

Do Open-path Eddy Covariance CO₂ Analyzers Need a Spectroscopic Correction for Fast Temperature Fluctuations in the Optical Path?

Ivan Bogoev Campbell Scientific, Logan, Utah, USA

David Holl University of Hamburg, Hamburg, Germany

Introduction

Open-path infrared H₂O and CO₂ gas analyzers are widely used in **eddy covariance** systems for measuring turbulent gas exchange between the ecosystem and the atmosphere. They use non-dispersive infrared (NDIR) spectroscopy to provide *in situ*, accurate, and fast response CO₂ concentration measurements.

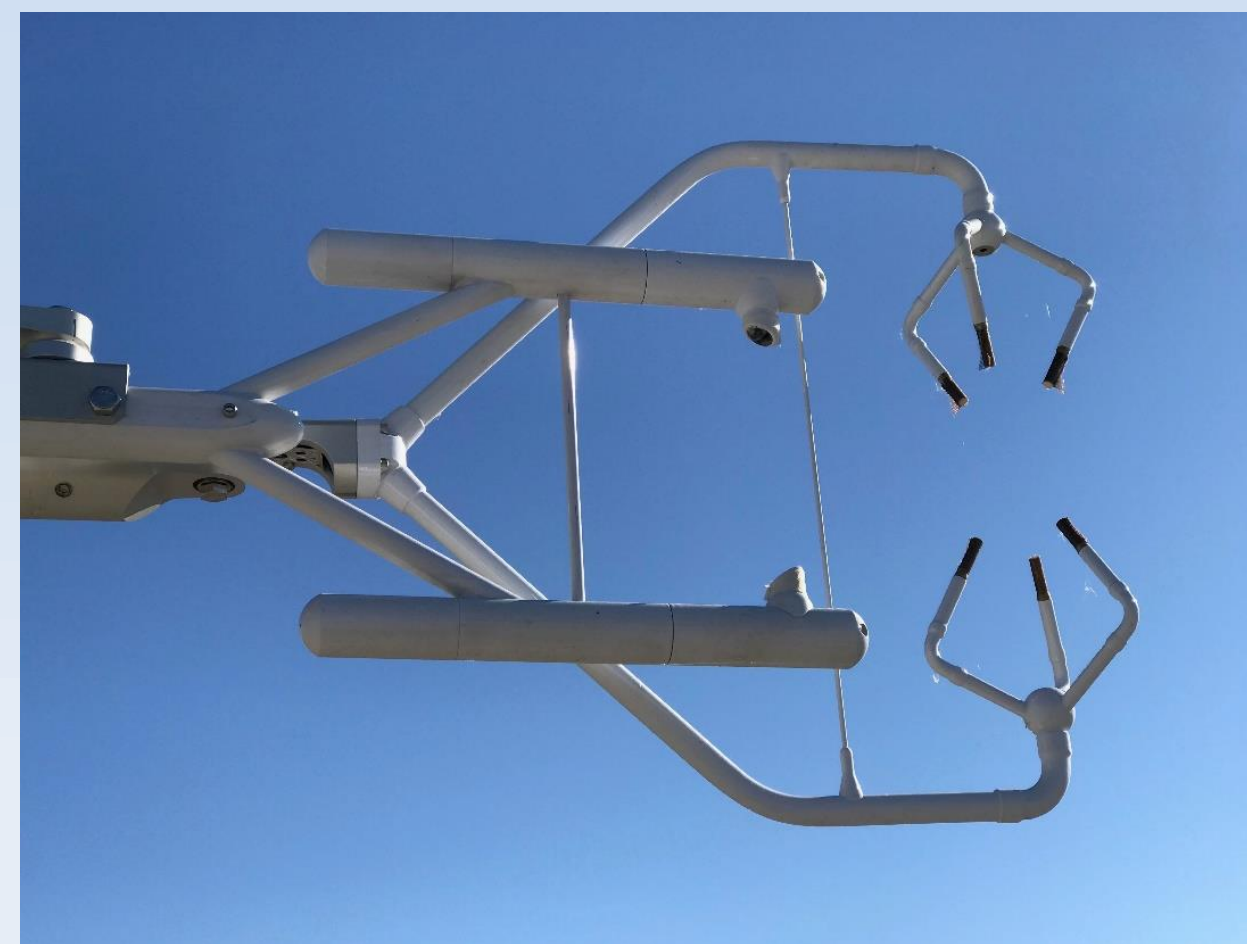


Figure 1: Eddy covariance infrared gas analyzer (EC150, Campbell Scientific, Inc.)

