IR absorption cross sections of propane broadened by H_2 and He between 150 K and 210 K

A. Wong [a], D.R.T. Appadoo [b], P.F. Bernath [a],*

[a] *Department of Chemistry and Biochemistry, Old Dominion University, VA 23529, USA*
[b] *Australian Synchrotron, 800 Blackburn Road, Clayton 3168, Australia*

A R T I C L E   I N F O

A B S T R A C T

Absorption cross sections of cold propane, pure and broadened with H_2 or He, have been recorded in the 650–1250 cm^{-1} region using an Enclosive Flow Cooling (EFC) cell located at the Australian Synchrotron Far-IR/THz beamline. The chosen temperatures range from 150 to 210 K to replicate similar atmospheric conditions of the giant planets. These cross sections have been normalized using data obtained from the Pacific Northwest National Laboratory, and can be used directly in comparisons with observed spectra and in radiative transfer models.

1. Introduction

The atmospheres of the giant planets contain numerous hydrocarbons that are formed from the photochemistry of methane [1]. These secondary hydrocarbons, such as acetylene, ethane and propane, can react further to generate larger polycyclic aromatic hydrocarbons, eventually leading to the formation of aerosol particles in polar regions by ion-molecule chemistry [2]. Depending on the location (latitude, longitude and altitude), the atmospheric composition, temperature and pressure can vary greatly due to complex dynamical and chemical processes. These factors result in complex spectra from the signatures originating from many different molecules and make it difficult to retrieve atmospheric concentration profiles.

In order to interpret such spectra and therefore be able to accurately model these planetary atmospheres, it is necessary to first characterize the component spectra (i.e., of small hydrocarbons) as accurately as possible. Unfortunately, there is a lack of accurate spectroscopic data for a number of these molecules. In the absence of accurate line parameters that are derived using traditional analytical methods [3-6] (e.g. assignment of transitions and fitting of molecular constants), it is possible to utilize absorption cross sections instead. Infrared absorption cross sections are empirically derived from laboratory transmission spectra of samples with a known temperature, pressure and composition [7]. Absorption cross sections can be used directly in radiative transfer models to retrieve molecular abundances.

Although several databases such as HITRAN [8], HITEMP [9], PNNL [10] and GEISA [11] exist, data in these sources are typically applicable to the Earth's atmosphere rather than those of the giant planets. HITRAN (http://hitran.org/) has, however, begun to collect line parameters for broadeners other than air. To address this issue, it is therefore necessary to measure spectra of these small hydrocarbons under conditions that replicate those of planetary atmospheres (composition, temperature and pressure) to produce accurate spectroscopic data.

Propane is one of several small hydrocarbons that have already been detected in planetary atmospheres like Saturn [12] and on one of its moons, Titan [13]. High resolution infrared absorption cross sections for hot propane are available in the 3 μm region for applications in hot Jupiter exoplanets [14]. Propane cross sections have been measured for applications to Earth's and Titan's atmospheres [15] as well as for combustion environments [16,17]. Previously we have reported absorption cross sections of cold propane in the 600–1250 cm^{-1} region that have been broadened with H_2 [18] and He [19]. These works were performed at the Canadian Light Source which has a limited temperature range down to 200 K. We present here, absorption cross sections of pure and H_2/He broadened propane in the same spectral region, at even colder temperatures from 150–210 K. These studies form part of a larger project to measure and analyze spectra of small hydrocarbons that have been observed (or are expected to be present) in the atmo-

Table 1
Summary of the experimental conditions used.

T (K)	Parameter	Pressure of H_2/He (kPa)			
		Pure	1.07[a]	4.00[a]	13.33[a]
210, 190, 170 and 150	Source	SR	MIR	MIR	MIR
	Resolution (cm^{-1})[c]	0.00096	0.005	0.01	0.04
	Aperture (mm)	1.3[b]	2	3.15	6.3

[a] These numbers refer to the total pressure after the addition of H_2 or He, before calibration (see below).

