Infrared absorption cross sections of propane broadened by hydrogen

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ABSTRACT

Fourier transform infrared absorption cross-sections of pure propane (C_3H_8) and propane broadened with H_2 have been calculated from transmittance spectra recorded at temperatures from 292 K to 205 K. Transmittance spectra were recorded at the Canadian Light Source (CLS) Far-Infrared beamline, utilizing both the synchrotron source and the internal glowbar source. The absorption cross-sections have been calibrated to Pacific Northwest National Laboratory (PNNL) reference cross-sections of propane and can be used to interpret astronomical observations of giant planets such as Jupiter and Saturn as well as exoplanets.

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1. Introduction

Propane is one of the many small hydrocarbons found in the Earth's atmosphere. The main source of atmospheric propane is fugitive emissions associated with oil and gas production with minor sources from biomass burning, oceans and volcanoes [1]. As a constituent of natural gas, it can be used to distinguish urban emissions from those due to oil and gas operations [2]. Although propane does not have a large direct radiative forcing, monitoring of atmospheric propane is still relevant because of its production of CO_2 and tropospheric O_3. In the troposphere, propane has a relatively long lifetime (about 14 days) and is oxidized by hydroxyl radicals into acetone and acetaldehyde [3,4]. This leads to the production of peroxyacetyl nitrate (PAN), which can transport NO_2 molecules over large distances; NO_x catalyzes the formation of tropospheric ozone [5,6].

The C-H stretching modes of propane, centered around 2963 cm^{-1} (3.37 μm), are the most intense bands of propane [7,8] and serendipitously, their absorption coincides with a He-Ne laser line at 3.39 μm [9]. As a result, it is possible to use He-Ne laser absorption spectroscopy to measure properties of propane such as its absorption coefficient [10,11] and concentration [12] in a fuel combustion environment. Absorption cross sections of propane at elevated temperatures and pressure have also been recorded [13,14] for the purpose of quantifying propane in combustion engines. Recently a set of high resolution pure propane cross sections were recorded at high temperatures [15] aimed at astronomical applications such as spectral analysis of the auroral regions of Jupiter.

The detection of propane is not just limited to Earth's atmosphere. In our Solar System, propane has been found in the atmospheres of the gas giant Saturn [16,17] and its moon Titan [18,19]. Propane is formed by hydrocarbon photochemistry starting from methane, e.g. [20]. Beyond our Solar System, gaseous propane has not yet been detected however there is a possibility of its existence in the atmospheres of cool brown dwarfs [21] and exoplanets as the presence of methane [22] in these objects has already been observed.

Propane has an equilibrium structure with C_{2v} symmetry and has 27 fundamental vibrational modes. Several of these vibrations have frequencies < 1500 cm^{-1} and only a few have been rotationally analyzed thus far by Fourier transform infrared (FTIR) spectroscopy: ν_9 (369 cm^{-1}) [23], ν_{21} (921 cm^{-1}) [24], ν_{26} (745 cm^{-1}) and $2\nu_9$-ν_9 (370 cm^{-1}) [25]. There are also two low frequency torsional modes (approximately 217 cm^{-1} and 265 cm^{-1} [26]) from the two methyl rotors which have been analyzed using microwave and submillimeter wave techniques [27]. At warm (even cold) temperatures, the torsional levels are highly populated and result in numerous hot bands that have appreciable intensities. These hot bands add to the spectral congestion and complexity of propane's gas phase spectrum, hindering the analysis when attempting to assign transitions and fit spectroscopic constants.

In the absence of accurate spectroscopic constants, absorption cross-sections provide an alternative method of using high quality laboratory data of "heavy" molecules. Absorption cross-sections

Table 1
Experimental conditions used for the individual scans.

1.066 kPa H_2 & C_3H_8				4 kPa H_2 & C_3H_8			
P (Pa)[a]	P_{eff} (Pa)[b]	T (K)	No. of scans	P (Pa)[a]	P_{eff} (Pa)[b]	T (K)	No. of scans
26.66	26.35	208.95	340	76.79	81.78	208.95	306
31.73	30.83	232.35	400	106.39	110.29	232.45	300
58.40	51.82[c]	262.15	406	101.72	109.35	262.15	300
71.33	67.43	291.85	344	115.86	115.87	292.35	311

13.33 kPa H_2 & C_3H_8				Pure Propane			
P (Pa)[a]	P_{eff} (Pa)[b]	T (K)	No. of scans	P (Pa)[a]	P_{eff} (Pa)[b]	T (K)	No. of scans
162.65	162.01	232.45	300	11.20	7.11[c]	204.35	104
146.25	144.05	262.35	300	31.73	30.17	231.95	266
173.32	169.45	292.15	300	40.93	38.15	262.55	156
				43.86	42.28	291.05	300
				46.00	51.12[c]	294.75	288

