



Spectral line parameters including temperature dependences of air-broadening for the $2 \leftarrow 0$ bands of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ at $2.3 \mu\text{m}$

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ABSTRACT

The first air broadening line shape parameters were determined for the $2 \leftarrow 0$ bands of $^{13}\text{C}^{16}\text{O}$ near 4166.8 cm^{-1} and $^{12}\text{C}^{18}\text{O}$ near 4159.0 cm^{-1} . Air-broadened Lorentz half-width coefficients, their temperature dependence exponents; air-induced pressure shift coefficients, their temperature dependences; and air line mixing coefficients were measured. Additionally, speed-dependent line shapes with line mixing employing the off-diagonal relaxation matrix element coefficients were applied to minimize the fit residuals. Finally, individual line positions and line intensities of the two isotopologues were constrained to the well-known theoretical quantum mechanical expressions in order to obtain the rovibrational (G , B , D and H) and band intensity parameters (including Herman–Wallis coefficients). For this, laboratory spectra were recorded at 0.005 cm^{-1} resolution using a temperature-controlled coolable absorption cell configured inside a Bruker IFS 125HR Fourier transform spectrometer. Gas temperatures and pressures for the spectra varied from 150 to 298 K and 20 to 700 Torr, respectively. Results were obtained from broad-band multispectrum least-squares fitting of the $4000\text{--}4360 \text{ cm}^{-1}$ spectral region. Four isotope-enriched pure sample spectra and twelve spectra with air + CO samples ($^{13}\text{C}^{16}\text{O}$ or $^{12}\text{C}^{18}\text{O}$, as appropriate) were fitted simultaneously. The results obtained for $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ are compared and discussed.

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1. Introduction

Precise and accurate knowledge of spectral line parameters for CO isotopologues is essential for ground- and satellite-based remote sensing. To support atmospheric monitoring, we recently obtained an extensive set of spectroscopic line parameters for the first overtone ($2 \leftarrow 0$) band of the main isotopologue $^{12}\text{C}^{16}\text{O}$ near 4260 cm^{-1} [1]. Our experiment was designed to measure the CO line shapes in the temperature–pressure ranges encountered in the terrestrial atmosphere; we therefore specifically targeted pressure broadening coefficients (Lorentz air-broadened widths, pressure shifts, line mixing coefficients and their temperature dependences and speed dependence) and also obtained line positions and intensities.

In the present paper, we now report the corresponding air broadening measurements for the $2 \leftarrow 0$ bands of $^{13}\text{C}^{16}\text{O}$ near 4166.8 cm^{-1} and $^{12}\text{C}^{18}\text{O}$ near 4159.0 cm^{-1} . Although these isotopic bands were already included in HITRAN [2] and GEISA [3], their line positions and intensities required validation. In addition, the Lorentz broadening coefficients for the $1 \leftarrow 0$ band of $^{12}\text{C}^{16}\text{O}$ were

assumed for all the isotopologues and bands ($1 \leftarrow 0$, $2 \leftarrow 0$ and $3 \leftarrow 0$) of CO in the databases. In fact, little specific investigation of the pressure broadening coefficients was available for these isotopic bands other than one room temperature study of $^{13}\text{C}^{16}\text{O}$ at 0.005 cm^{-1} resolution by Voigt et al. [4] who reported N_2 -broadened Lorentz half-widths and pressure shifts.

As in our first study [1], we employed a high resolution Bruker 125 HR Fourier transform spectrometer coupled to a temperature-controlled absorption cell [5] to record the spectra. Line parameters were retrieved simultaneously utilizing the multispectrum non-linear least-squares fitting technique [6]. The non-Voigt line shape profiles were applied in the analysis employing a rapid and accurate Voigt routine developed by Letchworth and Benner [7]. As described later, line position and intensity ‘constraints’ were imposed during the retrieval process, but individual widths, shifts, their temperature dependences, off-diagonal relaxation matrix elements and the speed dependence are all adjusted line-by-line. We simultaneously fit many spectra using pure and air-broadened enriched samples over a wide pressure range, and thereby minimize random errors to provide accurate values for all the measured parameters. We thus obtained internally consistent line positions, intensities, air-broadened widths, and air-induced pressure shifts,

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along with the temperature dependences of the widths and shifts. Most importantly, for the first time line mixing and speed dependence coefficients for the 2–0 bands $^{13}\text{C}^{16}\text{O}$ or $^{12}\text{C}^{18}\text{O}$ were directly measured.

