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EFFECTS OF N_2-CO POLARIZATION BEATING ON FEMTOSECOND COHERENT ANTI-STOKES RAMAN SCATTERING SPECTROSCOPY OF N_2 (POSTPRINT)

Sukesh Roy

Spectral Energies, LLC

Daniel Richardson, Paul J. Kinnius, and Robert P. Lucht

Purdue University

James R. Gord

Combustion Branch
Turbine Engine Division

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6. AUTHOR(S)

Sukesh Roy (Spectral Energies, LLC)
Daniel Richardson, Paul J. Kinnius, and Robert P. Lucht (Purdue University)
James R. Gord (AFRL/RZTC)

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Spectral Energies, LLC
5100 Springfield Street, Suite 301
Dayton, OH 45431

Purdue University
School of Mechanical Engineering
585 Purdue Mall
West Lafayette, IN 47907

Combustion Branch (AFRL/RZTC)
Turbine Engine Division
Air Force Research Laboratory, Propulsion Directorate
Wright-Patterson Air Force Base, OH 45433-7251
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14. ABSTRACT

The effects of broadband excitation employing femtosecond laser pulses on the coherent anti-Stokes Raman scattering (CARS) spectroscopy of N_2 are investigated. We have previously demonstrated that the dephasing rate of the coherence, established by the impulsive excitation of N_2 using femtosecond pump and Stokes beams, can be used for measuring gas-phase temperature in chemically reacting flows. The objective of the current work is to investigate the effects of polarization beating between N_2 and CO on the measured gas-phase temperature using time-resolved femtosecond CARS spectroscopy of N_2.

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Effects of N_2–CO polarization beating on femtosecond coherent anti-Stokes Raman scattering spectroscopy of N_2

Sukesh Roy,[1,a)] Daniel Richardson,[2] Paul J. Kinnius,[2] Robert P. Lucht,[2] and James R. Gord[3]
[1]*Spectral Energies, LLC, 5100 Springfield Street, Ste. 301, Dayton, Ohio 45431, USA*
[2]*School of Mechanical Engineering, Purdue University, 585 Purdue Mall, West Lafayette, Indiana 47907, USA*
[3]*Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio 45433, USA*

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The effects of broadband excitation employing femtosecond laser pulses on the coherent anti-Stokes Raman scattering (CARS) spectroscopy of N_2 are investigated. We have previously demonstrated that the dephasing rate of the coherence, established by the impulsive excitation of N_2 using femtosecond pump and Stokes beams, can be used for measuring gas-phase temperature in chemically reacting flows. The objective of the current work is to investigate the effects of polarization beating between N_2 and CO on the measured gas-phase temperature using time-resolved femtosecond CARS spectroscopy of N_2. © *2009 American Institute of Physics*.
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Femtosecond laser-based coherent anti-Stokes Raman scattering (CARS) spectroscopy for measuring gas-phase temperature and species concentrations has been the focus of intense research for the last several years.[1–4] The interest in femtosecond laser-based CARS spectroscopy is driven by the advent of off-the-shelf femtosecond laser systems, coupled with the potential for this technique to overcome the temperature and species-concentration measurement challenges encountered in nanosecond and picosecond CARS spectroscopy applied to gas-phase reacting media.[5] The ultrashort pulse width, wide bandwidth, and high repetition rate of femtosecond lasers facilitate (1) suppression of the nonresonant CARS signal, (2) establishment of a very strong coherence in the Raman medium through utilization of the full bandwidth, (3) measurements at rates of 1 kHz or greater,[3] and (4) performance of CARS measurements with only one laser beam, thereby eliminating the need for phase-matching of three laser beams in highly turbulent reacting flows.[6] In femtosecond CARS the ultrashort pump and Stokes beams coherently excite the accessible transitions of the probe molecule, creating a phase relationship between various transitions whose resonance frequencies differ slightly. This in-phase coherence created by the pump and Stokes pulses then dephases because of the frequency spread between the excited transitions within the vibrational band. When probed by a third laser beam, this dephasing is revealed as a temporal decay of the CARS signal. We have recently demonstrated that the coherence-dephasing rate during the first few picoseconds after the initial impulsive excitation is dependent only on the temperature and is nearly independent of collisions up to 50 bars.[7] This is very important for the application of this spectroscopic technique to high-pressure reacting flows where modeling the collisional dynamics for extracting temperature from experimental CARS signals is a very challenging task.[4]

