Absorption cross sections in the CH stretching region for propene broadened by helium and nitrogen

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Abstract

Propene infrared absorption cross-sections are important for quantitative analysis of atmospheric spectra. Propene has been observed in Titan's atmosphere and may be detected in the atmospheres of giant planets. Infrared absorption cross-sections of propene (C_3H_6) have been measured in the 2680-3220 cm^{-1} region by high-resolution Fourier transform spectroscopy. Samples of propene were held at 202, 232, 265, 295 K with helium and nitrogen broadening gas pressures of 10, 30, 100 Torr. The cross section files are available for download.

Keywords: infrared spectroscopy, absorption cross-sections, planetary atmospheres, Fourier transform spectroscopy, propene

1. Introduction

Propylene or propene (C_3H_6) is a small unsaturated hydrocarbon, next in size to ethene. It is an important alkene that is widely used in the chemical industry, for example, in the production of polypropylene. Propene is a short-lived (a few hours for the OH lifetime [1]) non-methane hydrocarbon found in the Earth's atmosphere with a low atmospheric mole fraction (about 10 ppt) throughout the year [2] with both biogenic and anthropogenic sources [3].

Propene has been detected in several extraterrestrial sources. Nixon et al. [4] detected propene in Titan's stratosphere using the ν_{19} band at 912.5 cm^{-1} with the Cassini Composite Infrared Spectrometer (CIRS) on the Cassini spacecraft that was in orbit around Saturn. The other C_3 hydrocarbons detected on Titan include propane, methylacetylene [5], allene [6], cyclopropenylidene [7], but not cyclopropane. Titan's atmosphere is mainly N_2 with a few percent CH_4, so N_2-broadened line parameters and cross sections are need. Marcelino et al. [8]

detected propene in the dark interstellar cloud TMC-1 using the IRAM 30-m radio telescope. Interstellar propene is formed by ion-molecule chemistry [9].

Hydrocarbons are also formed in the stratospheres of the giant planets starting from the photolysis of methane [10]. Propane has been detected on Saturn [11] and propene is predicted to be present [12]. The two main constituents of giant planet atmospheres are H_2 and He, so hydrocarbon spectra broadened by H_2 and He are needed.

Propene has C_s symmetry at equilibrium and 21 fundamental vibrational frequencies [13-14], ν_1-ν_{14} (a′) and ν_{15}- ν_{21} (a″). In the C-H stretching region there are 6 fundamental frequencies ν_1-ν_5 (3091.62, 3015, 2991.03, 2973, 2931.46 cm^{-1}) and ν_{15} (2954.30 cm^{-1}) [14]. In fact, there are 26 resolved vibrational bands in the CH stretching region as observed at 0.4 K with propene imbedded in He droplets [15]. Strong anharmonic resonances with several combination bands increases the number of features measured in the 3.3 μm region.

Sung et al. [14] have recorded high-resolution propene cross sections (pure and mixtures with nitrogen) in the 6.5-15.4 μm (650-1534 cm^{-1}) region in the 150 - 299 K temperature range. High-resolution infrared spectra near 3.3 μm (3000 cm^{-1}) for hot samples (400 - 700 K) were recorded by Buzan et al. [16] The Pacific Northwest National Laboratory (PNNL) infrared database has cross sections for propene with 1 atm (760 Torr) of nitrogen at 278, 298 and 323 K [17] that are now available in HITRAN [18]. Es-sebbar et al. [19] have measured cross sections in the 400 - 6500 cm^{-1} range for samples with temperatures between 296 and 460 K.

We report here on high-resolution propene absorption cross sections in the 2680 - 3220 cm^{-1} spectral region broadened by nitrogen and helium at 202, 232, 265 and 295 K. The nitrogen data are for Titan and the helium data for the giant planets. Spectra in the same spectral region with hydrogen as the broadener have also been recorded; they will be converted to cross sections and published separately.

Ground based measurements of hydrocarbons, including possibly propene, are feasible in the atmospheres of giant planets in the CH stretching region. Several hydrocarbons have been detected in emission in the auroral regions of Jupiter [20]. The Juno mission currently in orbit around Jupiter has a low resolution infrared spectrometer that also covers the CH stretching region [21]. Although the ν_{19} Q-branch at 912.5 cm^{-1} is the strongest feature in the propene infrared spectrum, the CH stretching region carries more integrated intensity [19] and is in a convenient spectral region for hydrocarbon spectroscopy.

