Femtosecond Pure-Rotational CARS for Gas-Phase Diagnostics

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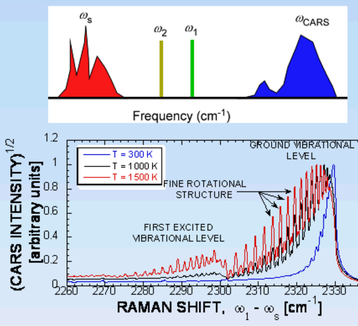
1. Background

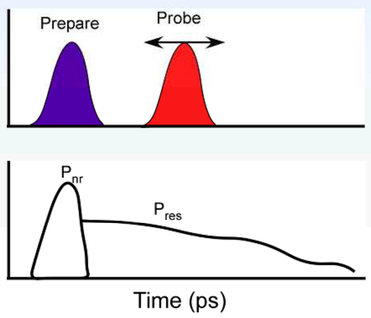
"Typical" Nanosecond CARS

- Measurements performed in the *frequency domain*
- The nanosecond approach has its limitations
- Nonresonant background
- Linewidth/collisional modeling
- Data rates are limited to around 10 Hz
- Limited single-shot precision: broadband Stokes dye laser statistics



Femtosecond CARS (fs-CARS)

- Nonresonant background suppression
- Near collision-free measurements
- Transform-limited fs pulses exhibit low amplitude and phase noise
  - Superior precision
  - Efficient signal generation
- Increased single-shot data rates (1-10 kHz)
- Paradigm shift for gas-phase community: *time-domain vs. frequency domain*

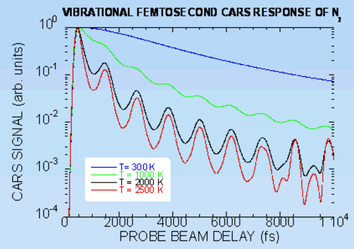


2. . Vibrational fs-CARS: Time-Domain and Single-Shot Measurements

- Transient Q-branch ($\Delta v = +1$, $\Delta J = 0$) Raman polarizations reflect *frequency spread dephasing*
- Direct *time-domain* measurements

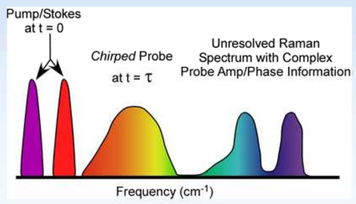
$$P_{res} \sim \sum_i \Delta N_i \left(\frac{d\sigma}{d\Omega}\right)_i \cos(\omega_i t)\exp(-\Gamma_i t)$$

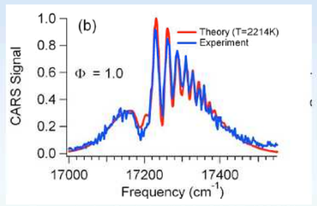
- Single-shot measurements require modification to the fs-CARS approach



Lucht et al., Apl. Phys. Lett **89,** 251112 (2006)

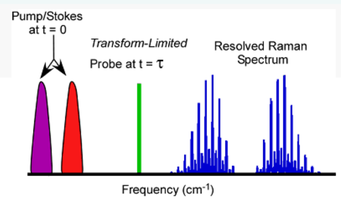
Chirped Probe Pulse (CPP)

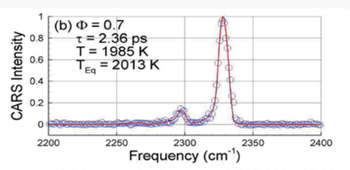




Roy *et al.*, *Opt. Lett* **34**, 3857 (2009)

Transform-Limited Probe Pulse (TLPP)





Miller *et al.*, *Opt. Lett* **35**, 2430 (2010)

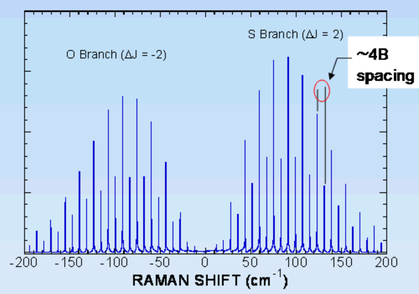
3. Can Pure-Rotational CARS be Applied in Similar Fashion?

