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journal homepage: www.elsevier.com/locate/jqsrtHe and H₂ broadened propane cross sections in the 3 μm region at cold temperaturesAndy Wong^a, Dan Hewett^{a,*}, Brant B. Billingham^b, James N. Hodges^a, Peter F. Bernath^a^a Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA^b Canadian Light Source Far-Infrared Beamline, 44 Innovation Blvd, Saskatoon, SK S7N 2V3, Canada

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ABSTRACT

Infrared absorption cross sections of pure propane, as well as propane broadened by He or H₂, have been obtained from spectra recorded using Fourier transform instruments located at the Old Dominion University (ODU) and at the Canadian Light Source (CLS). Pressure and temperature regimes for He and H₂ foreign gas broadening range from 10 Torr to 300 Torr between 298 K and 200 K. The integrated absorption cross sections were compared to reference data obtained from the Pacific Northwest National Laboratory (PNNL) spectroscopic database, with most values lying within ±10% of their expected values.

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1. Introduction

Propane is an important molecule present in planetary atmospheres. In the Earth's atmosphere it originates from biomass burning and fugitive emissions from fossil fuel production. Propane has been detected on both Saturn and Titan [1,2]. On Titan and the Giant Planets, hydrocarbons such as propane are the result of photochemical reactions starting from methane [3]. Methane has been detected in hot Jupiter exoplanets [4,5,6] so hydrocarbons such as ethane and propane are also potentially present in exoplanet atmospheres. The presence of hydrocarbons on the Giant Planets and exoplanets makes accurate propane spectra that simulate exoplanet conditions vital for propane detection and quantification.

Propane has 11 atoms and a C_{2v} equilibrium geometry. This results in 27 fundamental vibrational modes, 7 of which lie below 1000 cm⁻¹ [7]. These low energy vibrational levels give rise to many hot bands that have appreciable intensity at room temperature (and even cold) temperatures which add to the line density of high resolution spectra and further complicate the analysis. This results in spectroscopic constants that do not reproduce the observed spectra, making it difficult to model propane in planetary atmospheres and lead to inaccurate reports of atmospheric composition. This is where absorption cross sections become valuable, as they are only dependent on physical conditions such as composition, pressure and temperature, removing the necessity for com-

plex spectral analysis in order to obtain accurate molecular abundances.

Much of the previous work done on propane is focused on its presence here on Earth [8], and its role in combustion processes [9,10,11]. Infrared absorption cross sections are available in the 3 μm region with air as a broadening gas [8]. There has been some work directed at the conditions present on the Giant Planets [12], with absorption cross sections of pure propane being recorded at high temperatures to simulate the auroral regions of Jupiter [13].

This present paper builds upon previous work done in the Bernath group that obtained the absorption cross sections of propane broadened by helium and hydrogen between 650 and 1250 cm⁻¹, at temperatures ranging from 150 K to room temperature [7,14,15]. Here we focus on the 3 μm region of the infrared spectrum, at temperatures ranging from 200 to 298 K. The choice of broadening gases is vital for simulating the environments present in the atmospheres of Jupiter and Saturn, as their atmospheres are composed primarily of hydrogen and helium.

2. Experimental

2.1. Old Dominion University (ODU)

Spectra of pure and H₂-broadened propane were recorded with a Bruker IFS 120/125 spectrometer in the 3 μm region with the internal glowbar source. The spectrometer was fitted with a CaF₂ beamsplitter and a liquid N₂ cooled InSb detector. Both propane

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Table 1
Summary of the experimental conditions explored at ODU and CLS.

	ODU		
	T (K) 296, 270 and 240	Resolution (cm ⁻¹) ^a	# of co-adds
P (H ₂) Torr	0	0.005	400
	10	0.005	400
	30	0.005	400
	100	0.01	400
	300	0.01	400
	CLS		
	T (K) 298, 260, 230 and 200	Resolution (cm ⁻¹) ^a	# of co-adds
P (He or H ₂) Torr	0	0.005	400
	10	0.005	400
	30	0.01	400
	100	0.04	400

^a The resolution refers to what was used for the sample scans. Corresponding background scans were recorded at either the same or a lower resolution than what was used for the sample scans.

Table 2
Calibration factors for the ODU cross sections.

H ₂				H ₂				Pure		
Propane P (Torr)	H ₂ P (Torr)	T (K)	CF	Propane P (Torr)	H ₂ P (Torr)	T (K)	CF	Propane P (Torr)	T (K)	CF
1	10	240.15	0.9948	1.5	30	269.65	1.053	1	238.15	1.2656
1	30	239.15	1.0304	1.5	100	270.05	0.9954	1	269.65	1.4088
1	30	296.15	0.9421	2	100	239.15	1.0944	1	296.15	1.4307
1.2	10	269.65	0.9555	3	300	269.65	1.119			
1.5	10	296.15	0.9698							

and H₂ gases were obtained from Airgas (99.99% and 99.999% purity, respectively) and were used without further purification.

