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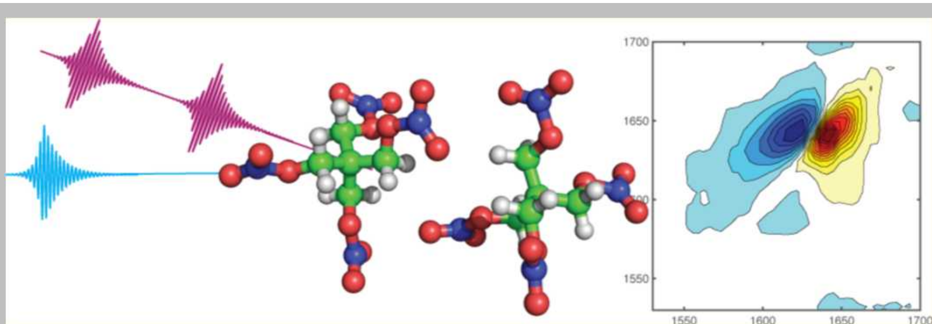

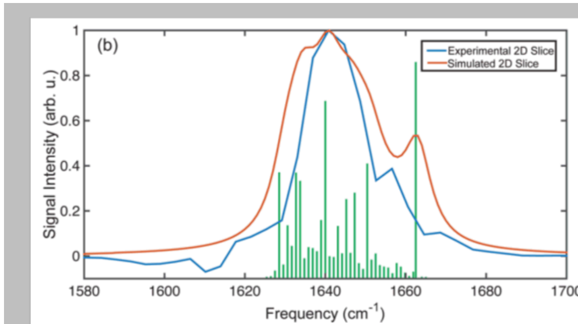

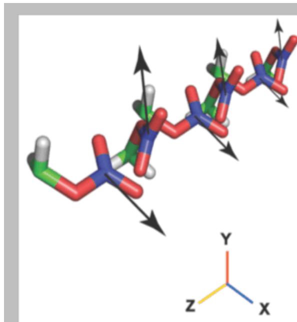

Energy Transfer Between Coherently Delocalized States in Thin Film PETN Revealed by 2D IR Spectroscopy.

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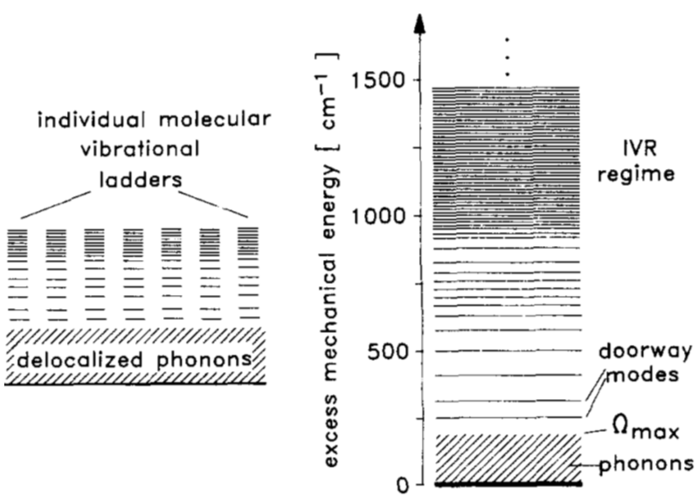
Outline

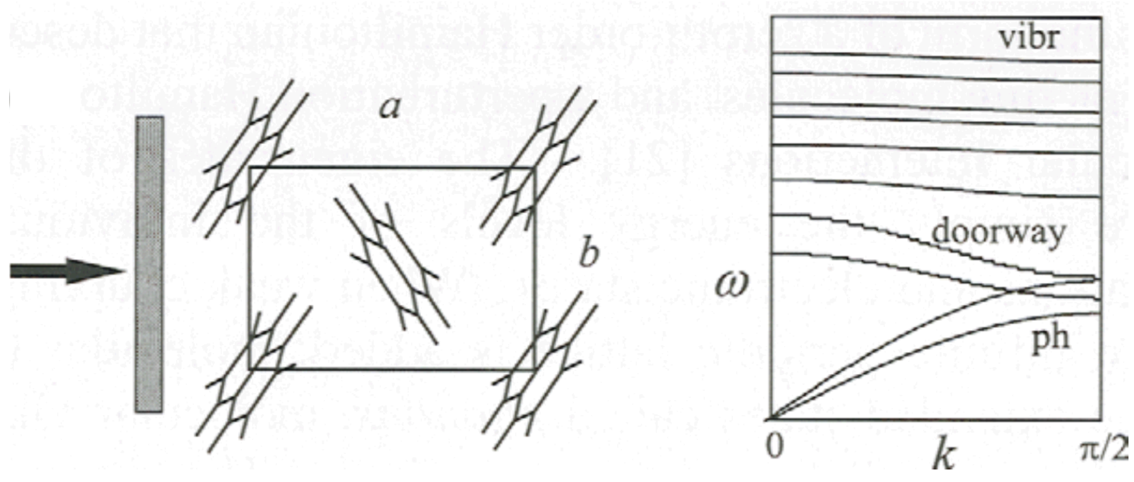
- Traditional picture of high-frequency vibrations in energetic solids.
- Correlation between intermolecular bonding and sensitivity of PETN analogs.
- Conceptual Introduction to Two Dimentional Infrared Spectroscopy: Direct measure of weak vibrational coupling.
- 2D IR spectra of thin film and acetone solutions of PETN under ambient conditions.
- Spatially delocalized NO_2 stretch and rapid intermolecular energy transfer via weak intermolecular interactions.

Vibrational Energy Transfer leading up to Reaction / Intermolecular bonds

- Multiphonon up-pumping (Dlott/Fayer)
  - *Low frequency vibrations (ring motions, bends) are strongly coupled to high frequency phonons.*
  - *Energy transferred up through phonons and doorway modes to spatially-localized, high-frequency vibrations (NO_2 stretch) weakly coupled to low frequency motions.*



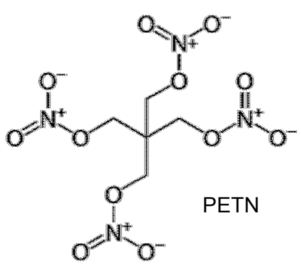
Dlott and Fayer, *JCP* 1990



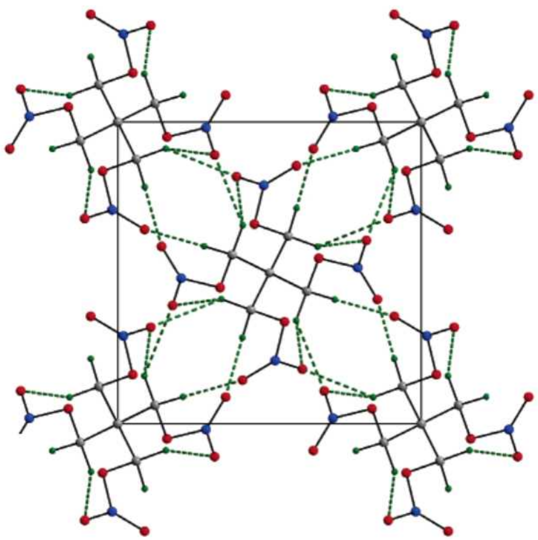
J. M. Winey and Y. M. Gupta, J. Appl. Phys. 90 (2001) 1669.