2. Experimental Method

The experimental procedure used is very similar to our recent work on ethane and neopentane in the same spectral region [22, 23]. Infrared absorption spectra of propene, pure and broadened by helium and nitrogen were recorded at the Canadian Light Source (CLS) far-infrared beamline. Propene samples were held in a White-type multiple reflection cell at a path length of 8.63 m ($\pm$0.02 m) and at four different temperatures (nominally 202, 232, 265, 295 K) with nominal broadening gas pressures of 10 Torr, 30 Torr and 100 Torr. In addition to these, a pure propene spectrum was also recorded at 295 K. Fig. 1 illustrates the absorption cross sections of propene broadened by helium at 297 K. No wavenumber calibration was necessary as the N_2O line

positions in a calibration spectrum matched the HITRAN values [18] to within about 0.0003 cm^{-1}.

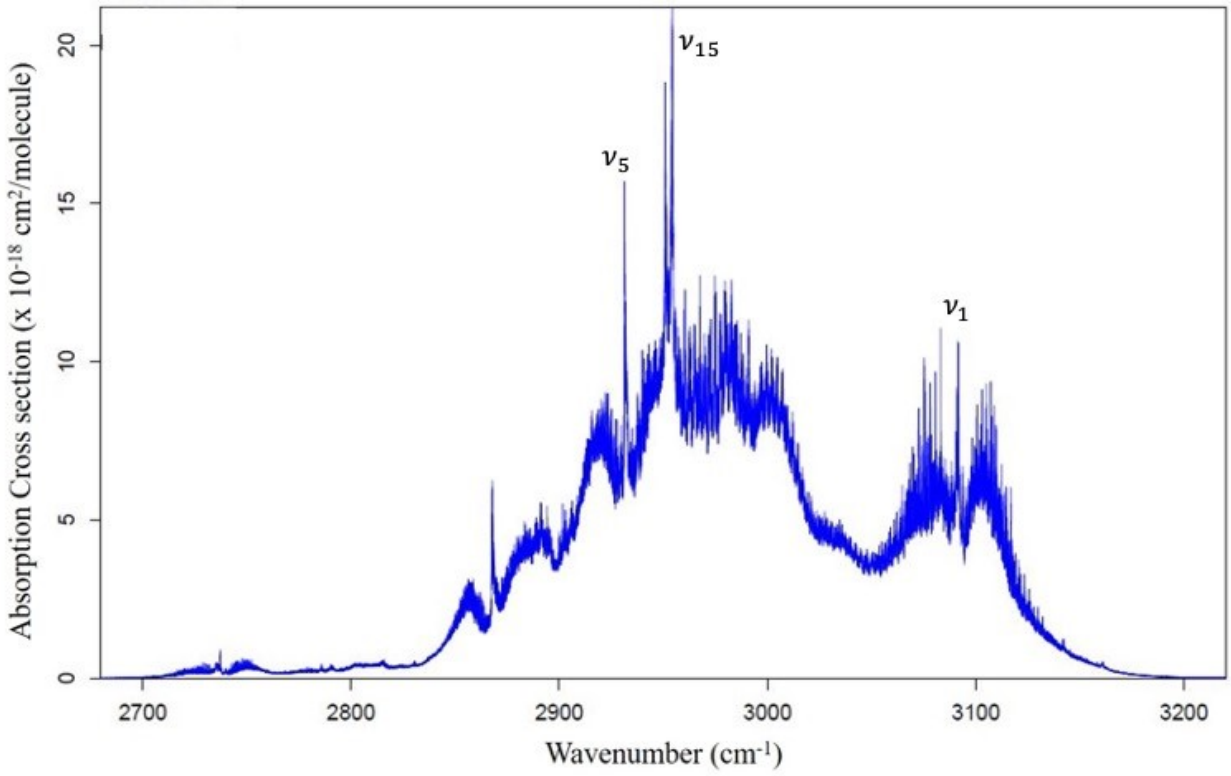

Figure 1. Absorption cross sections of propene (about 503 mTorr of propene at 30.5 Torr total pressure of He and propene at 297 K)

