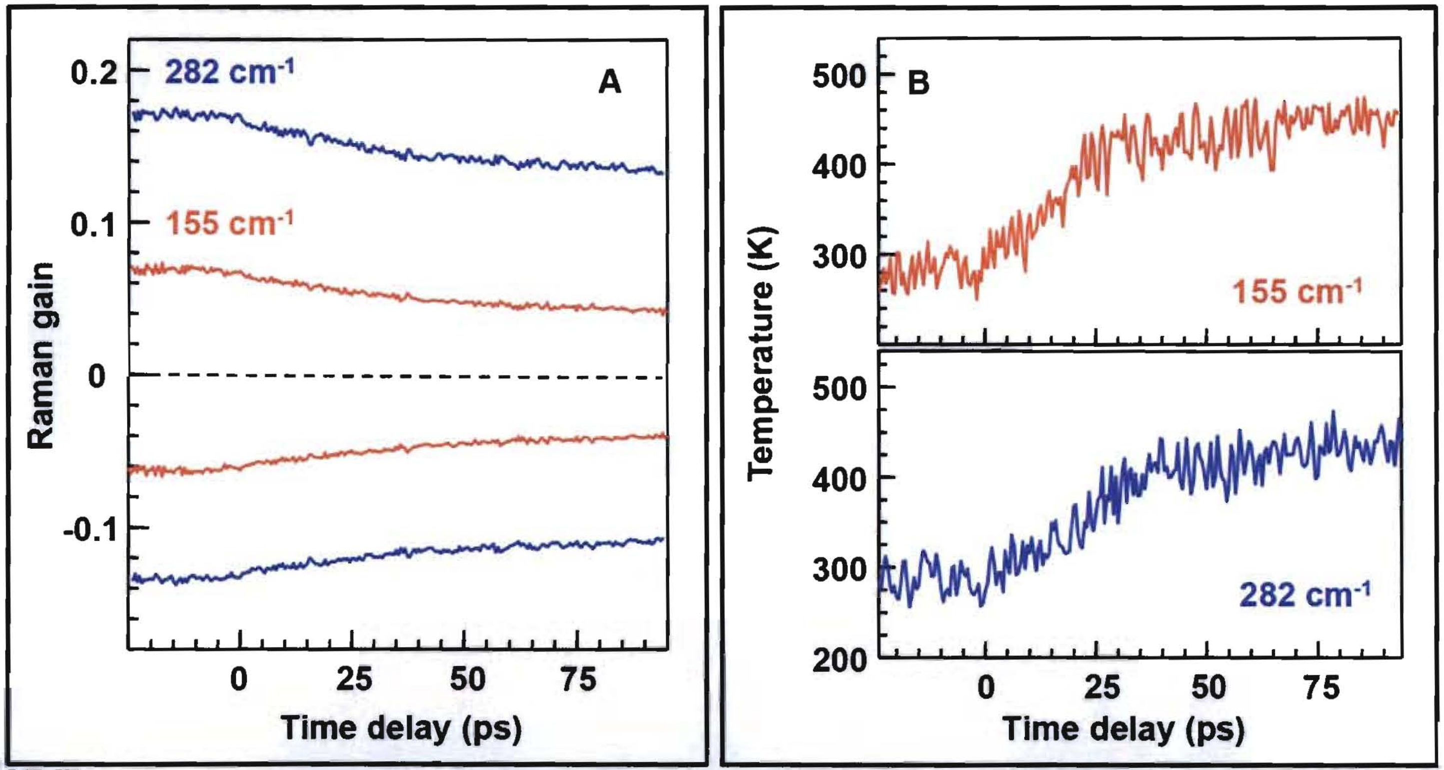
FSRS(T) experiments validate theoretical predictions

- **Experiment matches theory**
  - Low signal to noise in ratio due to small total change with temperature and long acquisition time making data sensitive to laser instability



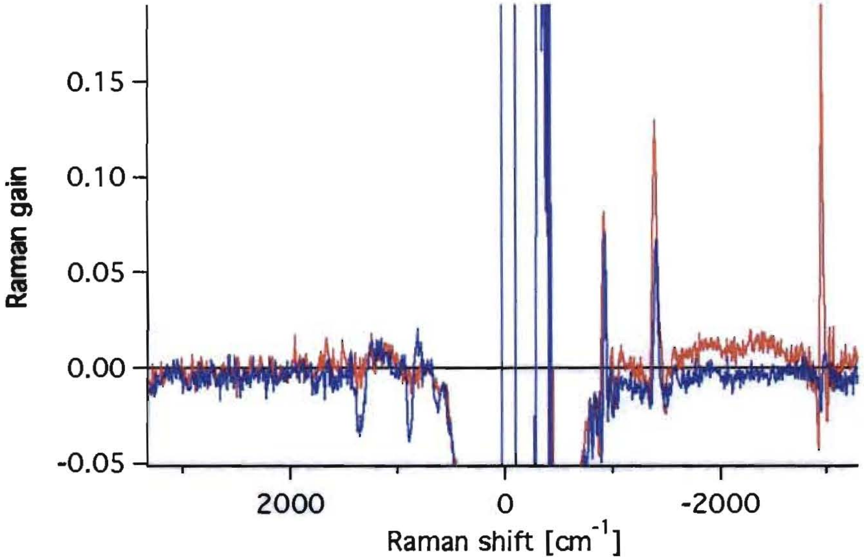
Transient FSRS(T) measurements are easier and more accurate

