Interference-free coherence dynamics of gas-phase molecules using spectral focusing

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Abstract: Spectral focusing using broadband femtosecond pulses to achieve highly selective measurements has been employed for numerous applications in spectroscopy and microspectroscopy. In this work we highlight the use of spectral focusing for selective excitation and detection of gas-phase species. Furthermore, we demonstrate that spectral focusing, coupled with time-resolved measurements based upon probe delay, allows the observation of interference-free coherence dynamics of multiple molecules and gas-phase temperature making this technique ideal for gas-phase measurements of reacting flows and combustion processes.

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OCIS codes: (300.6230) Spectroscopy, coherent anti-Stokes Raman scattering; (320.7100) Ultrafast measurements; (280.1740) Combustion diagnostics.

References and Links

1. T. Lang, K.-L. Kompa, and M. Motzkus, "Femtosecond CARS on H_2," Chem. Phys. Lett. **310**(1-2), 65–72 (1999).
2. P. Beaud, H.-M. Frey, T. Lang, and M. Motzkus, "Flame thermometry by femtosecond CARS," Chem. Phys. Lett. **344**(3-4), 407–412 (2001).
3. T. Lang, M. Motzkus, H. M. Frey, and P. Beaud, "High resolution femtosecond coherent anti-Stokes Raman scattering: determination of rotational constants, molecular anharmonicity, collisional line shifts, and temperature," J. Chem. Phys. **115**(12), 5418–5426 (2001).
4. R. P. Lucht, S. Roy, T. R. Meyer, and J. R. Gord, "Femtosecond coherent anti-Stokes Raman scattering measurement of gas temperatures from frequency-spread dephasing of the Raman coherence," Appl. Phys. Lett. **89**(25), 251112 (2006).
5. S. Roy, P. J. Kinnius, R. P. Lucht, and J. R. Gord, "Temperature measurements in reacting flows by time-resolved femtosecond coherent anti-Stokes Raman scattering (fs-CARS) spectroscopy," Opt. Commun. **281**(2), 319–325 (2008).
6. S. Roy, D. Richardson, P. J. Kinnius, R. P. Lucht, and J. R. Gord, "Effects of N_2–CO polarization beating on femtosecond coherent anti-Stokes Raman scattering spectroscopy of N_2," Appl. Phys. Lett. **94**(14), 144101 (2009).
7. W. D. Kulatilaka, J. R. Gord, and S. Roy, "Effects of O_2–CO_2 polarization beating on femtosecond coherent anti-Stokes Raman scattering (fs-CARS) spectroscopy of O_2," Appl. Phys. B **102**(1), 141–147 (2011).
8. M. T. Bremer, P. J. Wrzesinski, N. Butcher, V. V. Lozovoy, and M. Dantus, "Highly selective standoff detection and imaging of trace chemicals in a complex background using single-beam coherent anti-Stokes Raman scattering," Appl. Phys. Lett. **99**(10), 101109 (2011).
9. J. D. Miller, M. N. Slipchenko, T. R. Meyer, H. U. Stauffer, and J. R. Gord, "Hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering for high-speed gas-phase thermometry," Opt. Lett. **35**(14), 2430–2432 (2010).
10. S. Roy, W. D. Kulatilaka, D. R. Richardson, R. P. Lucht, and J. R. Gord, "Gas-phase single-shot thermometry at 1 kHz using fs-CARS spectroscopy," Opt. Lett. **34**(24), 3857–3859 (2009).
11. E. T. J. Nibbering, D. A. Wiersma, and K. Duppen, "Ultrafast nonlinear spectroscopy with chirped optical pulses," Phys. Rev. Lett. **68**(4), 514–517 (1992).
12. E. Gershgoren, R. A. Bartels, J. T. Fourkas, R. Tobey, M. M. Murnane, and H. C. Kapteyn, "Simplified setup for high-resolution spectroscopy that uses ultrashort pulses," Opt. Lett. **28**(5), 361–363 (2003).
13. D. Pestov, X. Wang, R. K. Murawski, G. O. Ariunbold, V. A. Sautenkov, and A. V. Sokolov, "Pulse shaping for mode-selective ultrafast coherent Raman spectroscopy of highly scattering solids," J. Opt. Soc. Am. B **25**(5), 768–772 (2008).

