4022. Measurements of CO_2 Spectroscopic Parameters in the Near-Infrared

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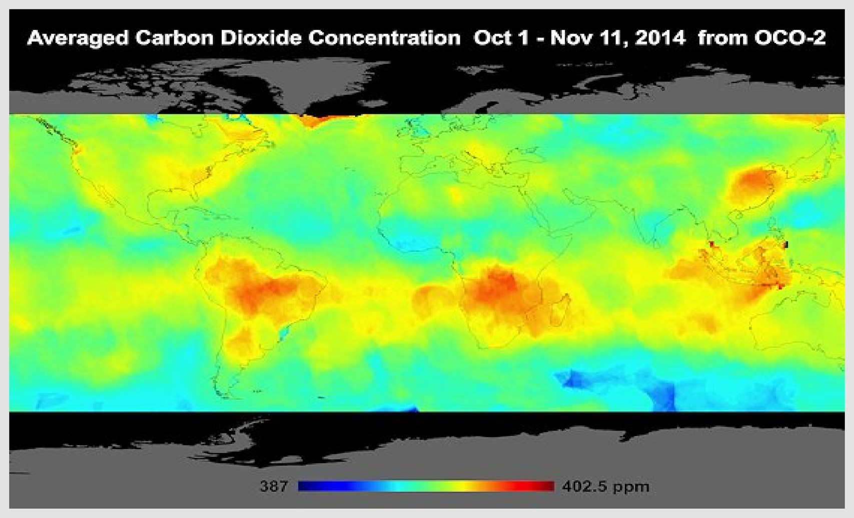
#1: Introduction

- Earth atmospheric measurements using CO_2 bands in the near-infrared region provide information on the global distribution of atmospheric carbon dioxide (see Fig. 1).
- Air-broadened line widths and shifts and their temperature dependences are needed for forward-model calculations in terrestrial remote sensing retrievals.
- Self-broadened line widths and shifts and their temperature dependences are needed to accurately characterize sensor signals for remote sensing of planetary atmospheres which are predominantly CO_2.

Fig. 1. OCO-2 global map of terrestrial atmospheric CO_2



http://science.nasa.gov/science-news/science-at-nasa/2014/19dec_oco/

In this poster…

➢ We report measurements and analyses of high-resolution spectra of self- and air-broadened CO_2 in several spectral regions between 1.6 and 4.5 µm at temperatures between 170 and 298 K.

➢ Parameters and their temperature dependences were determined for transitions of $^{12}C^{16}O_2$ and $^{16}O^{12}C^{17}O$ at 1.6 – 2.1 µm and positions for several isotopologues near 4.3 µm.

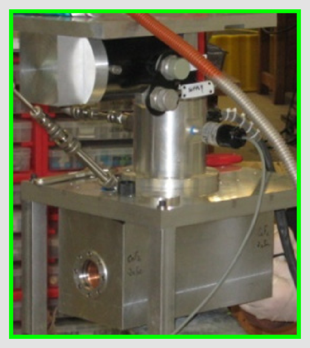
➢ Results are compared with other published measurements and with the HITRAN database values.

#2: Spectral Data

Several high-resolution Fourier transform spectrometers (FTS) were used.

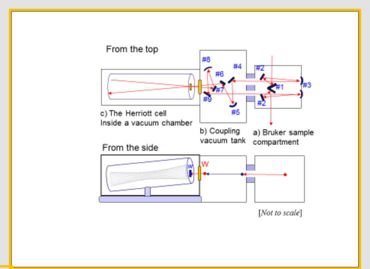
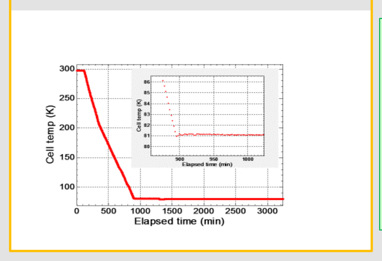
- Air- and self-broadened CO_2 spectra were recorded with several sample cells (2.46 to 121 m) at room temperature (~293 K) with the McMath-Pierce FTS at Kitt Peak at 0.01 cm^{-1} resolution [Malathy Devi *et al*., 2007a,b].
- Additional sets of CO_2 spectra were recorded at temperatures from 215 to 294 K with the Bomem DA3.002 FTS at NRC, Ottawa, at 0.008 – 0.009 cm^{-1} resolution [Predoi-Cross *et al*., 2007, 2009, 2010].
- The most recent spectra analyzed were recorded at 0.004 – 0.006 cm^{-1} resolution with the Bruker IFS 125 HR FTS at JPL using several different sample cells:
  - A two-chamber room temperature cell with optical paths 6.14 and 15.26 cm [Elliott *et al*., 2014].
  - A 20.38 cm straight cell coolable to < 80 K [Sung *et al*., *JMS* 262 (2010) 122-134].
  - A Herriott multipass cell, also coolable to < 80 K, with 20.9 m optical path [Mantz *et al*., 2014].