[b] A small aperture was used due to noise issues with the synchrotron radiation.

[c] The resolutions used for recording sample scans were based on previous studies [18,19].

spheres of planets, exoplanets and substellar objects such as brown dwarfs.

2. Experimental

Transmission spectra were recorded utilizing a Bruker IFS 125 HR spectrometer located at the Australian Synchrotron Far-IR/THz beamline. An enclosive flow cooling (EFC) cell, designed by Bauerecker [20], was used to achieve the desired temperatures from 150 to 210 K and has been previously installed using transfer optics described by Wong et al. [21]. To maximize signal in the region of interest (650–1250 cm^{-1}), the spectrometer and EFC cell were fitted with a KBr beamsplitter and KBr windows. Either the synchrotron radiation or the internal glowbar source was chosen depending on the required resolution; the detector of choice was a liquid N_2-cooled Mercury-Cadmium-Telluride mid-band (MCTm) detector.

The optical path through the cell was set to 20 passes (12.5 m) and cooled to a minimum temperature of 150 K using cold N_2 gas. Spectra were recorded at four temperatures starting from 210 K to 150 K (Table 1) and the cell was left to stabilize at each desired temperature for at least one hour. The cell temperature was measured by five type K thermocouples that are accurate to temperatures as low as 78 K and one Lakeshore thermocouple accurate to temperatures as cold as 4 K; typical thermocouple accuracies are better than ±2 K.

Propane (99%) was purchased from Coregas and used without further purification for all measurements. Conditions for pure propane required enough propane such that the ν_{26} band (near 750 cm^{-1}) remained below saturation. Sample pressures were monitored using a BOC Edwards wide range gauge (WRG) usable for pressures of up to 10 kPa (75 Torr). For broadened spectra, small amounts of propane were introduced into the cell before back-filling with either H_2 or He to the desired total pressure (Table 1). At each temperature 3 total pressures (gas plus broadener) at 1.07 kPa (8 Torr), 4 kPa (30 Torr) and 13.33 kPa (100 Torr) were used. H_2 and He were provided by the Australian Synchrotron (> 99% purity) and these higher pressures were monitored using an Edwards Active Strain Gauge (ASG) capable of operating up to 1 atm. As discussed below, these recorded pressures had to be calibrated.

For each condition, sample gases were left to equilibrate in the pre-cooled EFC cell for approximately 5 minutes to achieve temperature gradients of ±2.5 K across the cell before acquiring spectra. During each measurement, the flow rate of cold N_2 gas was adjusted such that fluctuations remained within ±3 K of the intended temperature.

