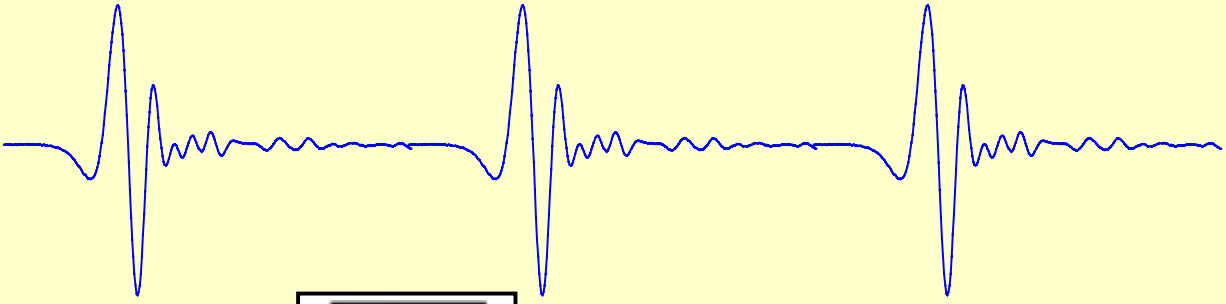
Learning New Chemistry and Physics with THz Light



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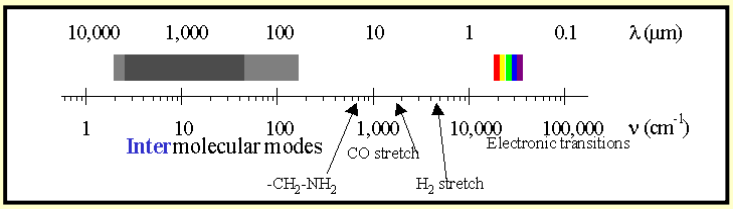
September 20, 2004

Overview



Characteristics of THz Pulse Spectroscopy

- measures electric field, E(t), directly $\Rightarrow \hat{n}(\omega) = n(\omega) - ik(\omega)$
- minimum detectable fractional absorption better than 1 in 10^4
- **transient FIR absorption with sub-picosecond temporal resolution !**

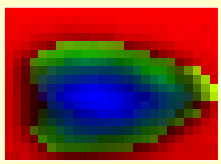
1 THz = 33.333 cm^{-1} = 4 meV = 300 micron λ

Transient Photoconductivity
- semiconductors (ultrafast switches)
- **Semiconductor nanocrystals**
- **nano-electronics, molecular electronics**
- **thermalization and relaxation processes**
- **frequency dependent conductivity**

Intramolecular Electron Transfer
- accelerating charge generates pulse

THz Imaging
- plastic and paper are transparent

Binary Liquid Mixtures
- H_2O & CH_3OH, CH_3CN, CH_3COCH_3
- CH_3OH & CH_3CN, CH_3COCH_3
- OH librational dynamics
- reverse micelles