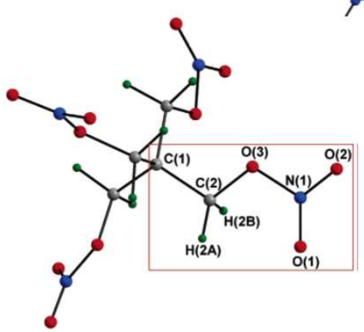
Vibrational Energy Transfer leading up to Reaction / Intermolecular bonds

- Sensitivity differences between Pentaerythritol tetranitrate (PETN) vs. analogs (e.g. Erythritol tetranitrate (ETN). *Stabilizing vs. destabilizing intermolecular interactions.*

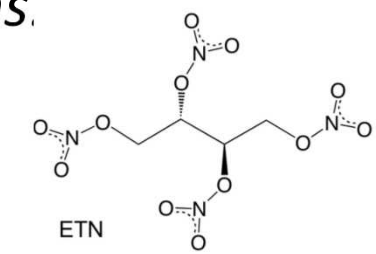


PETN

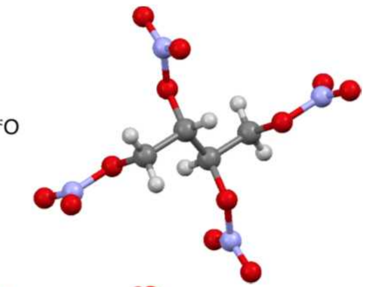


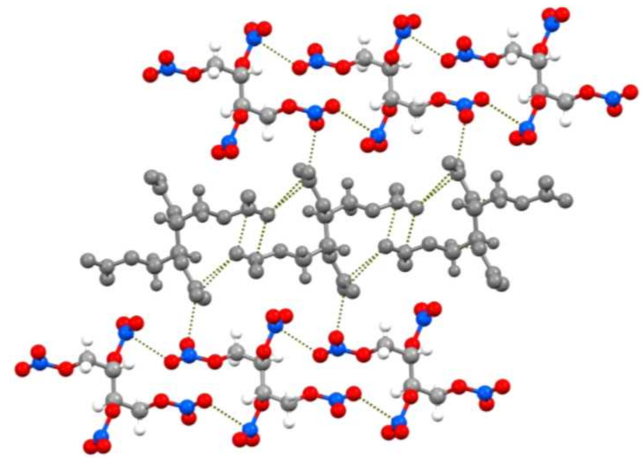


Zhurova et al, *JACS* 2006



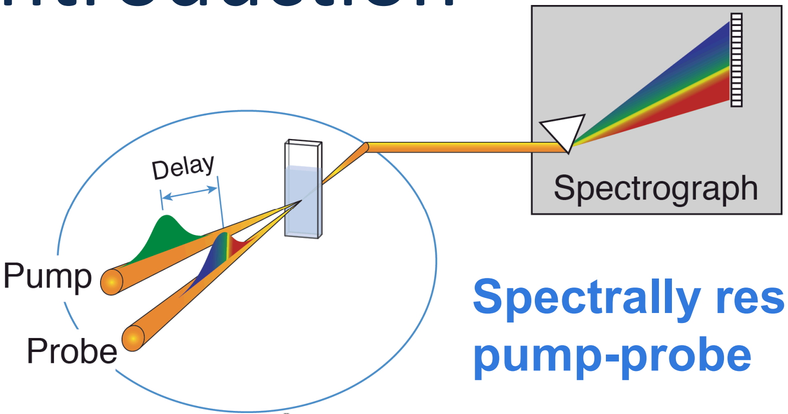
ETN



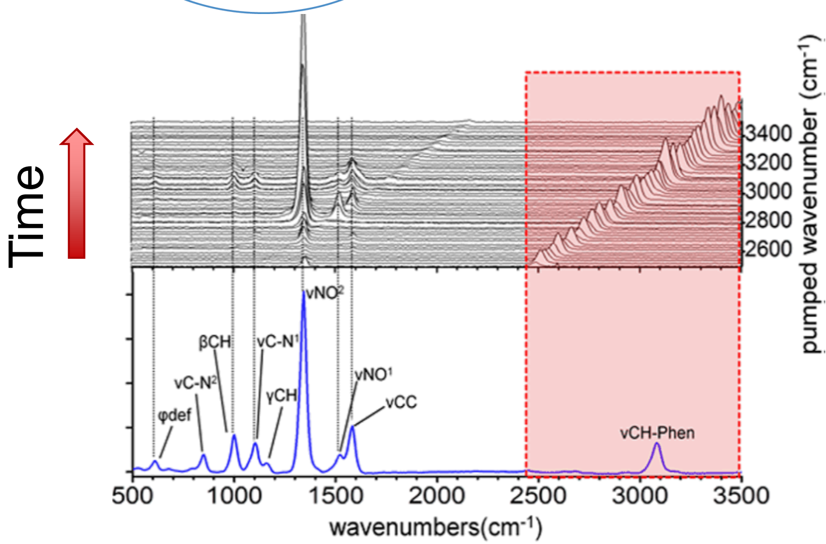


Manner et al, *Crystal Growth and Design* 2014

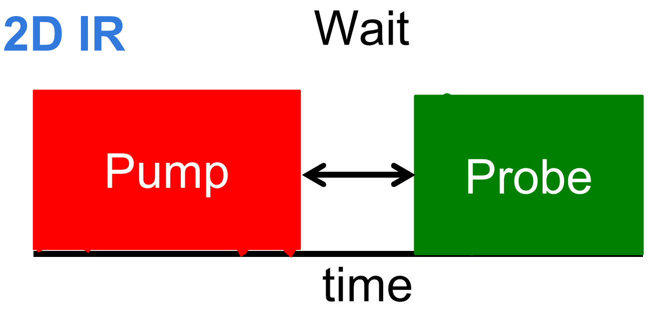
2D IR Spectroscopy: Conceptual Introduction

