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Absorption cross sections for ethane broadened by hydrogen and helium in the 3.3 micron region

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A B S T R A C T

The infrared absorption cross sections of ethane (C_2H_6) have been measured in the 3.3 µm region by high resolution Fourier transform spectroscopy. The ethane samples had temperatures of 203, 233, 263, 295 K with broadening gas pressures of 10 Torr, 30 Torr and 100 Torr of hydrogen or helium. These cross sections are useful for the interpretation of spectra of the giant planets.

1. Introduction

Ethane (C_2H_6) is the second most abundant hydrocarbon (after methane) in many planetary atmospheres. The main source of ethane in the Earth's atmosphere is from fugitive emissions from fossil fuel production [1]. For example, ground based Fourier transform spectroscopy of ethane in the 3.3 µm region has measured a recent increase attributed to shale gas production [1]. In this spectral region, high resolution absorption cross sections are available for ethane broadened by air [2]. A set of pseudo-lines have been derived these cross sections [1] and some Q-branches are in the HITRAN database [3]. Lower resolution absorption cross sections of ethane with 1 atm of N_2 broadening gas are available from the Pacific Northwest National Laboratory (PNNL) [4] and are now included in HITRAN. Villanueva et al. [5] have prepared a set of ethane line parameters in order to model cometary fluorescence.

Titan, the largest moon of Saturn, has a thick atmosphere (1.5 atm at the surface) of N_2 and CH_4 with strong ethane emission bands in the thermal infrared [6]. The CIRS (Composite Infrared Spectrometer) on the Cassini spacecraft recorded particularly extensive ethane bands from the nominally forbidden ν_4 torsional band at 289 cm^{-1} to the ν_8 band at 1468 cm^{-1} [6]. Absorption in low resolution solar occultation spectra at 3.4 µm have also been attributed partly to ethane [7]. On Titan, ethane originates from photochemical reactions of CH_4 induced by solar UV radiation [8].

Ethane is also found in the giant planets, Jupiter [9], Saturn [10], Neptune [11] and Uranus [12], again from CH_4 photochemistry. The main chemical reaction producing ethane is the recombination of two CH_3 radicals, e.g., [13]. For the giant planets, the broadening gases are H_2 and He, rather than N_2 and air for Titan and Earth, respectively. While ethane is typically seen in emission in the thermal infrared, it has also been detected in absorption at 3.06 µm on Saturn [14] and in hot 3 µm auroral emission on Jupiter [15]. Hot ethane emission cross sections have been obtained from laboratory spectra [16]. Ethane in the giant planets will also be observed with the NIRSpec instrument on the James Webb Space Telescope [17].

Recently, our group has published high resolution infrared absorption cross sections for ethane in the 1800–6200 cm^{-1} region with H_2 and N_2 as broadening gases [18]. However, the region containing the strong C–H fundamental vibrations was saturated because the goal was to obtain cross sections for the weak overtone and combination bands. In this follow-up paper, we report absorption cross sections for the C–H stretching region with H_2 and He as broadening gases for the interpretation of spectra of the giant planets.

2. Experimental method

Similar to the work described in reference [18], infrared absorption spectra of ethane, pure and broadened by hydrogen and

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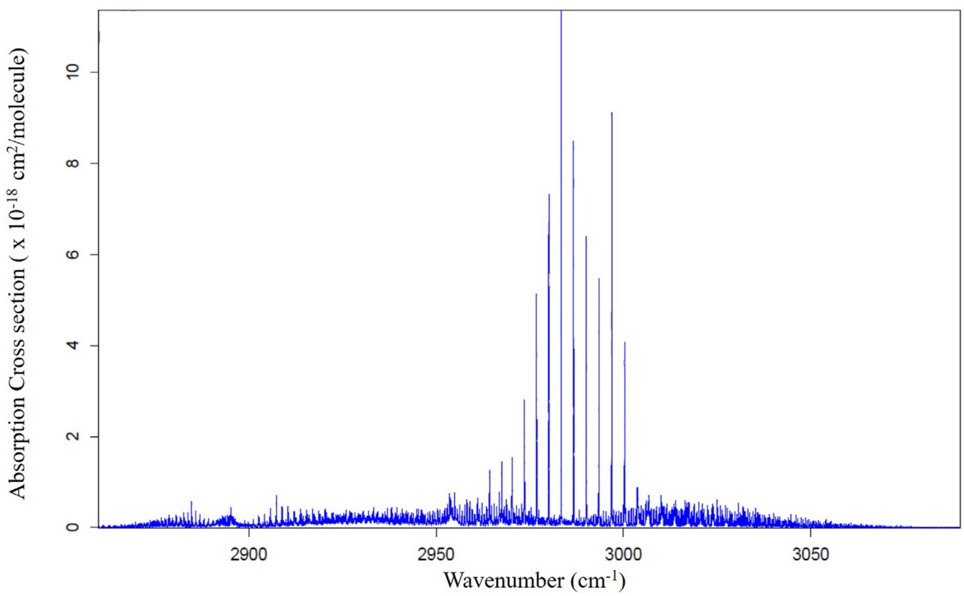

