Electronic-Resonance-Enhanced Coherent Anti-Stokes Raman Scattering of Nitric Oxide: Non-Perturbative Time-Dependent Modeling

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Outline of the Presentation

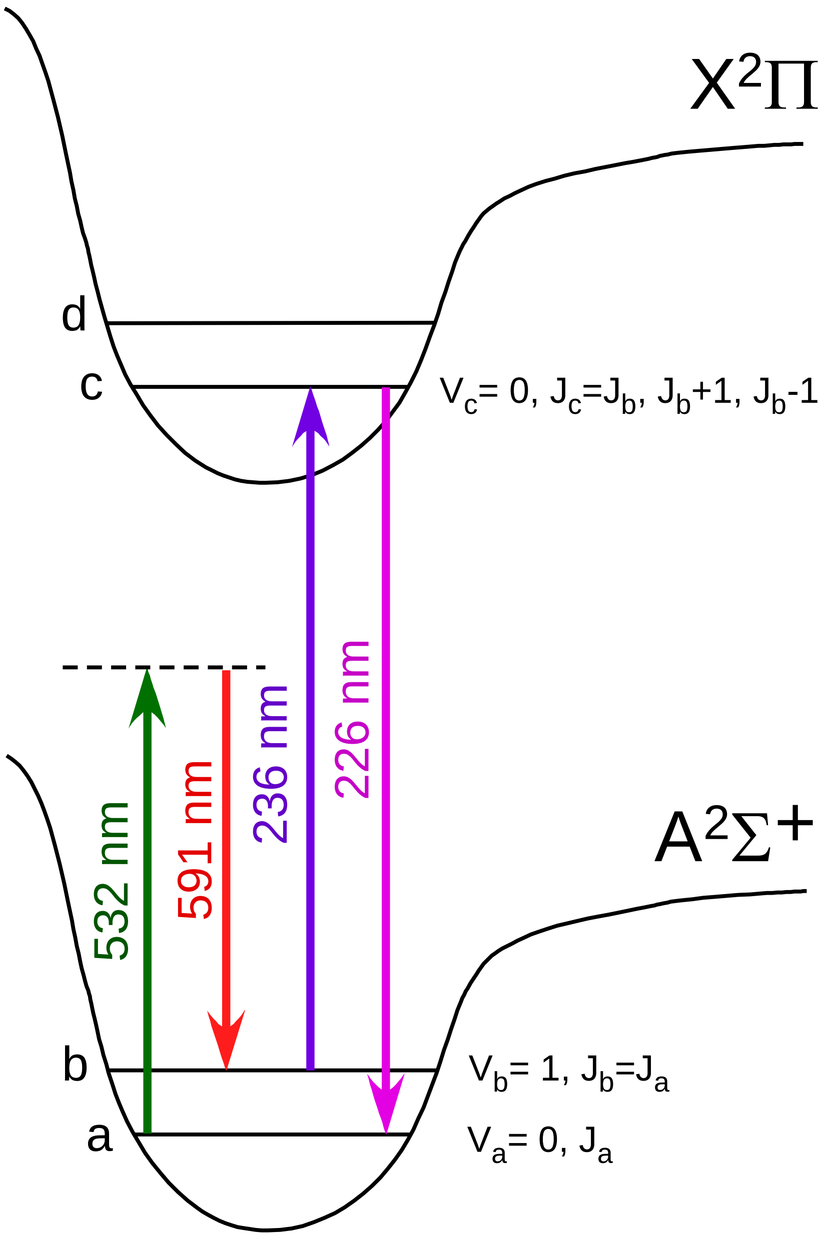
- Introduction and Motivation
- Scanning Stokes ERE CARS
- Density Matrix Modeling: Saturation and Stark Shifting Effects
- Broadband Stokes Vibrational ERE CARS
- Density Matrix Modeling of Broadband Stokes Vibrational ERE CARS
- Conclusions and Future Work

Introduction and Motivation

- **Oxides of nitrogen (NOx) are important atmospheric pollutants their major source being emissions is from combustion during transportation and power generation. Most NOx is produced in the form of nitric oxide (NO).**

- **ERE CARS is a very promising method for detecting NO in high-pressure combustion systems, overcomes numerous issues associated with LIF detection (quenching, laser beam absorption, interfering species, soot interferences).**

Vibrational Electronic Resonance CARS of NO



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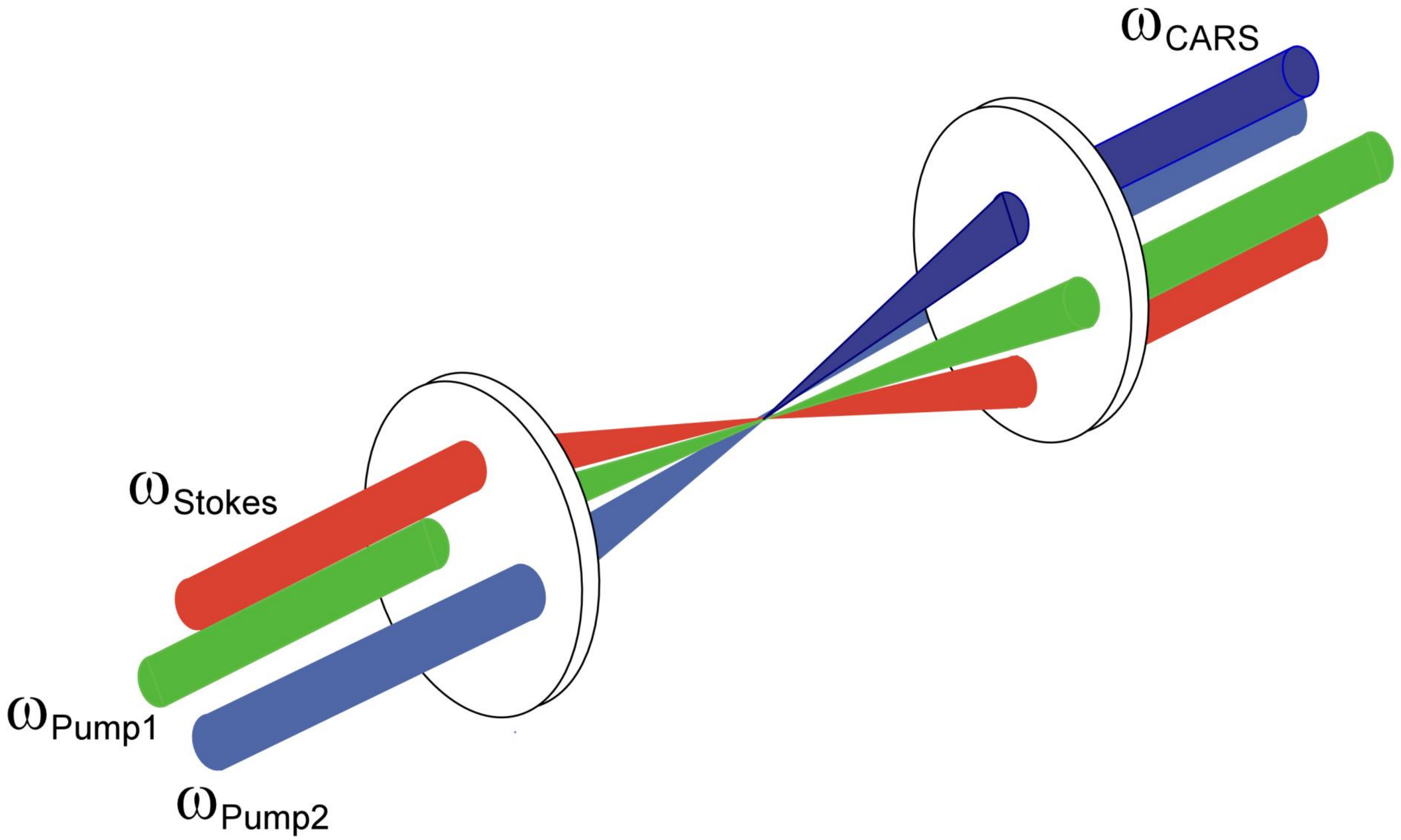
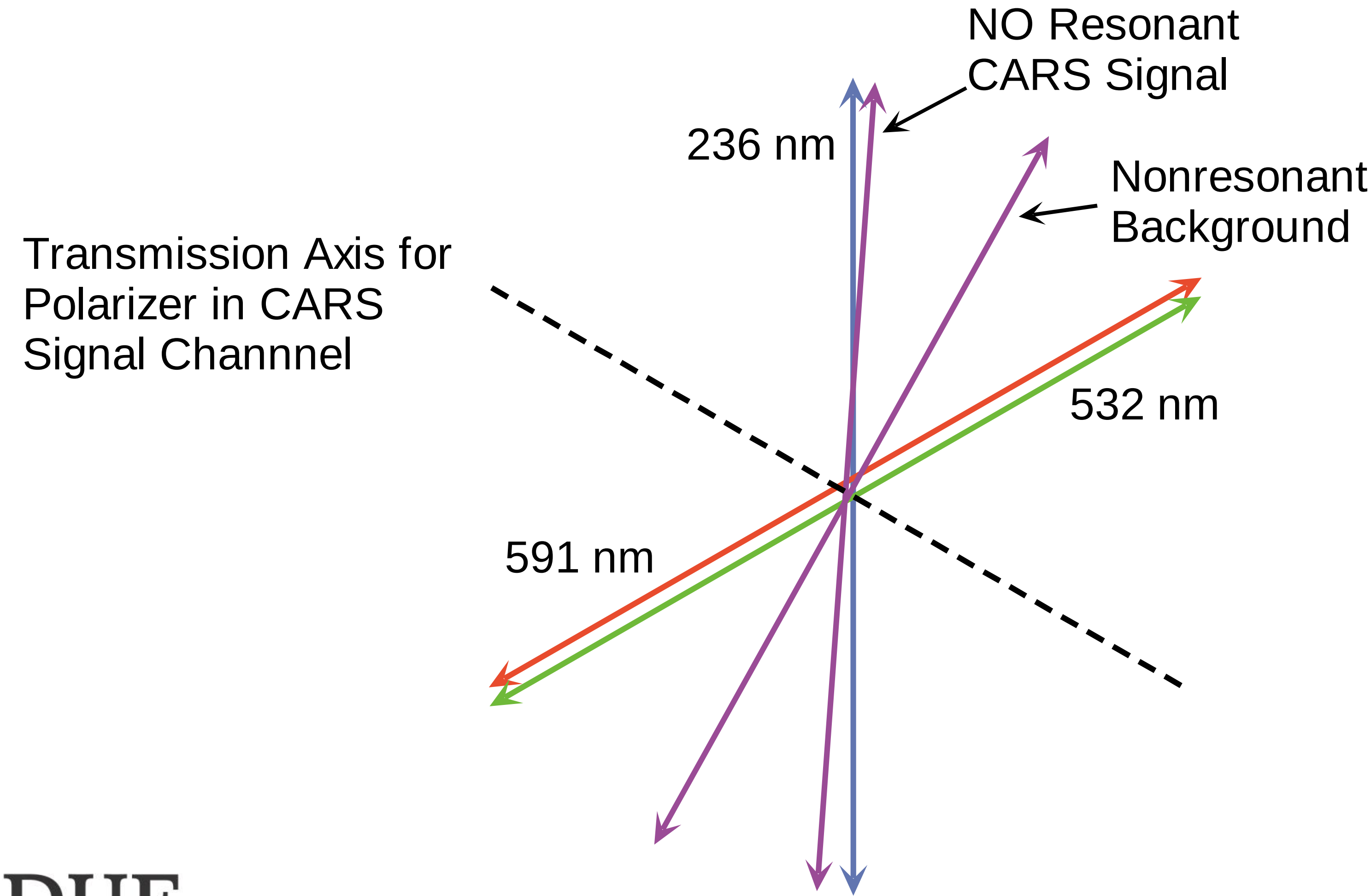
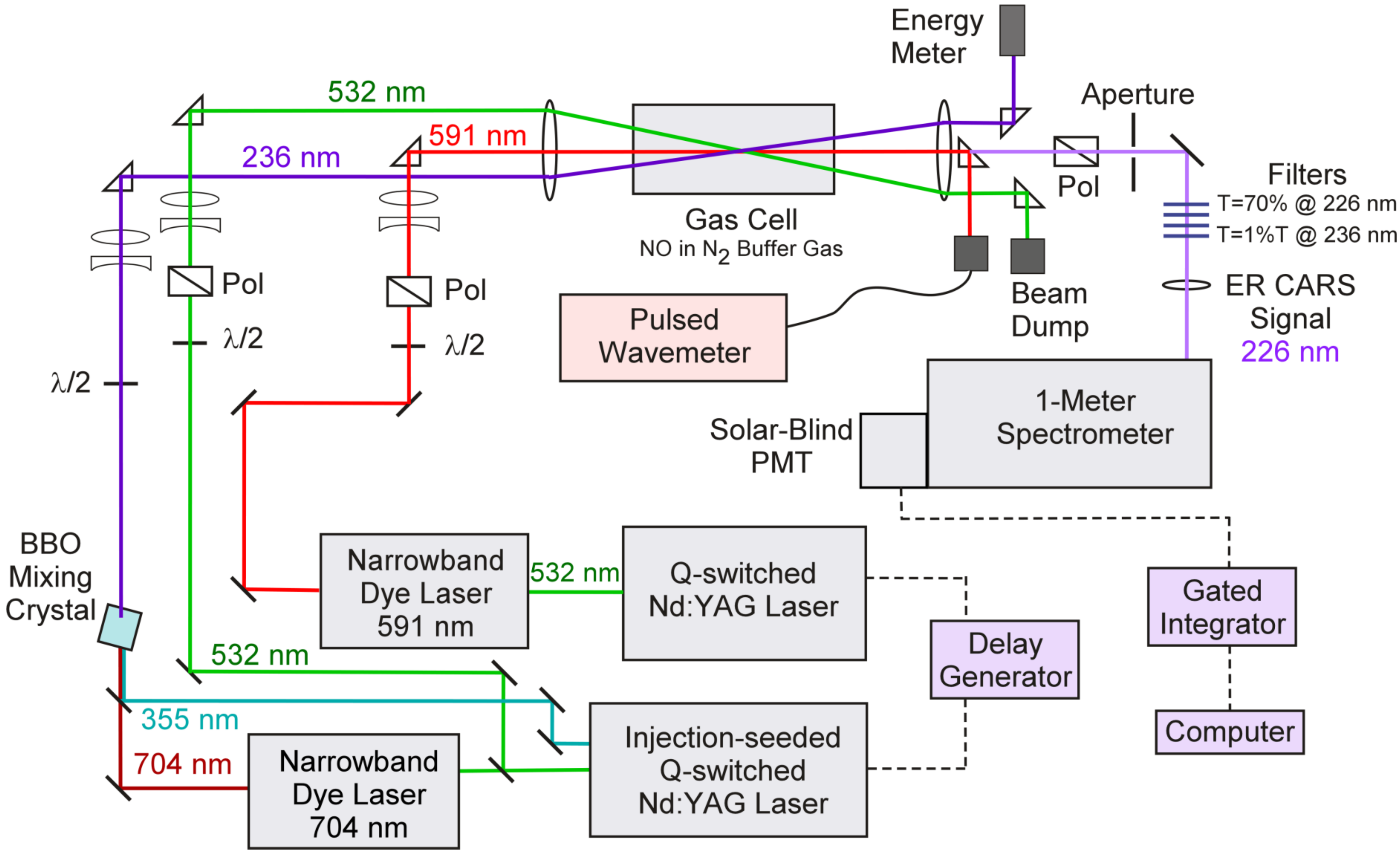
ERE CARS Phase Matching