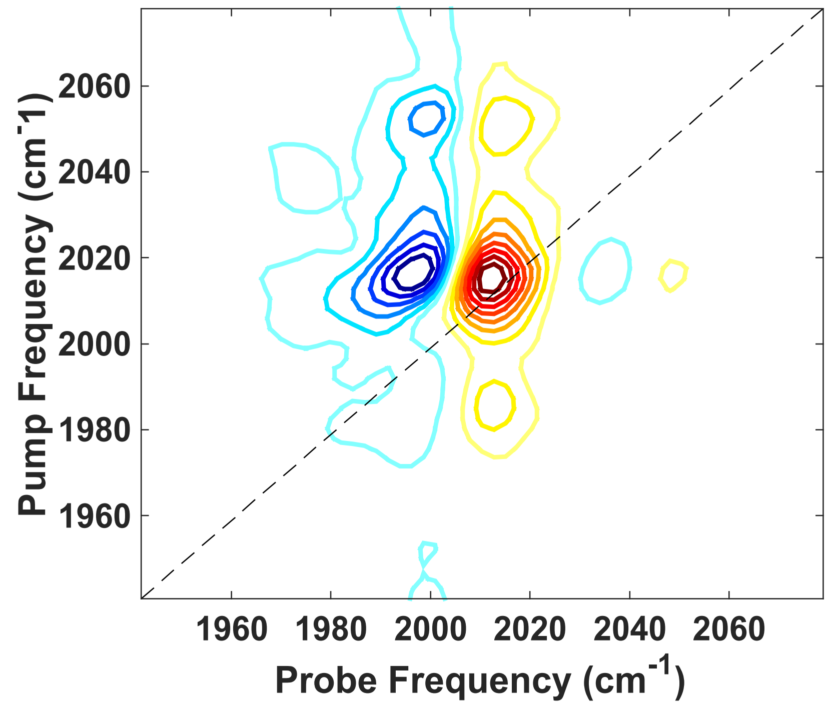


Spectrally resolved pump-probe



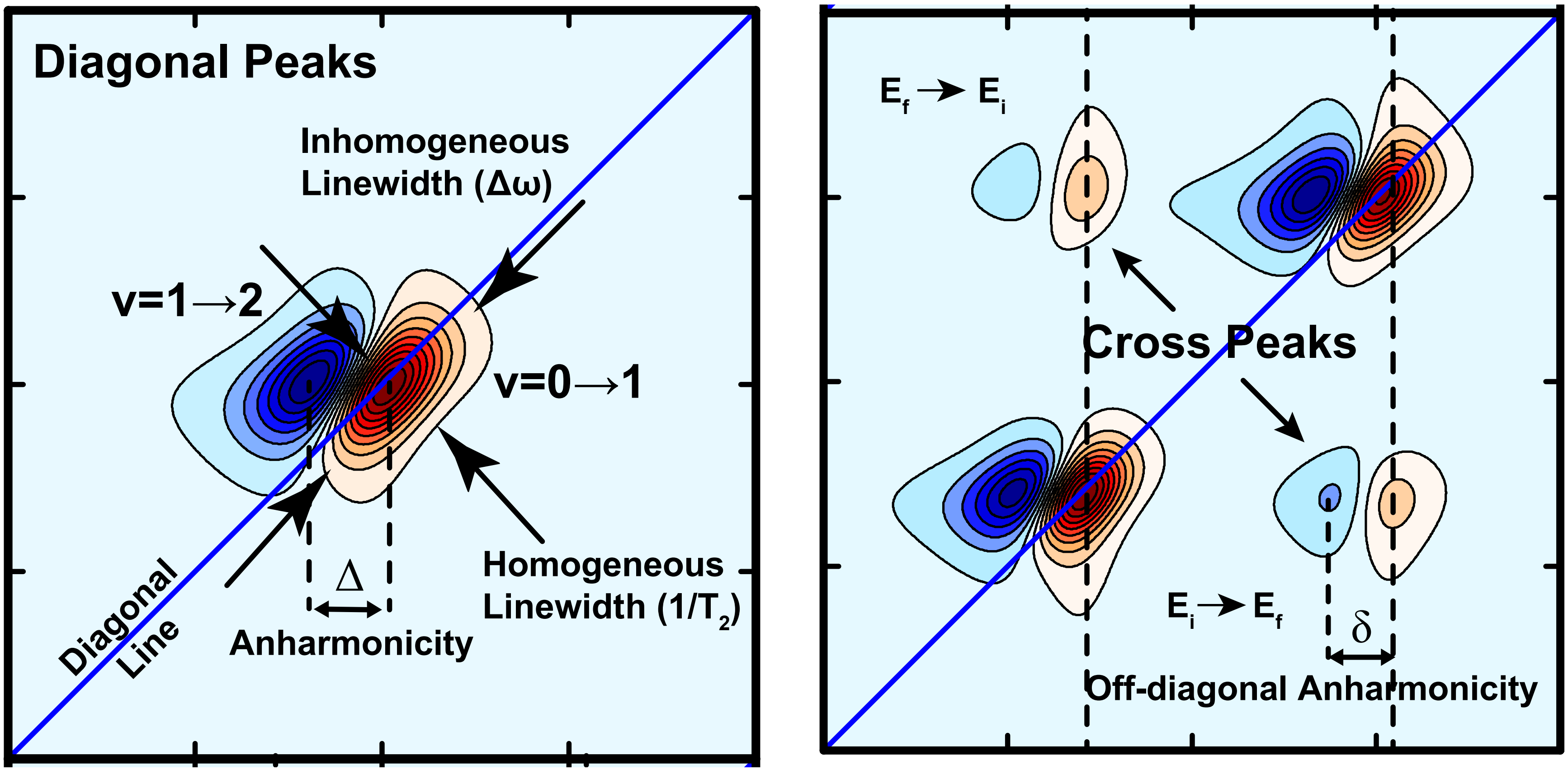
2D IR





2D IR directly measures the relationship between response to pump (e.g. absorption) and changes in the probe spectrum.