Samples of either pure or H₂-broadened propane were prepared in a single pass 20-cm cell fitted with wedged KBr windows and cooled with liquid ethanol to temperatures as low as 239 K. The pressure used for pure propane (100–200 mTorr) was such that the Q-branches near 3000 cm⁻¹ remained below saturation. For samples involving H₂-broadening, a similar amount of propane was introduced into the cell before being backfilled to a desired pressure of 10, 30, 100 and 300 Torr. A total of 400 scans were recorded for both sample and background before being averaged for each desired condition (Table 1).

2.2. Canadian Light Source (CLS)

A similar instrumental setup, employed in previous studies [7,14], was utilized for experiments performed at the CLS FIR beamline. The spectrometer was fitted with a KBr beamsplitter, InSb detector, internal glowbar source and a White-type multipass cell set to a total path length of 8 m.

Spectra were recorded at four temperatures (298, 260, 230 and 200 K) for either pure, He or H₂ broadened propane (10, 30 or 100 Torr). Samples at the CLS were prepared using similar methods to the experiments performed at ODU. A total of 200 sample scans (200 forward and 200 reverse) and 200 background scans (200 forward and 200 reverse) were averaged together for each experimental condition (Table 1).

3. Results and discussion

Absorption cross sections for both sets of data (ODU and CLS) were calculated using Eq. (1) [16] given below for reference.

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

In this equation, $\sigma(\nu, T)$ is the absorption cross section in cm² molecule⁻¹, ξ is the calibration factor (CF), 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 .

The cross sections were then integrated over a spectral window between 2550–3450 cm⁻¹ to include the entire C-H stretching region. Reference cross sections obtained from the Pacific Northwest National Laboratory (PNNL) were also integrated over the same spectral range and scaled using a factor [17], $F=9.28697 \times 10^{-16}$, to obtain units of cm²/molecule before integration.

Since the PNNL database provides cross sections at three temperatures (278, 298 and 303 K), all three cross sections were integrated and compared to each other. The integrated values are within 2% of each other (4.236×10^{-17} , 4.204×10^{-17} and 4.294×10^{-17} cm molecule⁻¹, respectively) and were averaged together to give 4.247×10^{-17} cm molecule⁻¹ as the reference value. Calibration factors for ODU (Table 2) and CLS (Table 3) were then obtained by dividing the averaged reference value by the integrated values from this work. Absorption cross sections for all temperatures and pressures listed in Tables 2 and 3 can be found as part of the supplementary data. The pressures listed in the tables and in the supplemental data are the measured pressures without applying the calibration factor for consistency, while the cross sections themselves have been calibrated.

All of the cross sections were calibrated to produce a consistent dataset, and the data present in the supplementary have been calibrated using the indicated correction factors. Fig. 1 compares a subset of H₂ broadened-data for the calibrated ODU (blue) and CLS (orange) cross sections. Both datasets from this work show good overlap and thus validate the calibration method used. A black trace for the PNNL data has also been added for reference to the pure propane panel, highlighting the accuracy of these cross sections. It is evident that there is some intensity discrepancy between the PNNL reference data and the cross sections from this

Table 3
Calibration factors for the CLS cross sections.

202 K											
H ₂				He				pure			
Propane P (Torr)	H ₂ P (Torr)	T (K)	CF	Propane P (Torr)	He P (Torr)	T(K)	CF	Propane P (Torr)	T (K)	CF	
0.025	10.6	201.85	0.9003	0.03	10.1	201.85	0.9348	0.03	201.75	0.9074	
0.03	30.5	201.85	0.9266	0.03	30.3	201.75	0.9175				
0.031	100.4	201.95	0.9351	0.031	99.9	202.25	0.927				
234 K											
H ₂				He				pure			
Propane P (Torr)	H ₂ P (Torr)	T (K)	CF	Propane P (Torr)	He P (Torr)	T(K)	CF	Propane P (Torr)	T (K)	CF	
0.035	10.5	233.65	0.9177	0.036	9.995	233.65	0.9387	0.036	233.75	0.9208	
0.037	29.6	233.75	0.9072	0.038	30.5	233.55	0.9209				
0.038	99.6	233.75	0.9207	0.035	100.1	233.75	0.9184				
262 K											
H ₂				He				pure			
Propane P (Torr)	H ₂ P (Torr)	T (K)	CF	Propane P (Torr)	He P (Torr)	T(K)	CF	Propane P (Torr)	T (K)	CF	
0.051	9.974	262.55	0.9151	0.053	10.35	262.25	0.9595	0.053	262.35	0.9221	
0.055	31.6	262.45	0.9272	0.054	30.2	262.35	0.9393				
0.053	99.9	262.55	0.9096	0.052	100.5	262.45	0.9249				
295 K											
H ₂				He				pure			
Propane P (Torr)	H ₂ P (Torr)	T (K)	CF	Propane P (Torr)	He P (Torr)	T(K)	CF	Propane P (Torr)	T (K)	CF	
0.082	10.8	295.35	0.9326	0.072	9.979	295.25	0.9281	0.081	295.35	0.9176	
0.085	29.4	295.35	0.9203	0.075	29.6	295.35	0.9302				
0.099	100.4	295.35	0.9136	0.080	100.1	295.35	0.9248				