Polarization Suppression of Nonresonant Background



Scanning ERE CARS Experimental System



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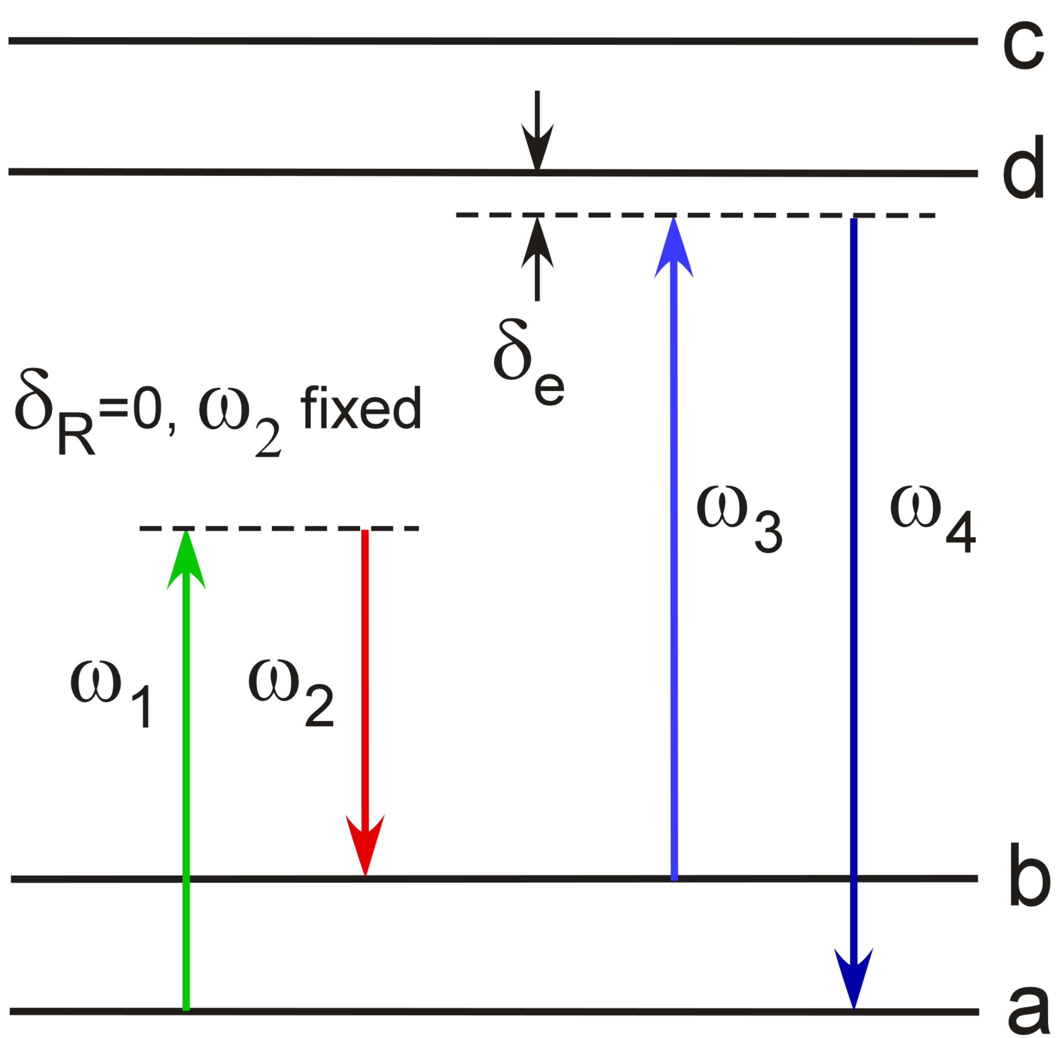
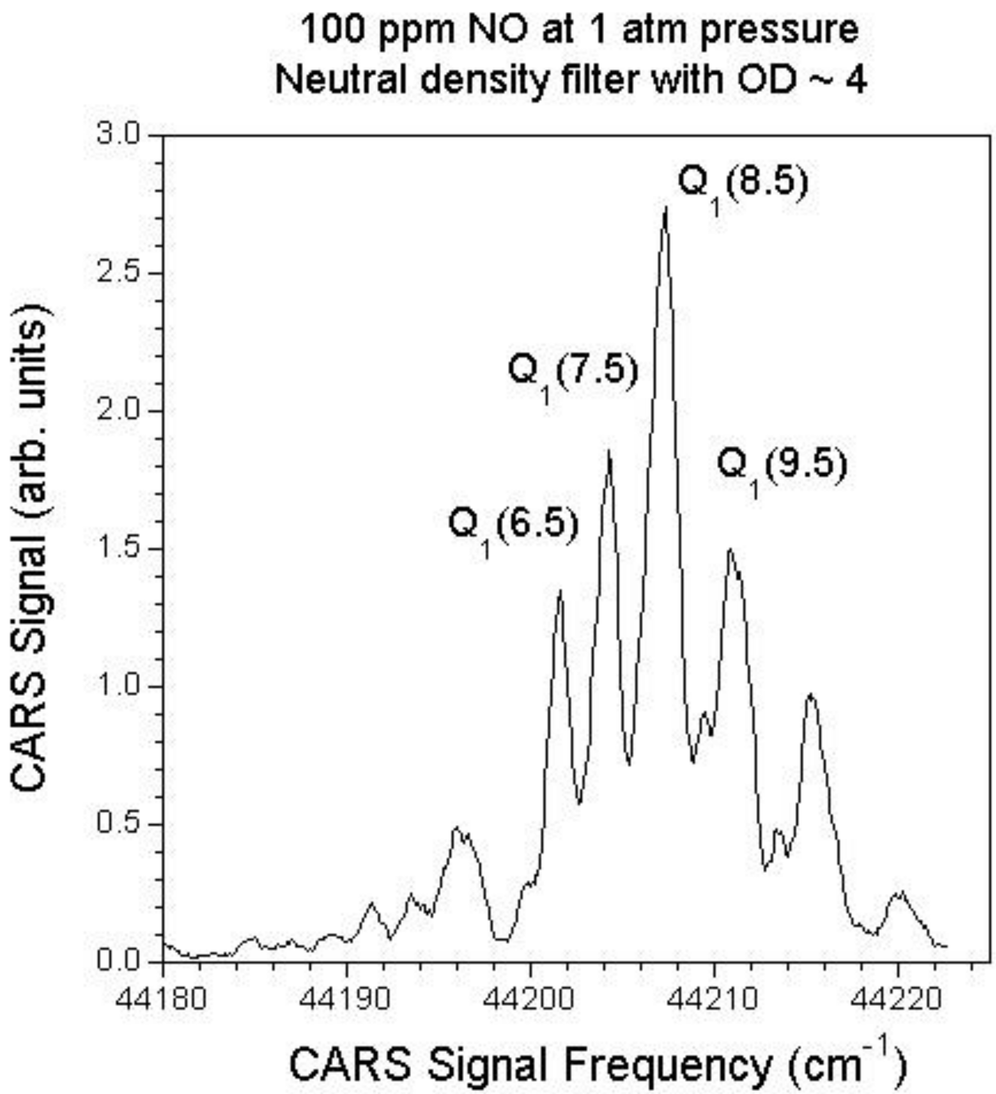
UV Probe Scan, Fixed Stokes Beam Frequency



UV Probe Scan, Fixed Stokes Beam Frequency



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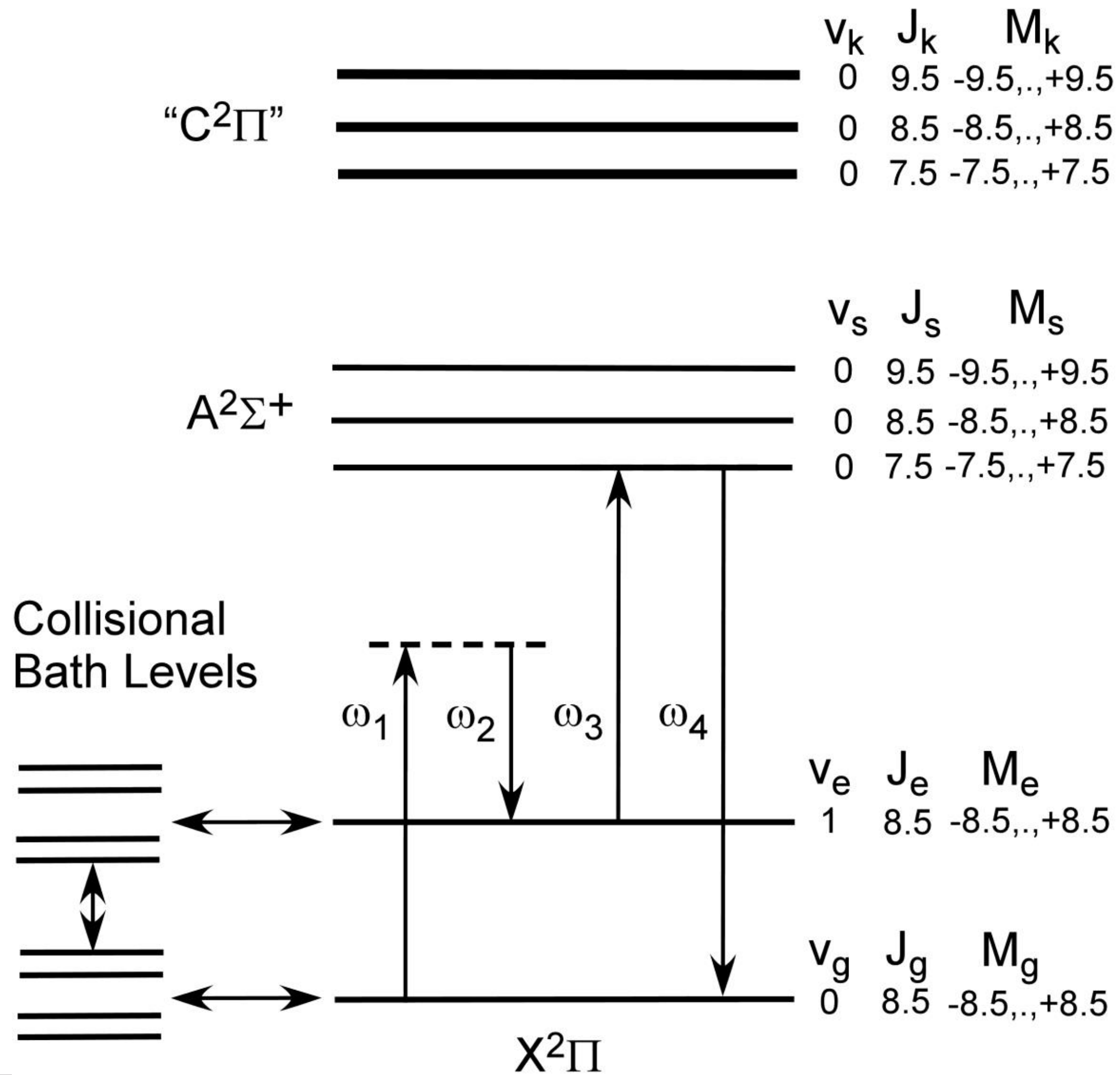
Numerical Model of CARS in Nitric Oxide: Raman $Q_1(8.5)$, Probe $P_1(8.5)$



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Time-Dependent Density Matrix Equations for the Laser Interaction

Rate of change of population of state j:

$$\frac{\partial \rho_{jj}}{\partial t} = -\frac{i}{\hbar}\sum_m (V_{jm}\rho_{mj} - \rho_{jm}V_{mj}) - \Gamma_j \rho_{jj} + \sum_m \Gamma_{mj}\rho_{mm}$$

Time development of coherence between states i and j:

$$\frac{\partial \rho_{ij}}{\partial t} = -\rho_{ij}(i\,\omega_{ij} + \gamma_{ij}) - \frac{i}{\hbar}\sum_m (V_{im}\rho_{mj} - \rho_{im}V_{mj})$$

Coupling of laser radiation and dipole moment for states j and m:

$$V_{jm} = -\vec{\mu}_{jm} \bullet \vec{E}(\vec{r},t) = -\vec{\mu}_{jm} \bullet \left[\vec{E}_1(\vec{r},t) + \vec{E}_2(\vec{r},t) + \vec{E}_3(\vec{r},t)\right]$$

Time-Dependent Density Matrix Equations for the Laser Interaction

The off-diagonal density matrix elements are written in terms of slowly varying amplitude functions and a term that oscillates at the frequency or frequencies of interest for each term:

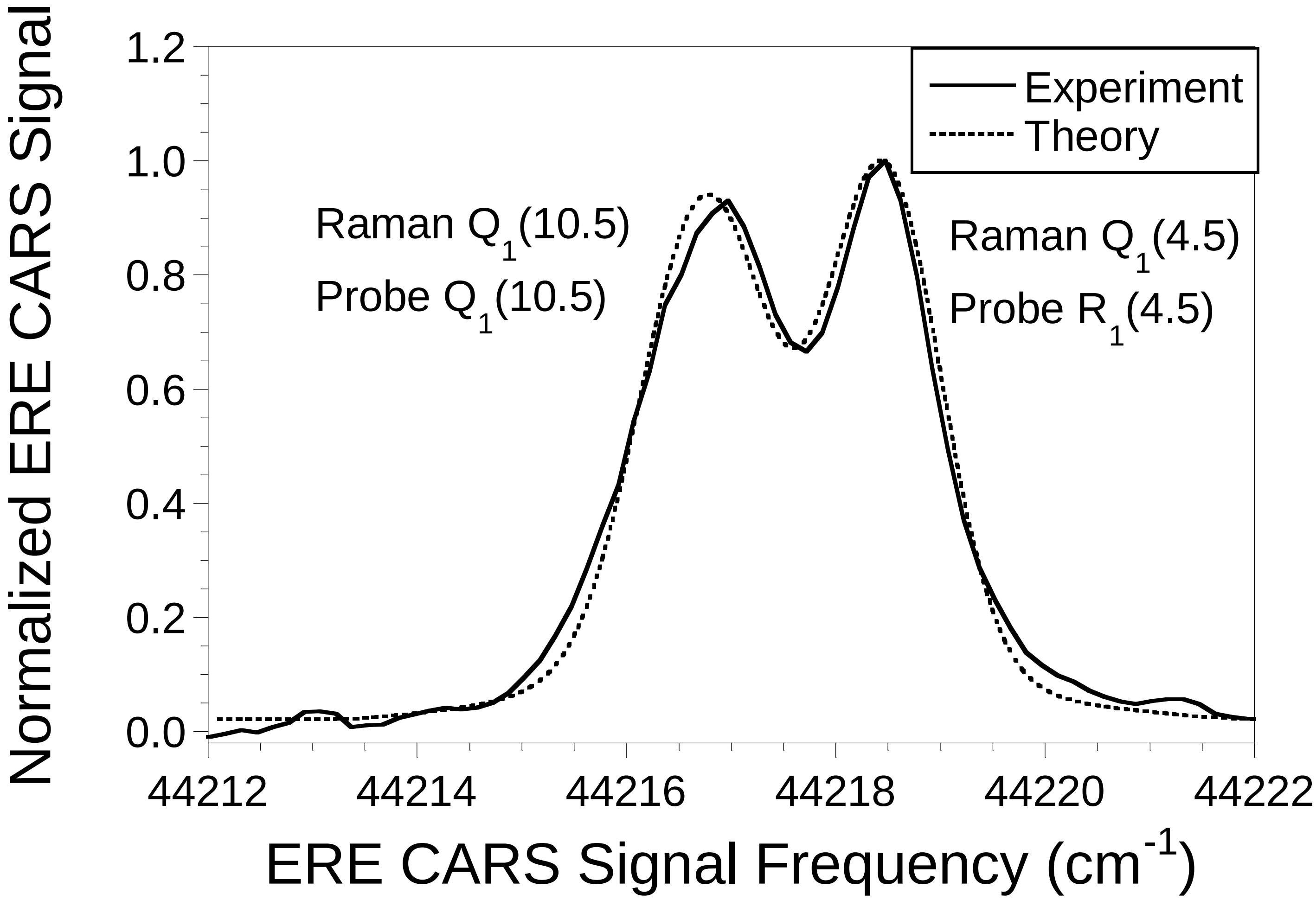
$$\rho_{kg}(t) = \sigma_{kg}(t)\exp\left(-i\,\omega_1 t\right) + \eta_{kg}(t)\exp\left(-i\,\omega_4 t\right)$$

$$\rho_{ke}(t) = \sigma_{ke}(t)\exp\left(-i\,\omega_2 t\right) + \eta_{ke}(t)\exp\left(-i\,\omega_3 t\right)$$

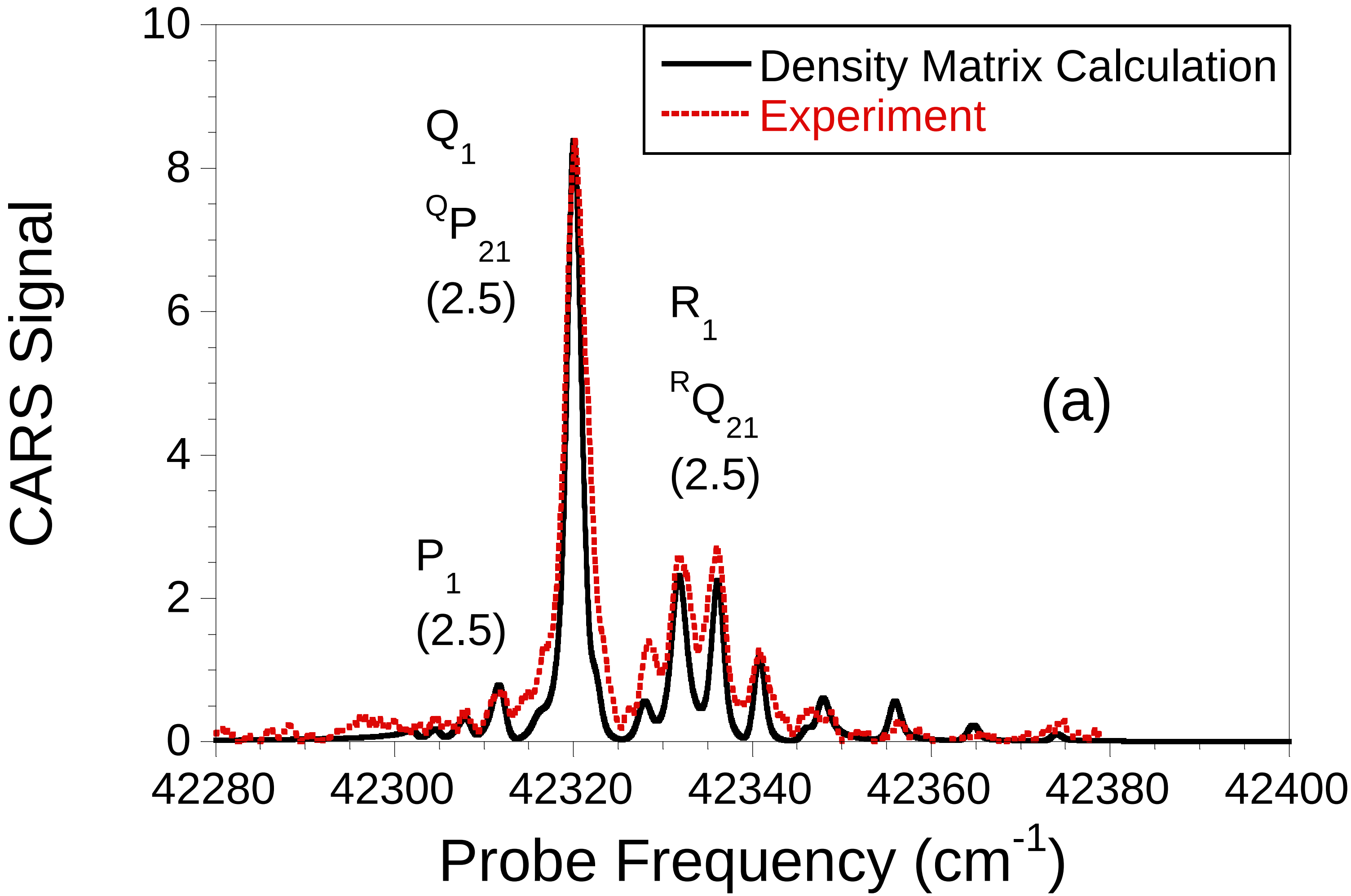
$$\rho_{eg}(t) = \sigma_{eg}(t)\exp\left[-i\left(\omega_1 - \omega_2\right)t\right]$$

The envelope functions and polarizations for the pump, Stokes, and probe beams are specified.

