



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Near infrared absorption cross sections for ethane broadened by hydrogen and nitrogen

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ARTICLE INFO

Article history:

Received 16 July 2019

Revised 1 December 2019

Accepted 1 December 2019

Available online 2 December 2019

ABSTRACT

Near infrared absorption spectra of ethane (C₂H₆) were recorded in the 1800–6200 cm⁻¹ region by high resolution Fourier transform spectroscopy (Bruker IFS 125 HR) at the Canadian Light Source (CLS). Absorption cross sections were obtained for pure samples and with nitrogen or hydrogen as broadening gases as appropriate for astronomical environments. Corrections to the cross sections were made using data from the Pacific Northwest National Laboratory (PNNL) infrared database.

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1. Introduction

Ethane is of considerable interest to the scientific community, particularly in the combustion sector, going back to the 1930s [1]. Much of the work done on ethane has focused on understanding the complex mechanism for the oxidation of ethane in flames with temperatures and pressures relevant to the combustion process [2]. Recently, ethane has been observed in absorption by time-resolved laser imaging in an ethane-air flame [3].

Ethane is also of considerable importance in planetary atmospheres. On Earth, it is the most abundant non-methane hydrocarbon and originates mainly from oil and gas production [4]. Ethane is also the second most abundant hydrocarbon on Titan, the largest moon of Saturn, behind methane [5,6]. It is also prevalent in the atmospheres of the four giant planets [7–10], on comets [11], and even as ice in Kuiper Belt objects [12]. The formation of ethane is thought to occur through the photolysis of methane, which results in CH₃ radicals and radical-radical recombination forms ethane [13].

The two methyl groups on ethane are staggered leading to D_{3d} symmetry at equilibrium, with a low torsional barrier of about 1000 cm⁻¹ [14]. Ethane is a symmetric top with 12 fundamental modes of vibration ranging from the torsion ν₄ (a_{1u}) at 289 cm⁻¹ to highest frequency C–H stretching mode ν₇(e_u) at 2985 cm⁻¹ [15]. The low frequency torsional mode leads to many hot bands and perturbations in the spectra. In spite of these perturbations, rotational assignments are available for most fundamental

bands, for example ν₇(e_u) and ν₅(a_{2u}) at 2896 cm⁻¹ [16]. Some combination bands and hot bands in the C–H stretching region have also been rotationally analysed in room temperature and jet-cooled spectra [15,17]. Hepp et al. [18] carried out a partial rotational analysis of the ν₆+ν₁₀ combination band at 4343 cm⁻¹. Hepp and Herman [19] summarize the vibrational assignments of ethane from 289 cm⁻¹ to 5956 cm⁻¹ based on high resolution spectra.

Quantitative analysis of ethane, however, in the 3-micron region and in the near infrared generally requires absorption cross sections. With the exception of Villanueva's work on the ν₇ band [20], line-by-line simulations are not satisfactory because of incomplete analysis and missing hot bands. High resolution infrared cross sections of ethane broadened by air from 197–297 K were measured by Harrison et al. [21] in the 3-micron region. These data are intended for ethane abundance retrievals in the Earth's atmosphere. For applications in the auroral regions of the giant planets and hot Jupiter exoplanets, high resolution cross sections of hot ethane (297–773 K) were measured by Hargreaves et al. [22] in the same spectral region. These cross sections were calibrated with the measurements of ethane broadened by 1 atm of N₂ recorded at the Pacific Northwest National Laboratory (PNNL) [23].

There is also a need for near infrared absorption cross sections of ethane at low temperatures for planetary applications. For Titan, ethane is found mainly in the stratosphere which has a temperature in the range of 80–180 K [6]. For example, the Visual and Infrared Mapping Spectrometer (VIMS) on the Cassini spacecraft [24] recorded solar occultation spectra of Titan from 0.89 to 5.1 μm at low spectral resolution. Maltagliati et al. clearly identified CH₄ and CO, but there were additional absorption features (e.g., at 2.3 μm, 4350 cm⁻¹) tentatively attributed to ethane. They

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comment on the lack of suitable laboratory data for ethane and used the PNNL cross sections (0.1 cm⁻¹ resolution, 1 atm N₂, 600–6500 cm⁻¹, at 278, 298 and 328 K). The Juno spacecraft is in orbit around Jupiter and the Jovian Infrared Auroral Mapper (JIRAM) [25] is recording spectra in the same range as VIMS. The only existing high resolution near infrared cross sections of ethane were determined near 1.68 μm at room temperature by Reed and Hodges [26] using cavity ring down spectroscopy. Our work provides high resolution absorption cross sections of the overtone/combination band region (about 1800–6200 cm⁻¹) for ethane from 196 to 297 K with H₂ and N₂ as broadening gases.