- More precise at "low" (<1000 K) temperatures
- Rotational transitions are closely spaced – more species with a single Raman instrument
- Rotational Raman spectra have wider bandwidth (200 cm^{-1}) than vibrational spectra (20 cm^{-1})
  - More rapid initial dephasing of the Raman coherence
  - Overall decay is collision instead of dephasing dominated
  - Strong signals at long probe delay – nonresonant background suppression
- "Rephasing" results from ~uniform energy 4B spacing in $\omega_{JJ'}$

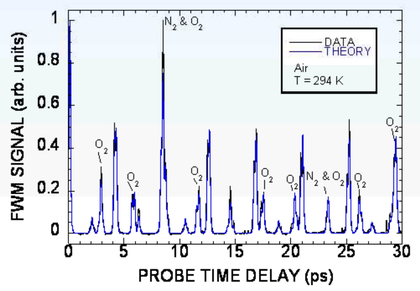
$$P_{res}(t) = \sum_k \sum_{\Delta J = \pm 2} W_{JJ'}^{(k)} \exp\left(-i\,\omega_{JJ'}^{(k)} t\right)\exp\left(-\Gamma_{JJ'}^{(k)} t\right)$$

$$W_{JJ'}^{(k)} = X_k\, \gamma_k \left(N_J - N_{J'}\right) F_{JJ'}\, b_{JJ'}$$

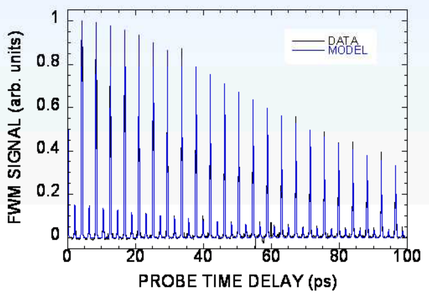
Frequency Domain N_2 Spectrum (ns-CARS)



Time Domain Air at 294 K with Scanned fs Probe

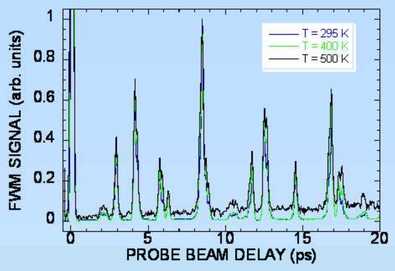


Time-Domain N_2 at 294 K with Scanned fs Probe

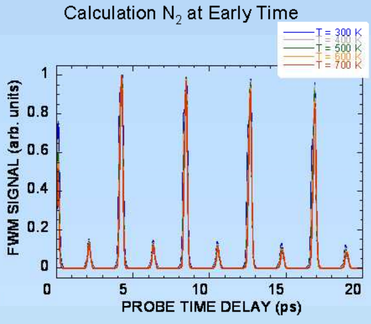


4. Temperature Sensitivity of Rotational Transients

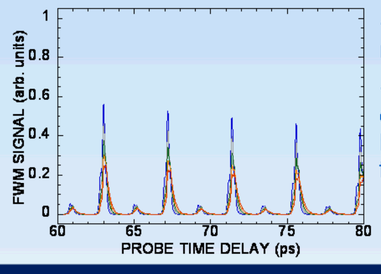
Experiment: Air in Tube Furnace



Calculation N_2 at Early Time



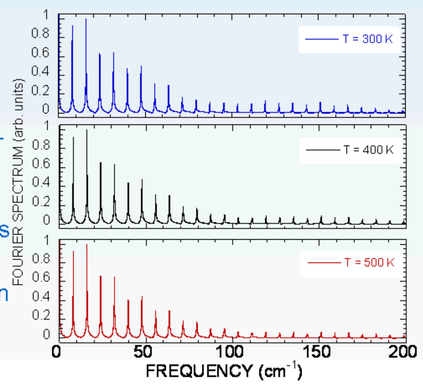
Calculation N_2 Late Time



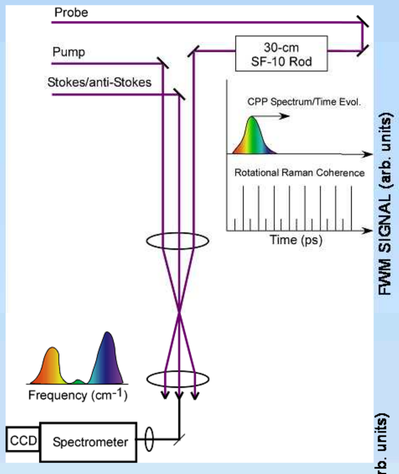
- Structure of the observed transients is not particularly sensitive to temperature
- Some increased sensitivity is observed at late times and arises from higher order corrections to the Raman frequencies