A high-resolution Fourier transform spectrometer (Bruker IFS 125HR) with a CaF_2 beam splitter, an InSb detector and a bandpass filter to cover the 2500-3280 cm^{-1} region was used. For different total pressures, the spectral resolution was varied: 0.003 cm^{-1} for the pure sample, 0.003 cm^{-1} for 10 Torr, 0.01 cm^{-1} for 30 Torr and 0.04 cm^{-1} for 100 Torr. Pressures were measured with three Baratron pressure gauges (Model 127AA up to 1 Torr, Model 627B up to 10 Torr and Model 626B up to 1000 Torr). The 1 Torr Baratron was a new gauge that was about 2 months old. The accuracy of the 1 Torr Baratron is about 1 mTorr or better than 1% for the propene pressures used. The 10 Torr Baratron was calibrated in January 2020, about 9 months prior to the experiment, and the 1000 Torr Baratron was calibrated in November 2019. The cell was cooled with an SP Scientific model RC211 refrigerated re-circulating 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 cell temperature uniformity was about 2-5 K. Table 1 shows the parameters used for recording the spectra.

Propene was added to the cell and helium (or nitrogen) was added until the desired total pressure was obtained. The continuum root-mean-square signal-to-noise ratios of the transmission spectra were in the range 2000-2800, except for the pure spectrum at room temperature with a value of

1800. The transmission spectra were converted to cross sections using [24]:

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

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. No intensity calibration factor was used.

Table 1: Experimental conditions for each spectrum

Helium

202 K			232 K		
Temp (K)	propene (mTorr)	Total (Torr)	Temp (K)	propene (mTorr)	Total (Torr)
201.95	257.5	10.6	232.15	315.4	10.47
201.95	248.3	30.2	232.15	334.4	30.2
201.95	248.3	100.3	232.05	347.4	100.3
265 K			295 K		
265.05	408.2	10.1	296.85	487.5	10.32
265.05	446.4	30.1	296.85	503.1	30.5
265.05	479.3	100.2	296.85	504.4	100.2

Nitrogen

202 K			232 K		
Temp (K)	propene (mTorr)	Total (Torr)	Temp (K)	propene (mTorr)	Total (Torr)
201.95	256.8	10.2	232.15	348.8	10.2
201.95	250.8	30.1	232.15	345.7	30
202.25	247.9	100.2	232.25	340.3	100.2
265 K			295 K		
265.05	405.9	10.2	296.75	483.5	9.9
265.05	445.6	30.3	296.85	502.9	30.2
265.15	479.2	100.6	296.85	506	100.2

Pure Sample

Temp (K)	propene (mTorr)	Total (mTorr)
296.75	482.9	482.9

Results and discussion

The 25 cross section files can be obtained from MoLLIST (Molecular Line Lists. Intensities and SpecTra) [25] website http://bernath.uwaterloo.ca/molecularlists.php. The cross sections should be multiplied by 10^{-18} and the units are cm^2/molecule.

The integrated areas of strong fundamental bands in the absorption cross sections are approximately constant independent of temperature, e.g. [26]. This property is often used for quality control or for calibration [22,24]. The integrated areas in the 2675 - 3210 cm^{-1} wavenumber region of our cross sections were compared with the corresponding integrated areas taken from the PNNL [17] database and cross sections provided by Es-sebbar et al. [19]. The integrated areas of our cross-sections range from 16.76×10^{-18} to 16.98×10^{-18} cm/molecule with an average value of 16.89×10^{-18} cm/molecule. The PNNL database provides composite spectra at temperatures 278, 298, and 323 K [17]. The individual spectra were taken by adding propene in a nitrogen mixture to make a total pressure of 760 Torr in a cell with a path length of 19.94 cm. PNNL spectra have a resolution of 0.112 cm^{-1}. The integrated areas range from 16.80×10^{-18} to 16.82×10^{-18} cm/molecule with an average value of 16.82×10^{-18} cm/molecule. Es-sebbar et al. [19] provide propene cross sections measured at various temperatures above 296 K but we only obtained cross sections for 296 K. 10% propene in a nitrogen mixture was used in gas cell with a path length of 10 cm. Spectral resolutions for the regions 400 - 3200 cm^{-1} and 3200 - 6000 cm^{-1} were 0.09 cm^{-1} and 0.18 cm^{-1} respectively. The integrated area is 16.49×10^{-18} cm/molecule for the 2675 - 3210 cm^{-1} range. The PNNL and Es-sebbar et al. [19] integrated areas differ by 0.42% and 2.38% from our work.