The objective of this work is to investigate the effect of intermolecular polarization interference of CARS signal on the coherence dephasing of the N_2 molecule after impulsive excitation using femtosecond pump and Stokes pulses.[8] It is important to understand the coherence-dephasing dynamics of the N_2 molecule in the presence of other molecules such as CO since the broad pulse widths of the pump and Stokes lasers simultaneously excite both molecules, as shown in Fig. 1. In air-fed reacting flows, N_2 is present everywhere and N_2 CARS is a very effective means of measuring gas-phase temperature. Femtosecond CARS spectroscopy has also been used to determine the concentration of molecular species in a mixture of liquids and gases. Leonarhdt *et al.*[9] first demonstrated the mode beating between pyridine and cyclohexane simultaneously excited by ultrashort pump and Stokes pulses. Knopp *et al.*[10] used femtosecond CARS spectroscopy to determine the concentration of gas species in a binary mixtures of ortho- and paradeuterium, and Pestov *et al.*[11] used femtosecond CARS to investigate the vibrational dynamics in water-methanol mixtures. Pestov *et al.*[11] observed a substantial change in the CARS signal-decay rates during the first 3 ps after the initial impulsive excitation when the concentration of methanol in water was varied from 100% to 25%. This variation in the decay rates was attributed to the formation of supermolecular structures.

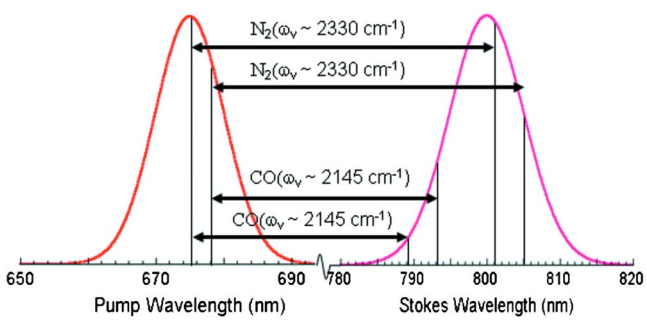

FIG. 1. (Color online) Raman excitation diagram of N_2 and CO with 80 fs pump and Stokes pulses. In the ground electronic state, 2330 and 2145 cm^{-1} correspond to the excitation of $v=0$ to $v=1$ transitions of N_2 and CO, respectively.

a)Electronic mail: sroy@woh.rr.com.