14. T. Hellerer, A. M. K. Enejder, and A. Zumbusch, "Spectral focusing: high spectral resolution spectroscopy with broad-bandwidth laser pulses," Appl. Phys. Lett. **85**(1), 25–27 (2004).
15. I. Rocha-Mendoza, W. Langbein, and P. Borri, "Coherent anti-Stokes Raman microspectroscopy using spectral focusing with glass dispersion," Appl. Phys. Lett. **93**(20), 201103 (2008).
16. B.-C. Chen, J. Sung, and S.-H. Lim, "Chemical imaging with frequency modulation coherent anti-Stokes Raman scattering microscopy at the vibrational fingerprint region," J. Phys. Chem. B **114**(50), 16871–16880 (2010).
17. A. F. Pegoraro, A. D. Slepkov, A. Ridsdale, J. P. Pezacki, and A. Stolow, "Single laser source for multimodal coherent anti-Stokes Raman scattering microscopy," Appl. Opt. **49**(25), F10–F17 (2010).
18. P. Adany, D. C. Arnett, C. K. Johnson, and R. Hui, "Tunable excitation source for coherent Raman spectroscopy based on a single fiber laser," Appl. Phys. Lett. **99**(18), 181112 (2011).
19. K. P. Knutsen, B. M. Messer, R. M. Onorato, and R. J. Saykally, "Chirped coherent anti-Stokes Raman scattering for high spectral resolution spectroscopy and chemically selective imaging," J. Phys. Chem. B **110**(12), 5854–5864 (2006).

1. Introduction

Coherent anti-Stokes Raman scattering (CARS) spectroscopy using ultrashort pulses has emerged as one of the most promising methods for the measurement of gas-phase molecules in reacting flows. The ability to reduce or eliminate the nonresonant contribution that typically plagues CARS measurements and the high data-acquisition rates are representative of the advantages afforded by the use of ultrashort pulses.

CARS using femtosecond (fs) pulses has been the focus of numerous research groups that employ several different experimental approaches for the study of gas-phase molecules. Time-resolved measurements over large time scales (>100 ps) have been used to study the rotational dynamics of H_2 [1], perform flame thermometry [2], and determine parameters associated with gas-phase molecules [3]. Time-resolved measurements over short time scales (~10 ps) have been used to examine the effects of temperature on frequency-spread dephasing [4], perform thermometry in diffusion flames [5], and examine the effect of polarization beating between close Raman transitions [6,7]. Several frequency-domain methods have also been studied. For effective use of femtosecond pulses for frequency-domain measurements, pulse-shaping methods are often applied to enhance the spectral resolution, as demonstrated in single-beam CARS [8] and hybrid fs/ps CARS measurements [9]. Additionally, pulse shaping has been used to obtain a direct transformation of the time-domain signal in the frequency domain through the use of a chirped probe pulse [10].

The CARS approach taken in this work also employs a pulse-shaping method, with spectral focusing being performed by chirping the pump and Stokes pulses and then changing the relative delay between the two pulses to excite a single Raman transition. This allows broadband femtosecond pulses to be used for exciting a single vibrational level, achieving very high spectral selectivity. However, in these experiments the resolution is limited because of the nature of the probing pulse. Since the probe pulse is broad compared to the narrowband excitation generated by the chirped pump/Stokes pulses, the resulting CARS signal arises because of the interaction of the widely dissimilar bandwidths of the pump/Stokes and probe pulses. While the use of a narrowband probe would lead to an increase in spectral resolution, it would result in a significant loss of signal due to a reduction in spectral intensity. This loss of signal would also occur for the same reason under conditions where the chirps of the pump/Stokes pulses were significantly increased. While not ideal, the resolution with this method was sufficient to enable us to resolve the resonant CARS signals for individual species in a mixture, which could not have been resolved using the original, unchirped broadband source. Furthermore, we were able to measure the frequency dephasing that has been shown to be highly temperature-dependent and the polarization beating between close Raman modes.

