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Self-broadening coefficients and improved line intensities for the ν_7 band of ethylene near 10.5 μm , and impact on ethylene retrievals from Jungfraujoch solar spectra



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ABSTRACT

Relying on high-resolution Fourier transform infrared (FTIR) spectra, the present work involved extensive measurements of individual line intensities and self-broadening coefficients for the ν_7 band of $^{12}\text{C}_2\text{H}_4$. The measured self-broadening coefficients exhibit a dependence on both J and K_a . Compared to the corresponding information available in the latest edition of the HITRAN spectroscopic database, the measured line intensities were found to be higher by about 10% for high J lines in the P branch and lower by about 5% for high J lines of the R branch, varying between these two limits roughly linearly with the line positions. The impact of the presently measured line intensities on retrievals of atmospheric ethylene in the 949.0–952.0 cm^{-1} microwindow was evaluated using a subset of ground-based high-resolution FTIR solar spectra recorded at the Jungfraujoch station. The use of HITRAN 2012 with line intensities modified to match the present measurements led to a systematic reduction of the measured total columns of ethylene by $-4.1 \pm 0.1\%$.

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1. Introduction

Ethylene (ethene, C_2H_4) is a tropospheric pollutant affecting plants [1], mainly produced by automobiles and in biomass fires [2,3]. In the atmosphere, photochemical

reactions of ethylene with molecular oxygen, nitrogen, the hydroxyl radical, and ozone produce formaldehyde, nitrous oxide and formic acid [4]. Ethylene is also present as a by-product of methane photochemistry in the atmosphere of outer solar system bodies, such as Jupiter and Saturn [5,6], Neptune [7] and Titan [8].

Remote sensing of ethylene in the infrared range relies on the 10 μm region. This spectral range corresponds to the excitation of 7 modes of vibration of $^{12}\text{C}_2\text{H}_4$, 4 of which

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being infrared active (see Fig. 1 of [9]). The corresponding ν_{10} , ν_7 , ν_4 and ν_{12} bands are located near 826, 949, 1026 and 1442 cm^{-1} , respectively [9]. Among these, the ν_7 band is the strongest, indeed used for remote sensing measurements of ethylene. Spectral line parameters for the ν_7 band of $^{12}\text{C}_2\text{H}_4$, as well as for the weak ν_{10} and ν_4 bands, were included into the HITRAN database as of the 2000 edition [10]. That information for the 10 μm range was later extended with the addition of line parameters for the ν_{12} band [11,12]. No changes occurred for ethylene in the latest edition of HITRAN [13].

The information available in HITRAN for the 10 μm region of ethylene is the result of several efforts. The energy levels structure associated with the 7 modes of vibration of $^{12}\text{C}_2\text{H}_4$ involved in this region has been extensively studied (see [12,14,15] for reviews). The integrated intensity of the ν_7 band (thus including the underlying ν_4 band and R branch of the ν_{10} band) has been measured several times [16–19], while measurements of individual intensities have been reported for only 32 lines of the ν_7 band of $^{12}\text{C}_2\text{H}_4$, located near the band origin between 940 and 970 cm^{-1} [20–25]. Blass et al. [24] mention a database of 510 assigned lines with intensities retrieved from Fourier transform infrared (FTIR) spectra and calibrated using 13 line intensities measured using a tunable diode laser spectrometer. To the best of our knowledge, this database was however not published. The line intensities available in HITRAN for the ν_{10} , ν_7 and ν_4 bands of $^{12}\text{C}_2\text{H}_4$ were generated by matching calculated relative intensities [26] to the intensities reported in [24]. Measurements of self-broadening coefficients have been reported for the ν_7 band [20,28] and one line of the ν_{10} band [29] of $^{12}\text{C}_2\text{H}_4$, as well as for a significant number of lines of the ν_7 band of $^{13}\text{C}^{12}\text{CH}_4$ [30]. In HITRAN [13], the self-broadening coefficient of all the lines is set to a default value of 0.09 $\text{cm}^{-1} \text{atm}^{-1}$, except for the ν_{12} band for which it is set to 0.125 $\text{cm}^{-1} \text{atm}^{-1}$ [12].