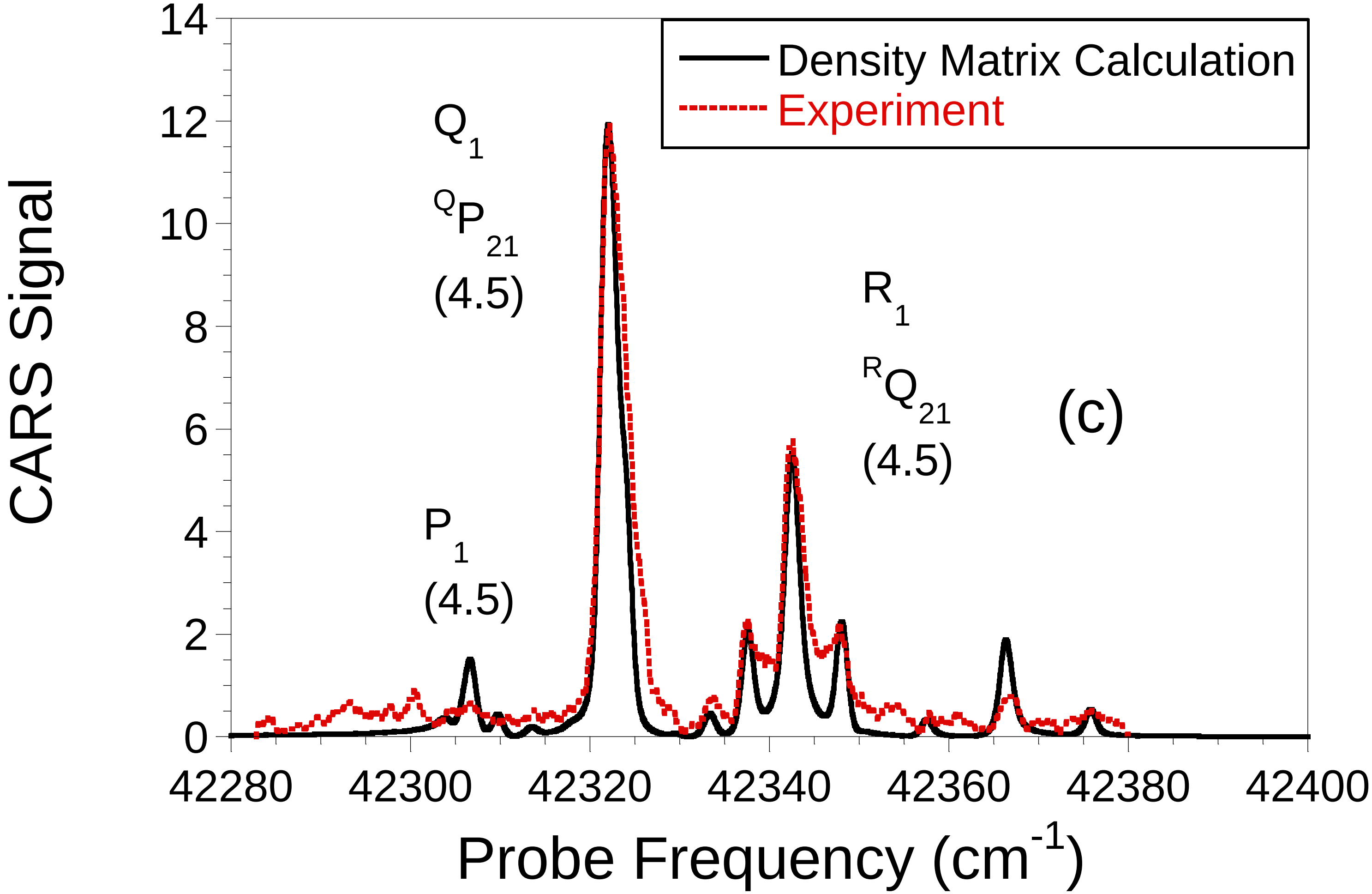
Vibrational ERE CARS in Nitric Oxide: Raman $Q_1(4.5)$, Probe $R_1(4.5)$ Raman $Q_1(10.5)$, Probe $R_1(10.5)$



Scanning Probe Vibrational ERE CARS in Nitric Oxide: Low Laser Powers



Scanning Probe Vibrational ERE CARS in Nitric Oxide: Low Laser Powers



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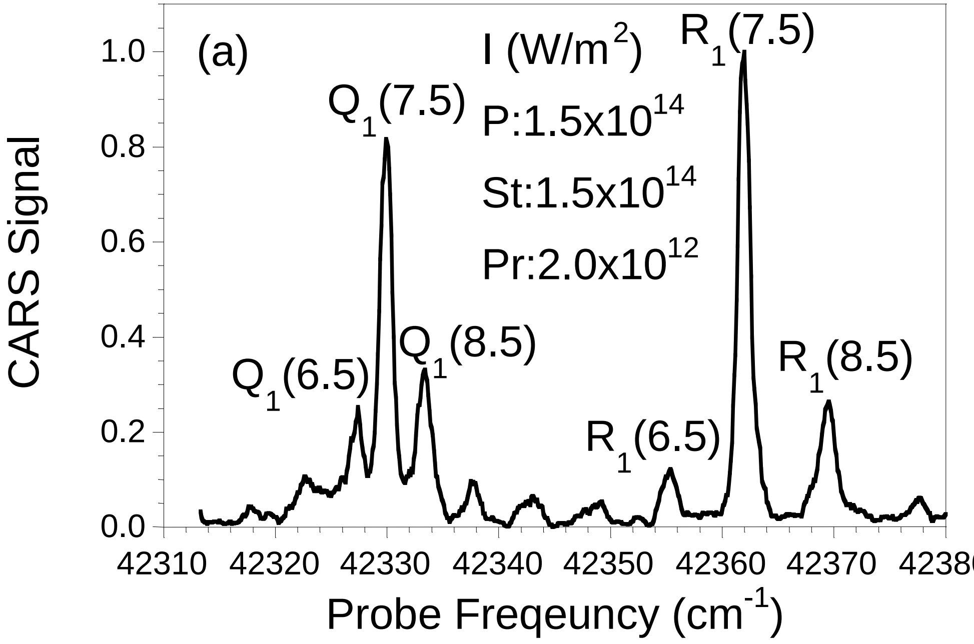
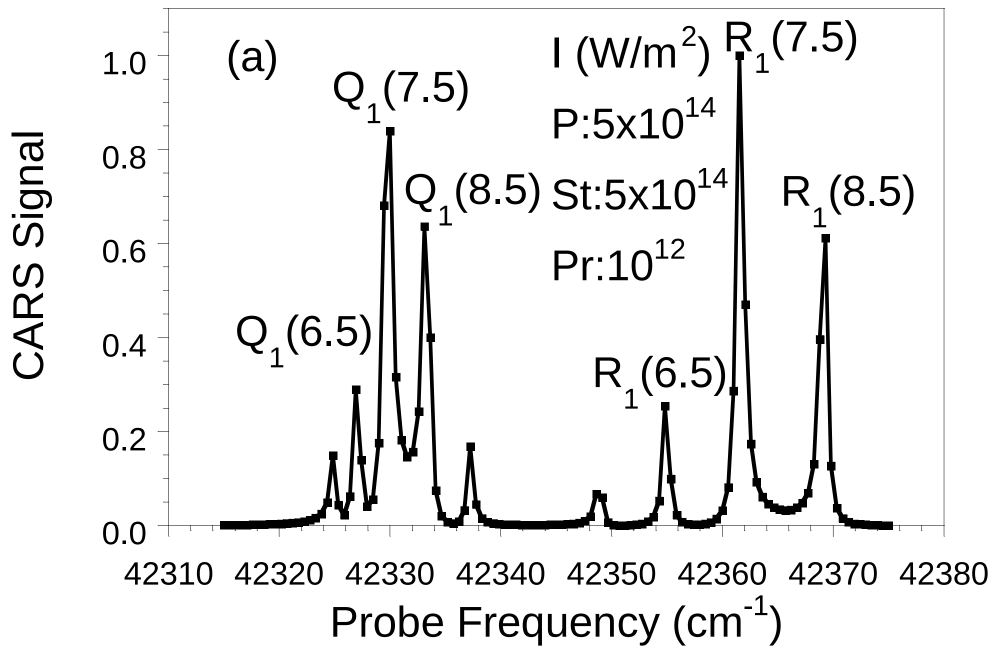
Scanning Probe Vibrational ERE CARS: Low Laser Powers



Expt



Theory

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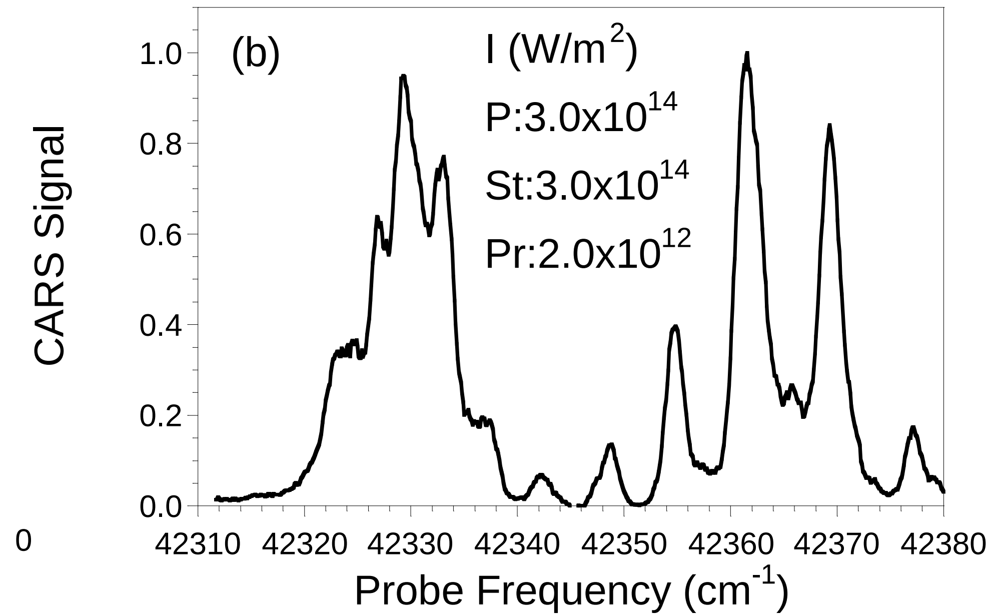
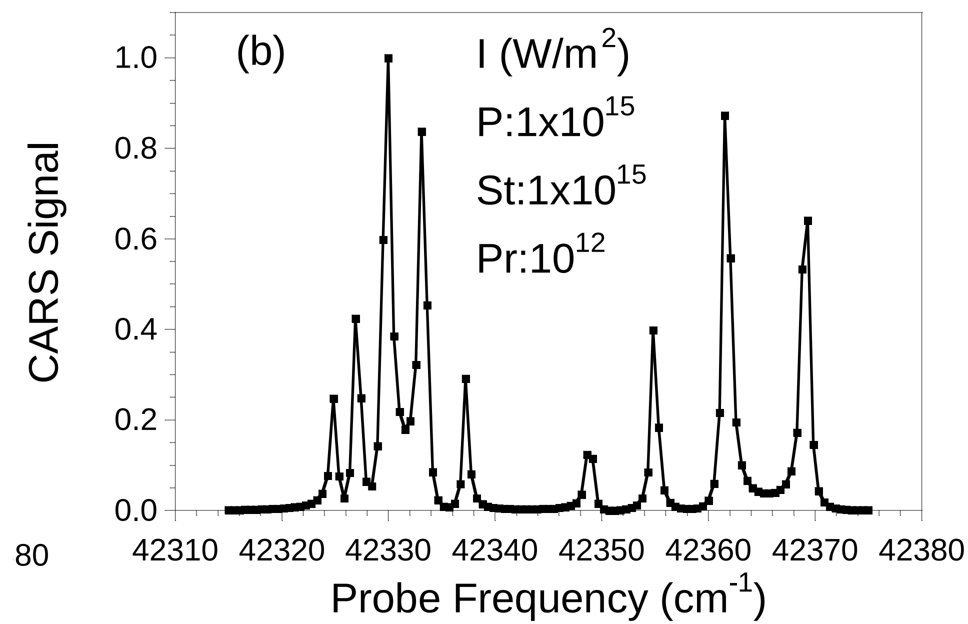
Scanning Probe Vibrational ERE CARS: Low Probe Power, Moderate Pump and Stokes Powers



Expt



Theory

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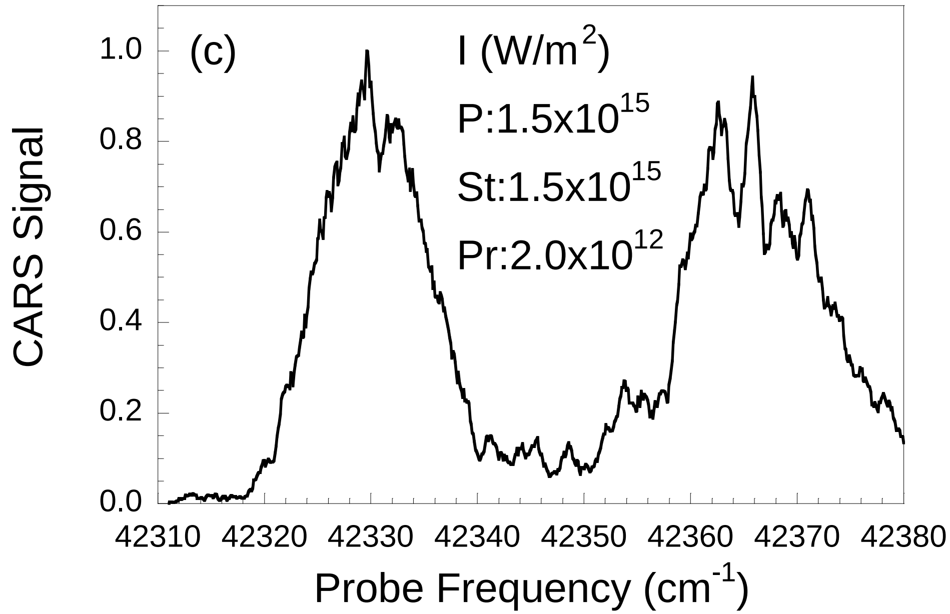
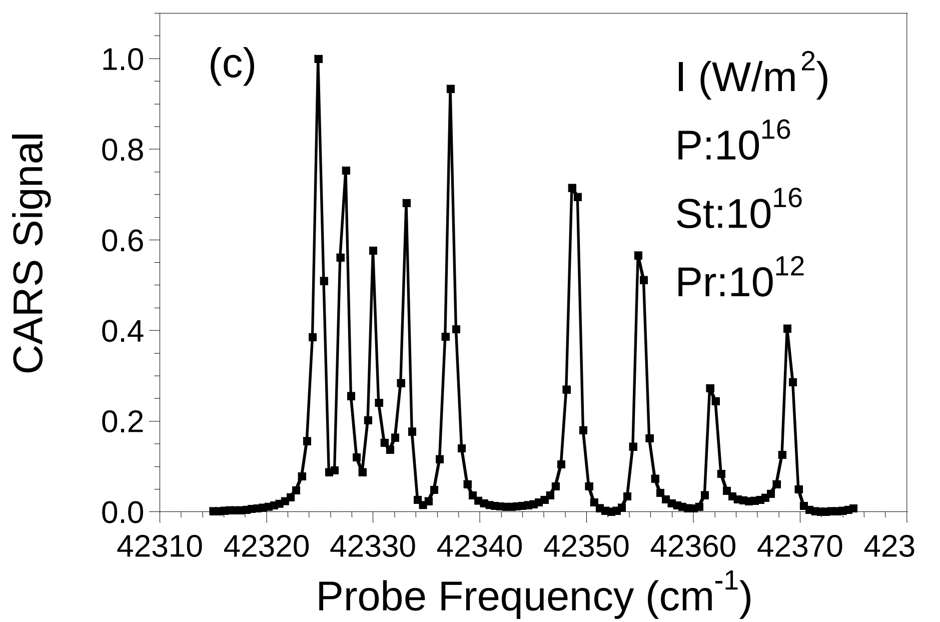
Scanning Probe Vibrational ERE CARS: Low Probe Power, High Pump and Stokes Powers