Individual files consisted of pairs of forward and reverse interferograms that were Fourier transformed using a Blackman-Harris 3-term apodization function to eliminate any residual effect of the instrument lineshape function and a zero-fill factor of 2. A total
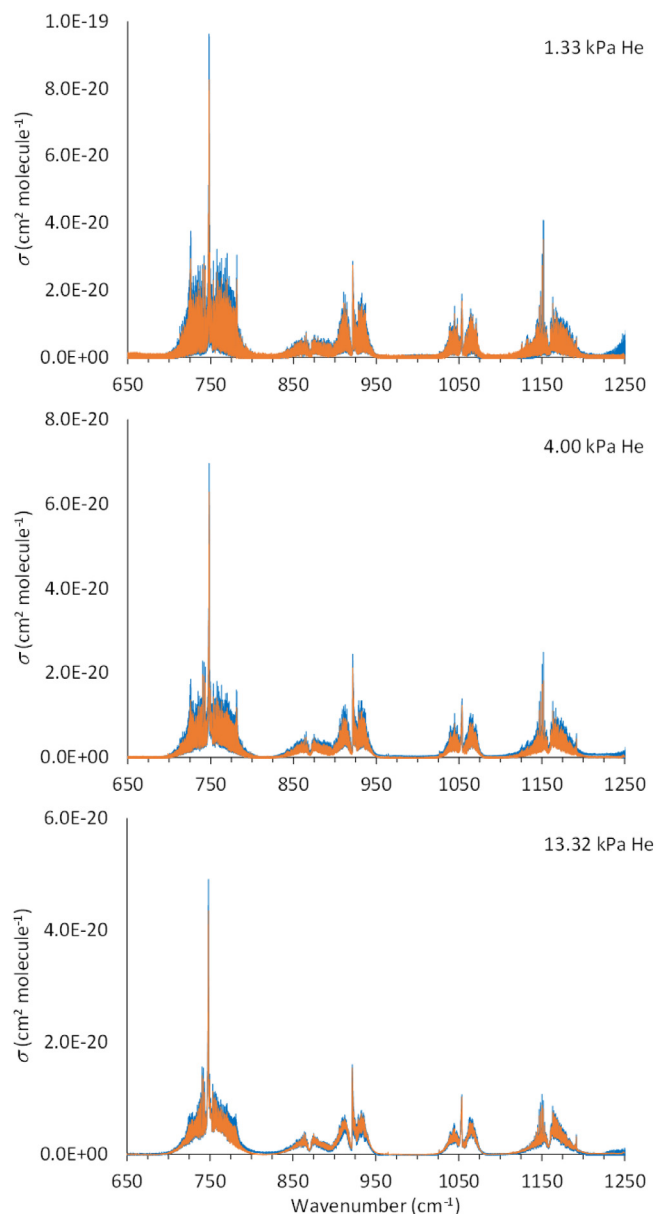

Fig. 1. Overlay of He broadened propane absorption cross sections σ_{CLS} (orange, 200 K) and the corresponding calibrated σ_{AS} (blue, 210 K). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of 300 scans were recorded for samples followed by an additional 300 scans for backgrounds and were co-added using a weighted average. Transmission spectra were obtained by dividing the single channel spectrum for the sample with the corresponding background. Slight adjustments were made to the background spectra to obtain satisfactory baselines in the transmission spectra. An additional post zero-fill factor of 8 was applied to the final transmission spectrum before being used for analysis to provide more points when calculating the absorption cross sections. These transmission spectra are available from the authors by request.

3. Results and discussion

3.1. Cross sections

The methods used for obtaining cross sections from the synchrotron data, σ_{AS}, and from the PNNL measurements, σ_{PNNL}, and

Table 2
Comparison of the observed (P) and derived (P_{eff}) values of propane for each experimental condition.

T (K)	Pure		H$_2$					
			1.33 (obs) 2.66 (cal) kPa[a]		4.00 (obs) 8.01(cal) kPa[a]		13.32 (obs) 26.7 (cal) kPa[a]	
	P^b (Pa)	P_{eff}^b (Pa)	P^b (Pa)	P_{eff}^b (Pa)	P^b (Pa)	P_{eff}^b (Pa)	P^b (Pa)	P_{eff}^b (Pa)
210	–[c]	–	146.65	61.26	199.98	69.96	266.64	103.79
190	40.89	11.87	94.66	38.87	133.32	45.77	186.65	55.89
170	28.44	9.99	67.99	26.32	95.99	33.16	133.32	40.27
150	20.66	9.56	42.66	14.36	67.99	26.56	81.33	36.55
T (K)	He							
			1.33 (obs) 2.66 (cal) kPa[a]		4.00 (obs) 8.01 (cal) kPa[a]		13.32 (obs) 26.7 (cal) kPa[a]	
			P^b (Pa)	P_{eff}^b (Pa)	P^b (Pa)	P_{eff}^b (Pa)	P^b (Pa)	P_{eff}^b (Pa)
210			66.66	32.30	107.99	62.76	133.32	80.70
190			67.99	33.06	107.99	70.02	146.65	107.34
170			66.66	32.31	66.66	27.94	107.99	63.24
150			26.66	9.76	67.99	29.25	81.33	38.89