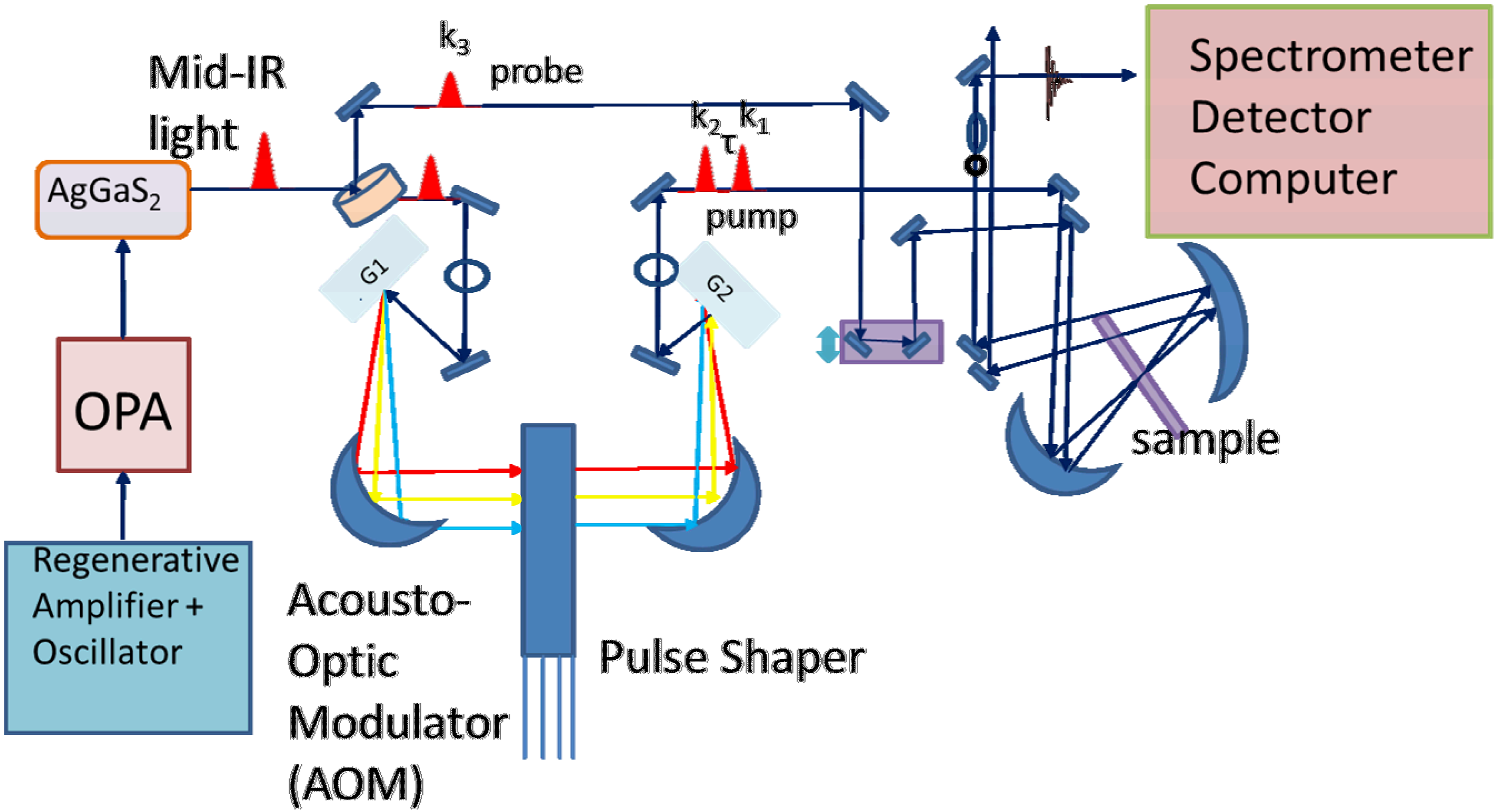
Interpreting a 2D IR Spectrum



Ghosh, A.; Ostrander, J.S.; Zanni, M.T. *Chem. Rev.* 2017

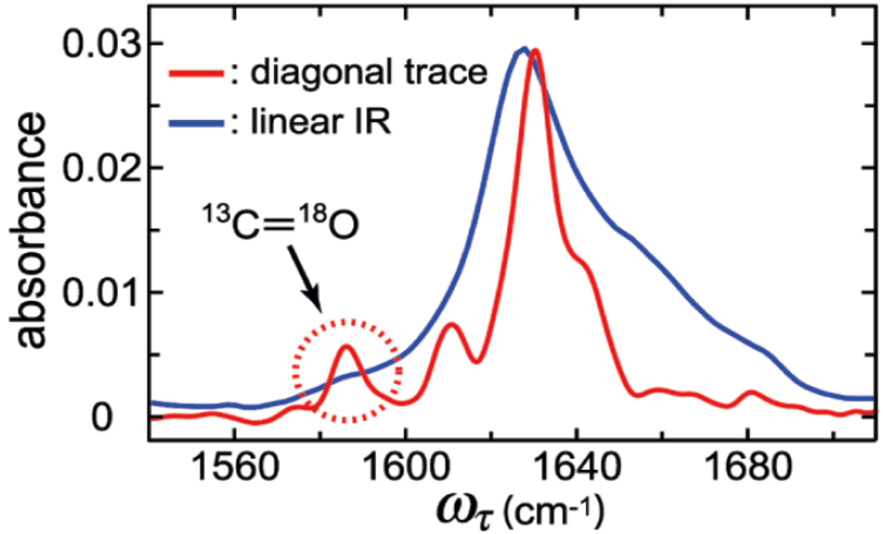
Homogenous/Inhomogeneous line width, anharmonicity and vibrational coupling directly measured in 2D spectra.

Rapid-scan 2D IR Spectroscopy



Scanning the t_1- t_2 delay using a pulse shaper: (1) Improves phase stability, (2) Reduces scanning time by a factor of 1000 and (3) Assures proper phase matching.