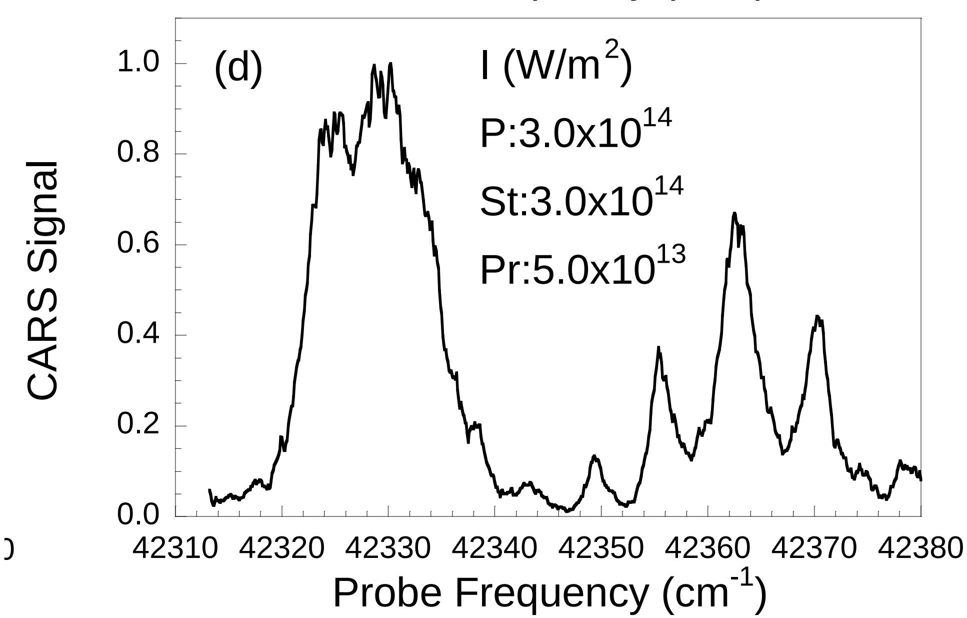


Expt

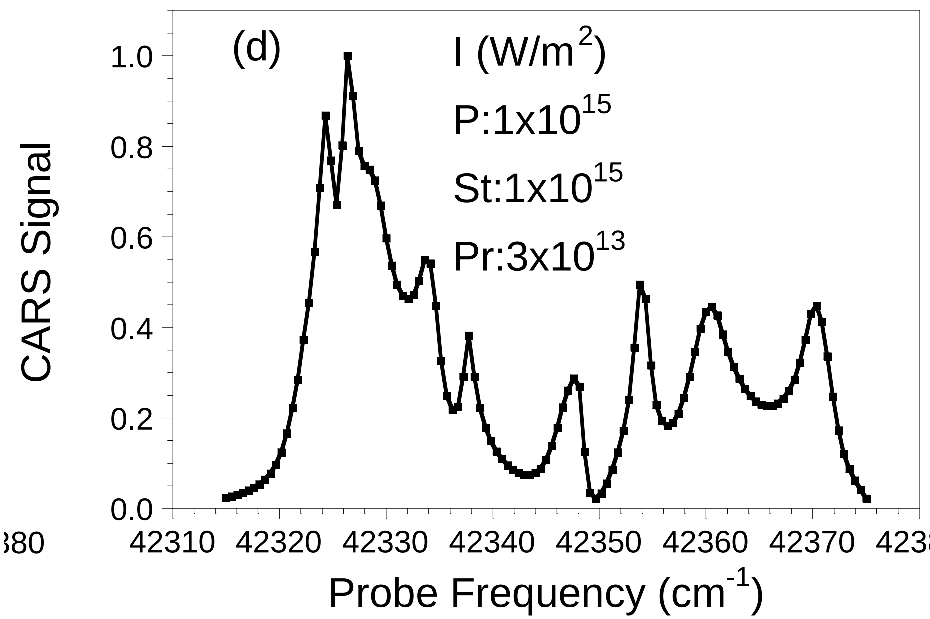


Theory

Scanning Probe Vibrational ERE CARS: High Probe Power, Moderate Pump and Stokes Powers

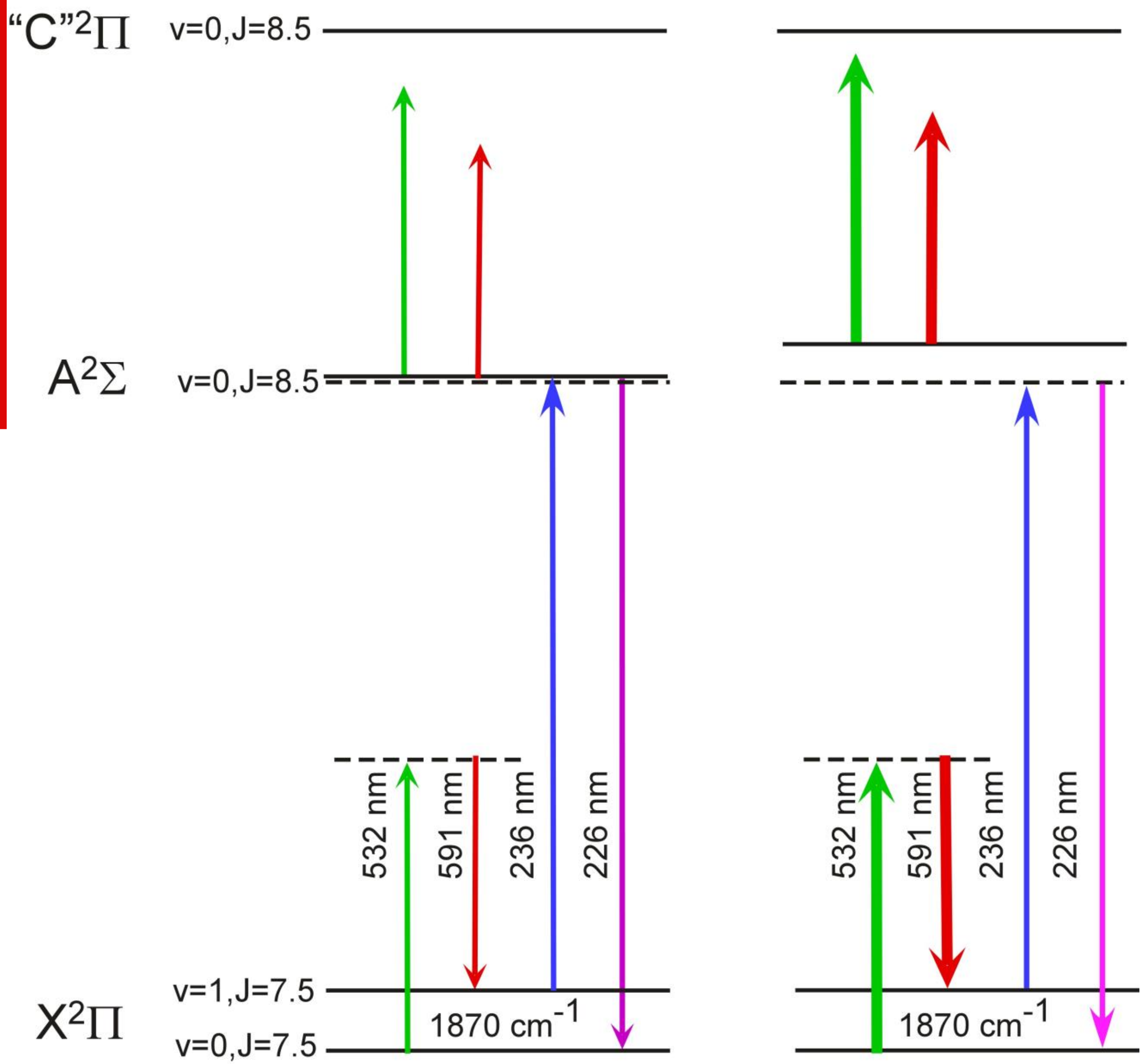


Expt



Theory

Scanning Probe Vibrational ERE CARS: Stark Shift Effects



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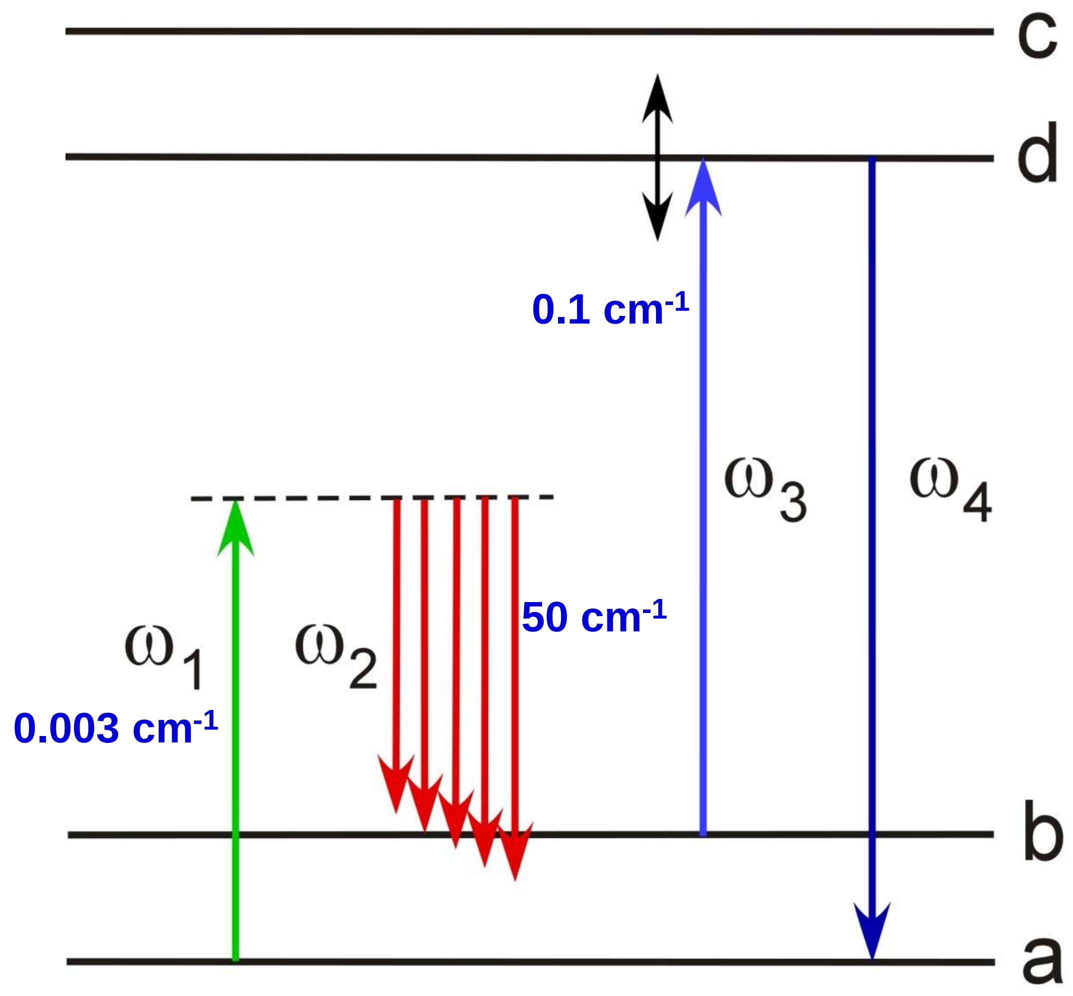
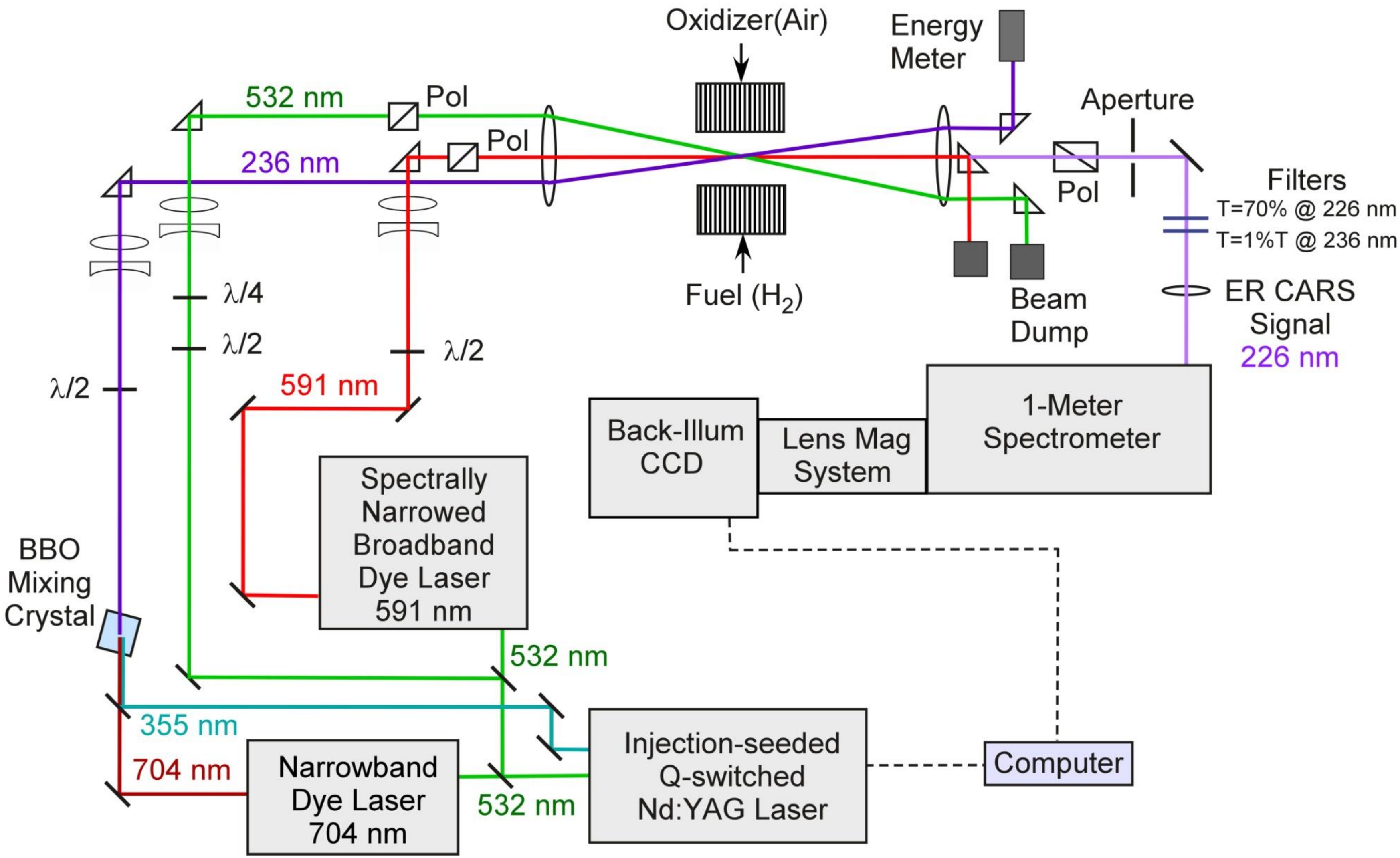
Broadband Stokes Vibrational ERE CARS



Broadband Stokes ERE CARS System



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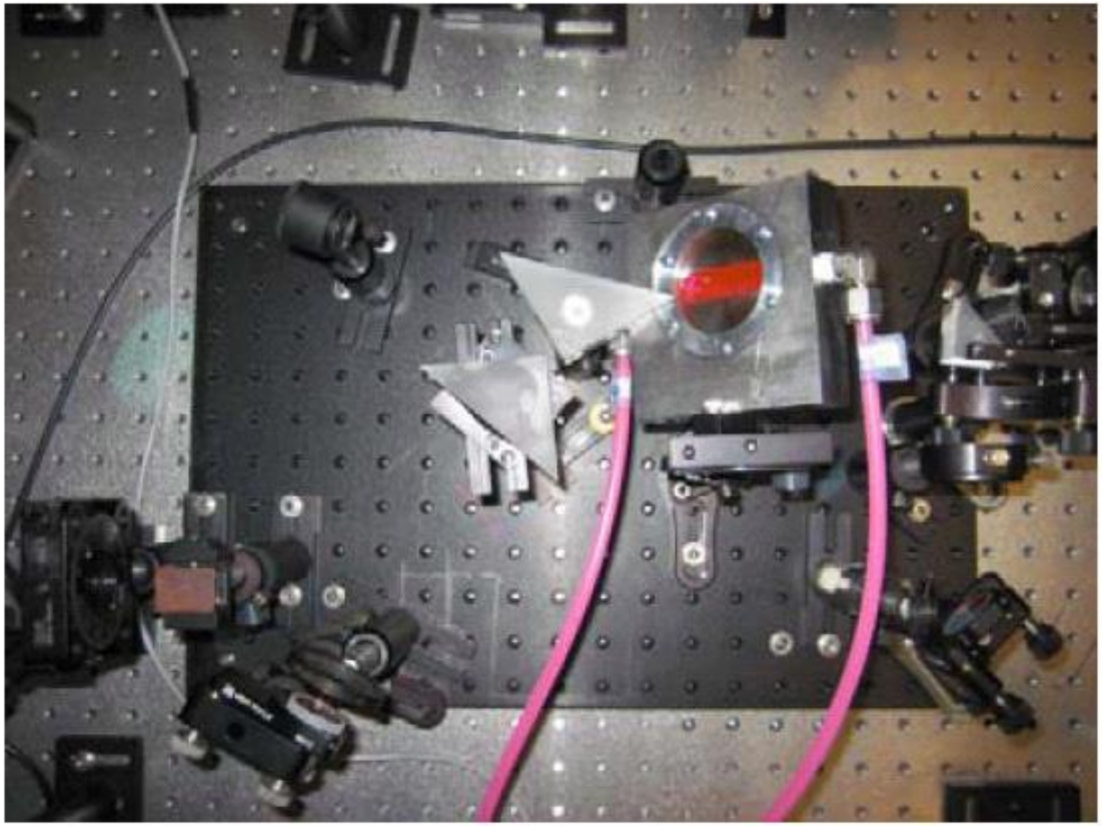
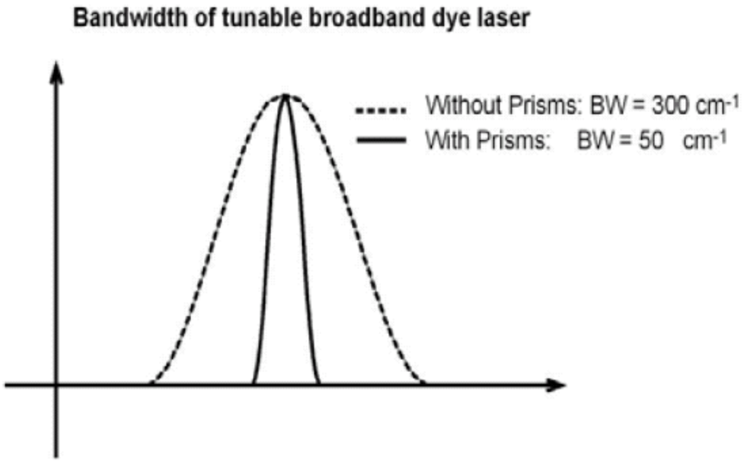
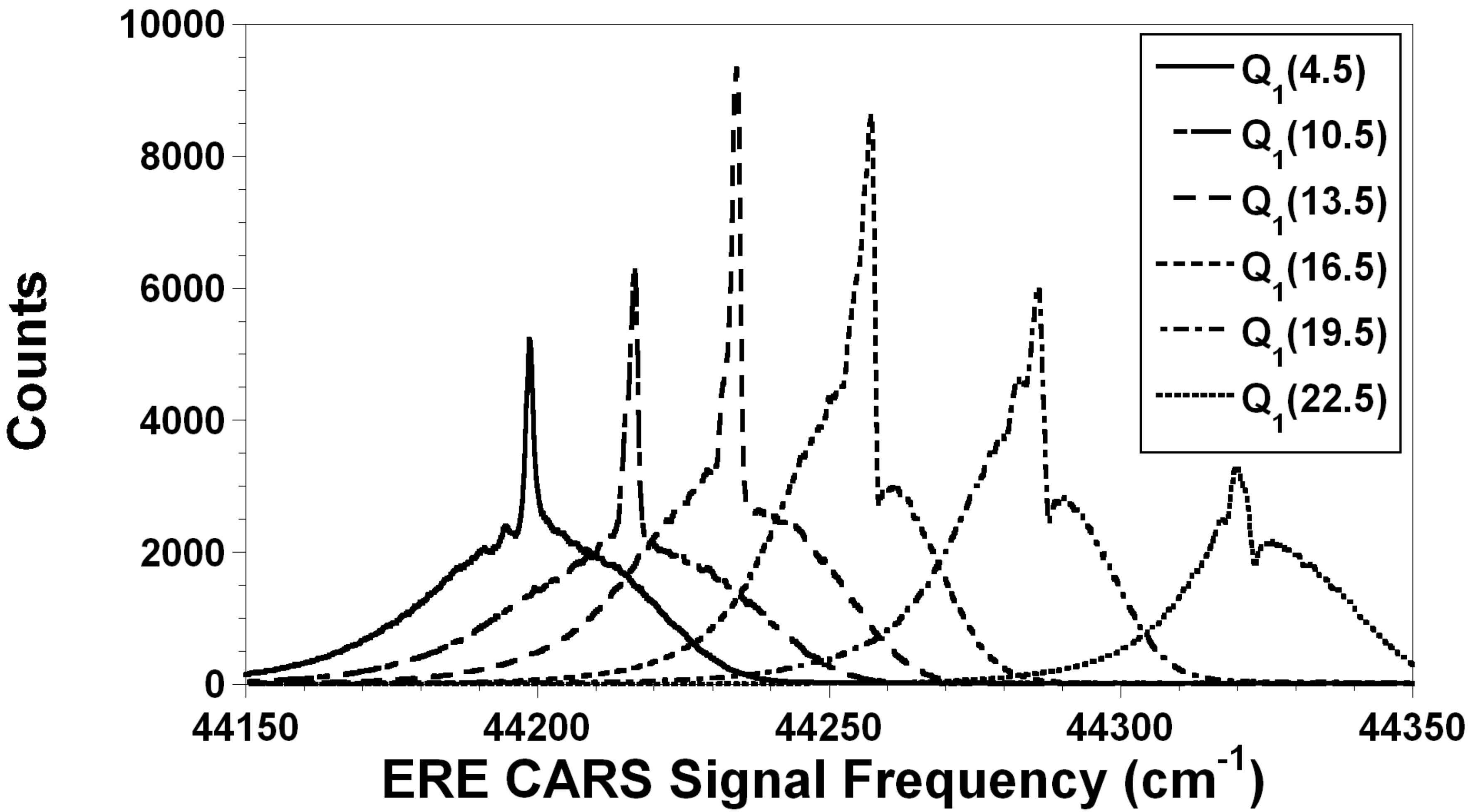
Broadband Stokes ERE CARS System: Spectrally Narrowed BBDL

