

High-Pressure Measurements of CO₂ Absorption near 2.7 μm

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Motivation

Future engine concepts for efficient and clean combustion incorporate ultra-dilute mixtures at pressures considerably higher than are employed in current internal combustion engine technologies. Dilute mixtures keep peak temperatures of combustion and hence pollutant formation rates low, while high pressures minimize energy loss during combustion. Pressures as high as 500 bar are within the present conceptual range of practical devices. Under such conditions, the fundamental physical nature of combustion processes is not well understood. New experimental techniques and diagnostic methods are required for quantitative and time-resolved measurements of reactants, intermediate species, products, and temperature to gain practical understanding of high-pressure combustion processes.

Overview

This work addresses the severe challenges to be faced in developing optical sensors for high-pressure applications. The extended-NIR wavelength region (2.5–3.0 μm) is chosen for this work due to the availability of DFB diode lasers in this wavelength range and the ability to access stronger vibrational bands of CO₂ compared with the NIR region. Direct absorption measurements made on transitions near 2743 nm show increasing deviation from the Voigt/Lorentzian simulations of spectral features as pressure increases. The deviation is larger in CO₂-air than CO₂-Ar mixture. This is attributed to the higher collision efficiency of CO₂ molecules with air and the smaller broadening of CO₂ transitions in Ar (See Table 1).

P [atm]	Deviation from Lorentzian	
	CO ₂ -Air	CO ₂ -Ar
5	15%	12%
10	24%	20%
15	35%	30%
20	47%	40%
30	70%	61%

Table 1: Average deviation of the measured absorption from the Lorentzian/Voigt simulation for the 2743 nm laser. Mixtures used: 0.54% CO₂-air and 0.49% CO₂-Ar. T = 296 K, L = 100 cm.

Measurements on transitions near 2752 nm show an interesting pattern of a shift from super-Lorentzian to sub-Lorentzian behavior when going from low to high wavenumbers. FTIR measurements are made from 3500 – 3800 cm⁻¹ covering the entire $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ vibrational bands of CO₂. These FTIR measurements demonstrate that this shift from super- to sub-Lorentzian behavior happens around 3633 cm⁻¹. The deviation from the Lorentzian behavior is shown to be as high as 100% in the far wings of the bands (Figure 1).

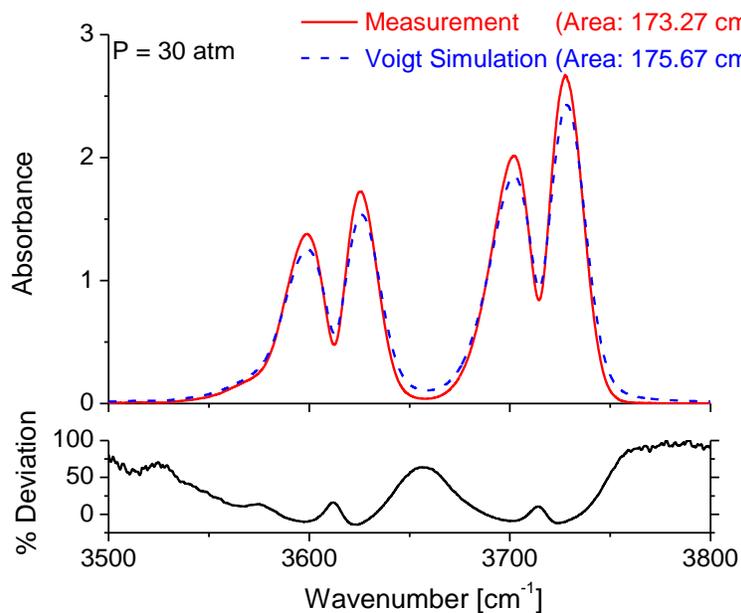


Figure 1. FTIR measurements for the CO₂ bands near 2.63 to 2.85 μm. T = 296 K, L = 5.77 cm, 1.49% CO₂ in air. P = 30 atm.

Various line shape simulations are used to model the experimental data. The empirical \mathcal{L} -factor model does a good job in the wings but significantly underestimates the band peaks. The line mixing model based on energy-corrected sudden approximation does an overall good job but overestimates the peaks by about 4 – 9% (See Figure 2). This suggests that diagnostic strategies using wavelengths away from the peaks can use the Niro model to infer accurate mole fraction values. The empirically determined ECS model parameters will have to be reevaluated for the 2.7 μm CO_2 band to improve the model performance near the peaks. This model predicts the wings of the bands quite accurately which suggests that line mixing is the dominant process here, and that the finite duration of collision effects are negligible at the measurement density (~ 30 amg) and about 100 cm^{-1} detuning from the band centers. The development of a high-pressure combustion sensor for sensitive CO_2 measurements will require the use of a multi-wavelength strategy and accurate predictive models for CO_2 spectra and the interference from water vapor.

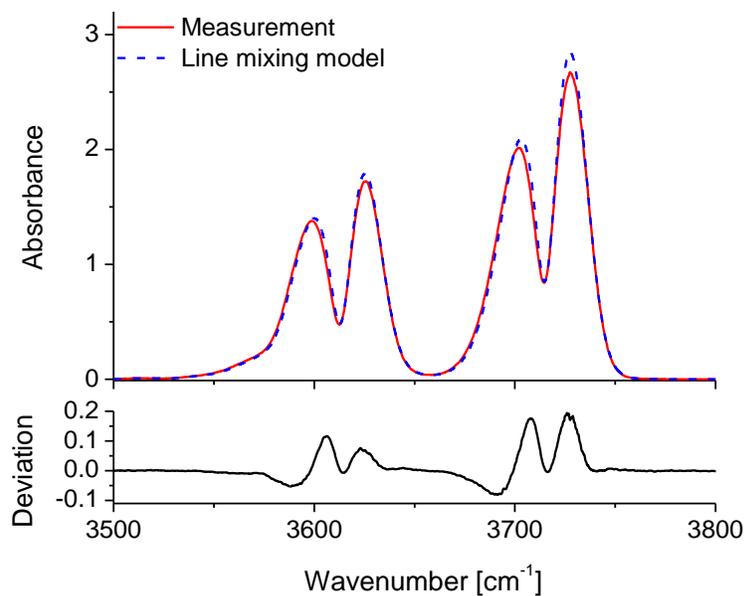


Figure 2. Comparison of the measurement with the line mixing model of Niro et. al. $T = 296\text{ K}$, $L = 5.77\text{ cm}$, 1.49% CO_2 in air, $P = 30\text{ atm}$.

Next Steps

Extend these fundamental measurements of collision effects at high pressure to develop design rules for sensors for practical combustion and propulsion systems operating at high pressures.

References

1. Farooq, J.B. Jeffries, R.K. Hanson, "High-pressure measurements of CO₂ absorption near 2.7 μm: Line mixing and finite duration collision effects", *Journal of Quantitative Spectroscopy and Radiative Transfer* **111** 949 – 960 (2010)
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3. F Niro, C Boulet, J.M. Hartmann, "Spectra calculations in central and wing regions of CO₂ IR bands between 10 and 20 μm. I: model and laboratory measurements" *Journal of Quantitative Spectroscopy and Radiative Transfer* **88** 483-98 (2004).