

Comb-based FTIR spectroscopy of CO perturbed by N₂ at 4.6 μm

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Abstract. Line-shape measurements of the fundamental vibrational band of CO at 4.6 μm perturbed by N₂ with a mid-infrared frequency comb-based Fourier-transform spectrometer were performed. Precise collisional line-shape parameters for 41 lines were determined, including the pressure broadening and shifting and speed-dependence of the collisional width. The results were compared with sparse literature data available.

1 Introduction

Carbon monoxide (CO) has its fundamental vibrational (0-1) band at 4.6 μm , which plays an important role in various fields. As an example, in atmospheric physics it can be used as an indicator of abundances of methane that is a contributor to global warming, in combustion processes serves as a tracer of combustion processes of fossil fuels and biomass. Since the nitrogen molecule (N₂) is the main constituent of atmosphere, the pressure broadening and shift parameters of N₂-perturbed CO are particularly important for the spectroscopic community. In this work, we applied mid-infrared frequency comb (FC)-based Fourier-transform spectroscopy (FTS) [1] to the measurement of the fundamental ro-vibrational band of CO perturbed by N₂. Using these measurements, we studied the effect of collisions on N₂-perturbed CO lines, which allows us to provide precise collisional parameters that are crucial for the terrestrial atmosphere observations.

2 Experimental Setup

The measurements were made with comb-based FTIR spectrometer. The mid-infrared FC was generated by an optical parametric oscillator (OPO) using a high-power mode-locked Yb-fiber laser [2] as the pump laser. The OPO idler operated at around 4.6 μm were used for spectroscopy of the fundamental band of CO. The f_{rep} (~125 MHz) and offset frequency of the mid-infrared FC were stabilized to RF references. The mid-infrared FC output passed through a 72-cm long cell filled with a CO-N₂ mixture, and the light transmitted through the cell was coupled to a fiber leading to a home-build FTS system. Interferograms with the length of about 2.4 m, corresponding to c/f_{rep} , were obtained, and the data were treated according to the procedure from [4] to remove the

instrumental line shape (ILS) of the FTS system. We also applied a correction to remove the additional ILS caused by the varying intensity of the interferogram.

3 Results

From two measurements of P- and R-branch, the normalized spectrum of the whole fundamental band of CO was retrieved, shown in the Fig.1.

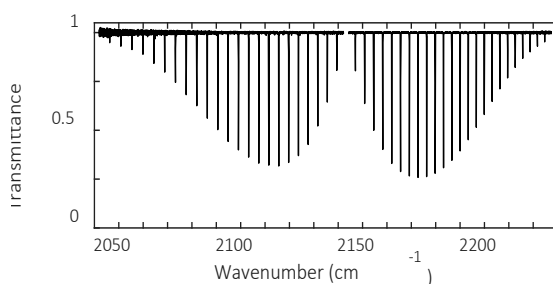


Fig. 1. Transmittance spectrum of the 72cm optical path cell filled with 100 Torr CO-N₂ mixture

On individual lines we performed line-shape fittings with Voigt profile (VP), Nelkin-Ghatak profile (NGP), and speed-dependent VP (SDVP). The w-shape systematic deviation from the VP is distinct in the pressure range of 10-100 Torr, which implies we see the effects not described by VP. The fitted lineshapes with NGP and SDVP agree with the experimental results better than VP over all the pressure range, and SDVP shows even better agreement than NGP at 10 Torr and 30 Torr. The example of the fits in the 10-100 Torr range for R7 line is shown in the Fig.2. Altogether we have performed the SDVP fits of 20 lines of P branch and 21 lines of R branch for 5 measurements with different pressures between 10 Torr and 400 Torr. Fitted Lorentzian widths and center frequencies showed linear dependence on pressure. The collisional broadening (γ) and shift (δ) coefficients were

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obtained from the slopes of the linear functions fitted to the pressure dependence of Lorentzian width and center frequency, respectively. Fig.3 shows the collisional broadening and shift, respectively, against line number (m).

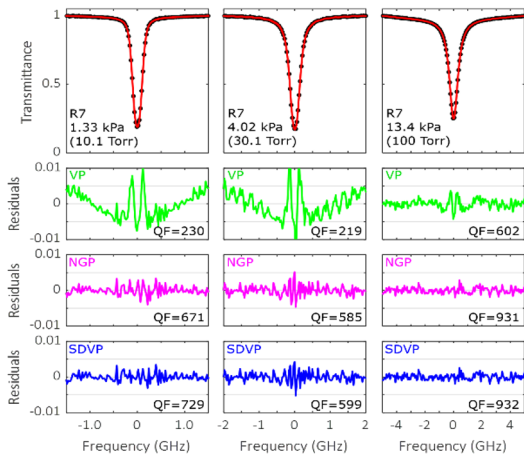


Fig. 2. The R7 line measured in 10-100 Torr range and residuals of line-shape fittings with three different profiles. QF: a ratio of the peak absorption to the standard deviation of the fit residuals.

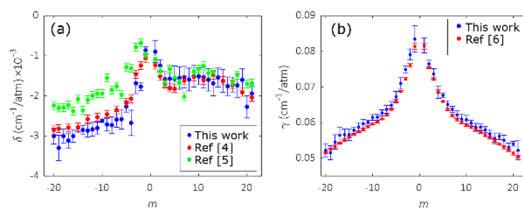


Fig. 3. The collisional shift (δ) and (b) broadening (γ) coefficients derived from the linear fits with the line number (m), where $m = -J$ for the P branch, and $m = J + 1$ for the R branch.

Our results for collisional shift coefficient (δ), shown in blue in the Fig. 3(a) agree with previous study using a tunable diode laser [4] (shown in red) within the error bars. However in comparison to results of previous measurements with FTIR [5] (green) we can see the systematic offset. In case of the collisional broadening (γ), the results of previous study using a tunable diode laser [6] (red in the Fig. 3(b)) have small systematic offsets providing approximately 2.3% smaller collisional broadening parameters than our results (blue).

4 Summary

Precise line-shape study of the fundamental vibrational bands of CO-N₂ was performed with mid-IR FC-FTS spectrometer. The spectrometer successfully obtained precise line shapes of a large number of lines under several pressure conditions in a short time. Since the spectral data of CO has high importance in spectroscopy community due to the role of atmospheric CO in the carbon cycle and the versatility as a probe in various astronomical observations, spectral data over a wider temperature range and comparison with theoretical calculations will be required for future studies.

5 Acknowledgments

This work was supported by National Science Centre, Poland (No.2016/23/B/ST2/00730 and 2019/35/D/ST2/04114). RC was supported by Polish Ministry of Education and Science in the framework of the project Polish Metrology; grant number PM/SP/0040/2021/1

References

1. P. Masłowski, et al., Phys. Rev. A **93**, 021802(R) (2016)
2. X. Li, et al., Rev. Sci. Instrum., **87**, 093114 (2016)
3. L. Rutkowski, et al., JQSRT **204**, 63-73 (2018)
4. C. Luo, et al., J. Mol. Spectrosc. **196**, 290–295 (1999)
5. J.-P. Bouanich, et al., J. Mol. Spectrosc. **178**, 157-164 (1996)
6. A. Predoi-Cross, et al., J. Mol. Spectrosc. **198**, 291–303 (1999)