Fig. 2a. The 20.38-cm copper cell enclosed in its vacuum box


The cell operates inside the Bruker FTS sample compartment.

Fig. 2b. 20.9-m Herriott cell enclosed in its vacuum box and coupled to the Bruker FTS through transfer optics

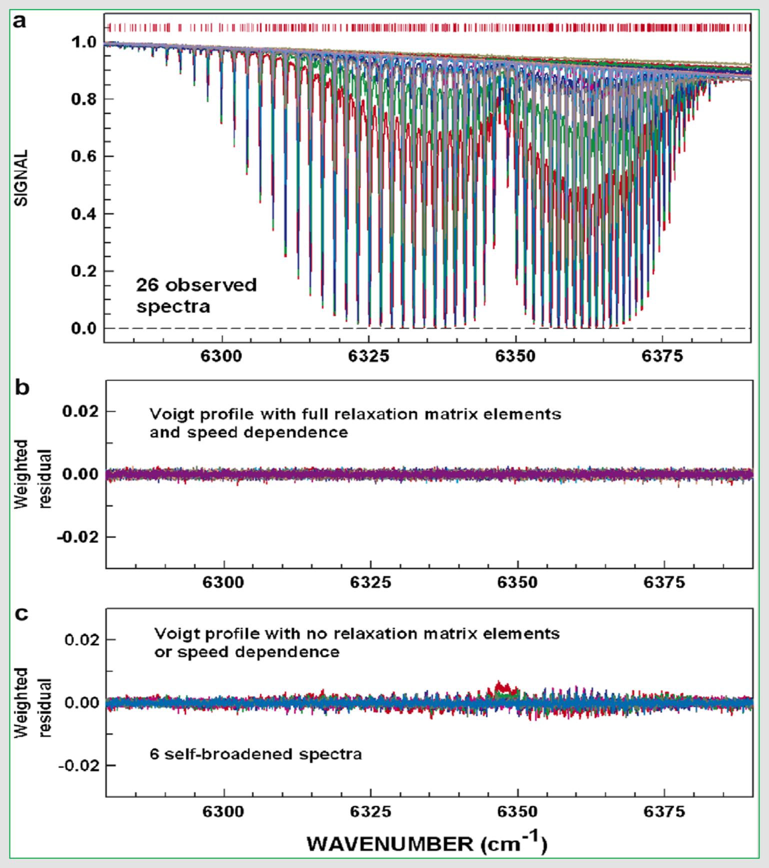
Both cold cells achieve excellent temperature control.

#3: Analysis

Nonlinear least squares multispectrum fitting [Benner *et al., JQSRT* 53 (1995) 705-721] was used in most of the studies described here to retrieve spectroscopic parameters consistent with sets of 16 or more laboratory spectra.

- All spectra were calibrated to the same wavenumber scale.
- Voigt line shape was initially assumed for most analyses; line mixing and speed dependence parameters were required for residuals within the noise level of the spectra.
- Room-temperature spectra were fit first; then the lower-temperature spectra were added.
- Spectra were given weights inversely proportional to their signal-to-noise ratios.

Fig. 3. Simultaneous fit of 15 self-broadened and 11 air-broadened CO_2 spectra at 1.58 µm at room temperature [Malathy Devi *et al*., 2007a].