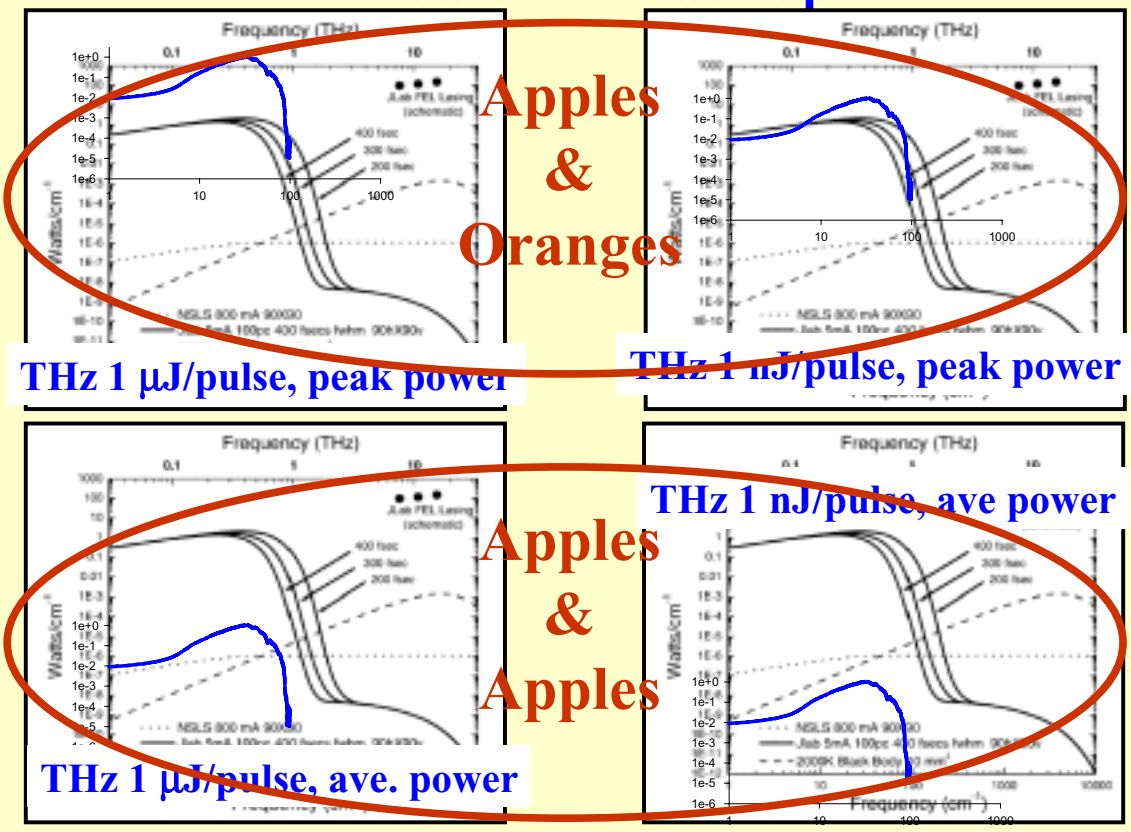
Relation to JLab THz Source …

Much of this could be done with accelerator-based sources

-100 fs pulse duration, or shorter.
- μJ to mJ per pulse, or more.
- kHz rep rates, or higher.
- At least 100 ns, or longer, between pulses for some studies.
- Synchronize intense NIR/visible/UV/x-ray pulses with far-IR.

- Nonlinear spectroscopy (2D THz, photon echoes, etc).
- Rapid, large-area THz imaging.
- (Ultra)high magnetic fields.

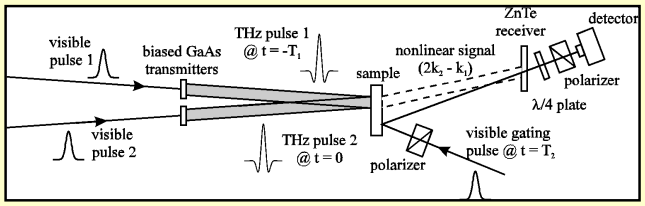
How do we stack up?

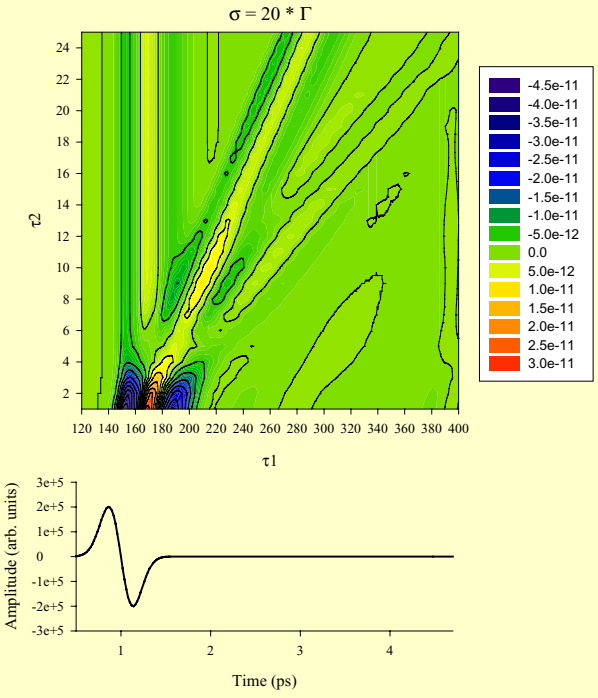


G. L. Carr et al., J. Biol. Phys. **29**, 319 (2003)

Two-Dimensional THz Spectroscopy

- Far infrared analog of two-dimensional NMR spectroscopy
- Spectra will show coupling between modes
  - Diagonal peaks=Same as 1D spectrum
  - Off-diagonal peaks=Shows which modes are coupled to one another
    - Can arise from anharmonicity in the potential or nonlinear dependence of the transition dipole on the mode coordinates
  - Probe the coupling between the 42 cm^{-1} and 49 cm^{-1} libron modes in crystalline L-alanine.
  - Probe the coupling between low-frequency modes in proteins
- 3rd order process
  - Complementary to the 5th order Raman process