2. Experimental method

High resolution infrared spectra of ethane, pure and broadened by nitrogen or hydrogen, were recorded at the Canadian Light Source (CLS) Far Infrared Beamline, similar to work done on propane [27] and isobutane [28] (Fig. 1). The ethane gas (Praxair, Canada) was research grade (99.999% purity) with less than 6 ppm total hydrocarbon impurity and a natural isotopic abundance. The samples were held in a 2-m White-type multipass cell set to a path length of 72 m at 4 temperatures and 3 broadening gas pressures (plus the pure sample), at approximately 205 (196 for H₂), 234, 265 and 295 K, and 10 Torr (1333 Pa), 30 Torr (4000 Pa) and 100 Torr (13332 Pa) for the total pressures. The samples were prepared by adding a small amount of ethane (0.1–0.7 Torr; 13–93 Pa) to the cell, recording the pressure, then adding the broadening gas and recording the total pressure. The pressure-path length was chosen to give a reasonable absorption (approximately 80%) for the 4000–4500 cm⁻¹ bands, which means that the C–H stretching region (about 2850–3080 cm⁻¹) is saturated and unusable (Fig. 1). The pressures were measured with two Baratron pressure gauges (627B up to 10 Torr and 626B up to 1000 Torr). The precision of the 10 Torr Baratron gauge is about 2 mTorr and the accuracy is about 0.3%. The 1000 Torr Baratron has an accuracy of about 1%. The cell was cooled with a NESLAB ULT-80DD refrigerated recirculating methanol bath. The cell temperature was monitored with 4 wire PT100 RTD (platinum resistance temperature detector) sensors with an estimated accuracy of ±2 K.

The spectrometer was a Bruker IFS 125 HR Fourier transform spectrometer fitted with a CaF₂ beamsplitter, internal globar source, a 6200 cm⁻¹ red pass filter and a liquid N₂-cooled InSb detector. The long wavelength edge of the InSb detector and short wavelength edge of the filter set the bandpass to 1800–6200 cm⁻¹. The spectral resolution varied depending on the total pressure: 0.005 cm⁻¹ (pure sample), 0.005 cm⁻¹ (10 Torr), 0.01 cm⁻¹

(30 Torr), and 0.04 cm⁻¹ (100 Torr). The background spectra were recorded at 0.08 cm⁻¹ resolution and Fourier interpolated to match the higher resolution spectra. The parameters used for recording spectra are shown in Table 1. For each spectrum a minimum of 400 interferograms (200 forward and 200 backward) were co-added, boxcar apodization was used and a zero-filling factor of 8 was applied.

Due to potential inaccuracies in the measurements, a calibration factor (CF) was applied to obtain accurate absorption cross sections. Note that these errors come from many sources such as the location of the baseline in the spectra but are lumped together as a “corrected” pressure. The Pacific Northwest National Laboratory (PNNL) database [23] has over four hundred vapor-phase infrared spectra which can be used for calibration. The PNNL spectra are reported at 3 sample temperatures (278, 298 and 323 K) with 1 atm of N₂ broadening gas. As discussed in more detail by Harrison et al. [21], the integrated area of the absorption cross sections of isolated fundamental bands are independent of temperature and can be used for calibration. The situation is more complex for the combination bands used in this case. As shown experimentally and theoretically by Breeze et al. [29], combination and overtone bands have a small temperature dependence because the stimulated emission term and the absorption term have different temperature dependences and do not cancel as they do for fundamental bands. Fortunately, in our case, the stimulated emission term can be neglected and the temperature dependence is expected to be small. For ethane the integrated areas from 3600 cm⁻¹ to 4575 cm⁻¹ are 1259.912, 1252.859, and 1281.412 for 278, 298 and 323 K, respectively, for an average of 1264.728 in PNNL units. The PNNL data are in units of ppm⁻¹m⁻¹, and conversion to the standard units of cm²/molecule requires multiplication by the constant 9.28697 × 10⁻¹⁶.