Pressure broadening of propene cross sections due to helium is shown in Fig. 2. The effect of nitrogen broadening is similar. As the pressure increases the peaks get smaller and lines broaden. A quasicontinuum appears in the 100 Torr data and pressure broadening is linear with pressure.

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.

The PNNL cross sections have an estimated accuracy of 3.2% based on independent measurements carried out at PNNL and NIST [17]. Es-sebbar et al. [19] provide cross sections with uncertainties of 5% for the CH stretching region. Based on the agreement of our integrated areas with independent measurements, we estimate that our cross sections have errors of about 4%.

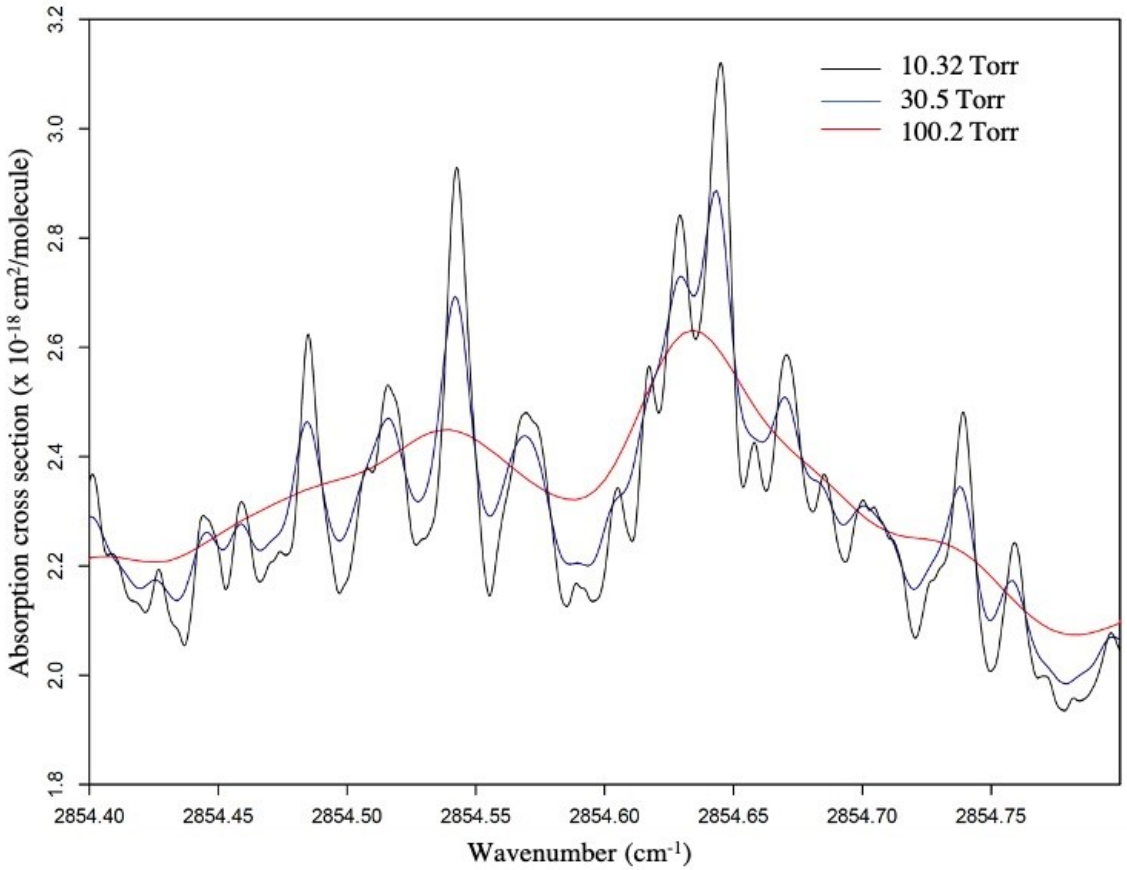

Figure 2. Absorption cross sections of propene broadened by helium at different total pressures at 295 K. (Black = 10.32 Torr, Blue = 30.5 Torr, Red = 100.2 Torr)