2D IR is more sensitive to coupling

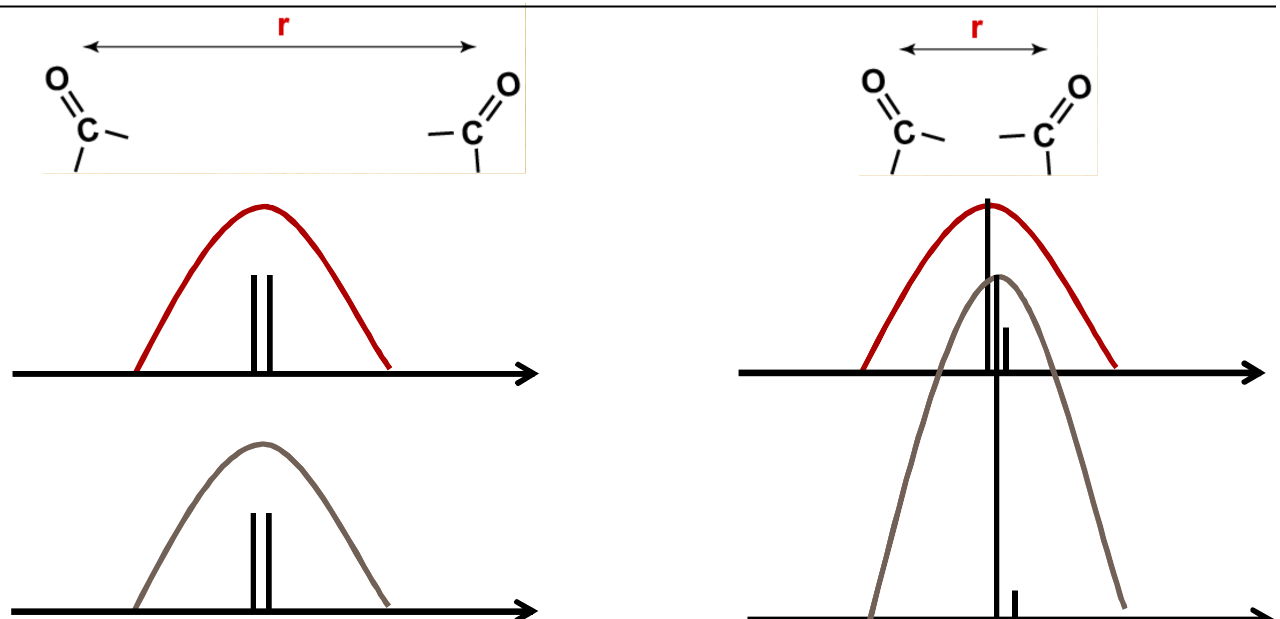


Linear IR ~ $|\mu|^2$

2D IR ~ $|\mu|^4$

FTIR $c|\mu|^2\ell$

2D IR $c|\mu|^4\ell$



Transition dipole strengths reveal coupling **(Grechko et al. *JCP*, 2012)**

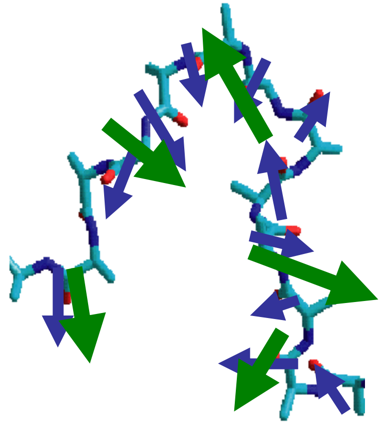
Spectroscopy/structure: amide I mode of peptides

Normal Modes

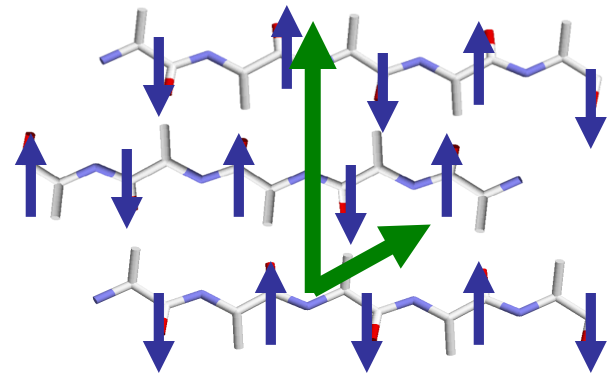
Local Modes

$$H = \begin{pmatrix} E_1 & \beta_1 & \beta_2 & \cdots \\ \beta_1 & E_2 & \beta_3 & \\ \beta_2 & \beta_3 & E_3 & \\ \vdots & & & \ddots \end{pmatrix}$$

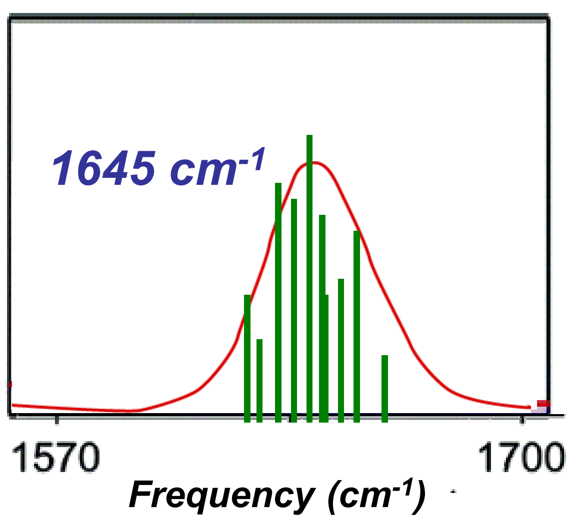
random coil

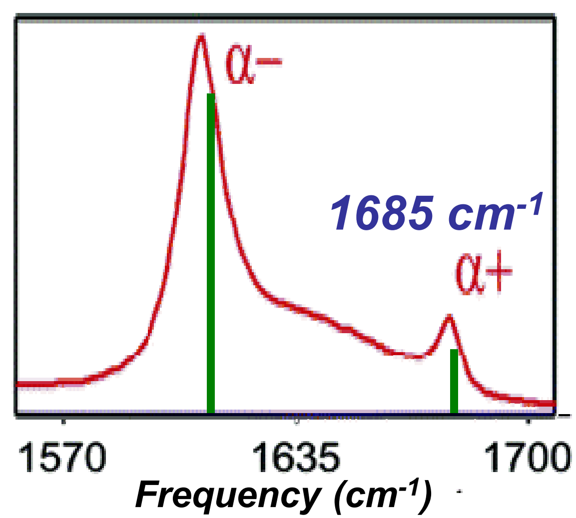


beta-sheet



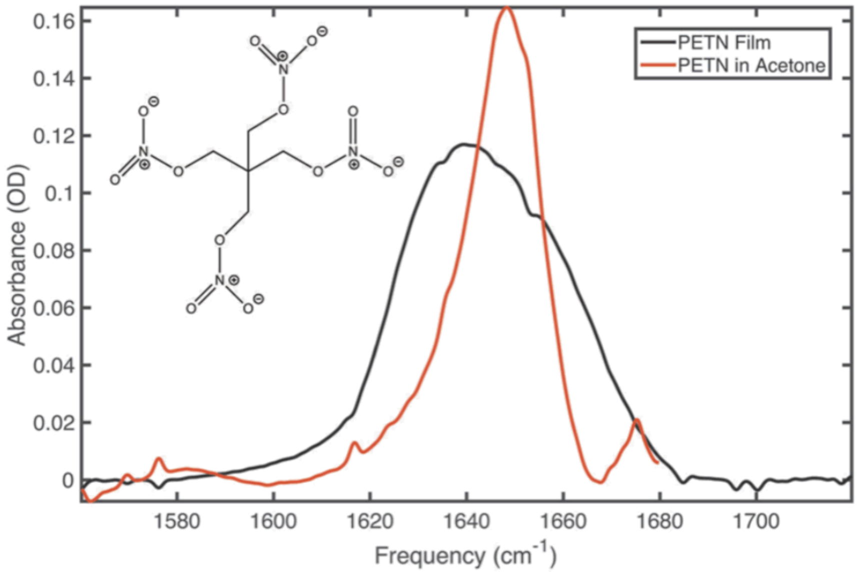
1636 cm^{-1}
(1620 for amyloid)