2-Dimensional (Nonlinear) THz Spectroscopy

Anharmonicity in intermolecular potential …

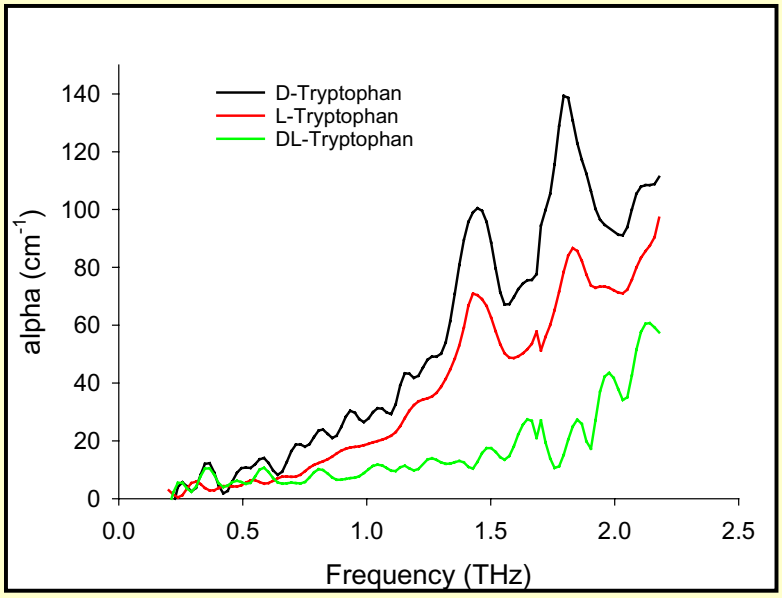
$$V(Q) = \sum_{i=1}^{s} \frac{1}{2} k_i Q_i^2 + \sum_{i,j,k} \frac{g_{i,j,k}}{3!} Q_i Q_j Q_k + \ldots$$

… or nonlinear dependence of transition dipole …

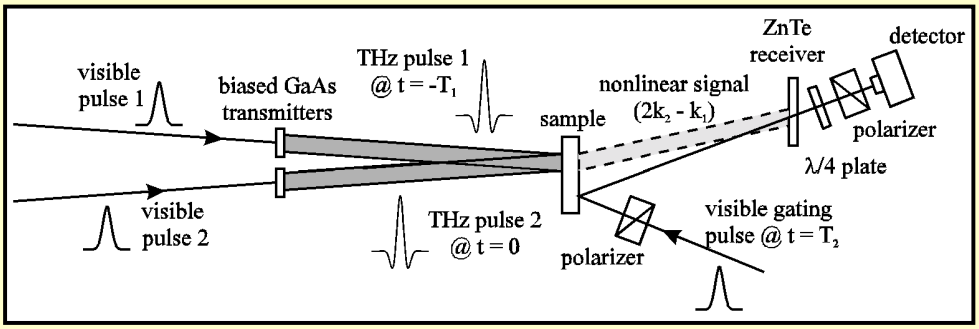
$$\mu(Q) = \mu_0 + \sum_{i=1}^{s} \mu_i Q_i + \sum_{i,j} \frac{\mu_{i,j}}{2!} Q_i Q_j + \ldots$$

Model System: Tryptophan Crystals

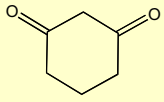
Intermolecular modes depend on enantiomers



Nonlinear two-dimensional THz spectroscopy

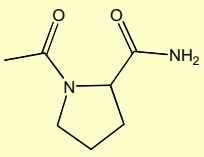


Previous work: 2D IR studies



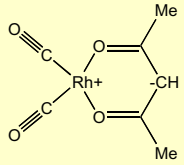
1,3-cyclohexane

Hochstrasser



acetylproline-NH_2

Hochstrasser

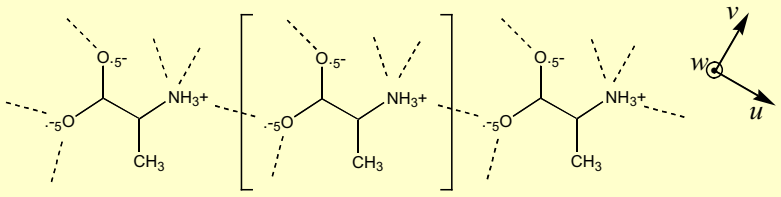


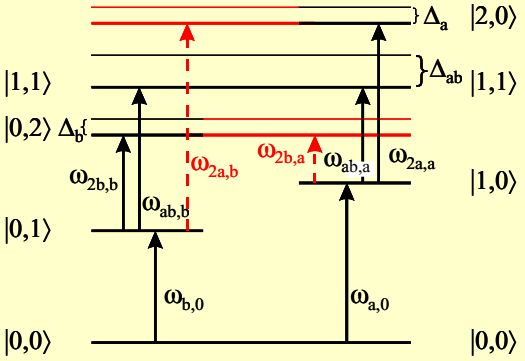
acetyl-acetonato dicarbonyl rhodium(I) (RDC)