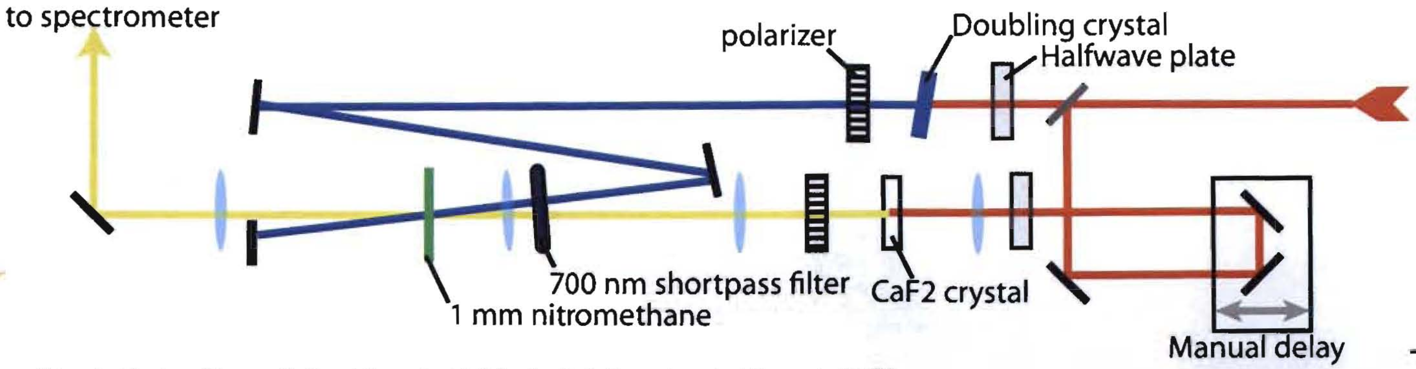
- **Shorter acquisition time leads to better signal to noise**
- **Slow (30 ps) heating due to vibrational relaxation following 200 fs electronic pump pulse of 2x400 nm photons**



For shock studies, FSRS over a broad frequency range can measure chemistry and temperature

- **We have recorded single shot FSRS on static samples**
  - 400 nm pump
  - Supercontinuum probe
  - 1 mm nitromethane

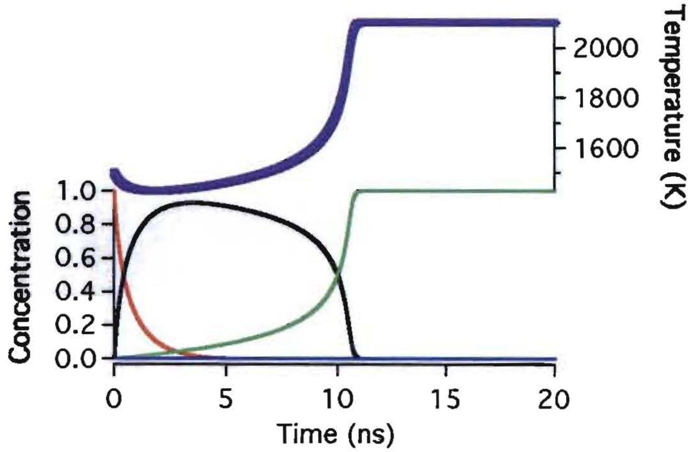




Why do we see chemistry on ps time scales where other experiments see effects on ns to μs time scales?

$A + \text{heat} \rightarrow B$

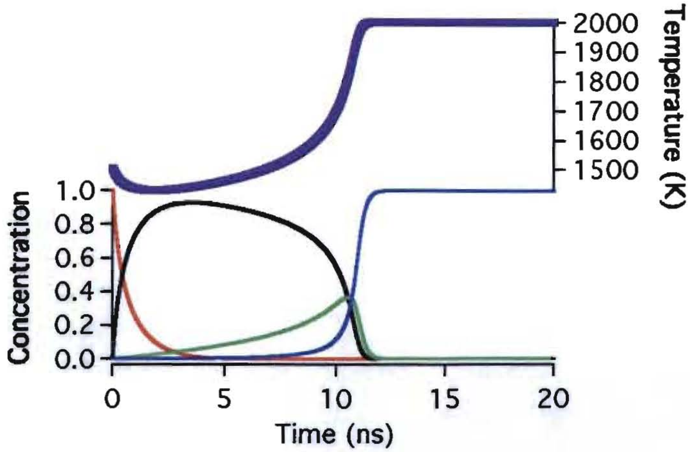
$B \rightarrow C + \text{heat}$



$A + \text{heat} \rightarrow B$

$B \rightarrow C + \text{heat}$

$C + \text{heat} \rightarrow D$



We are probably looking at earlier reactions

Light emission, temperature or pressure driven effects may not come from first reaction

Later reactions (even second) can be orders of magnitude later in time!

spectroscopy is not measuring mechanical variables!

Summary of work

- **Ultrafast dynamic ellipsometry (UDE) probes shock-induced material motion and changes in refractive index**
- **UDE has shown us the we are achieving the same shock states as experiments on longer timescales**
- **"Induction time" for chemical reaction in PVN is the same using IR absorption and transient absorption**
- **ps thermometry is possible with stimulate Raman scattering**

Next step: Investigate chemical reaction and temperature with single shot FSRS

Acknowledgements

- DTRA Basic Research funding
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- Leveraged against past and current projects funded by LANL Science Campaign 2
- Dr. Dan Hooks, Dr. Kyle Ramos and Tate Hamilton for HE crystal preparation