Motivation

In cold environments, physiologically unreasonable CO₂ uptake measurements are often observed (Wang, 2016). Self heating of the open-path gas analyzer is a possible explanation for the unreasonable measurements. However, the universality of the self-heating correction is questionable. (Wang, 2017). A new generation CO₂ analyzers with minimal power consumption still exhibit similar biases. (Figure 1).

Agreement of CO₂ fluxes measured by open- and closed-path gas analyzers can be poor, especially in low flux environments. (Wang, 2016). Recent studies find that CO₂ flux biases correlate with sensible heat flux, suggesting the bias is caused by temperature fluctuations in the open-path. Spectroscopic effects in laser-based open-path gas analyzers have been characterized (Burba et al., 2019), but there is little information about NDIR sensors.

Broad-band Non-Dispersive Infrared Spectroscopy

The absorption of infrared energy in the spectral band depends on the amount of the absorbing gas, the pressure, and temperature of the gas mixture:

$$A = \frac{N}{(\Delta\nu)} \int_{\nu_1}^{\nu_2} \left\{ 1 - \exp \left(- \frac{S_i \alpha_i c L}{\pi[(\nu - \nu_0)^2 + \alpha_i^2]} \right) \right\} d\nu \quad S_i = f(T) \quad \alpha_i = f(T, P)$$

A – Absorbed light energy in the spectral interval
 N – Number of absorption lines in the spectral band
 ν_0 – Wave number of the individual spectral line
 c – Density of the absorbing gas
 L – Path length

T – Air temperature
 P – Barometric pressure
 S_i – Strength of the individual line
 α_i – Half-width of the individual line
 $\nu_1 - \nu_2$ – passband of the IR filter

Methods

1. We derived integrated CO₂ in air absorption spectra in the infrared range typical for NDIR sensors between 4.18 and 4.33 μm (2309 to 2392 cm^{-1}). We obtained spectral-line parameters from the high-resolution transmission molecular spectroscopic database (HITRAN) for different pressures and temperatures and for CO₂ concentrations between 0 to 1000 ppm. We fitted an instrument calibration function using a third-order polynomial and ordinary least squares regression to the absorption-number density data set.
2. Additionally, HITRAN simulations were performed using a constant CO₂ number density of 29.95 mmol m^{-3} which was generated at ambient pressure (101.3 kPa) with different gas-mixture temperatures (244 K, 285 K, 326 K) and CO₂ concentrations (600, 700 and 800 ppm). To investigate the sensitivity of the integrated CO₂ absorption to changes in concentration, a simulation with a gas mixture containing 710 ppm CO₂ (30.352 mmol m^{-3} at 285 K) was generated.

References

Wang, L. et al., 2017: A Meta-Analysis of Open-Path Eddy Covariance Observations of Apparent CO₂ Flux in Cold Conditions in FLUXNET. J. Atmos. Oceanic Technol., 34, 2475–2487, <https://doi.org/10.1175/JTECH-D-17-0085.1>
Wang, W. et al., 2016: Performance Evaluation of an Integrated Open-Path Eddy Covariance System in a Cold Desert Environment. J. Atmos. Oceanic Technol., 33, 2385–2399, <https://doi.org/10.1175/JTECH-D-15-0149.1>
Burba et al., 2019: Accounting for Spectroscopic Effects in Laser-based Open-path Eddy Covariance Flux Measurements. Global Change Biology, 25-6, 2189-2202.
HITRAN online (<http://hitran.org>)