Fig. 1. Absorption cross sections of ethane (about 9 mTorr of ethane in 100.3 Torr total pressure of H_2 and ethane at 291.75 K).

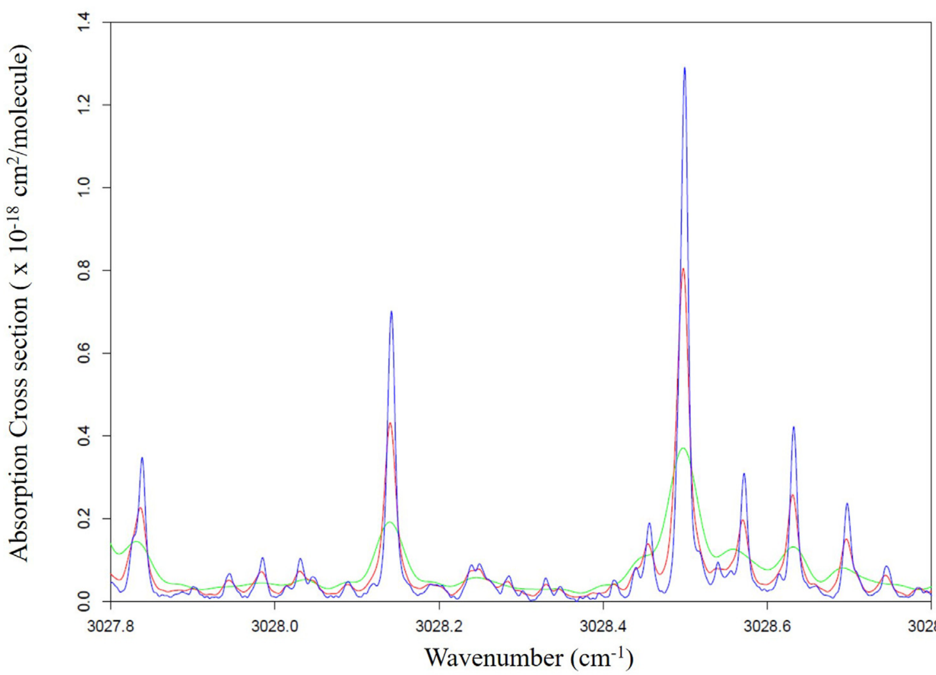

Fig. 2. Absorption cross sections of ethane broadened by hydrogen with different pressures at 295 K. (Blue = 10.29 Torr, Red = 30.1 Torr, Green = 100.3 Torr).

helium were recorded at the Canadian Light Source (CLS) far infrared beamline. 99.999% pure ethane with less than 6 ppm total hydrocarbon impurity was used. A path length of 8.63 m (± 0.02 m) was set in a White-type multiple reflection cell and samples were held at 4 temperatures (203, 233, 263, 295 K) with broadening gas pressures of 10 Torr, 30 Torr and 100 Torr. Pure ethane spectra were also recorded at each temperature. The pressure was chosen to give suitable absorption in the 2650–3200 cm^{-1} region. Fig. 1 illustrates the absorption cross sections of ethane broadened by hydrogen at 299.75 K.