Relying on high-resolution FTIR spectra, the present work involved extensive measurements of individual line intensities and self-broadening coefficients for the ν_7 band of $^{12}\text{C}_2\text{H}_4$. Discrepancies between the measured line intensities and the corresponding information available in HITRAN [13] were observed and modeled empirically. The measured self-broadening coefficients exhibit a dependence with J'' and K_a'' , the quantum numbers respectively associated with the total angular momentum of the molecule in the lower level of the corresponding transition and its projection on the principal axis of inertia a of the molecule, which was also modeled empirically. Both of these results were used to modify the spectroscopic information available in HITRAN. This work is described in Sections 2–4. The impact of these modifications on retrievals of atmospheric ethylene in the 949.0–952.0 cm^{-1} microwindow [2,3] was then evaluated using a subset of ground-based high-resolution FTIR solar spectra recorded at the Jungfraujoch station. This work is described in Section 5.

2. Experimental details

Six unapodized absorption spectra of a commercial sample of ethylene (Praxair, 99.95% stated purity, used

without further purification) were recorded with an upgraded Bruker IFS120HR Fourier transform spectrometer available in Brussels. The instrument was fitted with a Global source, a KBr beamsplitter, a low-pass optical filter with a cut-off wavenumber at about 2000 cm^{-1} and a HgCdTe detector. The spectra were recorded at room temperature [295(1) K], stabilized by an air-conditioning system. The sample pressure, absorption path length, maximum optical path difference and diameter of the entrance aperture of the spectrometer used are listed in Table 1. The sample pressure was measured using two MKS Baratron gauges model 690A, of 10 and 1000 Torr full scale range. All the spectra were recorded using a 1.45(2) cm long stainless steel cell located inside the evacuated spectrometer and closed with KBr windows. To avoid saturation of the absorption features, spectra S4–S6 were recorded with two 5-mm thick KBr windows fitted into the cell to reduce the absorption path length. The recorded spectra correspond to the average of 300–742 interferograms. They were corrected for the non-linear response of the MCT detector, using the algorithm implemented in the OPUS software provided by Bruker. A portion of the spectra recorded at the lowest and highest pressures is presented in Fig. 1.

The present effort being focused on measurements of line intensities and self-broadening coefficients, only a

Table 1

Sample pressure P , absorption path length ℓ , maximum optical path difference L (the corresponding spectral resolution is equal to $0.9/L$) and diameter d of the entrance aperture of the spectrometer. All the spectra correspond to a temperature of 295(1) K.

#	P (hPa)	ℓ (cm)	L (cm)	d (mm)
S1	1.544 (24)	1.45 (2)	450	1.50
S2	4.643(36)	1.45 (2)	450	1.50
S3	9.868 (51)	1.45 (2)	450	1.50
S4	25.7 (5)	0.4322 (15) ^a	450	1.50
S5	51.5(5)	0.4322 (15) ^a	150	1.50
S6	101.4 (8)	0.4322 (15) ^a	150	2.50

The absolute uncertainties given for the sample pressure P are the square root of the measurement uncertainty (estimated to be 0.5% of reading) and the peak-to-peak variations during the recordings.

^a The path length of spectra S4–S6 was included in the least squares fit.

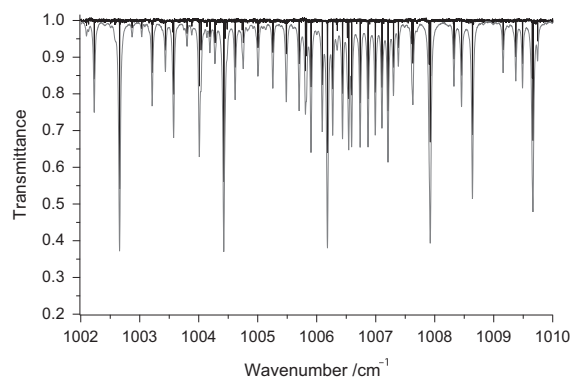


Fig. 1. Fourier transform spectra of ethylene near the r_{Q_6} branch of the ν_7 band of $^{12}\text{C}_2\text{H}_4$, recorded at the lowest (black curve, S1 in Table 1) and highest (gray curve, S6 in Table 1) pressures achieved in the present work.

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