2. Experimental details

The experimental set up, data acquisition method and data analysis techniques were identical to the ones used previously [1] and so only a brief overview is given here. All spectra were recorded at 0.005 cm^{-1} resolution with the Bruker IFS 125HR FTS configured with a tungsten lamp, a CaF_2 beam splitter and a LN₂-cooled InSb detector. The 20.38-cm long coolable absorption cell [5] was installed inside the sample compartment of the FTS and was operated at temperatures between ~ 298 and 150 K. The optical filter placed between the beam splitter and the secondary aperture restricted the bandpass to the $3550\text{--}5250\text{ cm}^{-1}$ interval; the aperture diameter was set to 1 mm. The sample pressures were continually monitored using calibrated capacitance manometers (Baratron pressure gauges) with 0–10, 0–100 and 0–1000 Torr pressure ranges as appropriate.

The specific experimental conditions for our spectral data are also provided in Table 1. Spectra with enriched samples of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ at room temperature were recorded first (at ~ 20 Torr). For the air-broadened spectra, an enriched sample of the

appropriate CO isotopologue was first admitted into the cell, and dry air (research grade) was then added to achieve the desired volume mixing ratios (0.06–0.14) needed to produce optimum absorption depths (50–80% absorbing) for both low- and high- J transitions. The sample temperatures were continually monitored by calibrated silicon diode temperature sensors attached to the cell body. The temperature stability during the entire scanning was observed to be better than ± 0.05 K.

Multispectrum fitting requires that the wavenumber scale of each spectrum be consistent to all the other spectra. In our first study [1], we calibrated selected H_2O positions between 3760 and 3900 cm^{-1} (against $2 \leftarrow 0$ $^{12}\text{C}^{16}\text{O}$ positions of Pollock et al. [8,9]) because these features were always present in our spectra; they arose from $\sim 5\text{--}10$ mTorr residual vapor inside the evacuated FTS chamber. The individual wavenumber calibration scaling factors, cv (cv is the multiplication factor applied to the observed line positions to obtain the corrected line centers), are listed in Table 1 for each spectrum.

The measured spectra in Fig. 1a and Fig. 2a cover the entire $4000\text{--}4360\text{ cm}^{-1}$ region where the $2 \leftarrow 0$ bands of the three CO isotopologues dominate. Each enriched sample in fact contained small amounts of the other isotopologues, and we therefore elected to combine two sets of the air-broadened data with four additional spectra recorded with samples of $^{13}\text{C}^{16}\text{O}$ (99% ^{13}C), $^{12}\text{C}^{18}\text{O}$ (95% ^{18}O) and $^{12}\text{C}^{16}\text{O}$ (99.5% ^{12}C). This permitted us to effectively ‘calibrate’ the isotopologue volume mixing ratios for each spectrum and then to determine the absolute line intensities of each transition.

Table 1
Summary of the experimental conditions of the CO spectra^a analyzed in this work.