Results

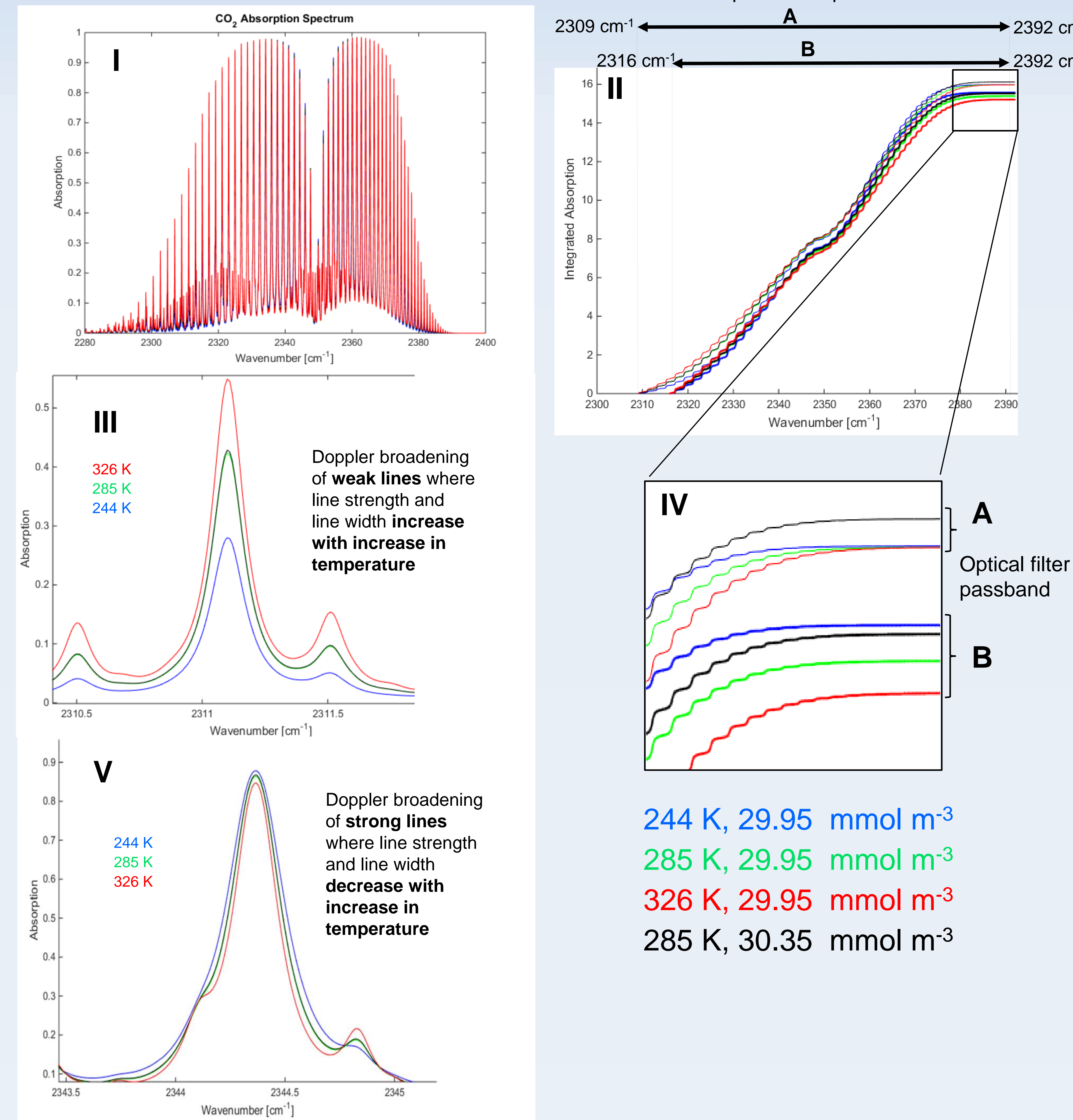


Figure 2: Absorption (I) and integrated absorption (II and IV) by CO₂ in the infrared range typical for NDIR analyzers at different temperatures. Doppler broadening of strong and weak absorption lines display opposite temperature effect (III and V).

Discussion

The HITRAN simulations show drastically different line strength and line broadening temperature coefficients (Figure 2, II and V) for the strong and weak absorption lines in the CO₂ active infrared spectral region (Figure 2, I) used by NDIR gas analyzers. An optical-filter with optimal center wavelength and passband (2309 to 2392 cm^{-1}). can balance these counteracting temperature effects and significantly reduce the temperature dependence of the integrated absorption (Figure 2 IV, passband A).

However, choice of the optimal filter passband is limited in practice because the central wavelength and passband of the optical filters:

- varies within manufacturing tolerances,
- shifts towards shorter wavelengths (larger wavenumbers) with an increase in the incident angle or when the filter is used in a non-collimated beam, and it
- shifts with temperature (longer wavelength with increase in temperature, blue shift with decreasing temperature)-meaning that this temperature sensitivity increases in cold environments.

In our simulation example using filter passband B, temperature line broadening leads to positive changes in air temperature being interpreted as negative changes in CO₂ concentration (Figure 2 IV and Figure 4).