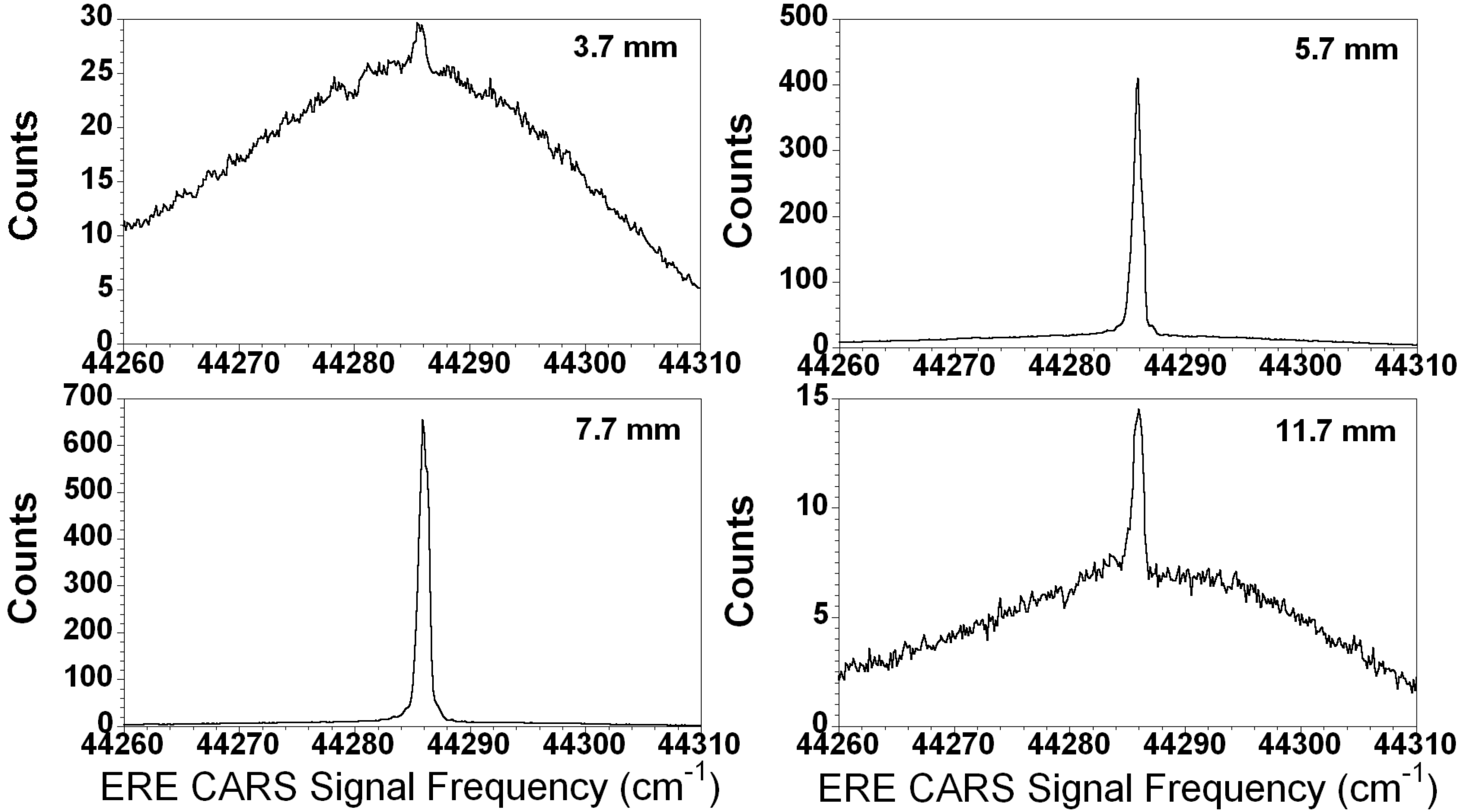




Broadband Stokes ERE CARS Signal in Jet of N2 with 1000 ppm NO at 300 K



Single-Shot NO ERE CARS in Counterflow H_2/Air Flame: Q_1(19.5) Line



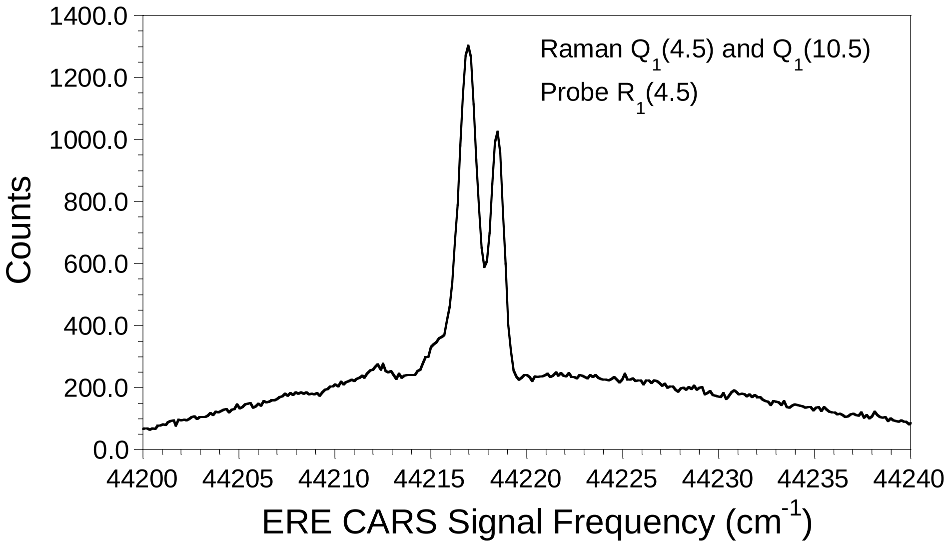
- **Estimated single-shot detection limit of 10 ppm based on an OPPDIF prediction of 30 ppm NO, 3.7 mm above the fuel nozzle**

DNI Modeling of Broadband Stokes Vibrational ERE CARS

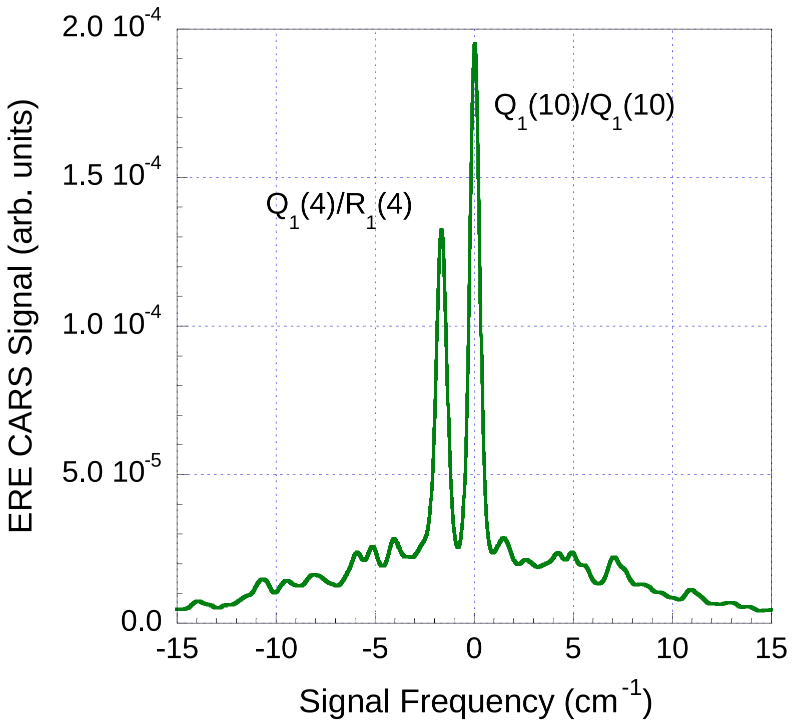
- **Same set of time-dependent density matrix equations as for scanning ERE CARS.**
- **Multi-mode laser models used for Stokes (50 cm^{-1} FWHM) and for probe (0.1-0.2 cm^{-1} FWHM). Random phase, Gaussian random amplitude for the modes.**
- **Time-dependent ERE CARS signal calculated. The signal is then Fourier transformed to generate the ERE CARS spectrum.**

DNI Modeling of Broadband Stokes Vibrational ERE CARS

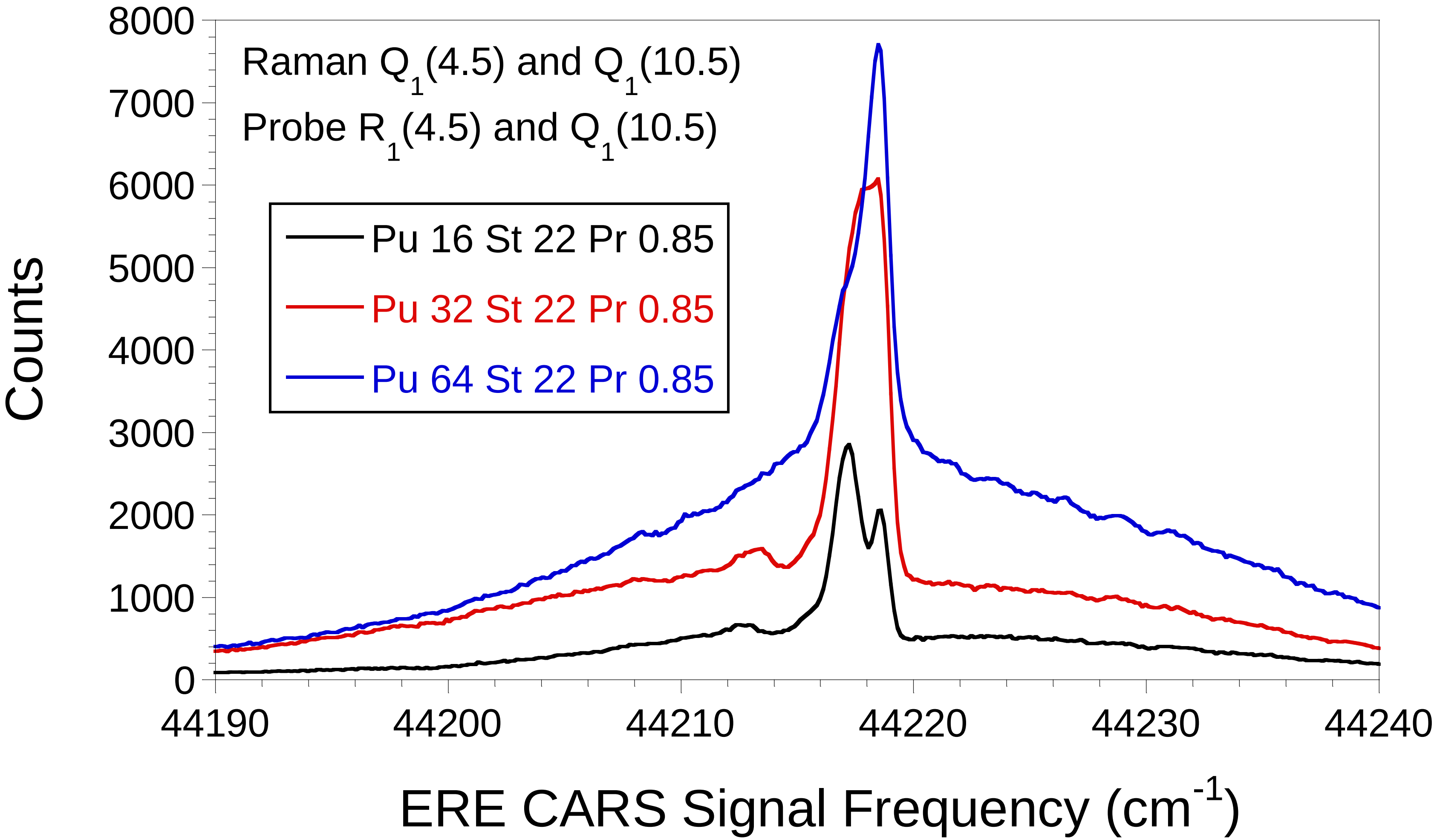
Experiment



Theory



Saturation Effects in Broadband Stokes Vibrational ERE CARS



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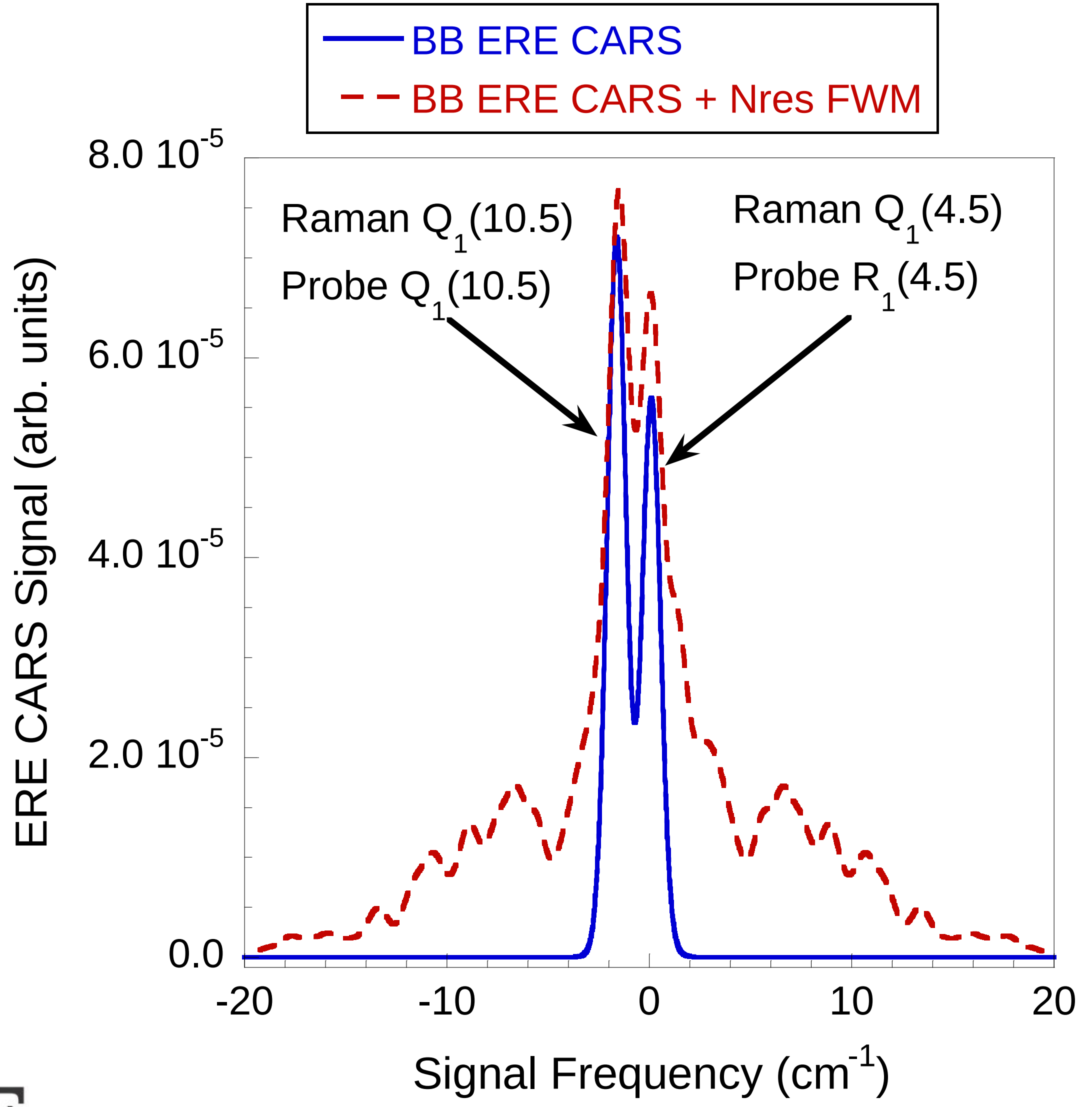
Conclusions

- Density matrix model for NO ERE CARS developed for both scanning and broadband ERE CARS.
- Theoretical spectra are in good agreement with experiment except for probe scans with high pump and Stokes powers.
- Multimode laser models for the Stokes and UV probe beams appear to give good results for the broadband Stokes ERE CARS process.

