Experimental Investigation of the Temperature-Dependent Self-Broadened S-Branch Raman Linewidths of CO_2

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This work reports the experimental determination of the temperature dependent S-branch Raman linewidths of pure CO_2 up to 1900 K, which are of utmost importance for accurately modelling the CO_2 rotational coherent anti-Stokes Raman scattering (RCARS) signal [1–3]. The linewidths are determined from the coherence decay time using a picosecond time resolved RCARS approach. The RCARS signal of CO_2 exhibits monoexponential dephasing behavior overlaid by a temperature dependent oscillation likely arising from coherence beating between the RCARS signals of the 01101e hotband and ground state of CO_2 which needs to be properly modelled in the fitting procedure (Figure 1 a). The obtained Raman linewidths deviate from so far available Q-branch linewidths from Rosenmann et al. [4] in absolute value and *J*-dependence for all studied temperatures (figure 1 b). Therefore, we expect a strong influence on evaluated temperature, when using the accurate S-branch linewidths as opposed to the Q-branch approximation. Also, we find non-monotonic J-dependence in the linewidths of thermal CO_2 for specific ranges of rotational states. Chen et al. [5] attributed a respective observations in optically centrifuged CO_2 to rotational to vibrational coherence transfer. Thus, our data provide additional insights into the coherence dynamics of CO_2 to improve modelling of the CO_2 RCARS signal.

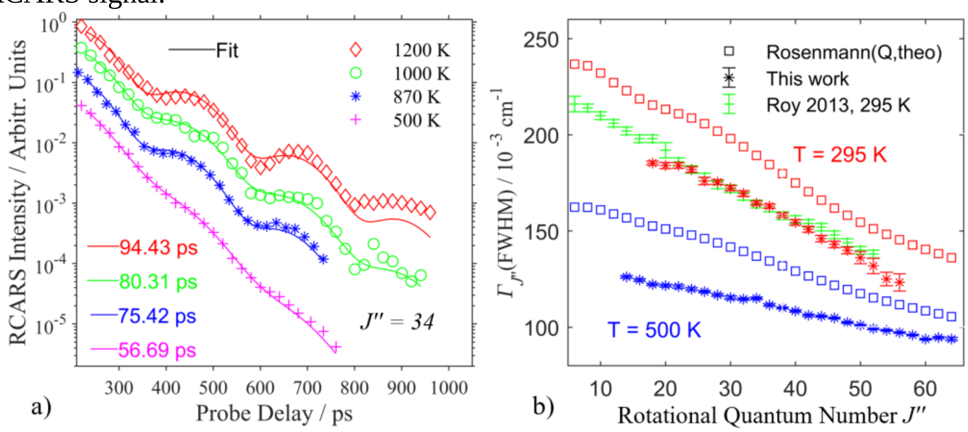

Figure 1 a) Time trace of the RCARS intensity of the J''=34 rotational line of CO_2 at selected temperatures. Solid lines indicate fits of a model considering coherence beating and monoexponential dephasing, with resulting decay constants indicated in the plot. b) S-branch rotational Raman linewidths at two selected temperatures compared against linewidth from Rosenmann et al. [4] (Q-branch) and Roy et al. [6] (S-branch, 295 K only).

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