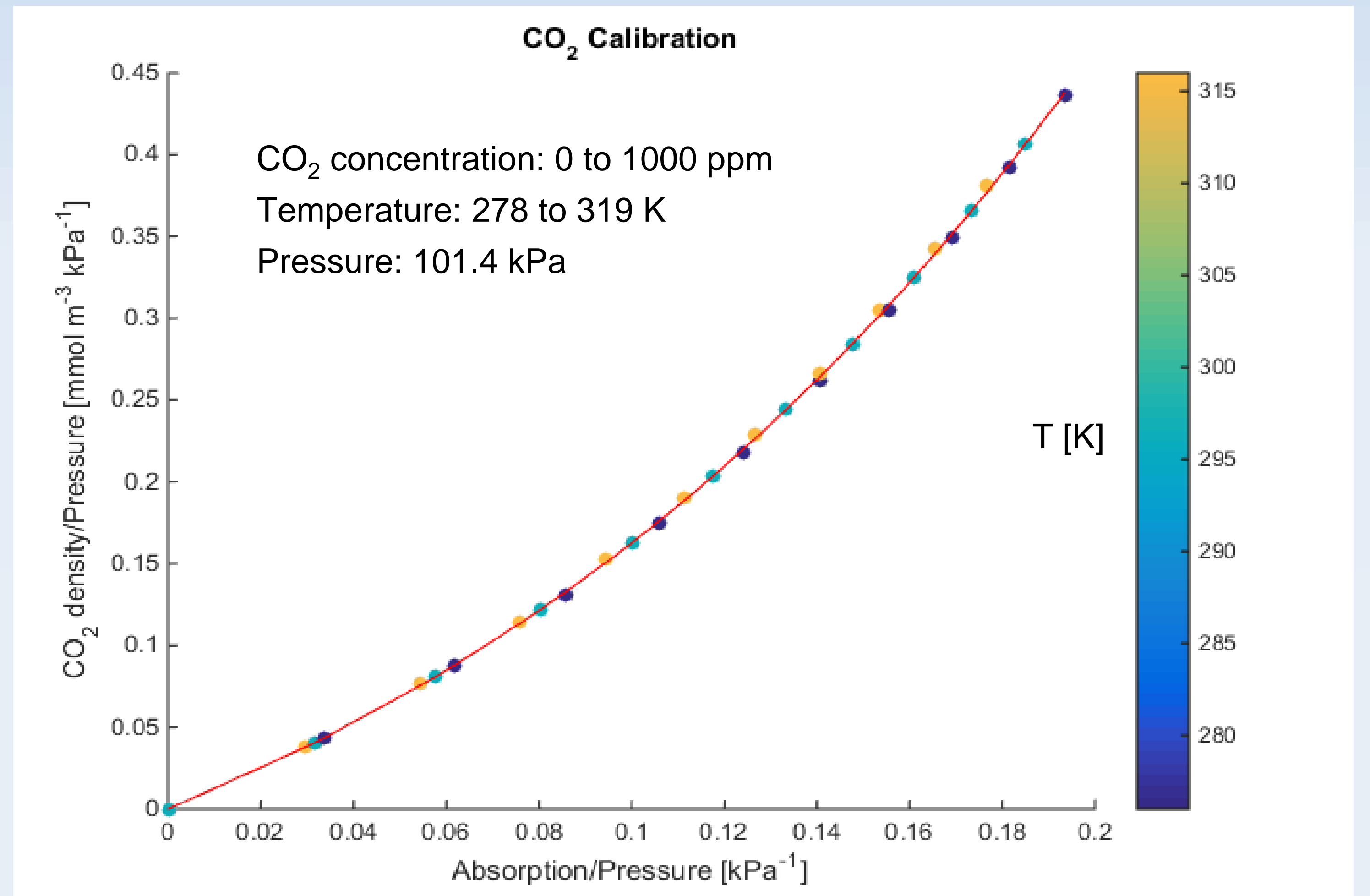


Figure 3: HITRAN-derived calibration data for a typical open-path gas analyzer using optical filter with passband B (2316 to 2392 cm^{-1}). The data are fitted with 3rd order polynomial.