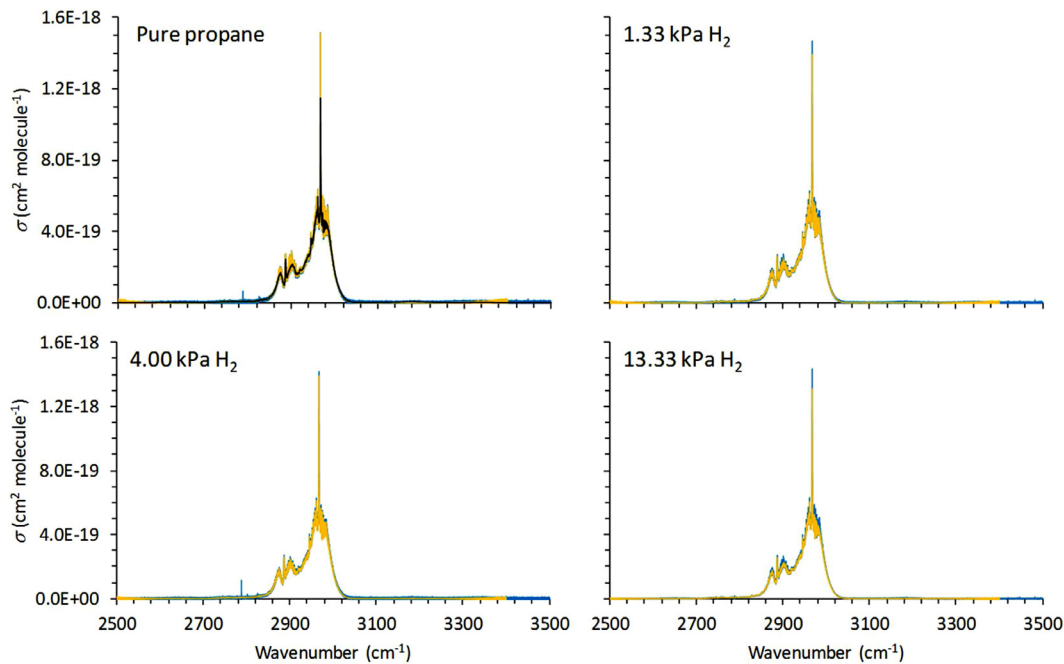


Fig. 1. Overlay of propane cross sections at 298 K with increasing amounts of H₂. The blue, orange and black traces represent data from ODU, the CLS and PNNL, respectively.

work; however, this is due to the different spectral resolutions used: a minimum resolution of 0.04 cm⁻¹ in this work compared to 0.112 cm⁻¹ for the PNNL data. The small feature near 2800 cm⁻¹ in the pure propane and 30 Torr H₂ cross sections is due to a noise spike.

The estimated error in the absorption cross sections based on past experience is about 5%. The error for PNNL spectra [17] is 3.2% (2 standard deviations) and a detailed previous error analysis [16] yields a value about 3%. However, our bias relative to PNNL

from the factors in Table 3 is 4% with a standard deviation of 3% consistent with overall estimated total error of about 5%. After calibration, the CLS and ODU data sets are comparable.

4. Conclusions

Absorption cross sections for pure propane and H₂ or He-broadened propane were obtained at ODU and the CLS in the 3 μm region at cold temperatures. Cross sections obtained from

ODU were calibrated with reference data from the PNNL database, whereas the majority of CLS cross sections required no calibration. These cross sections provide accurate spectral data that can be used to interpret observations of Giant Planets in the absence of spectroscopic information obtained from traditional line-by-line analysis. The stratospheres of the Giant Planets are colder than the 200 K minimum temperature obtained in the present work; extension to colder temperatures is planned.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jqsrt.2019.04.038](https://doi.org/10.1016/j.jqsrt.2019.04.038).

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