



# Infrared absorption cross sections for propene broadened by N<sub>2</sub> (450–1250 cm<sup>-1</sup>) and by H<sub>2</sub> (2680–3220 cm<sup>-1</sup>)



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## ABSTRACT

Propene (C<sub>3</sub>H<sub>6</sub>) has been measured in the planetary atmospheres of Earth and Titan, and may be detected in the giant planets by infrared spectroscopy. Propene infrared absorption cross sections have been determined in the 2680–3220 cm<sup>-1</sup> and 450–1250 cm<sup>-1</sup> regions by high-resolution Fourier transform spectroscopy with H<sub>2</sub> and N<sub>2</sub>, respectively, as broadening gases. Samples of propene were held at 202, 232, 265, 297 K.

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## 1. Introduction

Propylene or propene (C<sub>3</sub>H<sub>6</sub>) is an important small alkene that is found in the Earth's atmosphere [1]. Hydrocarbon ion-molecule and photochemistry starting from methane produces propene in the atmosphere of Titan, a moon of Saturn [2]. Infrared spectroscopy with the Cassini Composite Infrared Spectrometer (CIRS) on the Cassini spacecraft has detected propene on Titan using the strong band at 912.5 cm<sup>-1</sup> [3]. The atmosphere of Titan is about 95% nitrogen and 5% methane near the surface where the pressure is about 1.5 atm [4]. Sung et al. [5], therefore, have recorded high-resolution propene cross sections (pure and mixtures with nitrogen) in the 6.5–15.4 μm (650–1534 cm<sup>-1</sup>) region in the 150–299 K temperature range. Hydrocarbons are found in Titan's stratosphere where the pressure ranges from about 0.01 Torr to about 75 Torr [4], which sets the pressure range of interest.

The giant planets have atmospheres that are composed mainly of hydrogen and helium with a small amount of methane. For example, based on CIRS data, Saturn has a He/H<sub>2</sub> abundance ratio of 0.08 (H<sub>2</sub> abundance of 93% and He abundance of 7%) and a CH<sub>4</sub> abundance of about 0.5% [6]. Propane has been detected in Saturn's atmosphere [7] and propene is expected to be formed by photochemistry [8]. For giant planet spectroscopy, hydrocarbon spectra

and cross sections are needed with hydrogen and helium as broadening gases.

In addition to the Sung et al. [5] cross sections, 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 [9] that are now available in HITRAN [10]. Es-sebbar et al. [11] have published cross sections in the 400–6500 cm<sup>-1</sup> range. Very recently, we obtained high resolution propene cross sections [12] at 202, 232, 265, 295 K with helium and nitrogen broadening gas pressures of 10, 30, 100 Torr in the CH stretching region (2680–3220 cm<sup>-1</sup>). We report here on the corresponding data for propene broadened by hydrogen, and on propene broadened by nitrogen in the 500–650 cm<sup>-1</sup> region, a spectral region not covered by Sung et al. [5].

## 2. Experimental method

The experimental procedure used near 3000 cm<sup>-1</sup> is identical to our previous propene measurements in the same spectral region [12]. Infrared absorption spectra of propene, pure and broadened by hydrogen 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 (± 0.02 m) and at four different temperatures (nominally 202, 232, 266, 293 K) with nominal broadening gas pressures of 10, 30, 100 Torr. Propene was added to the cell and hydrogen (or nitrogen, below) was added until the desired total pressure was obtained. Pressures

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**Table 1**  
Experimental conditions for each spectrum.

With Hydrogen					
202 K			232 K		
Temp (K)	propene (mTorr)	Total (Torr)	Temp (K)	propene (mTorr)	Total (Torr)
202.15	258.7	10.3	232.15	352.1	10.0
202.05	249.4	30.4	232.15	314.1	30.3
202.05	247.6	100.3	232.15	341.4	100.4
265 K			297 K		
265.05	409.6	10.0	297.15	484.3	10.09
265.05	448.5	30.8	297.25	594.5	30.0
265.05	481.0	100.2	297.35	506.8	100.0
Pure Sample					
Temp (K)	propene (mTorr)	Total (mTorr)			
202.15	260.0	260.0			
232.15	353.5	353.5			
265.15	411.8	411.8			
297.85	488.0	488.0			
With Nitrogen					
202 K			232 K		
Temp (K)	propene (mTorr)	Total (Torr)	Temp (K)	propene (mTorr)	Total (Torr)
201.75	59.5	9.939	232.05	75.3	10.3
201.75	81.9	30.2	232.05	100.6	30.7
201.75	105.2	100.4	232.05	139	100.1
265 K			295 K		
265.25	96.8	10.2	294.35	103.7	10
265.25	119.2	30.1	294.35	128.5	31.2
265.25	148.6	100	294.35	153.9	100.2

were measured with three recently-calibrated Baratron pressure gauges (Model 127AA up to 1 Torr, Model 627B up to 10 Torr and Model 626B up to 1000 Torr).