Tokmakoff

L-alanine crystals

$CH_3CH(NH_3^+)COO^-$





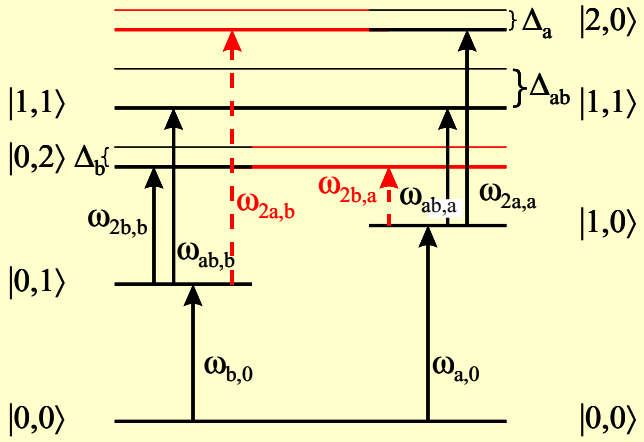
Anharmonicity in potential

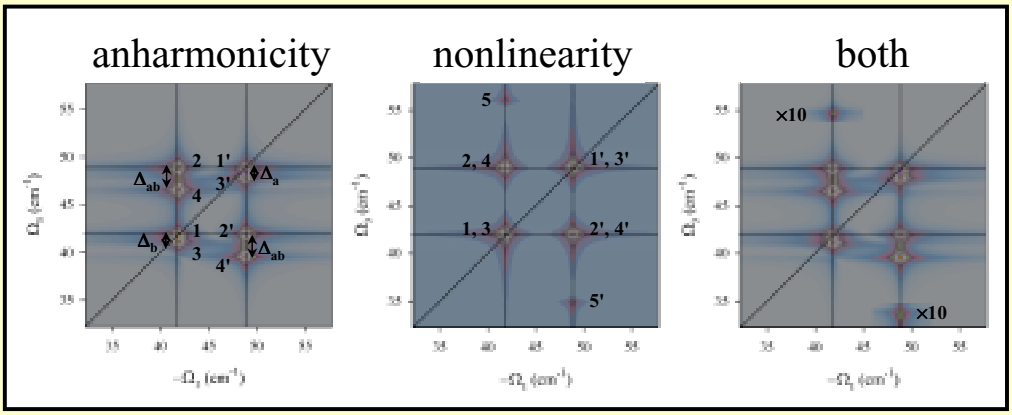
$$V(Q)=\sum_{i=1}^{s}\frac{1}{2}k_iQ_i^2+\sum_{i,j,k}\frac{g_{i,j,k}}{3!}Q_iQ_jQ_k+\ldots$$

Nonlinearity in dipole

$$\mu(Q)=\mu_0+\sum_{i=1}^{s}\mu_iQ_i+\sum_{i,j}\frac{\mu_{i,j}}{2!}Q_iQ_j+\ldots$$

Simulated Results





Summary: 2D THz Spectroscopy

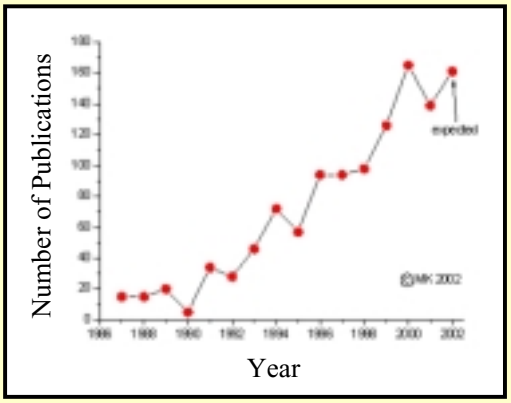
- Separate potential anharmonicity from dipole nonlinearity.

- Observe couplings between phonon modes.

- Observe FIR photon echo in liquids.