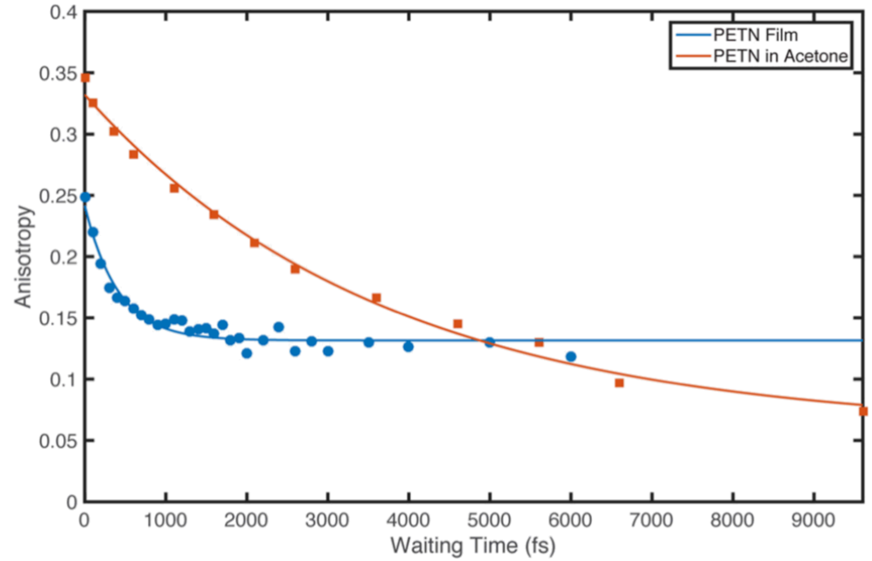




All physics that can be very accurately modeled.

Comparison between solid and solvated PETN (IR and pump-probe)

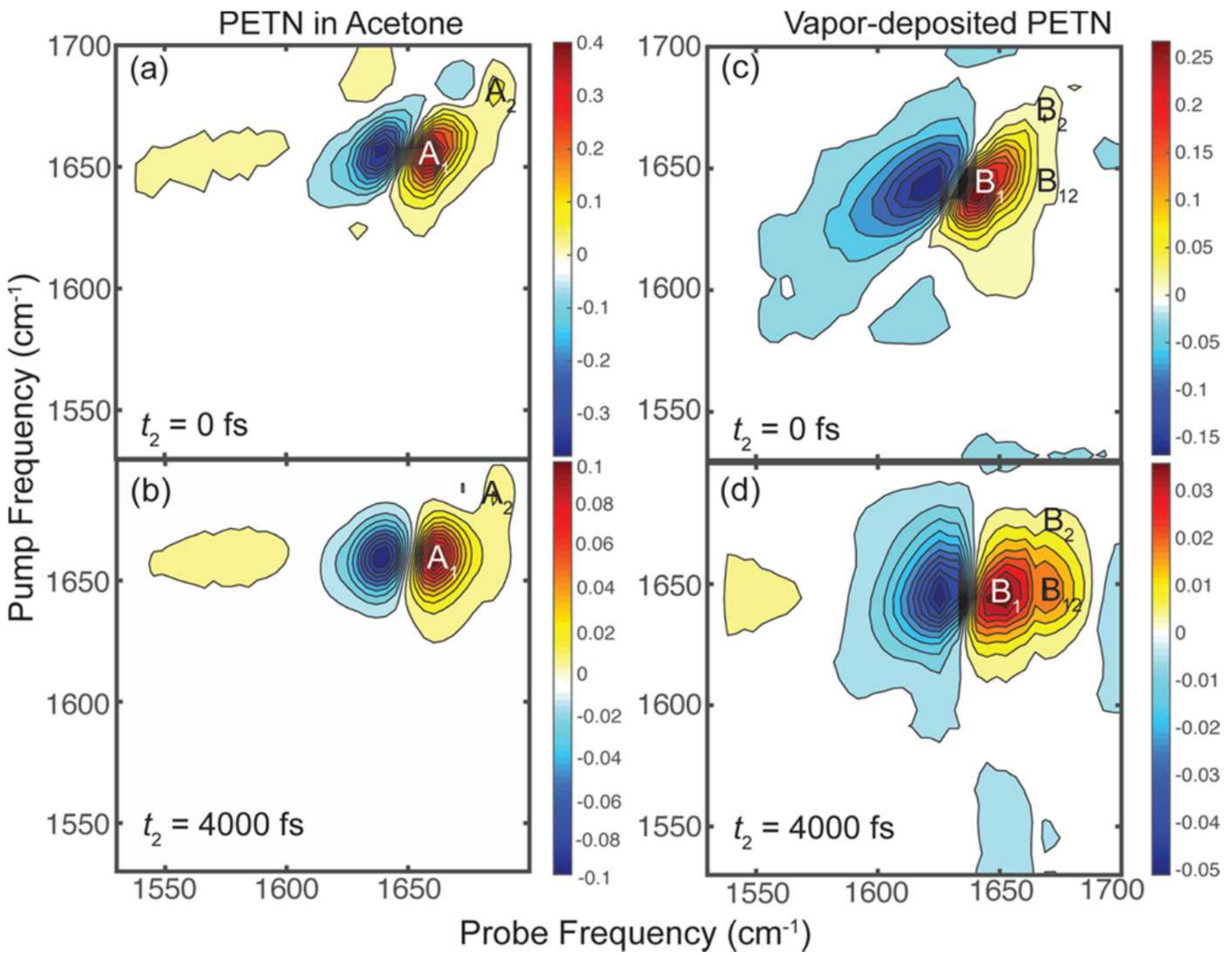




- FTIR spectra of thin film PETN spectrally broadened compared to PETN solution in acetone.
- Sub picosecond decay in dipole orientation only seen in thin film.

Evidence of vibrational coupling/energy transfer.

2D IR spectra of PETN



Cross peak observed in vapor-deposited PETN not present in solvated PETN data. **Additional evidence of coupling and shift vibrational energy.**

Transition Dipole Coupling Model (TDC) used to interpret FTIR and 2D IR features.