The integrated area from the PNNL spectra is compared to the integrated signal from the CLS spectra, and the CLS spectra are scaled accordingly to match the PNNL values. The CLS transmission spectra are converted to cross sections using [22]:

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

in which $\tau(\nu, T)$ 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 optical path length (m), and k_B is the Boltzmann constant (1.3806504 × 10⁻²³ J/K). CF is the calibration factor used to scale each spectrum to the PNNL average value.

The baselines of the cross sections were corrected with the help of the PNNL data. The calibration factor CF for each spectrum was calculated by taking the ratio between the integrated area of the PNNL absorption spectra and the integrated area of all of the CLS absorption spectra from this study, and are shown in Table 1. It should be noted that the pure spectra have a substantially lower signal to noise ratio, which affects the integration and normalization.

3. Results and discussion

The 32 calibrated high resolution infrared absorption cross sections can be obtained at the MoLLIST (Molecular Line Lists, Intensities and SpecTra) web site <http://bernath.uwaterloo.ca/molecularlists.php> and will be contributed to HITRAN. The data volume is 1.69 GB in total (zipped). Note that the values must all be multiplied by 10⁻²¹.

The overall precision and accuracy of these absorption cross sections is hard to assess and the various error sources are discussed in detail by Harrison et al. [21]. Fortunately, the precision can be estimated because there are repeated measurements of pure ethane taken under essentially identical conditions. The N₂

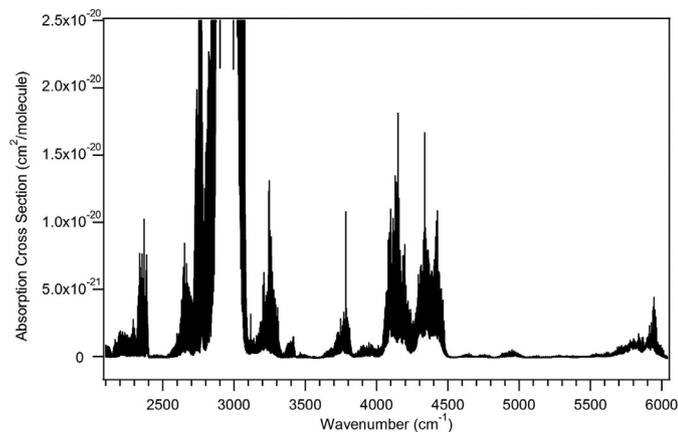


Fig. 1. Overview absorption cross sections of ethane (0.332 Torr of ethane in 100.2 Torr total pressure of ethane and N₂ at 234.45 K).

Table 1

Experimental conditions for each spectrum. CF is a calibration factor discussed in the text, and the corrected ethane pressure is the true pressure after the calibration factor is implemented.

N ₂					N ₂				
205 K					265 K				
Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)	Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)
205.05	0.15	0.15	1.100	0.136	265.45	0.45	0.45	1.083	0.412
205.05	0.148	10.2	1.071	0.138	265.25	0.45	10.1	1.101	0.409
205.15	0.225	30.1	1.079	0.209	265.25	0.502	30	1.092	0.46
205.25	0.248	100	1.076	0.230	266.15	0.619	100	1.094	0.566
234 K					295 K				
Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)	Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)
234.25	0.248	10.1	1.073	0.231	294.95	0.576	0.576	1.080	0.533
234.35	0.347	30.3	1.085	0.320	294.65	0.502	10	1.093	0.459
234.45	0.332	100.2	1.090	0.305	294.65	0.579	30	1.104	0.524
					294.75	0.697	101	1.102	0.632
H ₂					H ₂				
196 K					265 K				
Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)	Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)
195.95	0.058	0.058	0.912	0.064	265.25	0.453	0.453	0.981	0.462
195.85	0.151	10	0.962	0.157	265.15	0.452	10	0.992	0.456
195.85	0.154	30	0.963	0.160	265.15	0.502	30	0.98	0.512
195.85	0.155	100	0.952	0.163	265.15	0.618	100	0.98	0.631
232 K					297 K				
Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)	Temp (K)	Ethane (Torr)	Total (Torr)	CF	Corrected Ethane (Torr)
232.35	0.242	0.242	0.946	0.256	297.85	0.574	0.574	0.981	0.585
232.35	0.242	10	0.983	0.246	297.05	0.57	10.02	0.998	0.571
232.35	0.344	30	0.969	0.355	296.35	0.579	29.9	0.991	0.584
232.35	0.33	100	0.964	0.342	296.55	0.693	100	0.984	0.704

