Recent advances in picosecond and hybrid femtosecond/picosecond CARS techniques for gas phase analysis

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Accurate time- and spatially resolved measurement of temperature remains a critical focus of combustion diagnostics. The local temperature field and gradient not only govern chemical reaction rates but also physical quantities such as gas expansion and heat transfer. Coherent anti-Stokes Raman spectroscopy (CARS) has been applied for concentration measurements and ro-vibrational thermometry in gas-phase applications for more than three decades, and is often held as the gold standard optical technique for the non-intrusive determination of temperature in gas-phase systems. Current developments in picosecond (ps) coherent anti-Stokes Raman spectroscopy (CARS) and hybrid femtosecond/picosecond (fs/ps) CARS techniques have enabled breakthroughs in measurement capabilities for gas phase molecular analysis.

Utilizing a ps probe pulse in gas phase CARS investigations is in many ways an optimized approach. Collisional dephasing of many gas phase molecules occurs on the ps timescale for a range of pressures, thus, ps probe pulses are uniquely formatted to directly probe such processes. For instance, time-resolved ps-CARS has been recently employed to acquire high-fidelity measurements of collisional dephasing and, hence, Raman broadening coefficients [1-4], although for quickly dephasing molecules care must be taken to quantify the time-convolution with the probe window. A key advantage of ps-probing in CARS experiments is the capability for both excellent frequency resolution (transform-limited bandwidth a small fraction of 1 cm^{-1}), while simultaneously maintaining the advantages of time-resolved CARS with high peak power pulses, such as very high signal level, suppression of nonresonant background, and direct measurement of coherence dephasing effects.

Hybrid fs/ps CARS techniques [5] take advantage of *both* impulsive fs coherence excitation and high power, well-resolved, ps probing. Many breakthrough developments have recently been enabled by further developments with hybrid fs/ps CARS. Two-beam 1D ultrabroadband CARS has been demonstrated for, in principle, the simultaneous measurement of all Raman-active species and molecular manifolds in a gas phase mixture [6], demonstrated in Fig. 1. The first gas phase 2D-CARS measurements generating thousands of spatially correlated CARS spectra within a single laser shot have been demonstrated [7] in the harsh environment of a flame. A very recent development within our laboratory has been the development of ultrabroadband 2D-CARS – enabling planar imaging of Raman active-modes and spectra with an excitation bandwidth demonstrated beyond 4000 cm^{-1}.

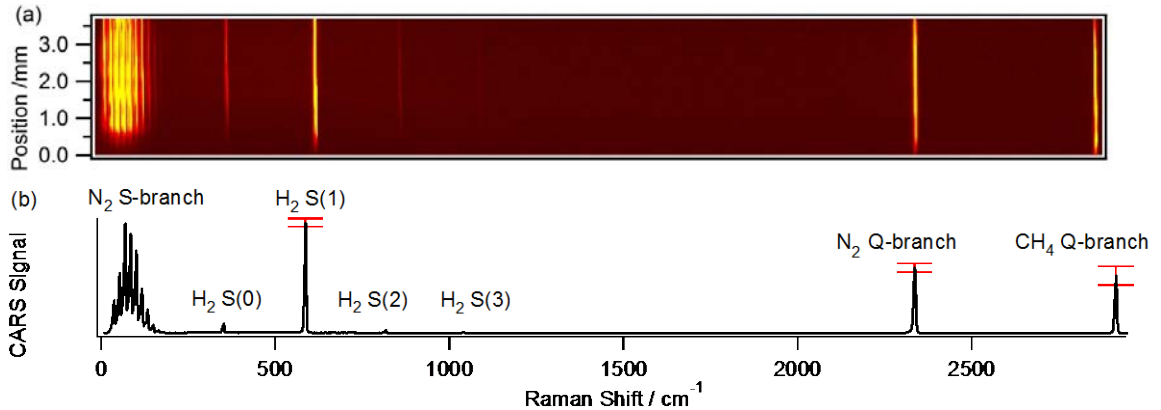

Fig. 1. (a) CCD image of a single shot acquisition of ultrabroadband CARS in a mixture of N_2, H_2, and methane. The log of signal intensity is presented. (b) CARS spectrum taken from a single pixel-row of the CCD image in panel (a). Error bars represent single-shot standard deviation in signal intensity when normalized to the N_2 pure-rotational branch.

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