Future Work

- Comparison of NO measurements by ERE CARS and LIF in high-pressure counterflow flames – the high-pressure flame facility at Purdue needed some extensive modification, should be operational this spring.
- Incorporation of the AC Stark effect in the density matrix code.
- Investigation of saturation and Stark effects for broadband Stokes ERE CARS.

DNI Modeling of Broadband Stokes ERE CARS in Nitric Oxide



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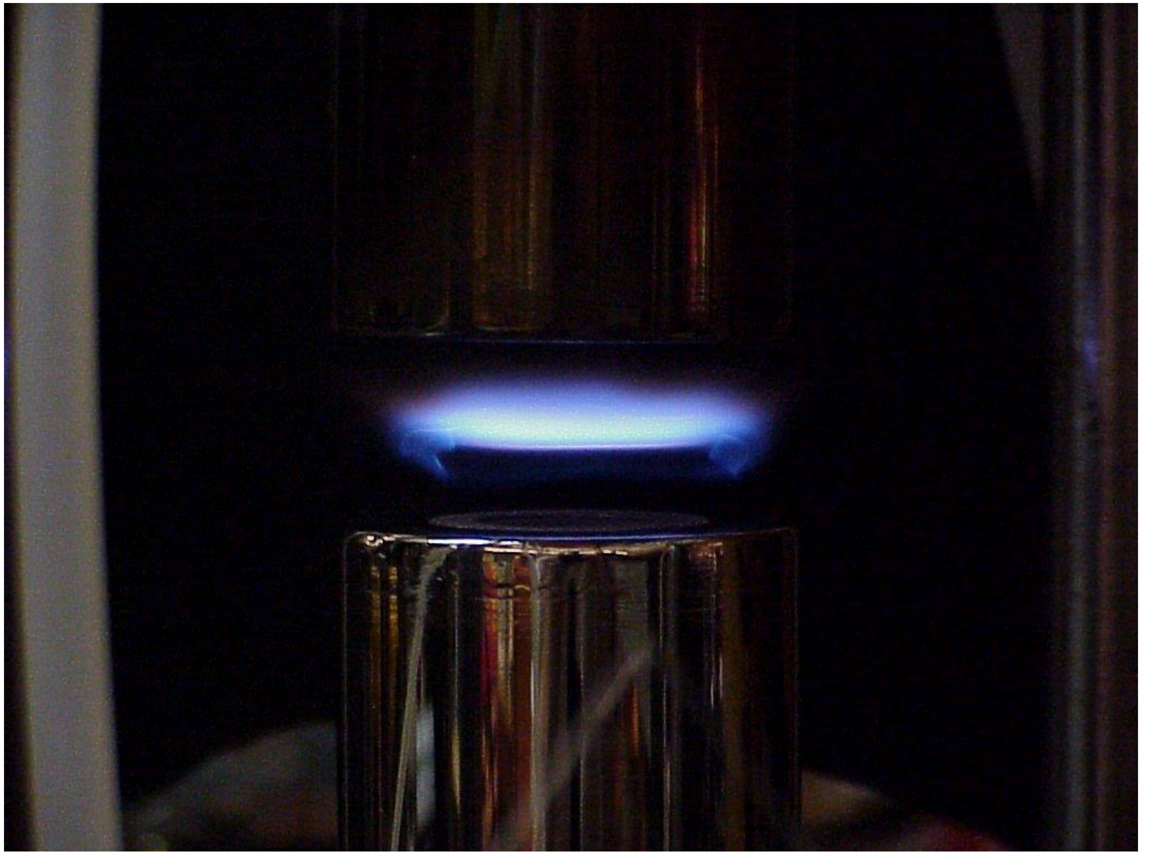
NO Measurements in Nonpremixed Counterflow Flames

Fuel and oxidizer nozzles separated by 20 mm

Fuel = H_2
Oxidizer = air or O_2

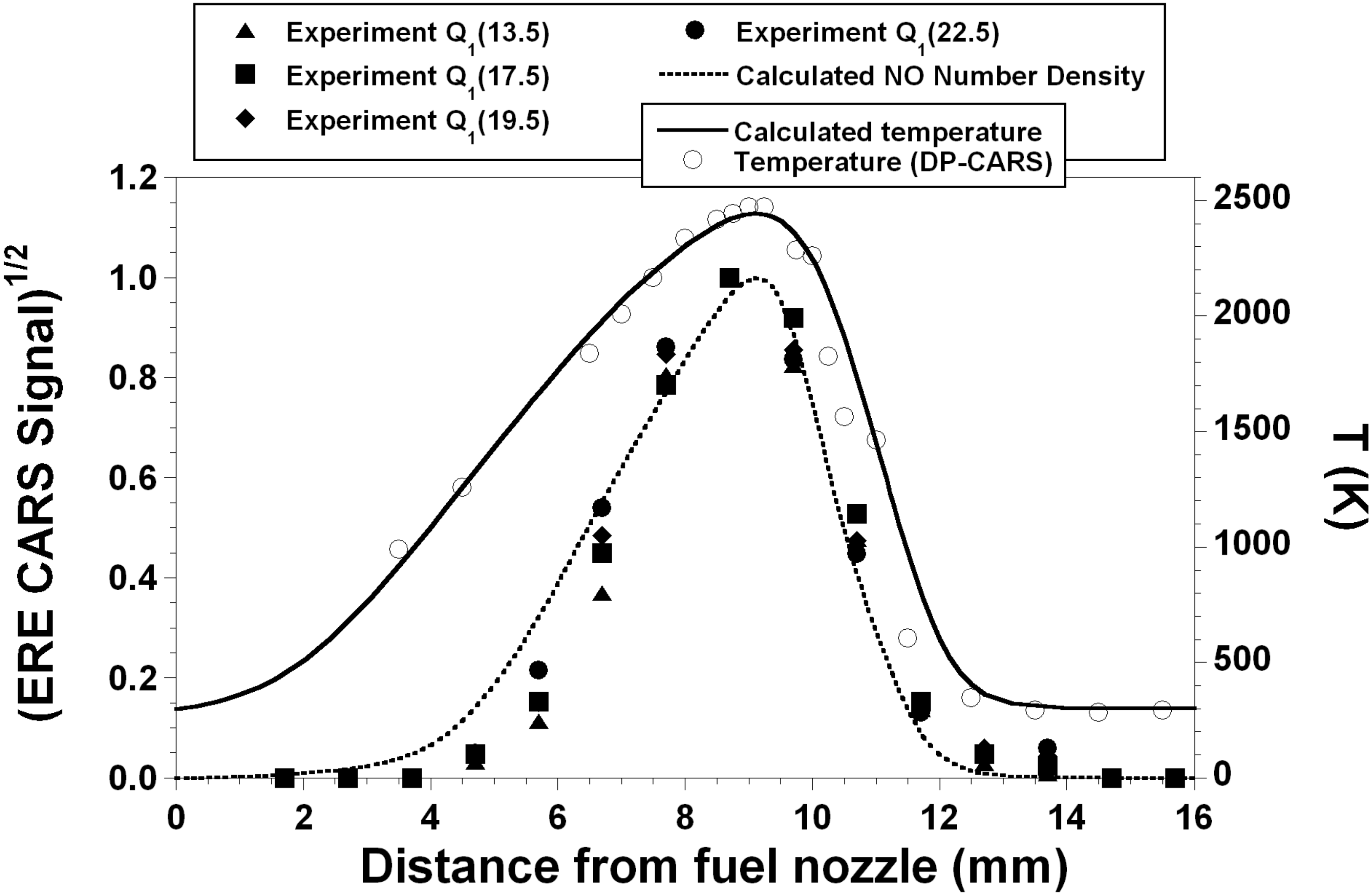
Fuel or Oxidizer Diluents = N_2, CO_2



Broadband Vibrational ERE-CARS System Experimental Parameters

- Pump, Stokes and probe beam energies were 60 mJ/pulse, 40 mJ/pulse, and 1.2 mJ/pulse, respectively in the probe volume; beam waists ~200 μm
- 1-meter spectrometer with blazed grating (3600 gr/mm) was used to isolate the signal which was recorded using a back-illuminated CCD imaging camera (Andor Technology Model DU440-BU)
- Spectrometer's spectral dispersion = 0.146 cm^{-1} /pixel
- H_2/Air Flame measurements were made with 1 mm spatial resolution

ERE CARS Measurements of NO profiles in Counterflow H_2/Air Flame



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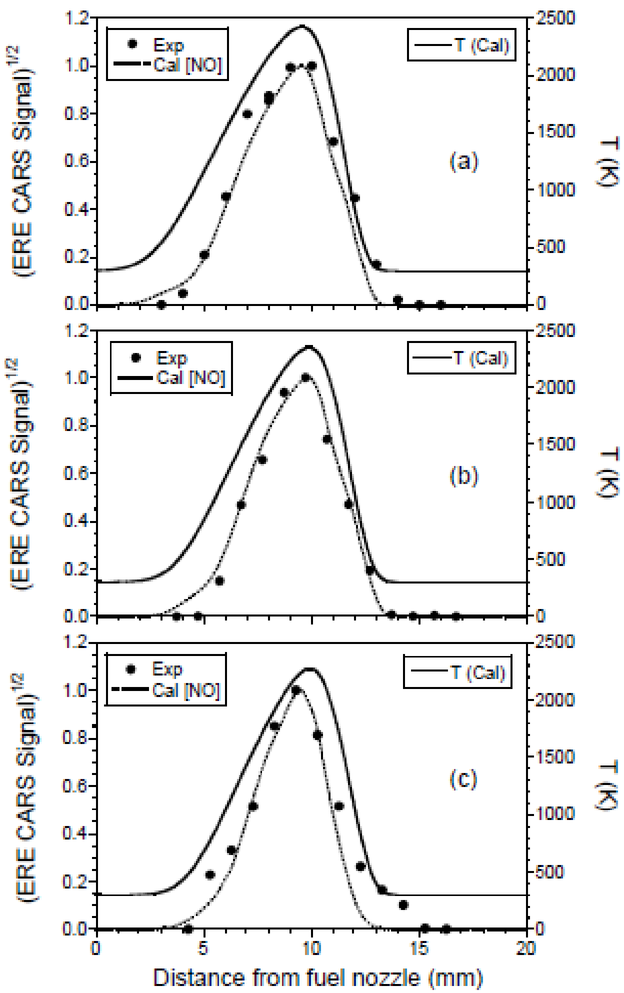
Comparison of Experimental and Calculated NO Concentration Profiles in H_2 / Air counter-flow flames with dilution of H_2 with either N_2 or CO_2