The spectral-focusing method is well established and has been used in many applications, particularly microscopy and microspectroscopy for high-contrast imaging [11–19]. Typically, the broadband pulses are chirped through the use of a grating compressor, adaptive pulse shaper, or optical glasses with well-known group velocity dispersion (GVD). In our approach

we use a pulse near 690 nm to act as the pump pulse and a pulse near 800 nm to act as the Stokes pulse. These pulses are both chirped using 30.5-cm-long SF-10 glass rods that introduce ~60900 fs^2 of group delay at 690 nm and ~48600 fs^2 at 800 nm. The auto-correlation of the unchirped 690 nm probe is shown in Fig. 1(c) along with the cross-correlation of the chirped Stokes and unchirped probe and the cross-correlation of the chirped pump/Stokes and unchirped probe. Typically, the total GVD of the pump and Stokes pulses is matched to ensure optimal signal generation. While the unmatched GVD here reduces the signal efficiency, it is a minimal reduction because of the close central frequencies and large GVD used. Figure 1 highlights the key features of the experimental setup, provides a schematic illustration of the principle of spectral focusing using a time-frequency diagram, and provides pulse-characterization information.
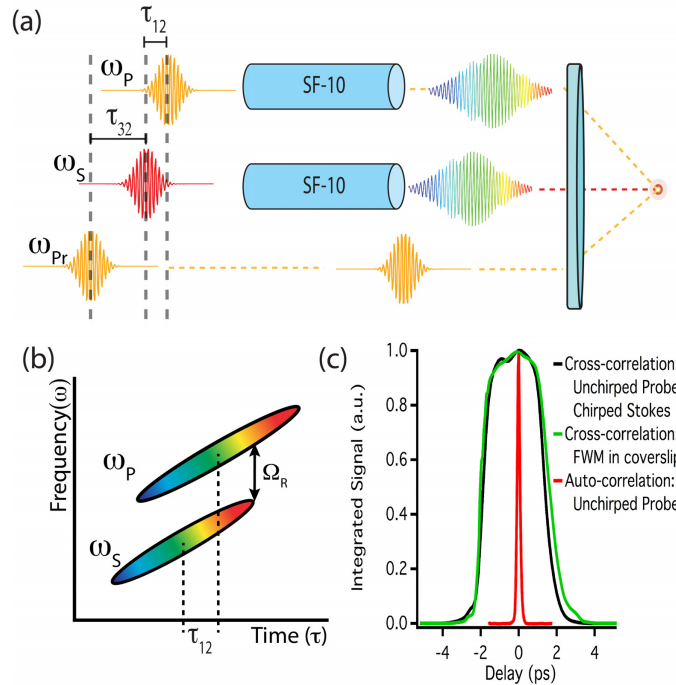

Fig. 1. (a) Schematic layout of the experimental setup. (b) Time-vs.-frequency diagram for chirped pump and Stokes pulses. The excited Raman transition (Ω_R) is dependent on the relative delay (τ_{12}) between the two pulses. (c) Cross-correlation (black) of the unchirped probe and chirped Stokes, cross-correlation (green) between the chirped pump/Stokes and unchirped probe, and auto-correlation (red) of two unchirped probe pulses.

2. Experimental

A commercially available, regenerative Ti:sapphire amplifier that pumps an optical parametric amplifier (OPA) was used to generate the three pulses. The 690-nm pulse from the OPA was split to serve as the pump and probe pulses, while the 800-nm output of the amplifier served as the Stokes pulse. Both the chirped Stokes and the unchirped probe pulses propagate along computer-controlled delay arms before being focused into the test cell along with the chirped pump pulse through the use of a three-dimensional BOXCARS geometry to meet the spatial-overlap and phase-matching requirements. The CARS signal emerging from the probe volume is collimated and detected with a high-speed photodiode that is locked into the output trigger of the amplifier. This configuration was used to perform two experiments. In the first experiment, the delay between the pump and Stokes pulses was fixed in time, while the delay of the probe pulse was varied to allow observation of the coherence-