A Bruker IFS 125 HR Fourier transform spectrometer with a CaF_2 beam splitter, a bandpass filter in the region 2650–3200 cm^{-1} and an InSb detector was used. The spectral resolution (Bruker definition) was varied according to the total pressure: 0.005 cm^{-1} (10 Torr), 0.01 cm^{-1} (30 Torr), 0.04 cm^{-1} (100 Torr) and 0.005 cm^{-1} (pure sample). The resolution for the background spectra were 0.04 cm^{-1}. Ethane pressures were measured using a 10 Torr Baratron pressure gauge, 627B, which has an accuracy of about 0.3%. The total pressures were measured with a 1000 Torr Baratron guage (Model 626B) with an accuracy of about 1%. Platinum resistance temperature detectors (4 wire PT100 RTD), which have an estimated accuracy of ± 2 K, were employed in monitoring cell temperature and a NESLAB ULT-80DD refrigerated recirculating methanol bath was utilized to cool the cell. Table 1

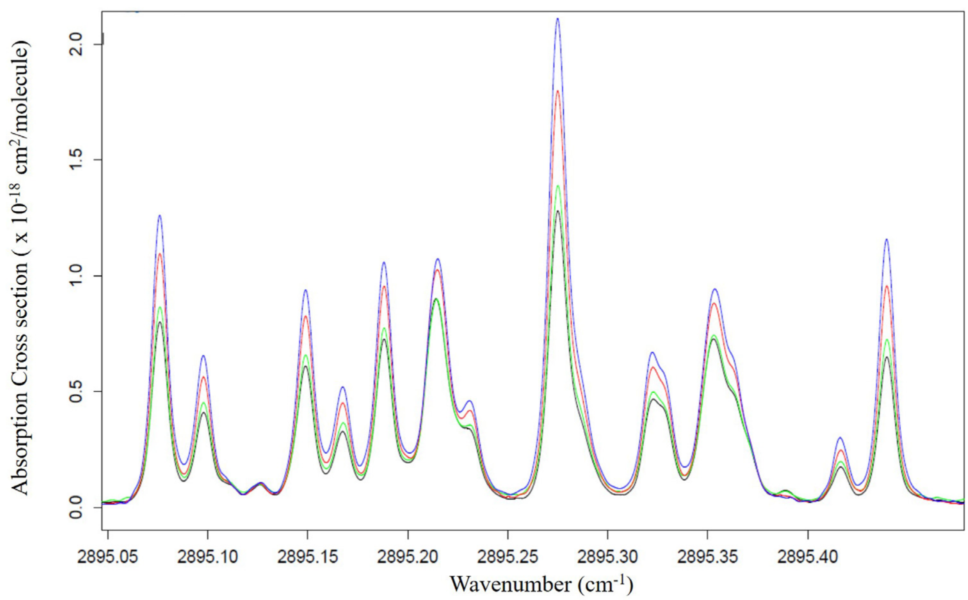

Fig. 3. Absorption cross sections of ethane broadened by hydrogen with different temperatures for 10 Torr of total pressure. (Blue = 202.05 K, Red = 232.95 K, Green = 262.45 K, Black = 291.85 K).

Table 1
Experimental conditions for each spectrum.

Helium					
203 K			233 K		
Temp (K)	Ethane (mTorr)	Total (Torr)	Temp (K)	Ethane (mTorr)	Total (Torr)
201.85	2.62	10.4	232.95	3.03	10.2
201.75	3.09	30.1	232.95	2.46	30.5
201.85	3.47	100.3	232.95	4.76	99.8
263 K			295 K		
262.35	4.30	9.9	292.05	5.71	10.4
262.25	2.47	30.6	292.15	3.14	30.4
262.35	6.48	100.5	291.95	8.66	100.8
Hydrogen					
203 K			233 K		
Temp (K)	Ethane (mTorr)	Total (Torr)	Temp (K)	Ethane (mTorr)	Total (Torr)
202.05	2.53	11	232.95	3.45	10.45
201.95	2.80	30.7	232.95	2.37	29.8
201.85	2.87	100	232.95	5.16	99.5
263 K			295 K		
Temp (K)	Ethane (mTorr)	Total (Torr)	Temp (K)	Ethane (mTorr)	Total (Torr)
262.45	4.30	10.7	291.85	4.51	10.29
262.45	2.72	30.8	291.45	4.09	30.1
262.45	6.19	100.5	291.75	7.62	100.3
Pure Samples					
Temp (K)	Ethane (mTorr)	Total (Torr)	Temp (K)	Ethane (mTorr)	Total (Torr)
201.85	2.50	2.50	232.75	3.10	3.10
262.35	3.94	3.94	291.85	4.68	4.68

shows the parameters used for recording the spectra. An initial zero-filling factor of 8 was used and an additional factor of 4 was applied to make the final cross sections.