N_2 10% CO_2

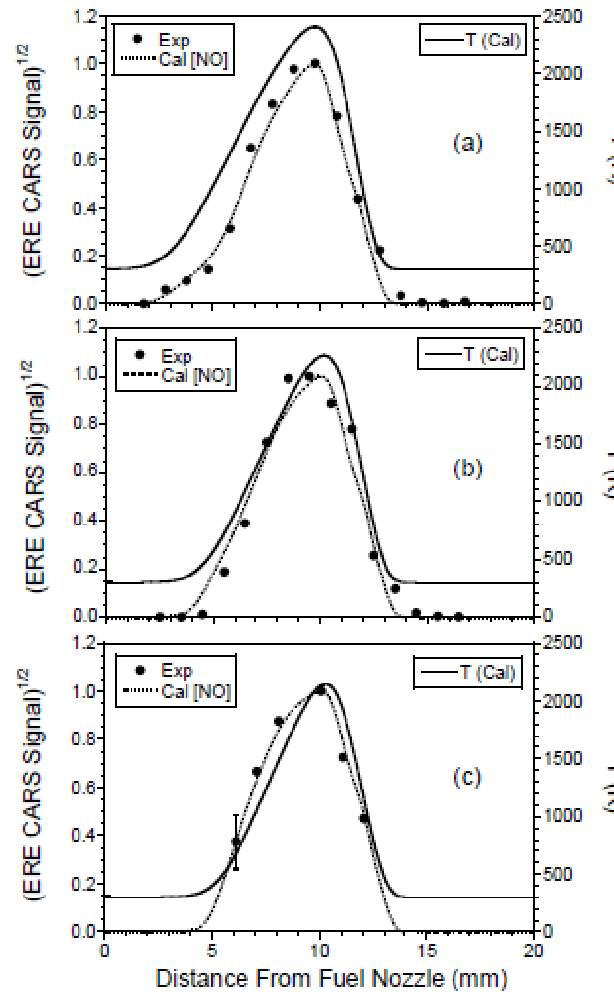
480 ppm ⟷ 420 ppm

N_2 25% CO_2

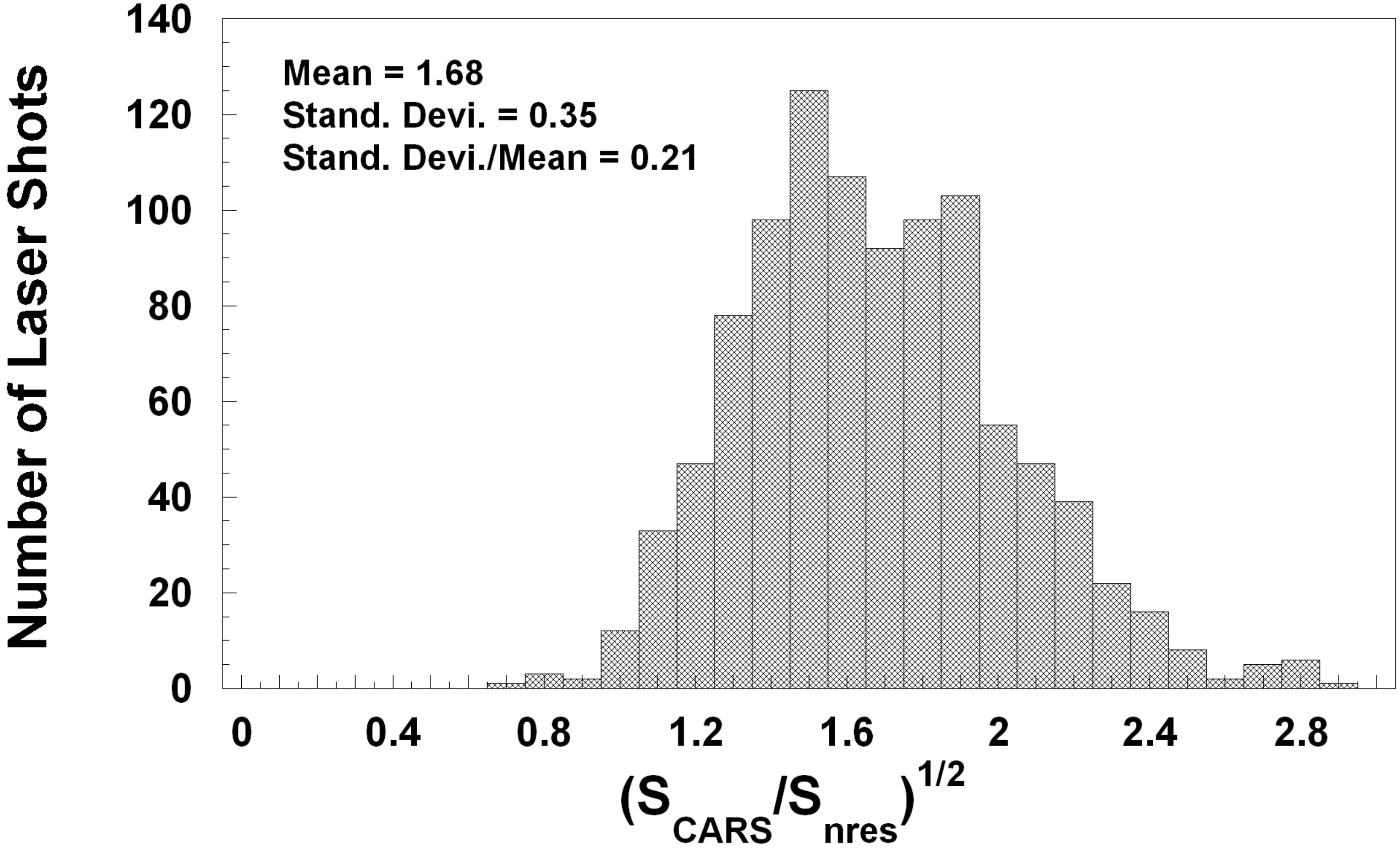
300 ppm ⟷ 180 ppm

N_2 35% CO_2

200 ppm ⟷ 80 ppm

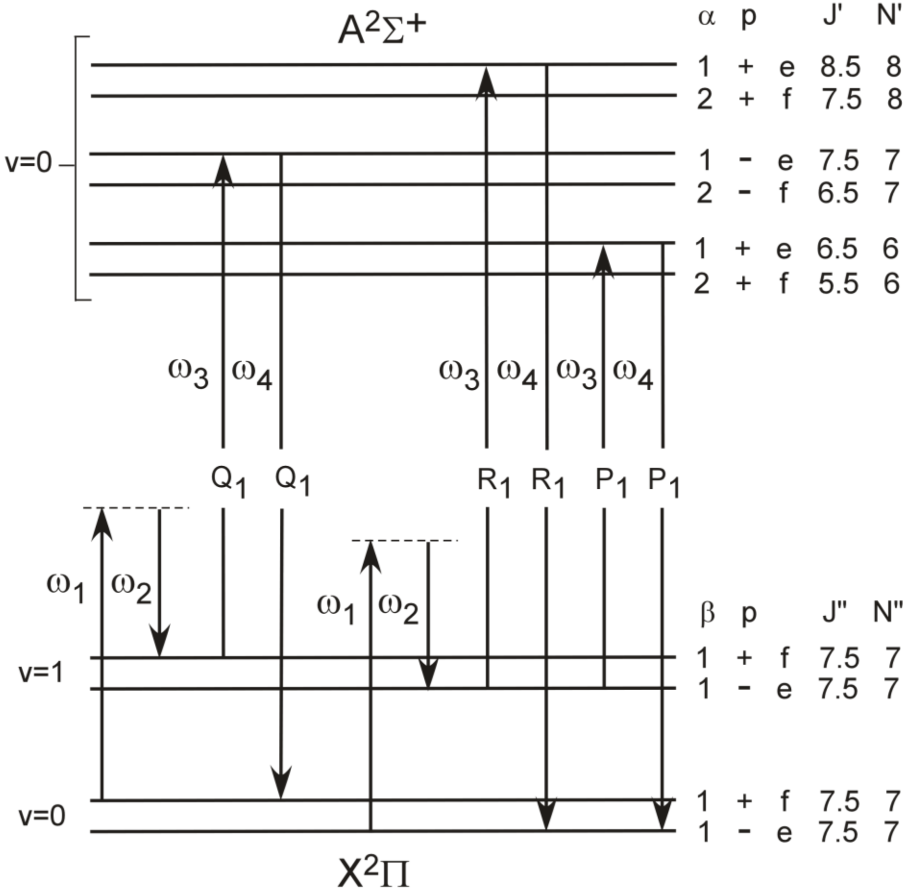


Statistics of Single-Shot NO ERE CARS Measurements in the Counterflow H_2/Air Flame: $Q_1(19.5)$ Line, 10.7 mm from Fuel Nozzle

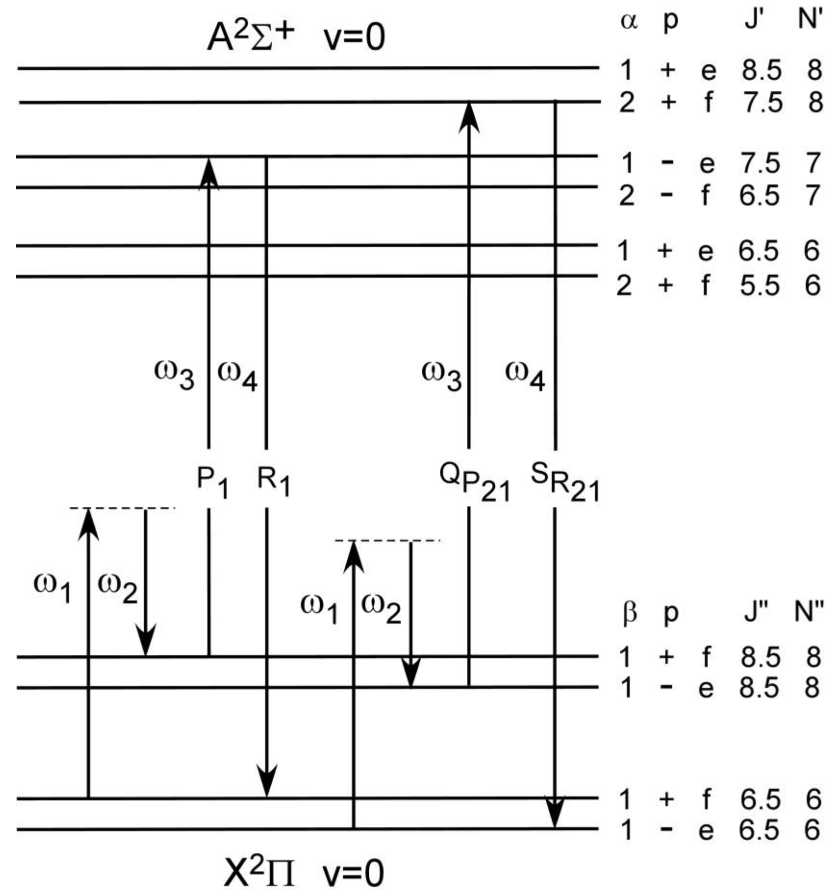


Broadband Pure Rotational NO ERE CARS

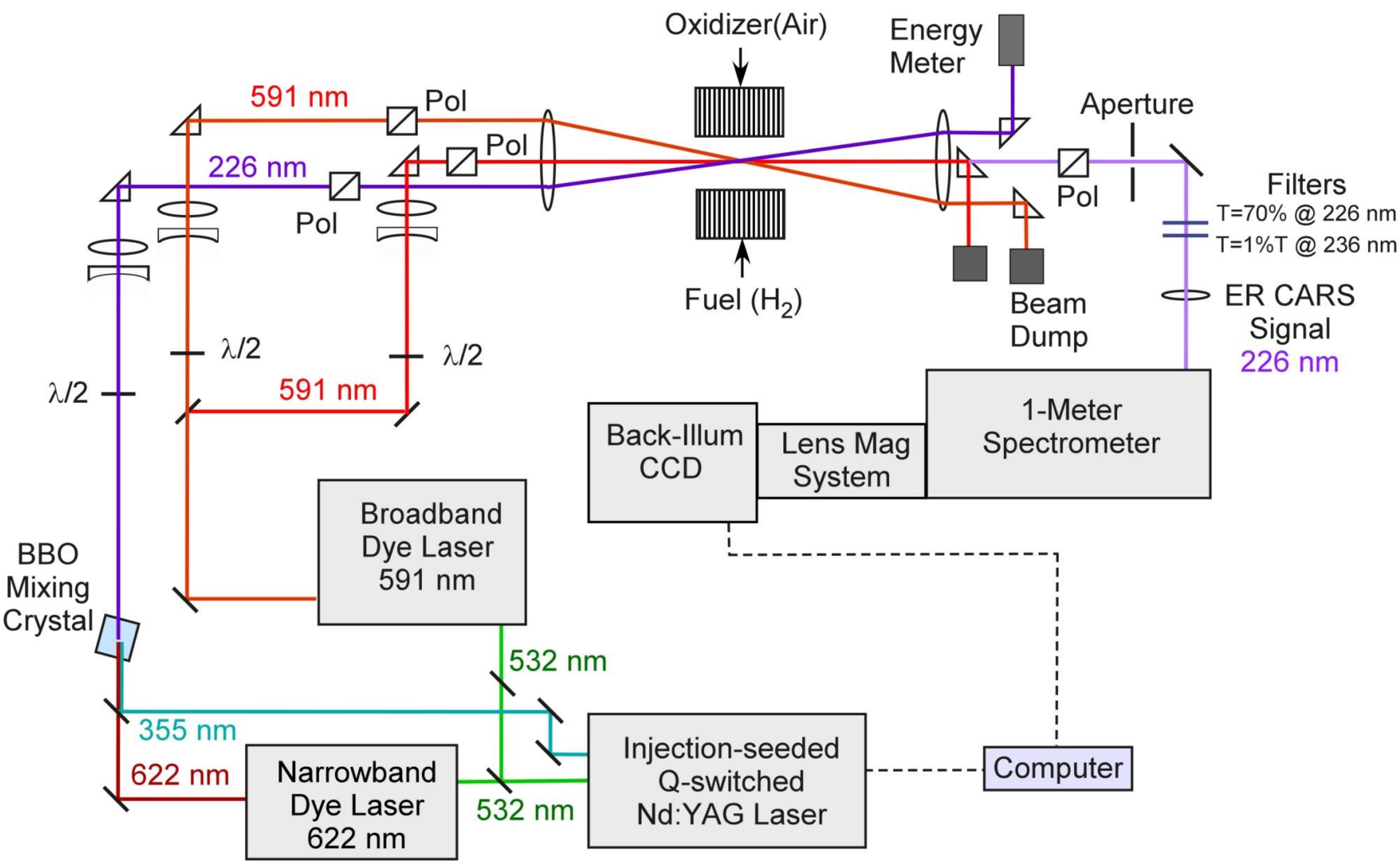
Vibrational ERE CARS



Pure Rotational ERE CARS



Pure Rotational NO ERE CARS



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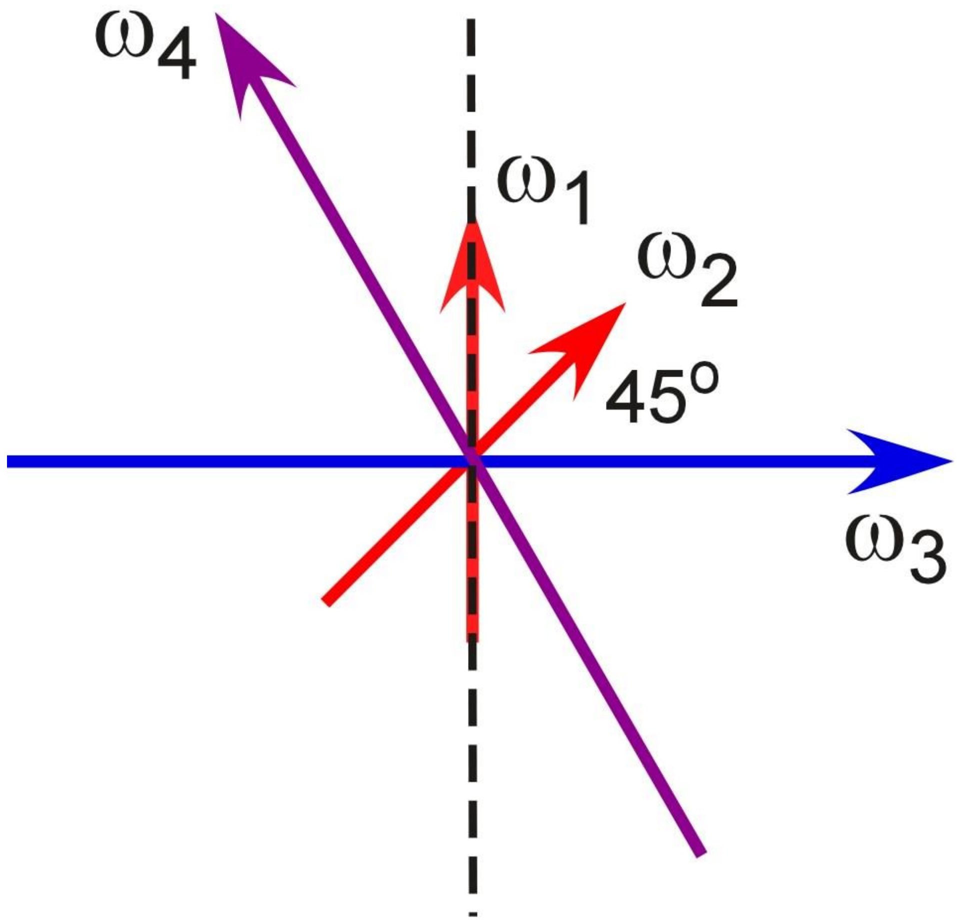
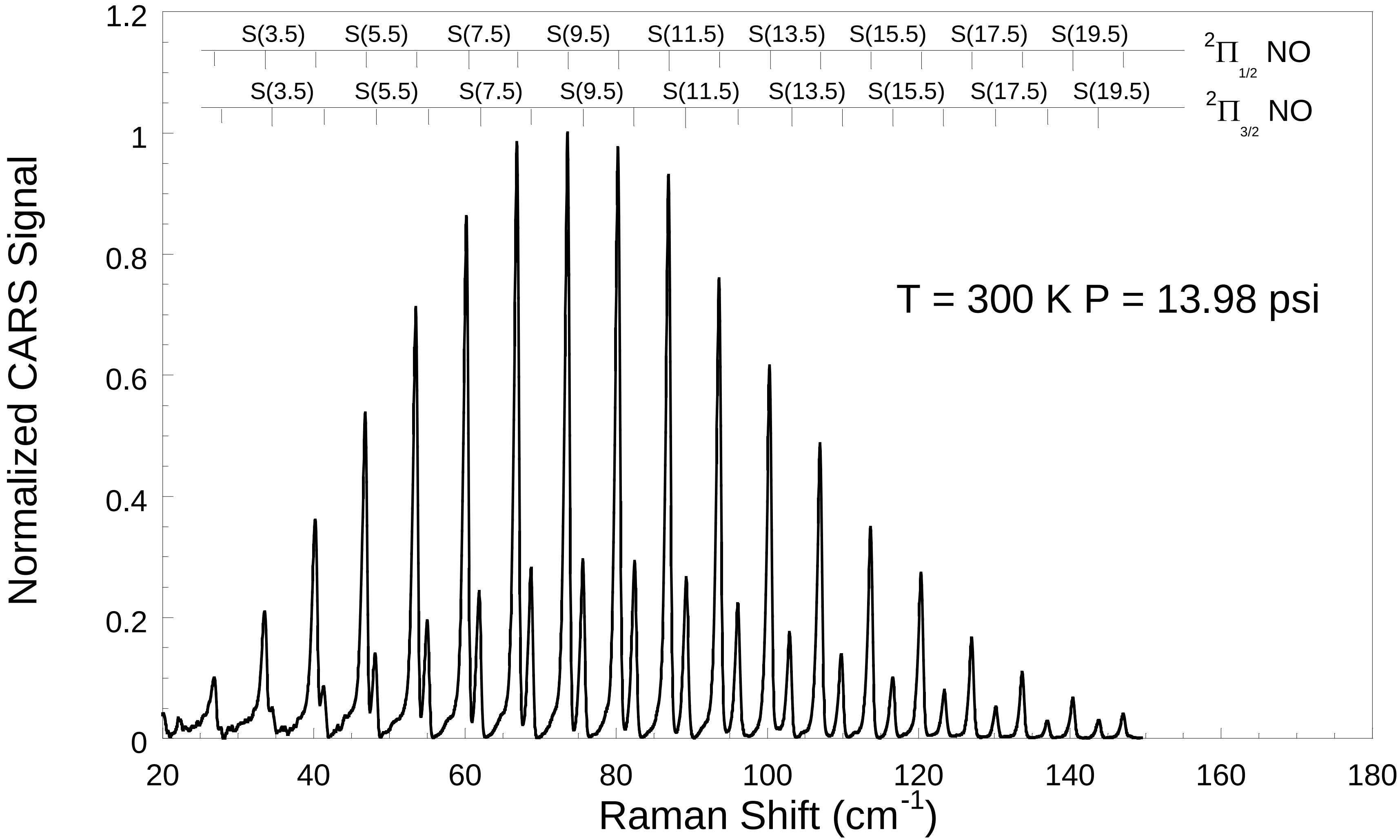
Polarization arrangement of pump (ω_1), probe (ω_3), Stokes (ω_2) and the resulting signal beam (ω_4) for Pure Rotational CARS



Pure Rotational CARS/ERE-CARS System Experimental Parameters

- For pure rotational CARS (without Electronic Resonance)
  - 355 nm UV beam with FWHM approx. 0.003 cm^{-1} , was used as probe beam
  - a 532 nm beam was used to pump the broadband Stokes beam at 591 nm which was split into 2 parts. FWHM of 591 nm beam was 300 cm^{-1} with energy of about 30 mJ/pulse for each beam
  - Measurements were made with varying ratios of NO and N_2 in a pressure vessel 6 cm in diameter and 25 cm long
- For pure rotational ERE CARS
  - the probe beam was at 226 nm with energy < 1mJ /pulse with FWHM approx. 0.1 cm^{-1}
  - the two 591 nm beams were combined and the resulting beam had approx. 50 mJ/pulse at the probe volume

Pure Rotational NO CARS



- **Stokes beam with FWHM 300 cm^{-1} covers numerous Raman transitions.**
- **Probe beam wavelength of 355 nm at spectral dispersion of 0.059 cm^{-1} /pixel.**