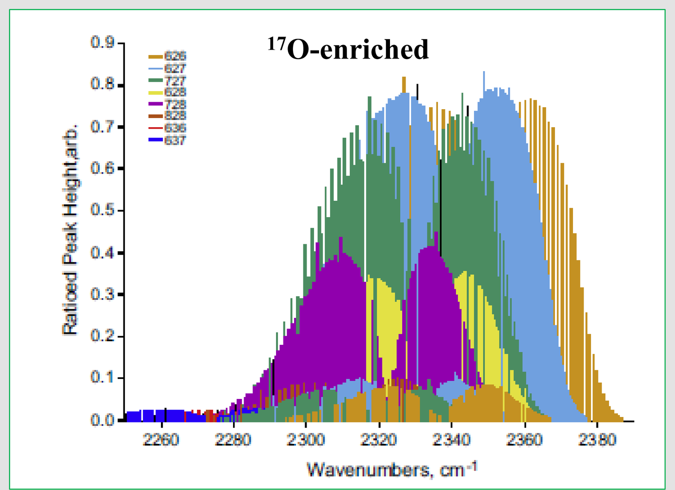
Red tick marks in panel (a) indicate positions of lines included in the fit.

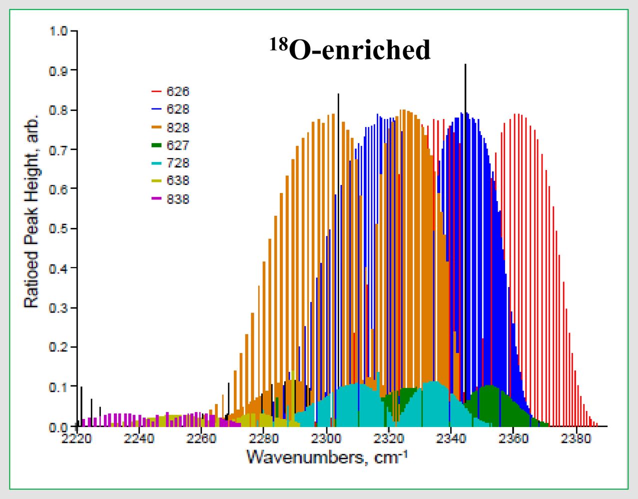
Self-broadened CO_2:
Sample pressures 9.9 to 897 Torr
Path lengths 2.46 to 49.0 m

Air-broadened CO_2:
Sample pressures 25.1 to 924 Torr
Volume mixing ratios 0.02 to 0.07
Path lengths 49.0 to 121.2 m

#4: Results – Line Positions and Intensities

Fig. 4. Line Positions: ^{17}O-, ^{18}O- and ^{13}C-enriched CO_2 isotopologues at 4.3 µm [Elliott *et al*., *JMS* 304 (2014) 1-11; Elliott *et al*., *JMS* (2015) accepted]





Spectra of various enriched CO_2 samples in the v_3 region with assigned transitions color coded by isotopologue. The 00011–00001 (v_3 fundamental) bands from normally less-abundant isotopologues have significant intensity, and numerous hot bands from these species are also observed.

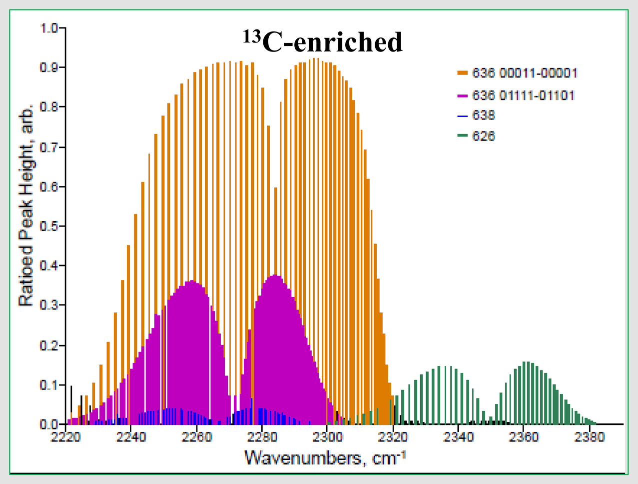


Fig. 5. Intensities in the $^{12}C^{16}O_2$ (and one $^{13}C^{16}O_2$) bands near 1.6 µm [Malathy Devi *et al*., 2007]