[a] The total observed pressure (obs) after the addition of H$_2$ or He. The actual observed pressures (cal) are obtained using the factors given in Fig. 2. The calibrated total pressures are therefore 2.66, 8.01 and 26.7 kPa for H$_2$ and He broadened spectra, not the observed values of 1.33, 4.00 and 13.32 kPa, respectively.)
[b] These values reflect the observed and calibrated pressures of propane used.
[c] The baseline for this scan was not good and therefore the transmittance spectrum was not usable during the analysis.
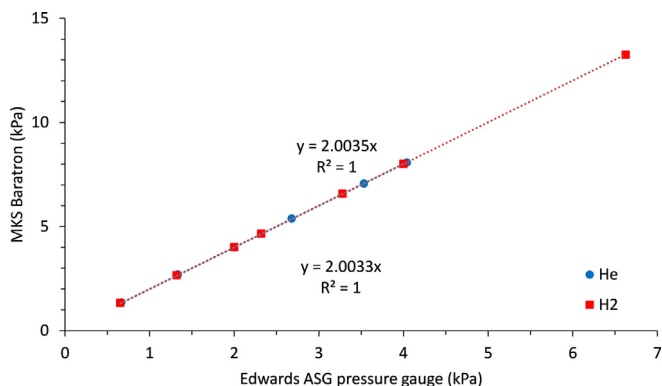

Fig. 2. Calibration of the high-pressure Edwards ASG gauge to the MKS Baratron for He and H$_2$.

their corresponding integrated values (int(σ_{AS}) and int(σ_{PNNL})), are similar to those described previously and are only mentioned briefly here [18,19]. For this work, AS and PNNL refer to data obtained from the Australian Synchrotron and reference data from the Pacific Northwest National Laboratory spectroscopic database [10], respectively. The comparisons with PNNL spectra are given below in the form of absorbance simulations that are converted into cross sections (in cm^2/molecule) using the factor 9.28697×10^{-16}.

Spectra from this work were Fourier transformed to a reduced resolution of 0.112 cm^{-1} in order to match what was used by the PNNL database. Absorption cross sections were then calculated using Eq. (1) [7] and integrated between 680 – 970 cm^{-1}. Reference propane data from the PNNL database were also integrated across the same spectral range, after being scaled using a factor $F = 9.28697 \times 10^{-16}$. The int($\sigma_{AS}$) values were then normalized with the calibration factor ξ so that int(σ_{AS}) = int(σ_{PNNL}), resulting in new P_{eff} values given in Table 2. The P_{eff} values were then used to calculate cross sections using spectra recorded at their original resolution and are attached as part of the supplementary material.

$$\sigma(\nu, T) = -\xi \frac{10^4 k_B T}{Pl} \ln \tau(\nu, T) \qquad (1)$$

where $\sigma(\nu, T)$ is the absorption cross section, ξ is the calibration factor, k_B is the Boltzmann constant (J K^{-1}), T is the temperature (K), P is the pressure (Pa), l is the pathlength (m) and τ is the transmittance as a function of ν (cm^{-1}) and T.

From the values given in Table 2, it is evident that none of the observed values are in agreement with the calibrated P_{eff} values. This in turn reflects discrepancies between the calculated int(σ_{AS}) and int(σ_{PNNL}) values and indicates that some error (from poorly calibrated pressure gauges) occurred during the experiment. The WRG pressure gauge used in the experiment is based on the thermal conductivity of gases and is calibrated for air, not propane, H$_2$ or He; there was also a problem with the ASG gauge calibration. To confirm this assumption and to validate the PNNL calibration method, a cross-check was performed by comparing these results to data from previous work [18,19] that was recorded at the Canadian Light Source (CLS).