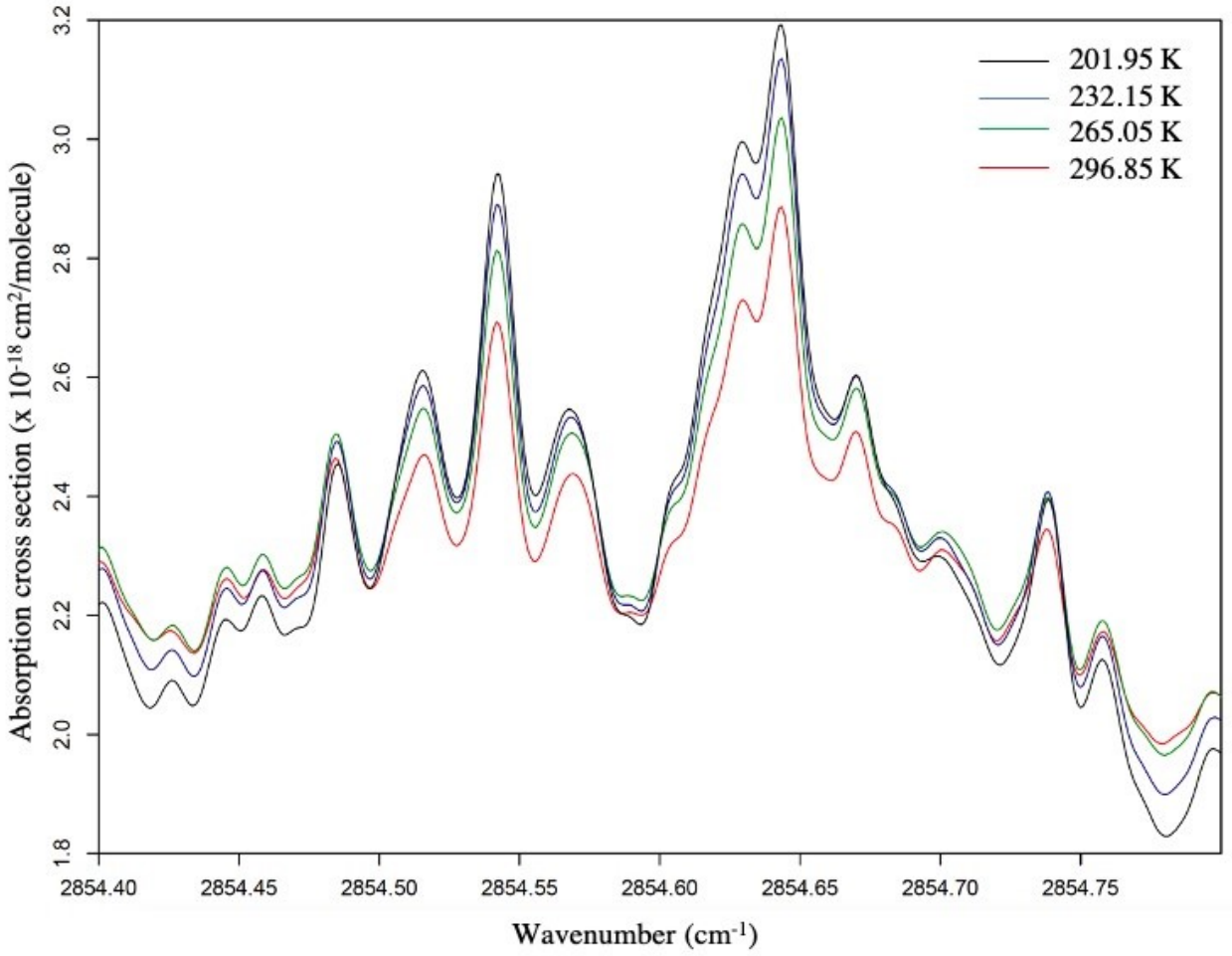

Figure 3. Absorption cross sections of propene broadened by helium at different temperatures for 30 Torr of total pressure. (Black = 202 K, Blue = 232 K, Green = 265 K, Red = 297 K)

Conclusion

This paper presents high resolution absorption cross sections of propene in the 2680 - 3220 cm^{-1} region from 202 K to 295 K using helium and nitrogen as broadening gases. These low temperature cross sections in the CH stretching region are expected to be useful in the detection of propene in planetary atmospheres.

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