broadening experiments were carried out in October 2018 and the H₂ broadening experiments in April 2019. The analysis of the two data sets was also carried out independently about 6 months apart. Comparison of the pairs of final cross sections for pure samples at 265 and 295 K shows that they differ by about 2%, which is an estimate of the precision of the measurements. The accuracy of the PNNL cross sections used for calibration is 3.2% [23]. The error in assuming no temperature dependence in the calibration cross sections is hard to assess but looking at the variation of the calibration factors with temperature (Table 1), could be 1–2%. Adding the errors in quadrature and rounding up gives an overall accuracy of about 5%, which is typical for our measurements.

The effects of temperature and pressure on the cross sections are shown in Figs. 2 and 3, respectively. Pressure broadening is readily observed in Fig. 2, where the higher pressure spectra have smaller, broader peaks than the low pressure spectra. The lines broaden linearly with pressure and the peak heights decrease. The Lorentzian wings of the lines start to overlap, and a quasi-continuum starts to appear in the 100 Torr data.

The effect of temperature is two-fold (Fig. 3): the lines broaden with the square root of the temperature due to Doppler broadening and the peak heights decrease. In addition, the population of the higher *J* and *K* levels increase from the Boltzmann distribution and lines at the edge of the band below 4050 cm⁻¹ strengthen. This drains population from lower *J* and *K* levels and strengthens the torsional hot bands. Overall the spectra become more congested and the prominent lower *J* and *K* features weaken as the temperature increases.

The effect of pressure broadening is shown in more detail in Fig. 4.

Hydrocarbons such as ethane are found in the atmospheres of the giant planets and Titan. For Titan this covers a temperature range of 80–180 K and 100–0.01 mbar (75 Torr–0.0075 Torr)

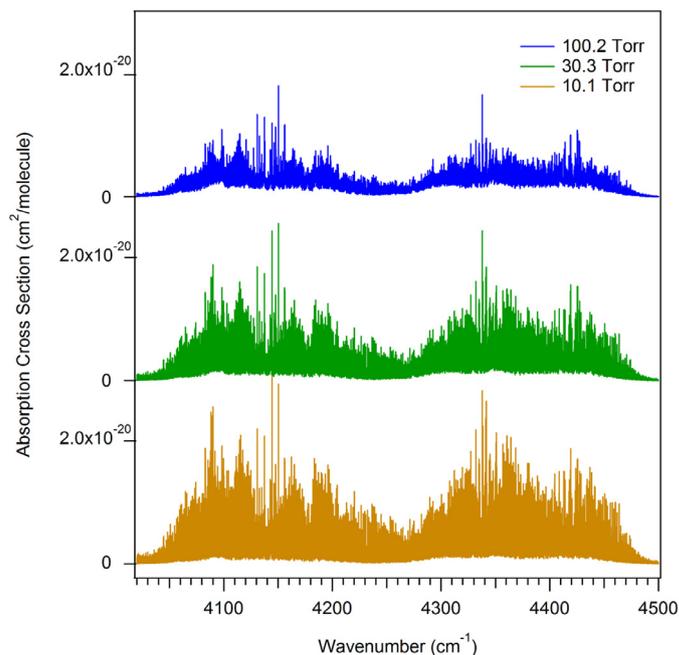


Fig. 2. A series of ethane cross sections with different pressures of nitrogen taken at 234 K (total pressures are 10.1 Torr, 30.3 Torr, and 100.2 Torr).

with N₂ as the primary broadening gas [30]. For Jupiter's stratosphere, the temperature and pressure ranges are about 120–190 K and 100–0.0001 mbar (75–0.00075 Torr) with H₂ as the primary broadening gas [31]. For planetary applications, our measurements cover the appropriate pressure range and are made with the two