4. Comparison with σ_{CLS}

4.1. Intensities

A transmission spectrum can be calculated using previously reported σ_{CLS} by interpolating the values of T, P and l and then using Eq. (1) to determine τ_{CLS}. The derived P_{eff} values are then used to calibrate the σ_{AS} which are then compared to σ_{CLS} [18,19] to confirm the validity of the calibration method. A subset of He-broadened cross-sections at 210 K (σ_{CLS}) and 200 K (σ_{AS}) are presented in Fig. 1. Some minor differences between the two sets of data can be seen in part due to the different temperatures. However, in general the calibrated σ_{AS} are in good agreement with previously reported σ_{CLS} within the 5–10% estimated errors. It is possible to extrapolate the σ_{CLS} to the colder temperatures (i.e. 190 K, 170 K and 150 K), however the expected τ_{CLS} would be less accurate due to extrapolation errors and therefore a comparison at these colder temperatures was not performed.

4.2. He and H$_2$ calibration

In addition to calibrating the WRG used for propane, it was also necessary to test the accuracy of the ASG gauge that was used to monitor the total pressure with the added He and H$_2$ broadeners. To do so, a series of He and H$_2$ readings were performed with the ASG gauge and then cross-checked with pressures recorded on a MKS Baratron accurate up to 10 kPa (Fig. 2). The data points were then fitted with linear regressions to determine calibration factors of 2.004 ± 0.003 (for He) and 2.003 ± 0.002 (for H$_2$). We assume

that the calibration factors for both He and H_2 remain consistent up to a reading of 13.33 kPa on the ASG gauge, which corresponds to 35.61 kPa for both He and H_2. This also accounts for the differences that are observed between the two sets of absorption cross sections given in Fig. 1.

5. Conclusion

Transmission spectra of pure and broadened propane were recorded between 600 – 1250 cm^{-1} at the Australian Synchrotron Far-IR/THz beamline utilizing the EFC cell to achieve temperatures as cold as 150 K. The chosen temperature and pressure ranges, along with broadening conditions, reflect the atmospheric conditions that have been observed on the giant planets.

Absorption cross sections have been obtained from each transmission spectrum and normalized to the PNNL database cross sections of propane. In all, 27 absorption cross sections are provided as supplementary data, corresponding to the 27 distinct experimental conditions reported in Table 2. Large calibration factors were required due to poor calibration and inaccuracies of the pressure gauges used. The data presented was also cross-checked with data from previous studies at the Canadian Light Source by interpolating σ_{CLS} to calculate expected transmission spectra. These comparisons validated our propane calibration factors. In addition, the gauge used to measure the total pressure used for the He and H_2 broadened spectra was calibrated by comparison with a Baratron pressure gauge. The typical errors in the cross sections based on experience and a more detailed error analysis in ref. [7] are 5–10%.

These new cross sections provide accurate spectroscopic data for pure and broadened propane without the need for high resolution rotational analyses. Line parameters such as broadening coefficients can also be extracted from these cross sections and used in radiative transfer models. Furthermore, the cross sections can be directly used to determine the abundances of propane in the giant planets.

In the FIR region, traditional light sources have low brightness which results in low signal-to-noise ratios for high resolution spectra. As a result, a large amount of acquisition time is required when utilizing the maximum resolution of the spectrometer. In this case, it is necessary to use the synchrotron source in order to obtain the best results. Since synchrotron radiation can be considered as nearly a point source, it overcomes the aforementioned issues of signal-to-noise levels and brightness. However, as the required resolution is decreased (e.g. increased sample pressure) the synchrotron advantage is lost with increasing aperture size and therefore the internal glowbar source is sufficient to provide high quality spectra.

Acknowledgement

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2018.06.026.

References

[1] Strobel DF. The photochemistry of methane in the jovian atmosphere. J Atmos Sci 1969;26:906–11.

[2] Wong AS, Lee AYT, Yung TL, Ajello JM. Jupiter: aerosol chemistry in the polar atmosphere. Astrophys J 2000;534:L215–17.

[3] Tchana FK, Flaud JM, Lafferty WJ, Manceron L, Roy P. The first high resolution analysis of the low lying ν_9 band of propane. J Quant Spectrosc Radiat Transf 2010;111:1277–81.