dephasing dynamics of the Raman transitions. The coherence dynamics result from the simultaneous excitation of the rovibrational transitions within the Raman band. Initially, these transitions are in-phase; however, they begin to drift out of phase after a short time because of the slight differences in their frequencies, leading to the measured coherence dephasing. Since these dynamics are dependent on the rovibrational transitions, they are very sensitive to the population distribution across the various states and can be used to extract accurate temperature information based on the change in the dephasing rate.[4,6] In the second experiment, the relative delay between the pump and Stokes pulse was varied and the probe pulse was maintained at a fixed delay; this allows the CARS spectrum to be directly mapped as a function of the relative pump/Stokes delay, which is essential for providing a Raman spectrum of the sample mixture. These two methods were combined to measure the dynamics of a single species in a mixture.

3. Results and discussion

Initially, a 10-bar, 1:1 binary mixture of O_2 and CO_2 was examined. The ν_1 (1556-cm^{-1}) mode of O_2 and the ν_1 (1388-cm^{-1}) and $2\nu_2$ (1285-cm^{-1}) modes of CO_2 can be excited simultaneously using a broadband source; this results in an integrated signal, which comprises contributions from each molecule as well as interference between the different vibrational modes of the molecules. Through the use of spectral focusing, it is possible to isolate each Raman mode individually and observe the species-dependent coherence-dephasing dynamics of individual molecules or the mixture. In Fig. 2(a) the mapping of the CARS spectrum as a function of the delay between the pump and Stokes pulse is shown for O_2 and CO_2. By fixing the pump/Stokes delay at the positions shown in Fig. 2(a) and scanning the delay of the probe pulse, it is possible to measure the coherence-dephasing dynamics. Figure 2(b) displays the measured dephasing for pure O_2 and for O_2 in the mixture, and Fig. 2(c) shows this information for CO_2.
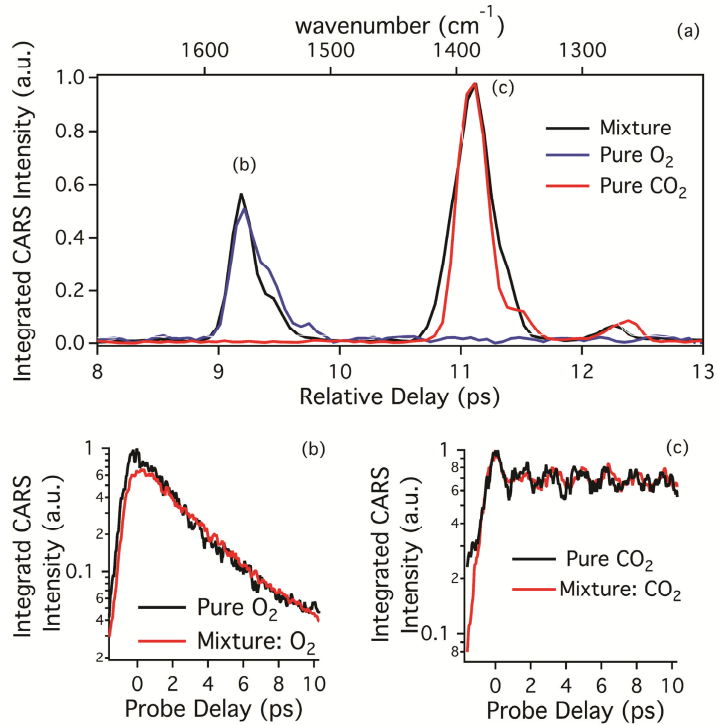
Fig. 2. (a) CARS response as a function of pump/Stokes delay for a 1:1 mixture of O_2 and CO_2 at 10 bar. (b) and (c) Integrated CARS response as a function of probe delay for each species in the mixture (red) and in the pure gas (black).