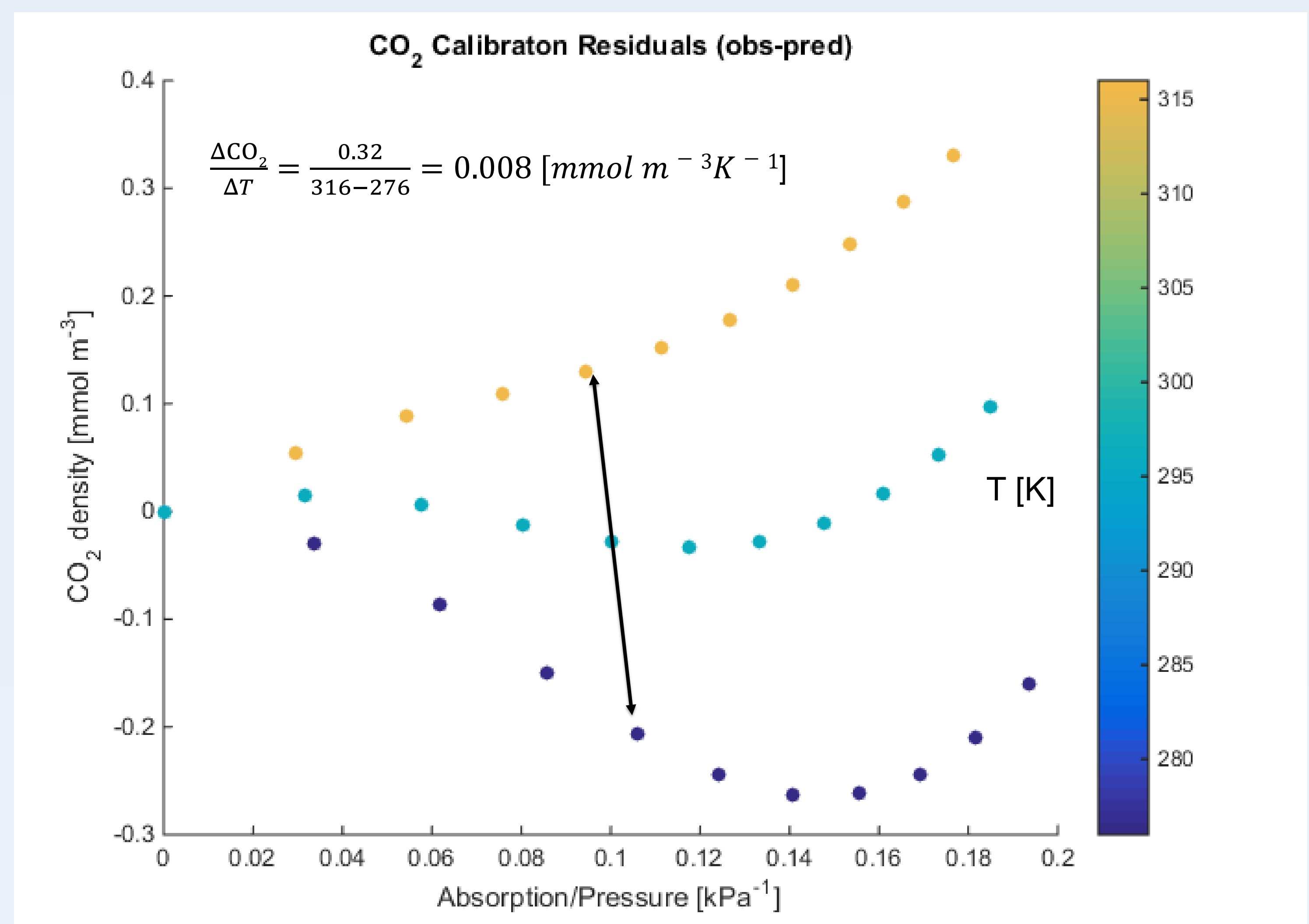


Figure 4: Residuals from the polynomial fit show that the calibration has a temperature bias: underestimation of CO₂ density at warmer and overestimation at colder temperatures, respectively.

Conclusions

- Weak and strong CO₂ absorption lines in the mid-infrared spectral region used by NDIR spectroscopy show opposite temperature sensitivity (Figure 2. III and V).
- Theoretically, an optimal spectral range exists, where the temperature broadening effects of strong and weak lines is balanced, and the temperature sensitivity of the integrated absorption is significantly reduced (Figure 2. IV)
- In practice, the optimal spectral range cannot be achieved due to optical filter tolerances. Consequently, this could introduce temperature induced bias in CO₂ measurements by NDIR analyzers (Figure 4).
- Temperature fluctuations in the optical path of open-path NDIR gas analyzers cause line broadening spectroscopic effects and if uncorrected introduce potential systematic biases in the measured CO₂ fluxes.