Temperature (K)	Pressure (Torr)	Volume mixing ratio (CO)	cv^c
CO^b			
297.35 ^d ($^{12}\text{C}^{16}\text{O}$)	20.23	1.0	0.9999999252
298.10 ^e ($^{13}\text{C}^{16}\text{O}$)	20.92	1.0	0.9999999229
298.15 ^f ($^{12}\text{C}^{18}\text{O}$)	20.16	1.0	0.9999999207
298.00 ^d ($^{12}\text{C}^{16}\text{O}$)	250.78	1.0	0.9999999253
$^{13}\text{C}^{16}\text{O}^e$ in air			
298.10	97.17	0.07320	0.9999999040
298.10	356.74	0.14465	0.9999999220
298.10	702.68	0.07355	0.9999999080
241.15	171.05	0.07405	0.9999999230
241.15	349.18	0.13455	0.9999999230
241.15	649.30	0.13492	0.9999999190
190.95	151.22	0.07418	0.9999999230
191.15	302.96	0.12500	0.9999999230
191.15	509.36	0.07516	0.9999999220
150.95	97.14	0.13820	0.9999999210
151.15	250.38	0.06680	0.9999999200
151.15	716.07	0.13790	0.9999999200
$^{12}\text{C}^{18}\text{O}^f$ in air			
298.10	98.42	0.07130	0.9999999200
298.10	348.82	0.14310	0.9999999220
298.10	699.84	0.07153	0.9999999230
241.15	196.32	0.13170	0.9999999210
241.15	398.98	0.09563	0.9999999230
241.15	647.25	0.13265	0.9999999210
191.15	198.51	0.14820	0.9999999230
191.15	297.54	0.05620	0.9999999210
191.15	499.58	0.05972	0.9999999220
151.15	107.25	0.14040	0.9999999330
151.15	259.03	0.05740	0.9999999220
151.15	702.01	0.14130	0.9999999210

1 atm = 101.3 kPa = 760 Torr.

^a 99.5% natural CO spectrum recorded with ~ 8 Torr CO in 20.38 cm cell cooled to 173 K was used to calibrate the wavenumber scales of all the spectra in this study and in [1] but not included in the fits. For all spectra the length of the coolable absorption cell was 20.38 cm.

^b These four spectra were included in both ($^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$) fittings.

^c Wavelength calibration correction scaling factor cv applied to each spectrum.

^d 99.5% natural CO.

^e ^{13}C -enriched (^{13}C , 99%) CO.

^f ^{18}O -enriched (^{18}O , 95%) CO.

3. Data reduction and analysis

Generally, for multispectrum non-linear least squares fits, the work begins by applying a theoretical prediction of line parameters (e. g. HITRAN 2008 [2]) to just a few spectra. A very important aspect of the technique is constraining the positions and intensities to the standard quantum mechanical equations for simple linear and diatomic molecules. Rather than determining the individual line positions, ν_i , and intensities, S_i , the fitting procedure adopts Eq. (1) to solve for the rovibrational constants (G , B , D and H) and Eqs. (2) and (3) for the transition moment constants (vibrational band strength S_v , and the Herman–Wallis type parameters a_1 , a_2 , a_3 and a_4)

$$\nu_i = G' - G'' + (B'J'(J'+1) - D'\{J'(J'+1)\}^2 + H'\{J'(J'+1)\}^3) - (B''J''(J''+1) - D''\{J''(J''+1)\}^2 + H''\{J''(J''+1)\}^3) \quad (1)$$

$$S_i(T_0) = \frac{S_v \nu_i L_i F}{Q_r \nu_0} \exp\left(\frac{-C_2 E''}{T_0}\right) \left[1 - \exp\left(\frac{-C_2 \nu_i}{T_0}\right)\right] \quad (2)$$

$$F = 1 + a_1 m + a_2 m^2 + a_3 m^3 + a_4 J'(J'+1) \quad (3)$$

ν_i and S_i correspond to the transition wavenumber (cm^{-1}) and intensity ($\text{cm}/\text{molecule}$ at 296 K) of the i th line, where prime and double prime refer to the upper and lower vibrational levels, respectively. The values of S_i and S_v reported here are the intensities per CO molecule in a natural sample, not per molecule of the particular absorbing isotopologue. In Eq. (2), L_i are the Hönl–London factors and C_2 represents the second radiation constant. J is the rotational quantum number, Q_r the rotational quantum partition function, ν_0 is the band center (equal to $G' - G''$), E'' is the lower state energy, and T_0 is the temperature of the absorbing gas. The values of the rotational quantum partition function Q_r used in the present study were 224.074297 for the $^{13}\text{C}^{16}\text{O}$ and 112.464588 for the $^{12}\text{C}^{18}\text{O}$ corresponding to $T_0 = 296$ K [10]. We found that the a_1 , a_2 and a_3 terms were sufficient to describe fully the $2 \leftarrow 0$ bands since

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