For O_2 the expected exponential decay is observed for both the pure gas and the mixture. In CO_2 the signal remains nearly constant because of the overlap of multiple vibrational modes. This also results in a beating pattern that can be observed in both the pure gas and the mixture with very good agreement. These results are consistent with those in the literature.[7] Additionally, the good agreement between these curves for the pure gas and the gas mixture indicates that it is possible to measure the decay for a specific species in the mixture without the influence of the other species, which is extremely valuable for temperature measurements. In temperature measurements with broadband excitation, the various Raman modes of species interfere, creating a decay that has contributions from each mode as well as the mixing of the modes. This decay is further complicated by the influence of the relative concentrations of each species, making it challenging to extract accurate temperature information. With the use of spectral focusing, the species can be excited individually, allowing their temperature-sensitive decays to be measured free from interference due to other species in the mixture. Figure 3 shows the measured decay for a 1-bar 1:1 mixture of O_2 and CO_2 and pure O_2 and CO_2 at temperatures of 300, 500, and 700 K. For O_2 we observe the expected increase in decay rate as additional modes are populated at elevated temperatures and very good agreement between the mixture measurement (Fig. 3(a), solid lines) and pure-gas measurement (Fig. 3(b), filled circles). The accuracy and precision of time resolved measurements for thermometry is typically 2-3% in temperature ranges of 300-2400K. As with the data at elevated pressure, we see very different behavior for the CO_2 and O_2. Again, very little change occurs in the overall decay, but an increase in the amplitude of the slow oscillation is observed as the temperature is increased.
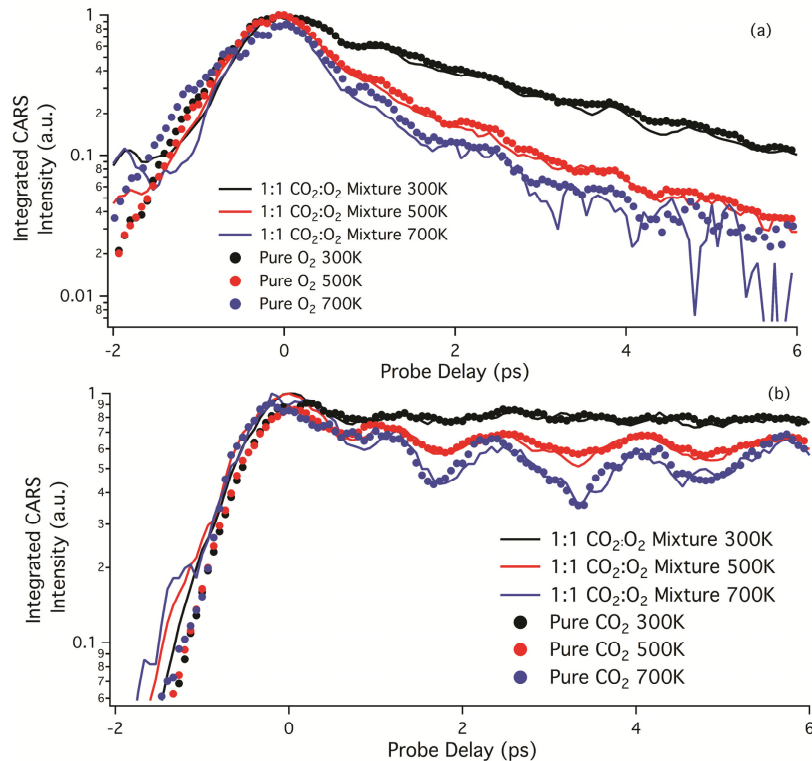
Fig. 3. Integrated CARS response as a function of probe delay for a 1-bar, 1:1 mixture of O_2 and CO_2. (a) Measurements at 300, 500, and 700 K with selective excitation of O_2 in the mixture (solid lines) and in the pure gas (filled circles). (b) Measurements in the same temperature regime with selective excitation of CO_2.