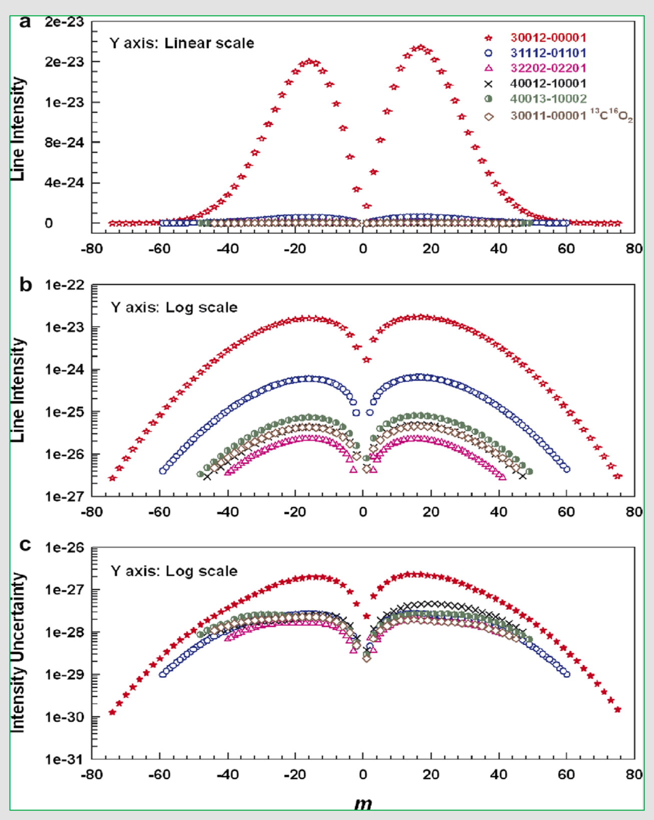
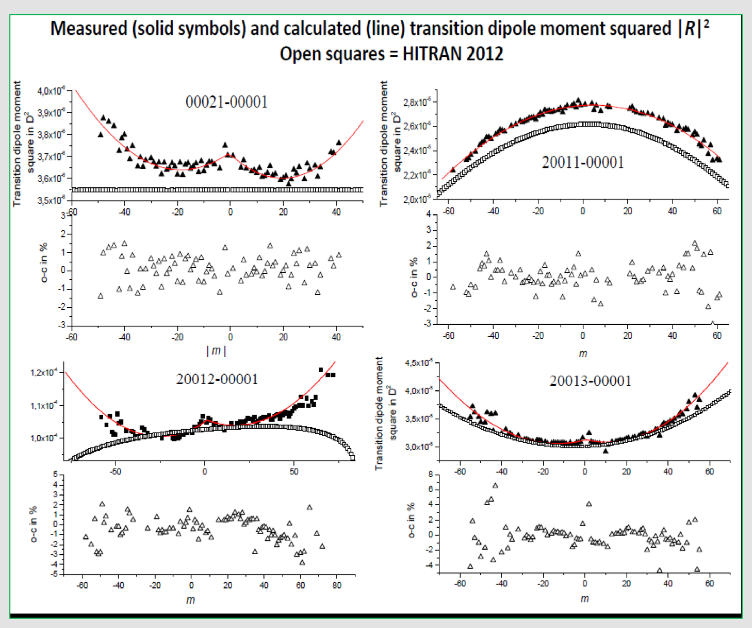


Fig. 6. Intensities: $^{16}O^{12}C^{17}O$ at 2.1 µm compared to HITRAN 2012 [Jacquemart *et al*., in preparation]



#5: Results – Line Widths, Pressure-induced Shifts, Line Mixing and Speed Dependence

Fig. 7. Comparison of 1.6 µm $^{12}C^{16}O_2$ Self- and Air-Broadened Widths (left panel) and Shifts (right panel)