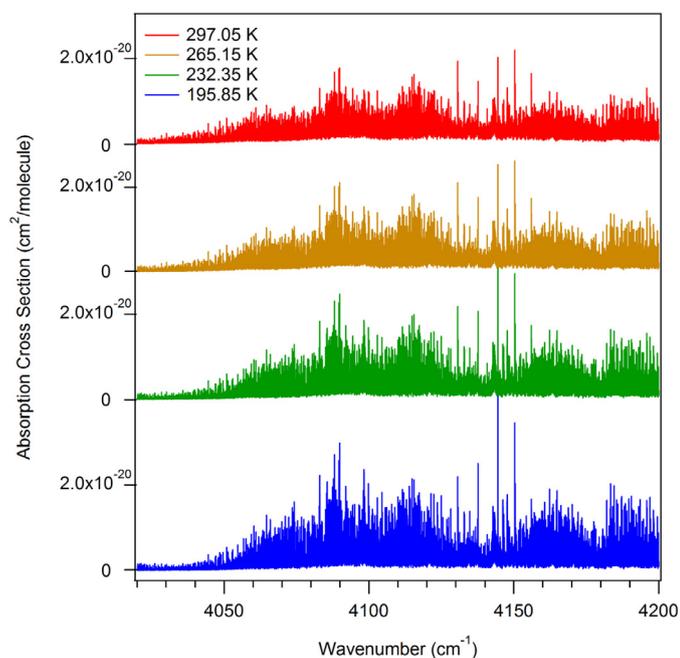


Fig. 3. A series of ethane cross sections at different temperatures for 10 Torr of hydrogen (195.85 K, 232.35 K, 265.15 K, and 297.05 K).

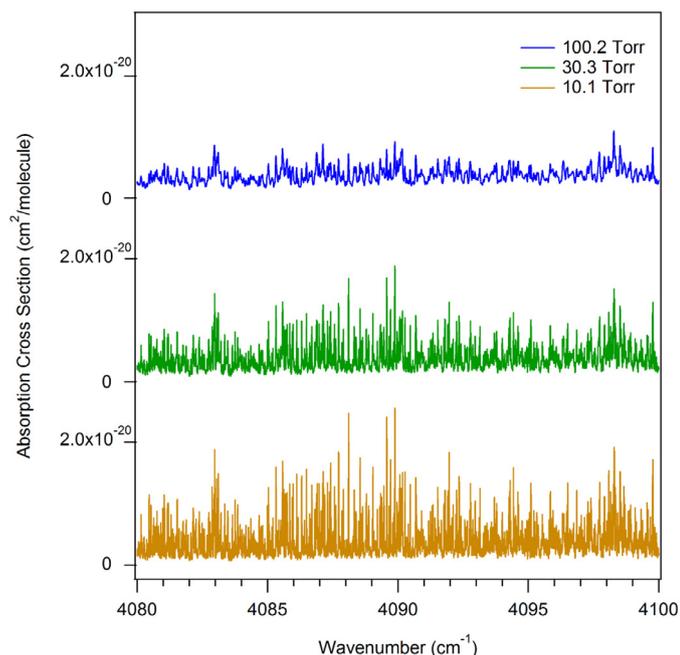


Fig. 4. An expanded section of Fig. 2 showing the effect of pressure broadening.

main broadening gases; however, lower temperatures are desirable. At the moment, the low temperature limit is set by the NESLAB chiller. Lower temperatures are planned by cooling the White cell with cold nitrogen vapor boiled from liquid nitrogen.

This work on the ethane overtone region is part of a larger project on cold hydrocarbon cross sections with data published so far, for example, on propane [27] and isobutane [28]. The spectra for ethane in the C–H stretching region near 3.3 μm have already been recorded with a smaller pressure-pathlength using hydrogen and helium as broadening gases; these data are being analysed for publication. These data will provide cross sections for the saturated region missing in the current paper.

4. Conclusion

High resolution absorption cross sections of ethane have been obtained from 1800 cm^{-1} to 6200 cm^{-1} from 196 to 297 K using N_2 or H_2 as broadening gases. These 32 cross sections are particularly useful for interpreting the near infrared observations of Titan and Jupiter made with the VIMS instrument on Cassini and JIRAM on Juno. Our cross sections will improve the simulation of spectra of Titan and the giant planets, although caution must be used in extrapolating the data to lower temperatures. Lower temperatures are desirable to more closely match the conditions on the giant planets and Titan, as the stratospheres of these objects are cooler than 196 K.

Declaration of Competing Interest

We have no conflicts of interest regarding this work.

Acknowledgements

The NASA Outer Planets Research and Planetary Data Archiving and Restoration Tools program (PDART) provided funding. Research described in this paper was performed at the Canadian Light Source, which is supported by the Canada Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research.

Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2019.106780.

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