In addition to CO_2 and O_2, a 10-bar mixture with a 2:2:1 ratio of nitrogen (N_2), carbon monoxide (CO), and acetylene (C_2H_2) was examined. The use of a broadband excitation source would result in the simultaneous excitation of ν_1 (2330 cm^{-1}) of N_2, ν_1 (2145 cm^{-1}) of CO, and ν_2 (1975 cm^{-1}) of C_2H_2 and a measured CARS response containing information from all three species. Again, the application of the spectral-focusing technique allows individual modes of each of the three species to be resolved independently, as shown in Fig. 4(a). It is also possible to measure the coherence-dephasing dynamics for each of these three species independently, as shown in Fig. 4(b)–4(d). Furthermore, the beating pattern that occurs as a result of interference between two vibrational modes of different species can be measured. Figure 4(e) illustrates that when the delay between the pump and Stokes pulses is such that the excitation frequency lies between two vibrational modes, a beating pattern can be observed after ~2 ps of delay. The oscillations at ~5 THz correspond to the difference frequency between the ν_1 mode of CO and the ν_2 mode of C_2H_2. The modulation depth of these beat frequencies has been used to determine the relative concentrations of the species [6].
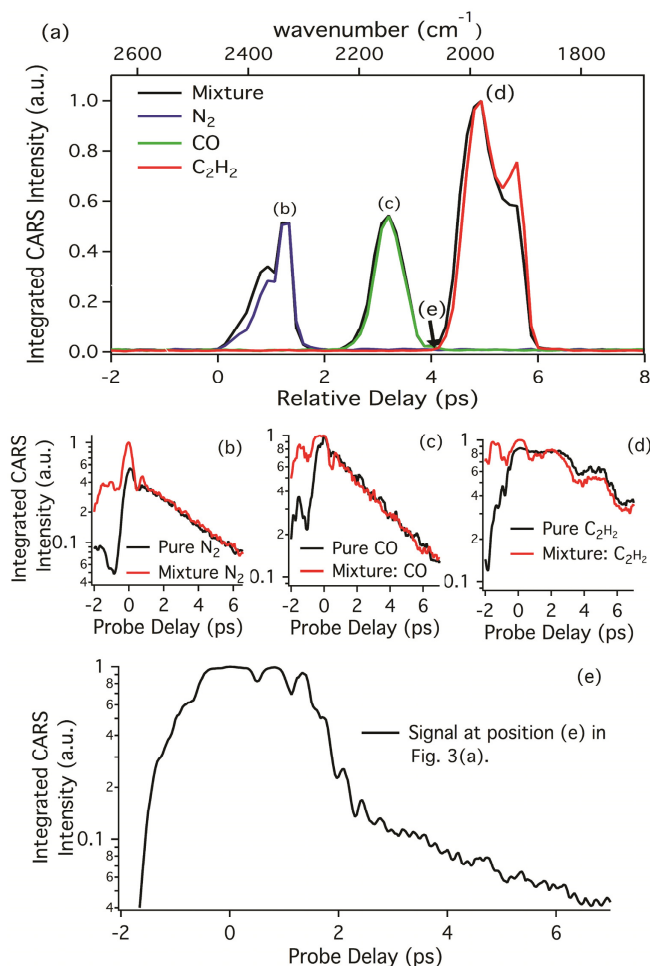
Fig. 4. (a) CARS response as a function of pump/Stokes delay for a 2:2:1 mixture of N_2, CO, and C_2H_2 at 10 bar. (b)–(d) Integrated CARS response as a function of probe delay for each species in the mixture (red) and in the pure gas (black). (e) CARS response at position (e) in Fig. 4(a), showing the beating between the ν_1 mode of CO and the ν_2 mode of C_2H_2.

4. Conclusion

To summarize, we have shown that simple spectral-focusing methods based upon the chirping of broadband pulses with optical glass can be applied to gas-phase CARS. This method not only allows the CARS signal to be mapped directly as a function of the relative delay between the pump/Stokes pulses but also is capable of resolving spectral features that are not observable with broadband sources. Furthermore, we have shown that by using spectral focusing to select the appropriate delay for excitation of a single vibrational mode and scanning the probe delay, it is possible to observe the temperature-dependent coherence dephasing for an individual species in a mixture. This method provides a simple way to determine temperature in reacting flows and combustion processes based on a single gas-phase species by eliminating any contribution to the coherence dephasing that may be present because of additional interfering species.

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