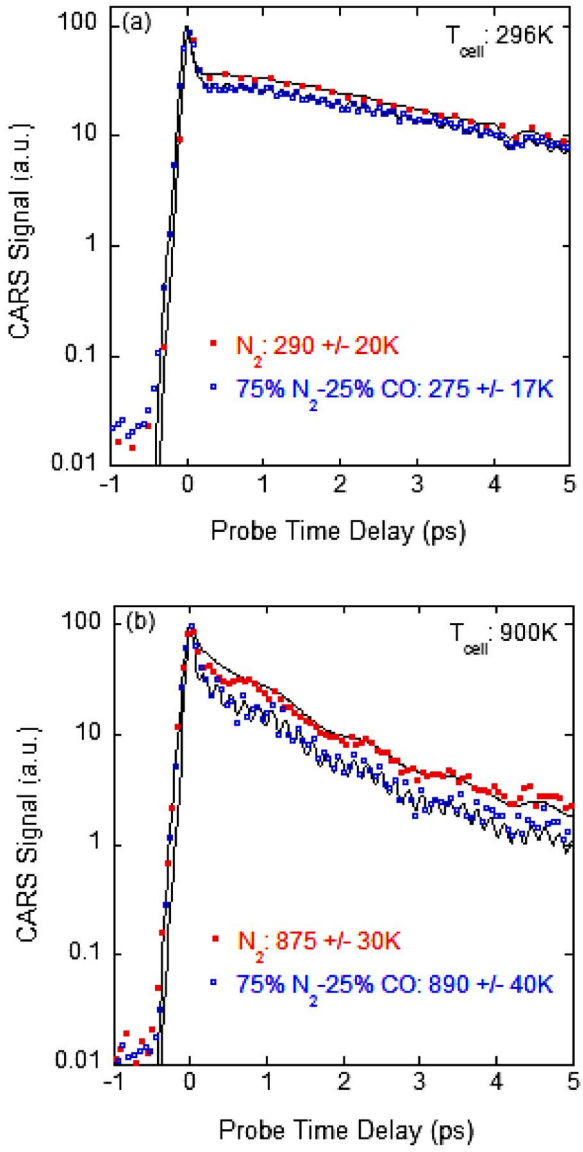

FIG. 2. (Color online) Time-resolved femtosecond CARS signal for pure N_2 and for a mixture of 25% CO and 75% N_2 at various temperatures. The symbols represent experimental data points and the solid lines correspond to the best-fit results obtained by fitting the experimental data points with the data calculated from the theoretical model described in Ref. 2.

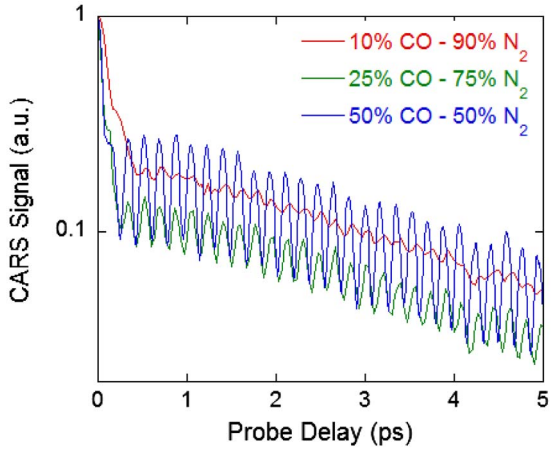

FIG. 3. (Color online) Time-resolved femtosecond CARS signal for mixtures of N_2 and CO, showing the vibrational beat frequency between the two CARS polarization. The decay rate of the CARS signals is unchanged as the concentration of CO is varied.

Since our thermometry approach depends on the coherence-dephasing rates after the initial excitation, it is important to know whether the excitation of a secondary molecule such as CO will significantly alter the dephasing rates because of the polarization interference of CARS signals from N_2 and CO, thereby complicating gas-phase temperature measurements achieved with femtosecond lasers.

The experimental system has been discussed in detail by Roy *et al.*[3] Briefly, a modelocked Ti:sapphire regenerative amplifier producing a 1 kHz train of 80 fs pulses at ~800 nm was used to pump an optical parametric amplifier (OPA) and also to provide the Stokes beam for the CARS signal-generation process. The signal output of the OPA at ~1350 nm was frequency doubled to generate the pump and probe beams for the current experiment. The pulse width of the pump and probe beams at ~675 nm was measured to be ~75 fs. The bandwidths of the pump and Stokes lasers were measured to be 220 and 160 cm^{-1}, respectively. The CARS signal around 583 nm was detected with a high-speed photodiode and a lock-in amplifier. Time-resolved CARS signals were obtained by delaying the probe beam with respect to the pump and Stokes beams. Experiments were performed in a heated gas cell where the ratio of the N_2 and CO was systematically varied. The temperature of the cell was limited to 900 K. Measurements were also performed in an atmospheric-pressure C_2H_4-air flame stabilized over a Hencken burner to investigate the effect of CO on the measured time-resolved N_2 CARS signal.

Figure 1 displays the femtosecond laser-based excitation diagram for N_2 and CO. It is shown that the pump and Stokes lasers have sufficient bandwidth that they simultaneously excite the Raman transitions of N_2 and CO at ~2330 and ~2145 cm^{-1}, respectively. Gas-phase temperature measurements for pure N_2 and for a mixture of 75% N_2 and 25% CO were performed in a gas cell over a temperature range of 300–900 K. The CARS signal decay due to frequency-spread coherence dephasing for 300 and 900 K are shown in Fig. 2. For a mixture of N_2 and CO, the modulations observed in Fig. 2 are due to the polarization beating between the fundamental vibrational modes at a frequency of ~5.56 THz, as expected from the 185 cm^{-1} difference in vibrational frequencies. The blue and red lines represent experimental data, and the black lines correspond to the best-fit results obtained by fitting the experimental data points with the data calculated from the theoretical model described in Ref. 2. In our previous work it was shown that the rate at which coherence dephasing occurs is dependent only on temperature during the first few picoseconds after the initial impulsive excitation.[2] The temperatures evaluated by fitting the theoretical results with the experimental ones are within the standard deviation of the fitting. In our earlier work we have noticed that this theoretical model is sensitive to within ±50 K for a temperature range of 300–2500 K. It is evident from Fig. 2 that the presence of 25% CO in 75% N_2 has not affected the coherence-dephasing rates significantly, which demonstrates that the excitation of secondary species such as CO does not affect the temperatures measured based on coherence dephasing of the N_2 molecule.