A small amount of ethane was added to the cell and hydrogen (or helium) was added until the desired total pressure was obtained and then recorded. For such small pressures of ethane, the 10 Torr Baratron was not suitable resulting in some inaccuracies in pressure measurements. A calibration factor (C) was therefore applied to obtain more accurate absorption cross sections. Spectra reported at temperatures of 278 K, 298 K and 323 K with 1 atm of nitrogen broadening gas from the Pacific Northwest National Laboratory (PNNL) database were used for this calibration. As discussed by Hewett et al. [18], the integrated area of the absorption cross sections can be used. After converting PNNL spectra to the units of 10^{-18} cm^2/molecule, the integrated areas from 2790 cm^{-1} to 3092 cm^{-1} for ethane are 28.365, 28.048 and 27.887 for 278, 298 and 323 K, respectively. The average integrated area is 28.1 × 10^{-18} cm/molecule. The transmission spectra were converted to cross sections using [16]:

$$\sigma(\nu, T) = -C\frac{10^4 k_B T}{Pl}\ln\tau(\nu, T)$$

where, $\tau(\nu, T)$ is the transmittance at wavenumber ν (cm^{-1}) and temperature T (K), P is the pressure of the absorbing gas in pascals (Pa), l is the path length in meters (m) and k_B (1.380649 × 10^{-23} JK^{-1}) is the Boltzmann constant.

Calibration factor C is the ratio between the averaged integrated area of the PNNL spectra and the integrated area from this study. Ethane pressures were corrected using C, as shown in Table 1. The cross sections were compared with Harrison et al.'s

[2] pure spectra and the wavenumbers were calibrated by a factor of 0.999998486. In addition, a spectrum at 294.95 K and a pressure of 0.3 Torr was recorded at Old Dominion University for comparison and confirmed that the wavenumber scale was calibrated to better than 0.001 cm^{-1}.

3. Results and discussion

The 28 calibrated cross section files can be obtained from MoLLIST (Molecular Line Lists. Intensities and SpecTra) website http://bernath.uwaterloo.ca/molecularlists.php and as supplementary data to this paper. The cross sections should be multiplied by 10^{-18} and the units are cm^2/molecule.

A room temperature ethane spectrum was recorded at Old Dominion University in the 1800–5000 cm^{-1} region. This spectrum was converted to cross sections and calibrated using impurity lines from the ν_3 band of CO_2 with the line positions taken from the HITRAN database. The integrated area from 2790 cm^{-1} to 3092 cm^{-1} is 25.88×10^{-18} cm/molecule which differs from the average of the PNNL spectra by 7.9%. Based on this independent measurement, the estimated absolute error in the cross sections is less than 10%.

Fig. 2 represents the effect of pressure due to hydrogen broadening. As the pressure increases the peaks get smaller and lines get wider. Pressure broadening is linear with pressure and as mentioned in Hewett et al. [18] a quasicontinuum appears in the 100 Torr data. The effect on cross sections due to helium broadening is similar.

The effect of temperature is shown in Fig. 3. The main effect of temperature is on population. For these low *J* and *K* transitions, the intensity increases and population increases as the temperature drops.

These data cover the saturated region missing in Hewett et al. [18] but with hydrogen and helium as broadening gases. The temperature and pressure ranges for Jupiter's stratosphere are about 120–190 K and 0.00075–75 Torr and hydrogen as a primary broadening gas [19]. Our measurements cover the pressure range but not the temperature range.

4. Conclusion

Absorption cross sections of ethane, broadened by hydrogen and helium from 203 to 295 K were obtained in the 2650–3200 cm^{-1} region. With these 28 cross sections, the full spectral region from 1800 to 6200 cm^{-1} for ethane is covered for hydrogen as the broadening gas. Extensive perturbations make an accurate quantum mechanical model of ethane in the 3 µm region difficult to obtain [5]. Our experimental cross sections can be used directly in radiative transfer models to improve the interpretation of spectra of the giant planets. They also can be used to estimate pressure broadening of the spectral features. However, measurements at lower temperatures are still needed because ethane is found in the stratospheres of the giant planets where temperatures are in the 100–200 K range.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Randika Dodangodage: Formal analysis, Writing - original draft. **Peter F. Bernath:** Methodology, Supervision, Writing - original draft. **Jianbao Zhao:** Investigation. **Brant Billinghurst:** Investigation, Supervision.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2020.107131.

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