Shameless Self-Promotion

Lots of Recent Activity and Interest in THz Radiation



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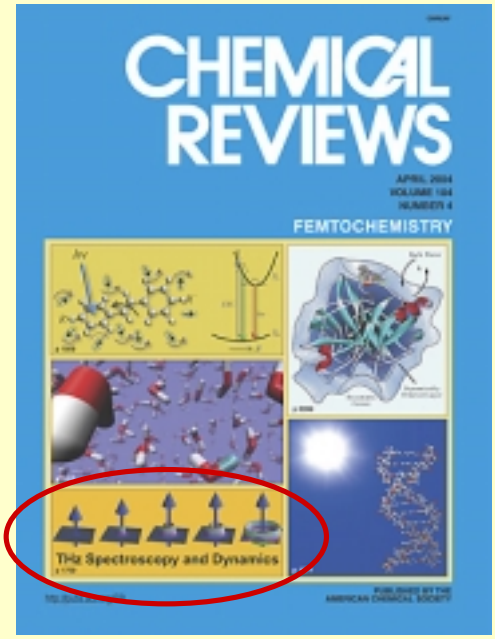
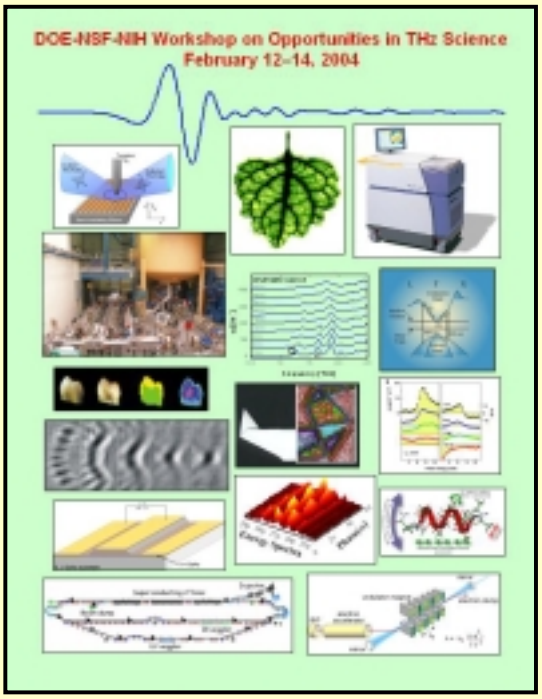
Additional THz Information

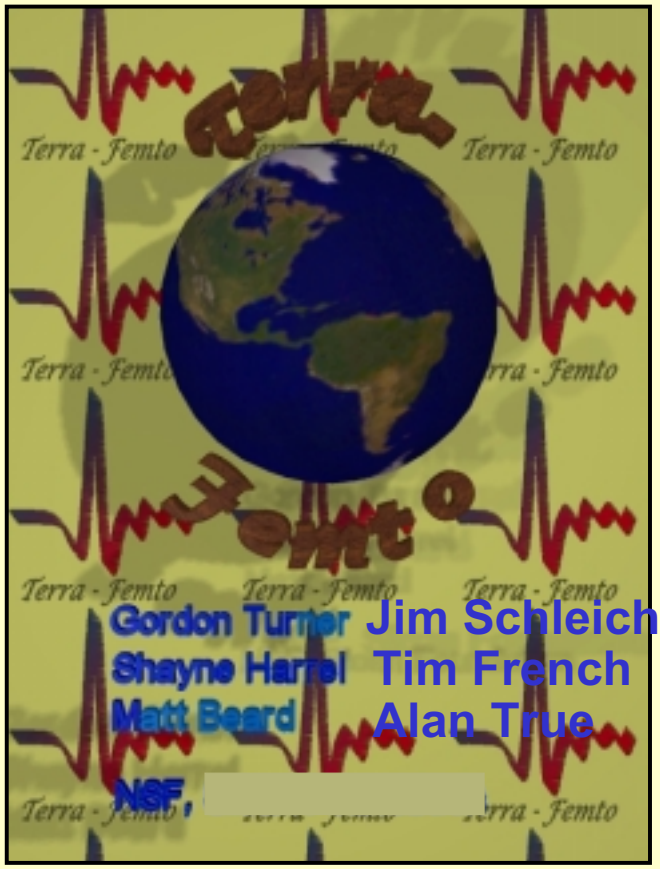
Reasonably comprehensive review:

C. A. Schmuttenmaer, "Exploring Dynamics in the Far-Infrared with Terahertz Spectroscopy" *Chemical Reviews*, **104**, 1759 (2004).





Report is available on DOE BES website.



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