Figure 3 shows the femtosecond CARS signal for mix-

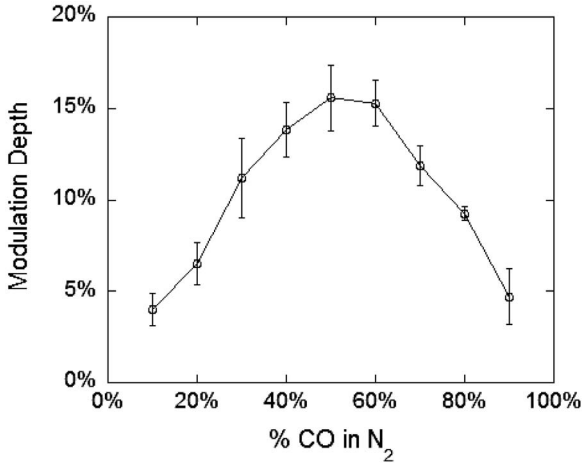

FIG. 4. Modulation depth of the beat frequency between N_2 and CO as a function of CO concentration in N_2. The pump and Stokes laser wavelengths were centered at ~675 and ~800 nm, respectively.

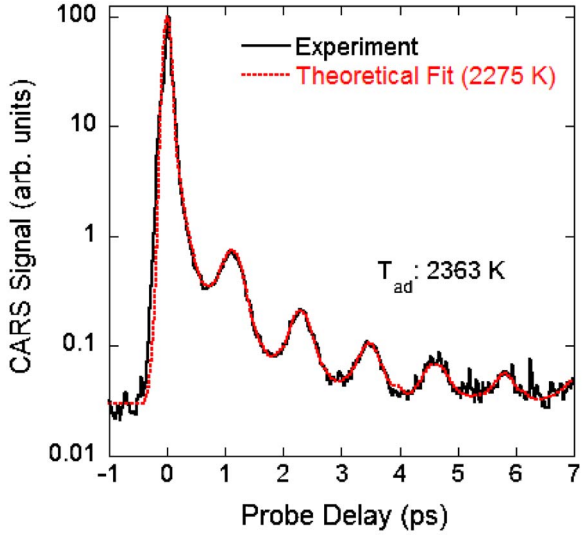

FIG. 5. (Color online) Time-resolved femtosecond CARS signal in an atmospheric-pressure C_2H_4-air flame for an equivalence ratio of 1.2.

tures of N_2 and CO at various concentration ratios. The modulation depth of the beat frequency between N_2 and CO changes with the concentration of CO in N_2, as expected. It is also clear that the effects of molecular interference might be completely negligible for a secondary molecule with concentration less than 5% of the primary molecule. As is evident in Fig. 4, the modulation depth of the beat frequency between N_2 and CO can be used to determine the concentration of the secondary molecule with respect to N_2. In Fig. 4 the modulation depth is shown as a percentage of the peak CARS signal at $t=0$ versus the percent CO in N_2.

Measurements were also performed in a near-adiabatic, atmospheric-pressure C_2H_4-air flame stabilized over a Hencken burner.[3] The typical CO concentration for this flame was varied between ~60 ppm and ~6% over an equivalence-ratio range of 0.6–1.2.[12] Figure 5 shows the time-resolved femtosecond CARS signal for an equivalence ratio of 1.2. It is clear that the Raman excitation of CO has no influence on the resulting N_2 femtosecond CARS signal. The extracted temperature is within ~4% of the adiabatic flame temperature (T_{ad}) of 2363 K. The evaluated (or best-fit) temperature has been determined to be within 50 K of the actual temperature.

In conclusion, it has been demonstrated that the excitation of secondary molecules such as CO with broad femtosecond laser pulses has no impact on the temperatures measured from time-resolved N_2 femtosecond CARS in reacting flows specifically for the concentrations available in typical reacting flows. It has also been shown that the depth of the modulation arising because of beating between the molecular signals has the potential for use in extracting concentrations of other major species (typically >5%).

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