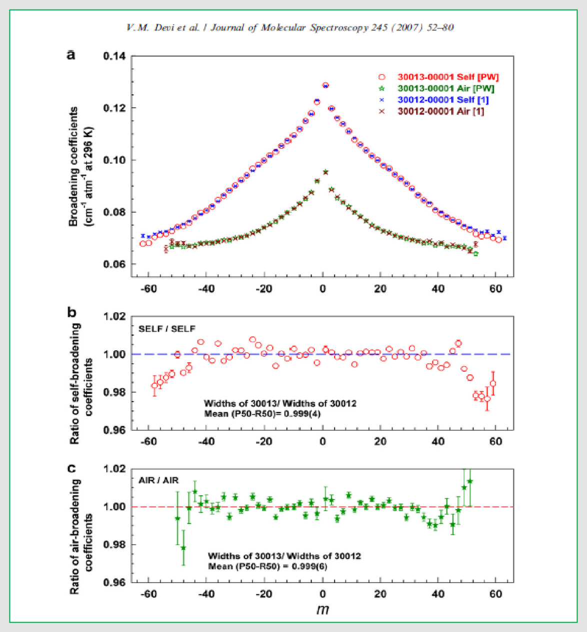
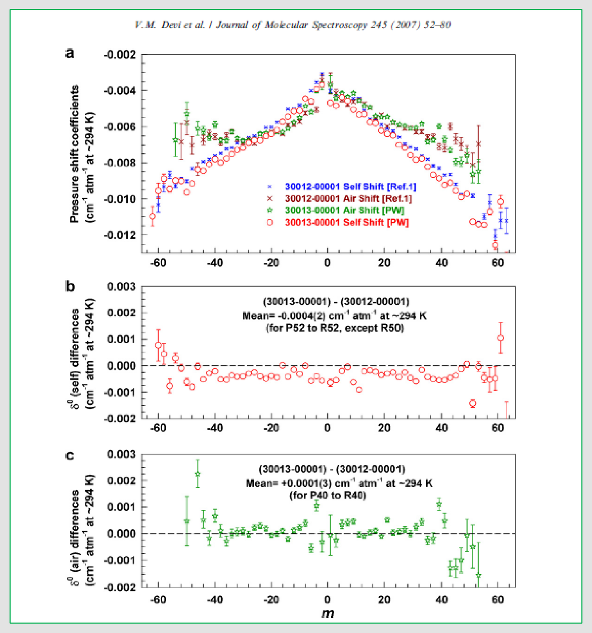
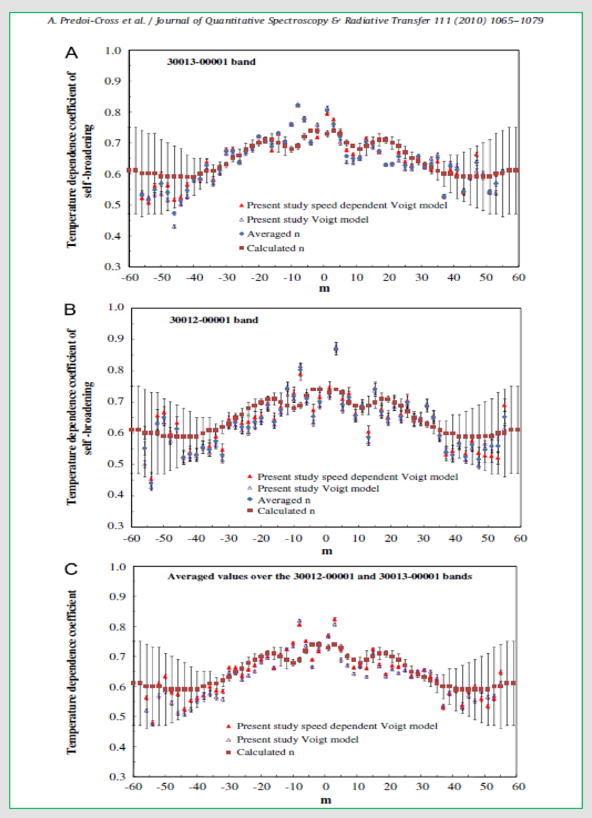
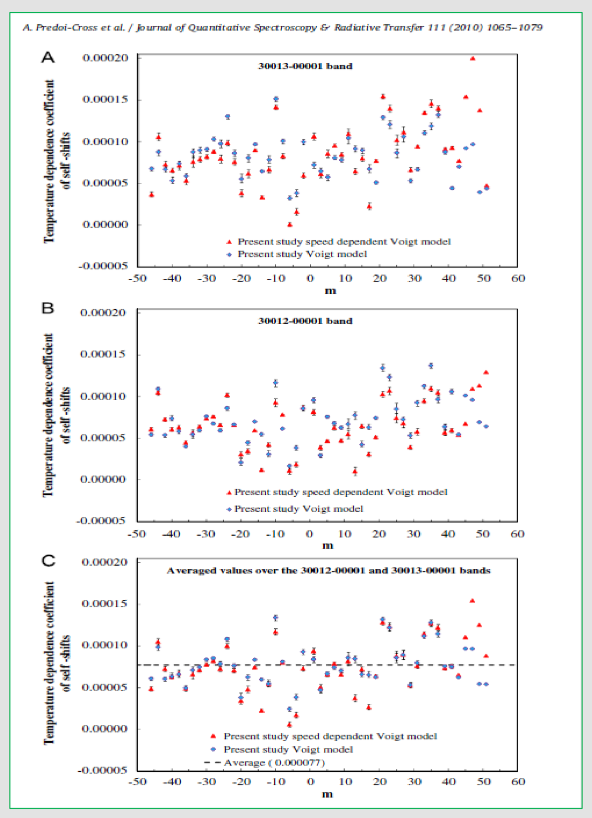