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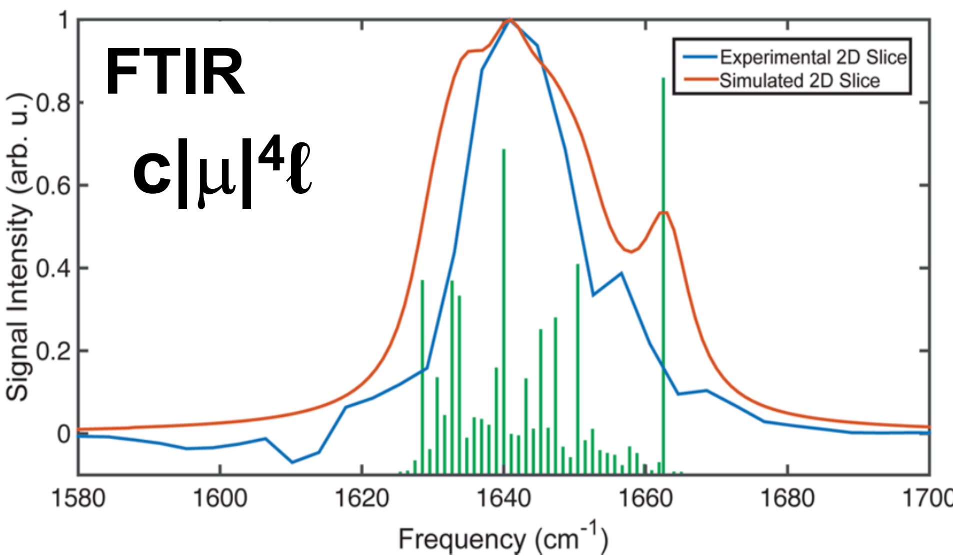
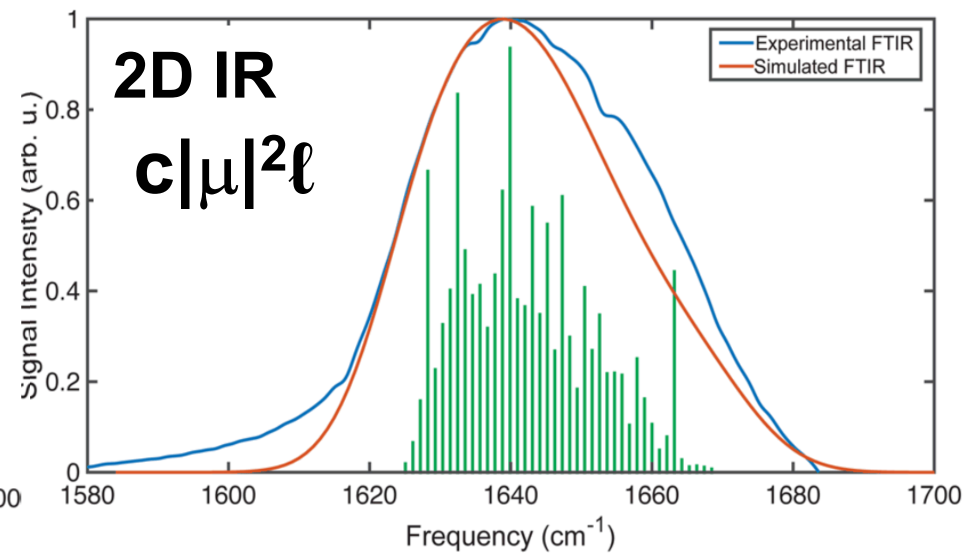
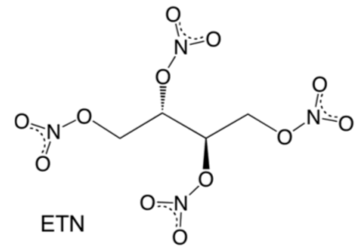


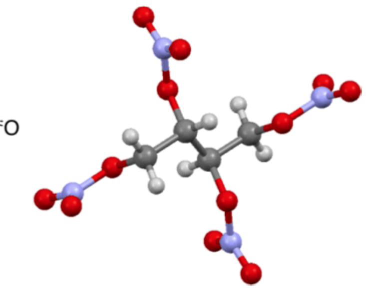


- DFT model of PETN dimer predicts intermolecular coupling between nitrate esters ($-4.60\ cm^{-1}$) larger than intra molecular couplings (~2 cm-1) .
- Transition Dipole Coupling Model (128 molecules) reproduces features in FTIR and 2D IR spectra.
- Transition Dipole strength *measured* from FTIR/2D-IR spectra show asymmetric NO_2 mode *delocalized over 15-30 nitrate esters*.

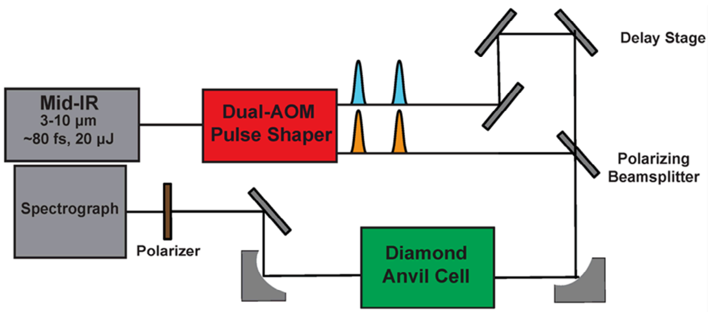
Future Directions:

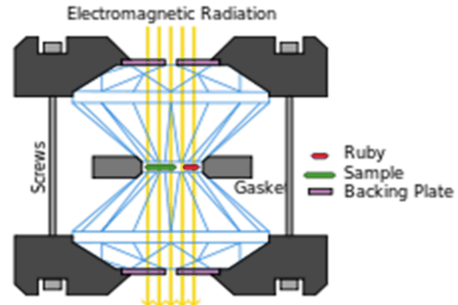
- Repeat for PETN analogs (e.g. ETN)



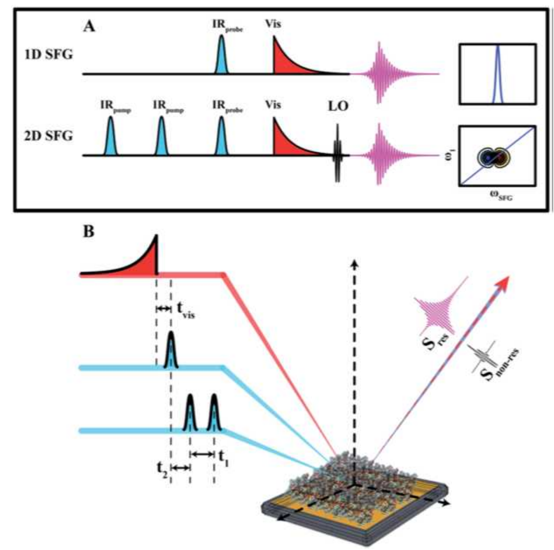


- Look for changes in delocalization under static compression (hydrostatic and non-hydrostatic).