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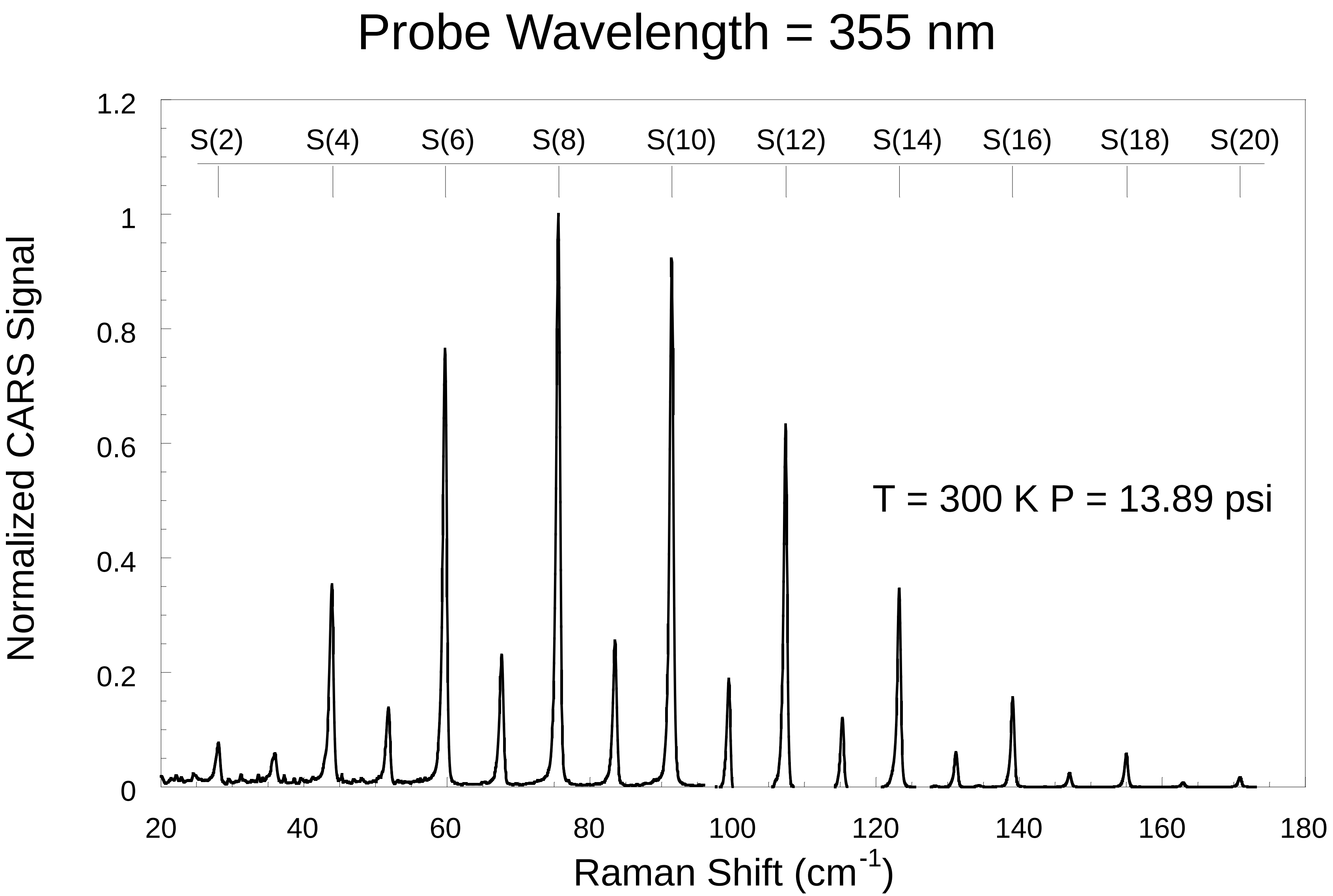
Pure Rotational N_2 CARS



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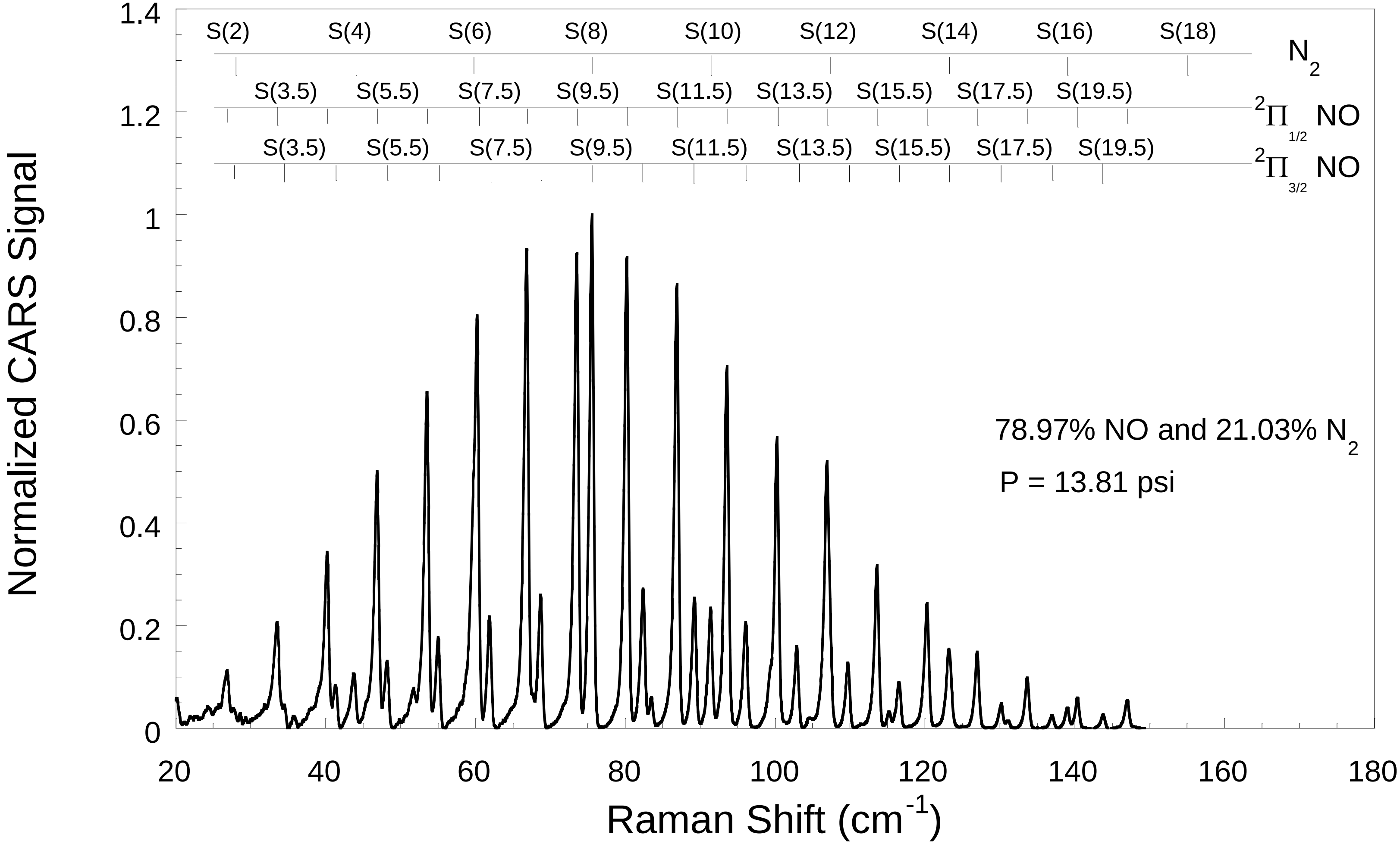
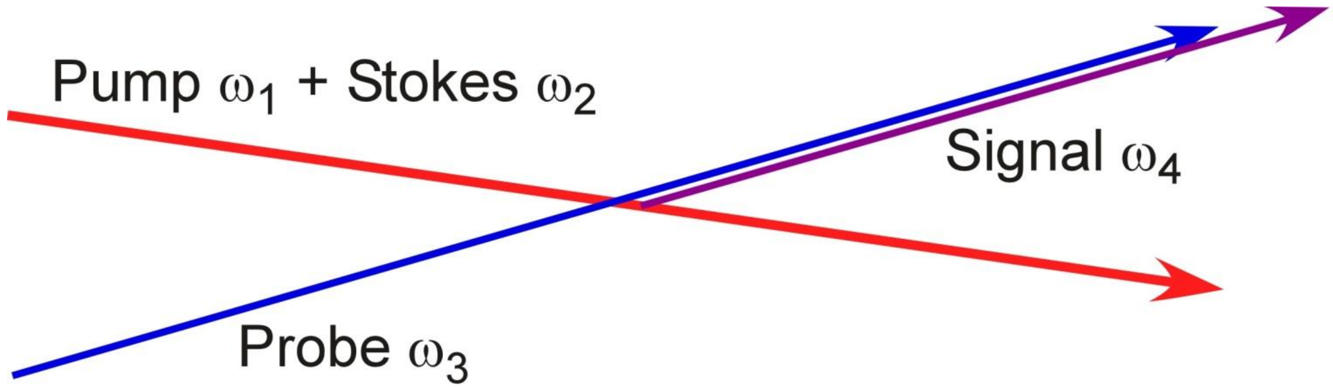
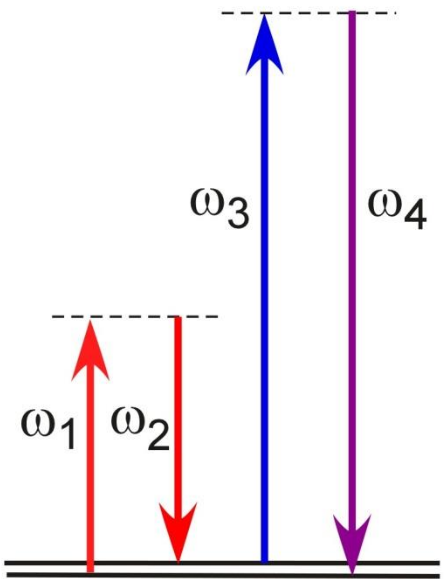
Pure Rotational NO+N_2 CARS



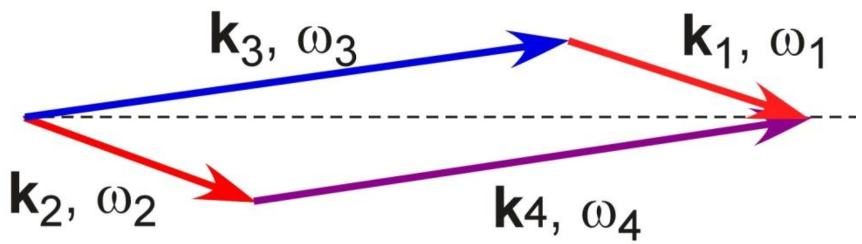
- **Significant overlap between the NO and N_2 pure rotational spectra. We expected this to provide real time, in-situ reference to get NO/N_2 concentration ratio along with temperature in flames.**

Two-Beam Pure Rotational ERE CARS





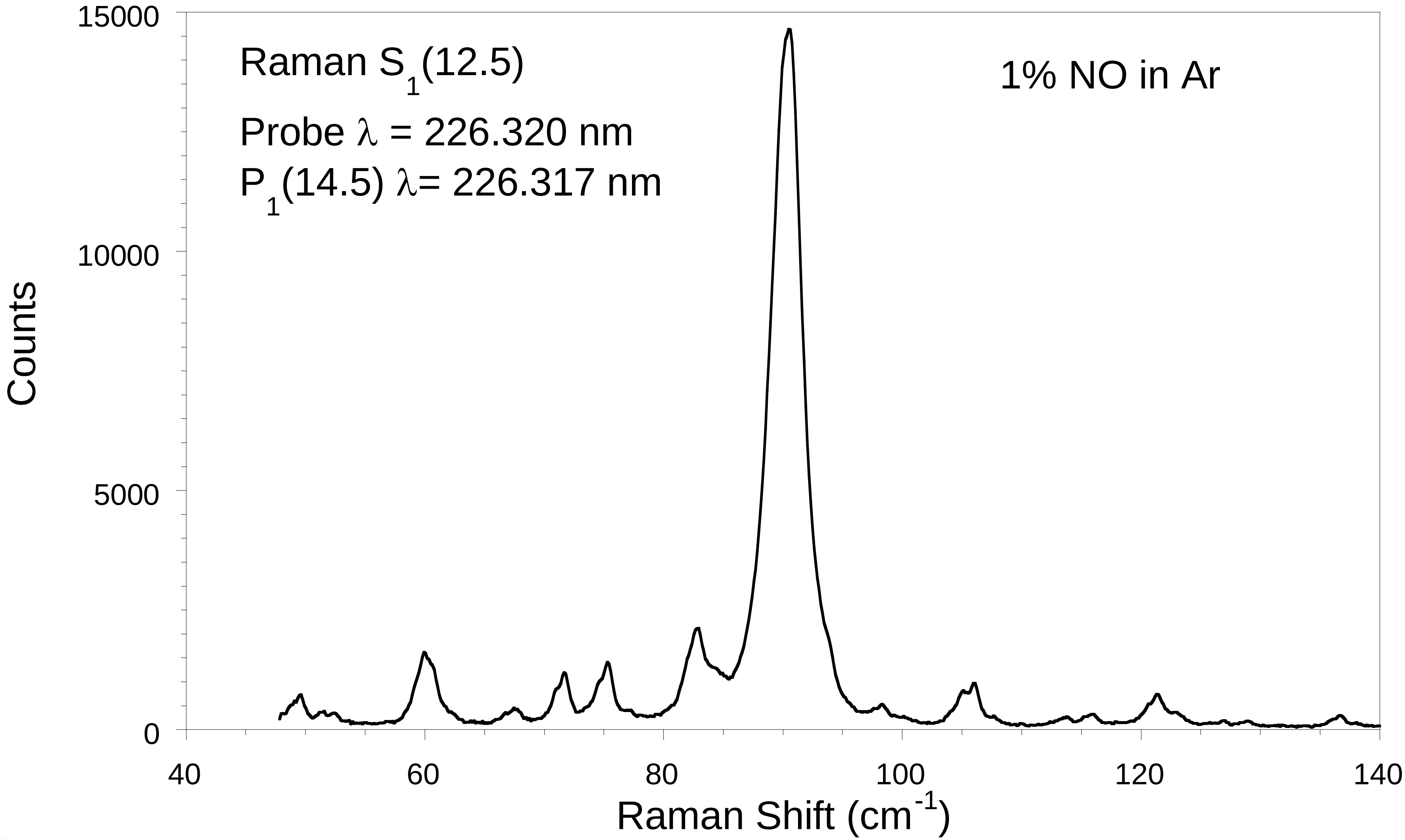
$$\omega_4 = \omega_1 - \omega_2 + \omega_3$$



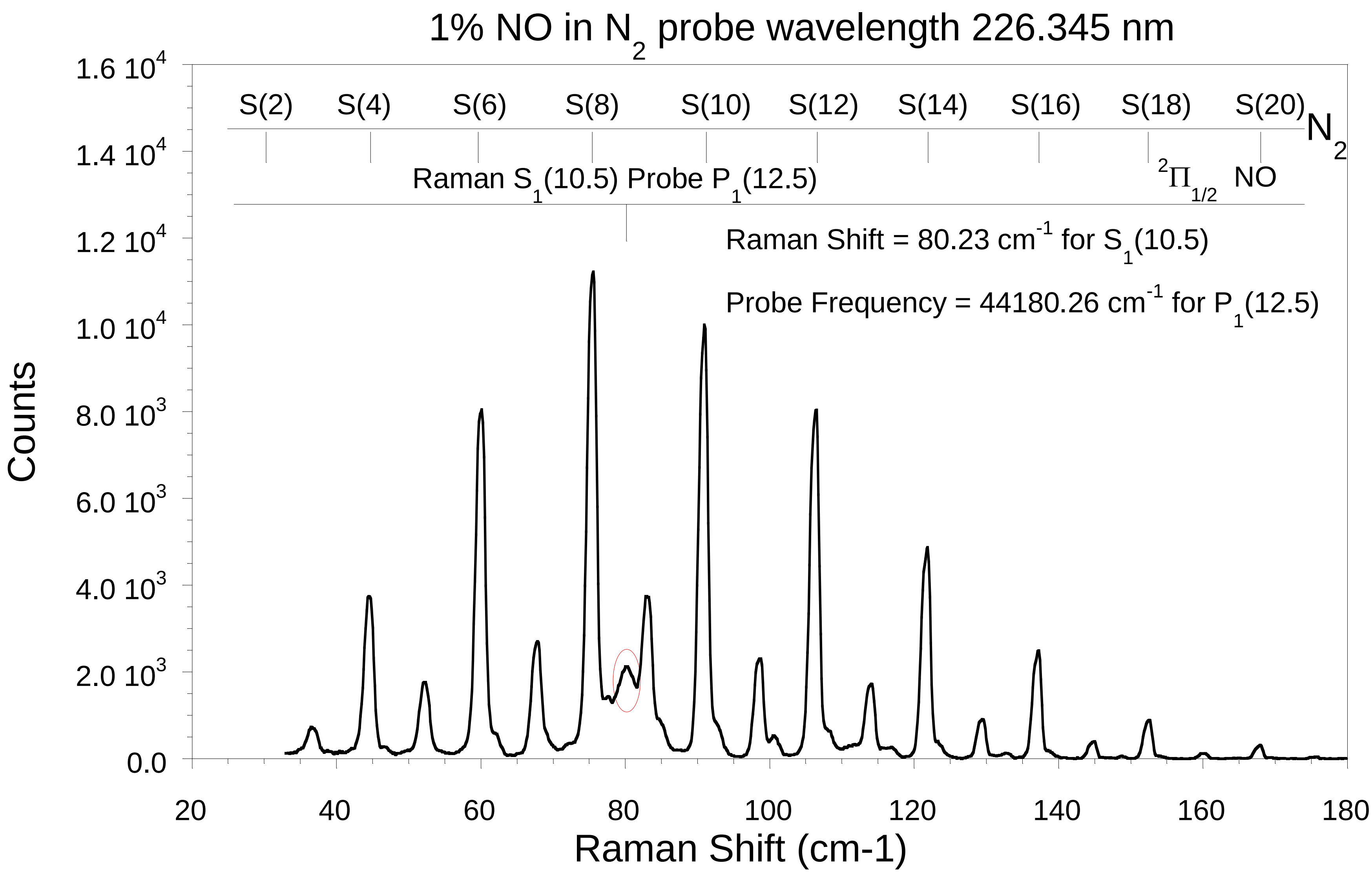
$$\mathbf{k}_1 + \mathbf{k}_3 = \mathbf{k}_2 + \mathbf{k}_4$$

Pure Rotational NO ERE CARS

Probe Wavelength = 226.317 nm, 1% NO in Ar



Pure Rotational NO ERE CARS



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Pure Rotational NO ERE CARS