Fig. 8. Temperature Dependences of Self-Broadened Widths and Shifts for 1.6 µm $^{12}C^{16}O_2$ (218 – 295 K)

Widths

$b_L^0(T) = b_L^0(T_0) \times (T_0/T)^n$

$b_L^0(T)$ = half width at T at 1 atm
T_0 = reference T (296 K unless otherwise noted)
n = temperature dependence exponent
(*Empirical power law*)

Shifts

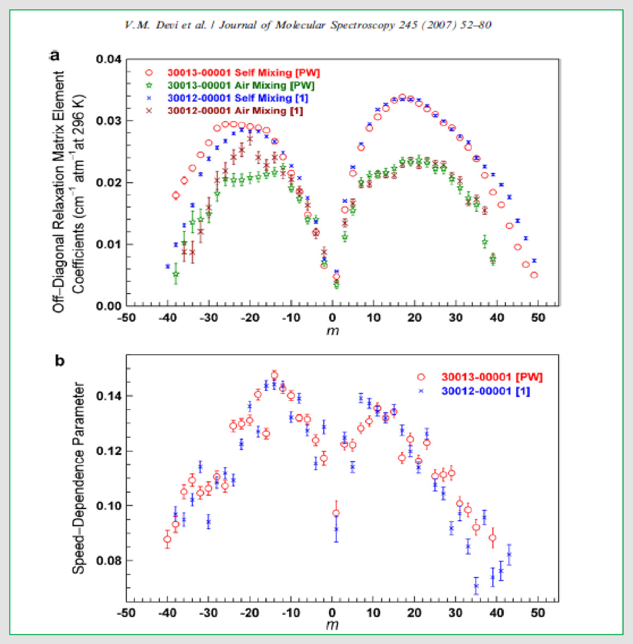
$\delta^0(T) = \delta^0(T_0) + \delta' \times (T - T_0)$

$\delta^0(T)$ = pressure-induced shift at T at 1 atm
T_0 = reference T (296 K unless otherwise noted)
δ' = temperature dependence coefficient
(*Note that we do not use a power law here.*)

Fig. 9. Experimentally-determined Line Mixing and Speed Dependence Parameters for $^{12}C^{16}O_2$ 1.6 µm transitions

Upper Panel: Measured Off-diagonal Relaxation Matrix Elements (Line Mixing Parameters)

Lower Panel: Measured Speed Dependence parameters



#6: Key Results

► $^{12}C^{16}O_2$ line parameters have been obtained in the 1.6 µm region with very high absolute accuracy, using high-resolution lab spectra from three different FTS systems.

► $^{16}O^{12}C^{17}O$, $^{17}O^{12}C^{17}O$, $^{17}O^{12}C^{18}O$, $^{16}O^{12}C^{18}O$, $^{18}O^{12}C^{18}O$, and $^{16}O^{13}C^{16}O$ line positions and spectroscopic constants have been determined in the 4.3 µm region with very high accuracy, using high-resolution lab spectra from the JPL FTS.

► High-quality laboratory spectra cannot be fit within their noise levels without non-Voigt line shapes (*i.e.*, speed dependence and line mixing).

Work in progress:

- $^{12}C^{16}O_2$ self- and air-broadening and shift parameters and line mixing, with temperature dependences, from 170 K to 298 K [V. Malathy Devi *et al.*].
- Further analysis of $^{16}O^{12}C^{17}O$ bands near 2.1 µm [D. Jacquemart *et al.*].

Results from our 2007-2010 work have been included in the 2008 and 2012 HITRAN updates. More recent measurement results will be included in future spectroscopic database updates (*e.g.*, HITRAN 2016).

Acknowledgements

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