[4] Perrin A, Tchana FK, Flaud J-M, Manceron L, Demaison J, Vogt M, et al. First high resolution analysis of the ν_{21} band of propane $CH_3CH_2CH_3$ at 921.382 cm^{-1}: evidence of large amplitude tunneling effects. J Mol Spectrosc 2013;315:55–62.

[5] Flaud J-M, Tchana FK, Lafferty WJ, Nixon CA. High resolution analysis of the ν_{26} and $2\nu_9–\nu_9$ bands of propane: modelling of Titan's infrared spectrum at 13.4 μm. Mol Phys 2010;108:699–704.

[6] Drouin BJ, Pearson JC, Walters A, Lattanzi V. THz measurements of propane. J Mol Spectrosc 2006;240:227–37.

[7] Harrison JJ, Bernath PF. Infrared absorption cross sections for propane (C_3H_8) in the 3 μm region. J Quant Spectrosc Radiat Transf 2010;111:1282–8.

[8] Gordon IE, Rothman LS, Hill C, Kochanov RV, Tan Y, Bernath PF, et al. The HITRAN2016 molecular spectroscopic database. J Quant Spectrosc Radiat Transf 2017;203:3–69.

[9] Rothman LS, Gordon IE, Barber RJ, Dothe H, Gamache RR, Goldman A, et al. HITEMP, the high-temperature molecular spectroscopic database. J Quant Spectrosc Radiat Transf 2010;111:2139–50.

[10] Sharpe SW, Johnson TJ, Sams RL, Chu PM, Rhoderick GC, Johnson PA. Gas-phase databases for quantitative infrared spectroscopy. Appl Spectrosc 2004;58:1452–61.

[11] Jacquinet-Husson N, Armante R, Scott NA, Chédin A, Crépeau I, Boutamine C. The 2015 edition of the GEISA spectroscopic database. J Mol Spectrosc 2016;327:31–72.

[12] Greathouse TK, Lacy JH, Bézard B, Moses JI, Richter MJ, Knez C. The first detection of propane on Saturn. Icarus 2006;181:266–71.

[13] Roe HG, Greathouse TK, Richter MJ, Lacy JH. Propane on Titan. Astrophys J 2003;597:L65–8.

[14] Beale CA, Hargreaves RJ, Bernath PF. Temperature-dependent high resolution absorption cross sections of propane. J Quant Spectrosc Radiat Transf 2016;182:219–24.

[15] Sung K, Toon GC, Mantz AW, Smith MAH. FT-IR measurements of cold C_3H_8 cross sections at 7-15 μm for Titan atmosphere. Icarus 2013;226:1499–513.

[16] Klingbeil AE, Jeffries JB, Hanson RK. Temperature- and pressure-dependent absorption cross sections of gaseous hydrocarbons at 3.39 μm. Meas Sci Technol 2006;16:1950–7.

[17] Mével R, Boettcher PA, Shepherd JE. Absorption cross section at 3.39 μm of alkanes, aromatics and substituted hydrocarbons. Chem Phys Lett 2012;531:22–7.

[18] Wong A, Hargreaves RJ, Billinghurst B, Bernath PF. Infrared absorption cross sections of propane broadened by hydrogen. J Quant Spectrosc Radiat Transf 2017;198:141–4.

[19] Wong A, Billinghurst B, Bernath PF. Helium broadened propane absorption cross sections in the far-IR. Mol Astro 2017;8:36–9.

[20] Bauerecker S, Taraschewski M, Weitkamp C, Cammenga HK. Liquid-helium temperature long-path infrared spectroscopy of molecular clusters and supercooled molecules. Rev Sci Instrum 2001;72:3946–55.

[21] Wong A, Medcraft C, Thompson CD, Robertson EG, Appadoo DRT, McNaughton D. High resolution far infrared spectroscopy of HFC-134a using a collisional cooling cell adapted to a synchrotron source. Chem Phys Lett 2015;634:225–9.