5. Fourier Transform Spectra

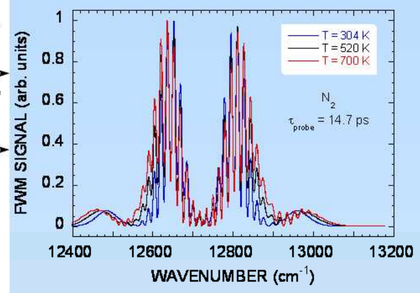
- Better temperature sensitivity observed in the frequency domain.
- Fourier spectra of the observed transients show Stoke/Stokes, anti-Stokes/anti-Stokes and Stokes anti-Stokes quantum beats
- Distinct migration of Fourier spectral energy to lower frequencies at temperature increases
- Next step: direct frequency domain measurements for single-shot data

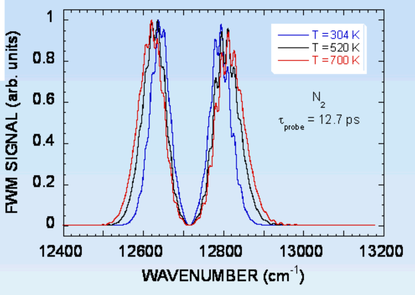


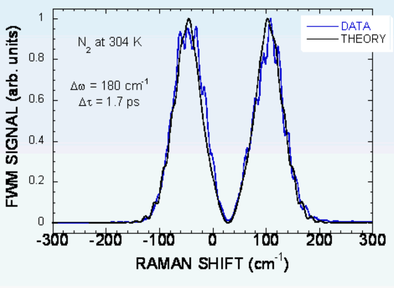
6. Initial CPP Rotational CARS Results



- Mechanically scanned probe data do not permit practical temperature measurement on a single laser shot
- Probe pulse is chirped by dispersive SF-10 rod
- CPP maps time-domain information into the frequency domain
- Rotational analog of CPP Vibrational CARS technique of Roy *et al.*
- Results are extremely sensitive to laser field phase and amplitude

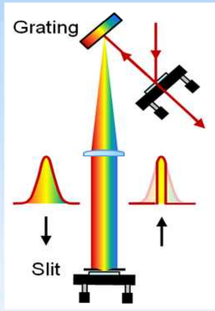


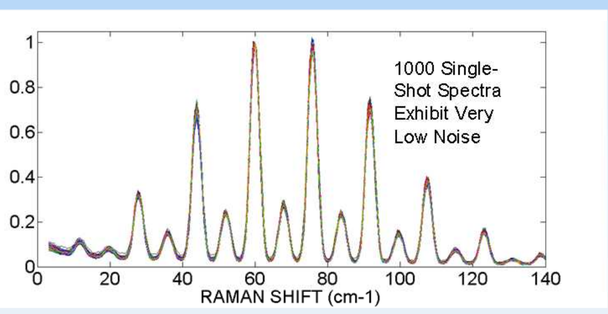




7. Early TLPP Measurements in Cold N_2

4-f Pulse Shaper





- 4-f pulse shaper slit removes probe bandwidth and stretches pulse to ~10 ps
- Available probe energy is reduced dramatically relative to CPP approach
- Raman spectra are well resolved and much simpler to interpret
- With 20-ps probe delay, these spectra are free of nonresonant background
- Single-shot spectra in N_2 display very low noise, a key advantage of fs pump/Stokes preparation

8. Summary and Conclusions

- Rotational CARS/CSRS is being developed for single-shot gas-phase measurements. We present some early results here
- The observed transients in N_2 and air are in good agreement with previous observations and are well-modeled
- Time domain transients are less sensitive to temperature than in the frequency domain
- Both CPP and TLPP are being investigated for single-shot measurements in the frequency domain
- CPP permits high probe-laser energies, but modeling of results is very sensitive to laser electric fields
- TLPP spectra are more readily modeled, but probe laser energy may be limited

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