- Use 2D-SFG to measure changes in changes in delocalization near PETN surface. *Compare to delocalization within crystal.*



Conclusions

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- We report the first 2D IR spectrum of explosive molecules in the solid-state.
- 2D IR spectra reveal one important pathway through cross peak growth in crystalline PETN not present in solvated PETN.
- PETN FTIR and 2D IR spectra are consistent with delocalized vibrations arising from intermolecular coupling.
- Delocalized high-frequency vibrations may have important implications for shock sensitivity of energetics.

Thanks to:

Josh Ostrander

Martin Zanni

Alex Tappan

Rob Knepper

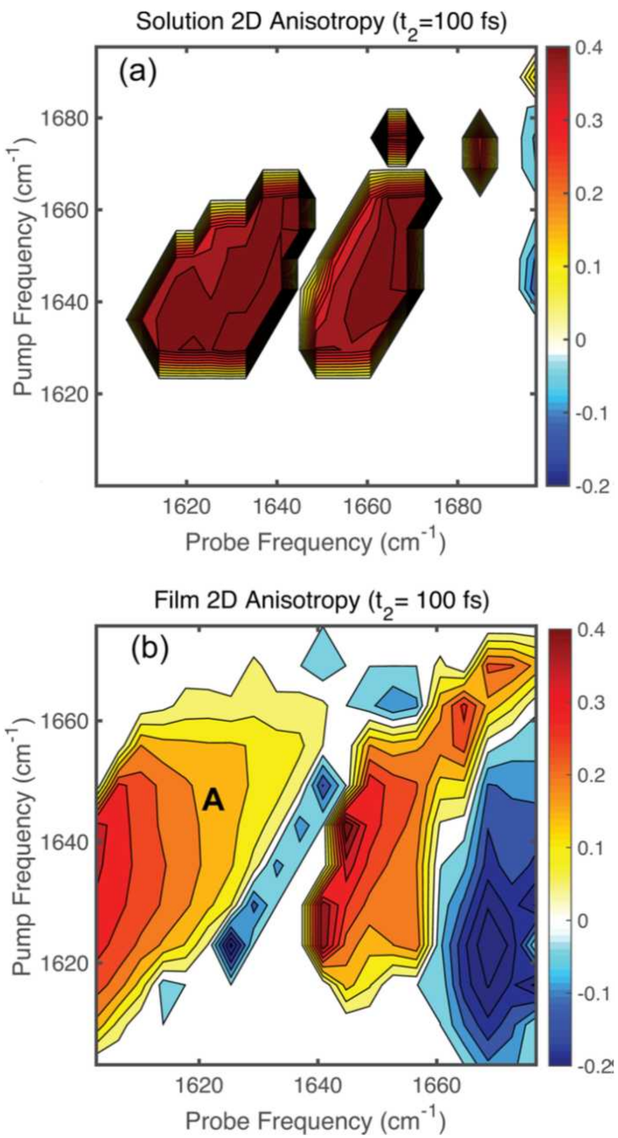
Michael Marquez

Jeff Kay

SNL LDRD (Material Science Investment Area).

… and you for your time.

Dipole randomization with frequency

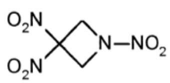


- Average orientation of excited vibrations randomize over time by rotation or vibrational energy transfer.
- Anisotropy of PETN varies from 0.4 (initial orientation maintained) to 0 (vibration delocalized in 3D). *–does not address negative features in 2D.*
- Homogeneous kinetics within the vibrational band in solutions of PETN.
- Frequency dependent relaxation kinetics to low frequency intramolecular and phonon modes in thin-films of PETN.

Previous pump-probe data on solvated explosive.

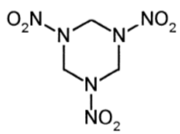
- Fast vibrational relaxation observed of the asymmetric NO_2 stretch in acetone or ethanol solutions for multiple explosives (2-6 ps).

TNAZ



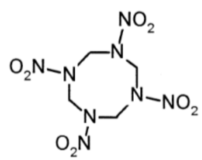
1585 cm^{-1}
6.31 μm

RDX



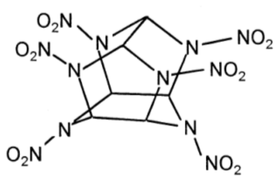
1582 cm^{-1}
6.32 μm

HMX



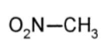
1570 cm^{-1}
6.37 μm

CL-20



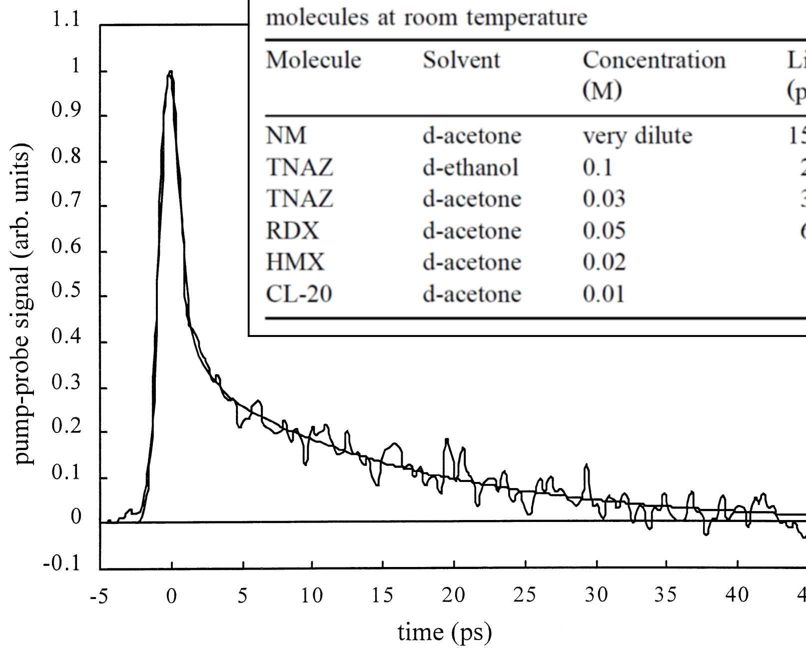
1597 cm^{-1}
6.26 μm

NM



1563 cm^{-1}
6.40 μm

Aubuchon et al, *Chem.Phys.Lett.* 1999



Nitro group asymmetric stretching mode lifetimes for several molecules at room temperature

Molecule	Solvent	Concentration (M)	Lifetime (ps)
NM	d-acetone	very dilute	15.9 ± 0.5
TNAZ	d-ethanol	0.1	2.4 ± 0.4
TNAZ	d-acetone	0.03	3.0 ± 0.5
RDX	d-acetone	0.05	6.2 ± 0.4
HMX	d-acetone	0.02	4 ± 1
CL-20	d-acetone	0.01	2 ± 1