[a] The pressure given in these columns refers to the pressure of C_3H_8 used.
[b] Effective pressures after normalization.
[c] Although included here, these cross sections are not usable as large pressure calibrations are required.

do not rely on accurate fits of spectroscopic parameters, rather only physical conditions such as temperature, pressure and sample transmittance. Another advantage of absorption cross-sections is that they are directly relatable to what is observed in substellar environments such as cool brown dwarfs, exoplanets and other planetary objects [15,28]. Spectroscopic data for propane is also available in several databases such as HITRAN [29] and GEISA [30], however these sources are more applicable to Earth's atmosphere rather than those of other planets. We present here infrared absorption cross-sections of pure, and H_2 broadened, propane as cold as 200 K.

The work is part of a program to record spectra of small hydrocarbons with H_2, He and N_2 broadeners as needed for the analysis of cool astronomical objects. In another experiment, spectra have been recorded at temperatures below 200 K to better match the stratospheric temperatures of Jupiter and Saturn. In this first paper, however, we present the warmer propane cross sections. We note that temperatures above 200 K can be found in the thermosphere and troposphere of the giant planets as well as in auroral regions.

2. Experimental

Propane (C_3H_8) (99.99% purity) and H_2 (99.99% purity) were purchased from Praxair and used without further purification and we assume the isotopic contamination of ^{13}C to be approximately 1.1% according to its natural abundance. Depending on the conditions, either pure C_3H_8 (or a C_3H_8-H_2 mixture) was used in a multipass White cell set to an optical path length of 8 m (base path length = 2 m) that was operated in a static mode [31].

The cell temperature was either left at ambient temperature (approximately 298 K) or cooled to temperatures as low as 205 K using a NESLAB ULT-80DD refrigerated re-circulating methanol bath [32–34]. Once the cell had reached the desired temperature, it was left to equilibrate overnight and monitored with PT100 RTD sensors. Fluctuations in temperature during each experiment were ±0.1 K. The spectrometer was fitted with a KBr beamsplitter and a liquid He-cooled Ge: Cu detector was used for optimum sensitivity between 600 – 1250 cm^{-1}. Table 1 summarizes the individual conditions used for each experiment. Experiments with H_2 as the foreign broadening gas were carried out first by filling the cell with a small amount of propane and then adding H_2 to reach total pressures of 8 Torr (1.066 Pa), 30 Torr (4 kPa) and 100 Torr (13.33 kPa) determined using two baratron gauges (MKS 626B13TBE up to

Table 2
Observed full-width half-maximum linewidths (FWHM) near 700 cm^{-1} for unblended lines and the resolution used to record the spectra.

H_2 (kPa)	Obs FWHM (cm^{-1})	Resolution (cm^{-1})	
		Sample	Background
Pure (n/a)	0.002	0.00096	0.01536
1.066	0.01	0.005	0.04
4	0.035	0.01	0.04
13.33	0.1	0.04	0.04

1000 Torr and Micro Precision 627B11TEV1B up to 10 Torr) with estimated uncertainties of ±0.4 Pa.

For scans with pure propane, the full resolution of the spectrometer was utilized (0.00096 cm^{-1}) along with the synchrotron radiation as the light source. For H_2-broadened spectra, the resolution was reduced to match the increasing linewidths and the source changed to the internal glowbar mid-IR source (Table 2). This is because the advantages of the synchrotron source (being a near pinpoint source, having both higher flux and higher signal-to-noise) are lost with increasing aperture size. Furthermore, signal-to-noise levels are increased with decreasing resolution and the efficiency of recording scans is increased. Forward and reverse pairs of interferograms were recorded and saved as individual files before being Fourier transformed. During the Fourier transform, a Blackman-Harris 3-Term apodization function and a zero-fill factor of eight were used. Zero-filling serves to mitigate the picket fence effect from the fast Fourier transform process by adding additional data points to interpolate between the sampled points. This results in smoother spectra with more accurate line positions, intensities and areas.

Background spectra were recorded before and after each sample and the single channel profiles were then co-added using a weighted average. The most suitable background was used in order to obtain the final transmission spectrum.

3. Results and discussion

3.1. Cross-Sections

Fig. 1 provides a series of vertically offset C_3H_8 absorption cross-sections (σ_{CLS}) broadened by approximately 1.066 kPa (8 Torr) of H_2 at progressively decreasing temperatures ranging from 292 K to 209 K in the 650 – 1250 cm^{-1} region. The absorption