Absorption spectra in this CH stretching region of propene were obtained using a high-resolution Fourier transform spectrometer (Bruker IFS 125HR) with a CaF<sub>2</sub> beamsplitter, an InSb detector and a bandpass filter to cover the 2500–3280 cm<sup>-1</sup> region. The spectral resolutions were varied for different total pressures: 0.003 cm<sup>-1</sup> for the pure sample, 0.003 cm<sup>-1</sup> for 10 Torr, 0.01 cm<sup>-1</sup> for 30 Torr and 0.04 cm<sup>-1</sup> for 100 Torr as needed to resolve the Doppler and pressure broadened lines. The propene sample pressures were selected so the Q branch at 2931.5 cm<sup>-1</sup> was not saturated.

Spectra for the band centered around 575 cm<sup>-1</sup> were obtained using a KBr beamsplitter, a Ge:Cu detector in a QMC Instruments cryostat at about 4 K. The 450–1250 cm<sup>-1</sup> bandpass was set by the KBr beamsplitter and windows at the lower end, and by a bandpass filter at the higher end. The nominal temperatures of the samples and pressures of N<sub>2</sub> broadening gas were the same as for the H<sub>2</sub>-broadened measurements. For different total pressures, the spectral resolution was varied: 0.00096 cm<sup>-1</sup> for the pure sample, 0.003 cm<sup>-1</sup> for 10 Torr, 0.01 cm<sup>-1</sup> for 30 Torr and 0.04 cm<sup>-1</sup> for 100 Torr. Cross sections for pure samples are not reported in this region because reliable cross sections could not be obtained because of very strong channeling (see below). The detailed temperatures and pressures are provided in Table 1. Note that the number of digits reported for the pressures in Table 1 correspond to the readout values from the Baratron gauges and they were carried in our calculations; the absolute accuracy of the pressure measurement is about 1%.

The transmission spectra were converted to cross sections using [13]:

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

where,  $\tau(\nu, T)$  is the transmittance at wavenumber  $\nu$  (cm<sup>-1</sup>) and temperature  $T$  (K),  $P$  is the pressure of the absorbing gas in pascals (Pa),  $l$  is the path length in meters (m) and  $k_B$  ( $1.380649 \times 10^{-23}$  J K<sup>-1</sup>) is the Boltzmann constant.

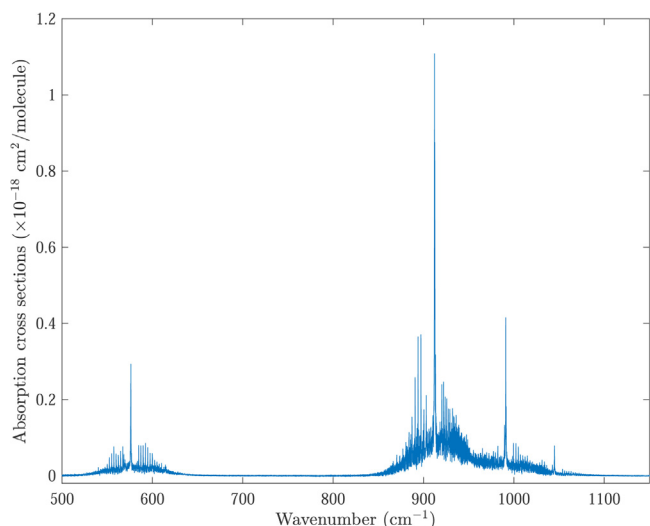
A wavenumber calibration was applied to the cross sections broadened by hydrogen in the CH stretching region. For the calibration, the pure spectrum at room temperature was compared to the corresponding calibrated spectrum recorded previously [12] and a calibration factor of 0.999999380 (corresponding to a shift of about  $-0.0018$  cm<sup>-1</sup>) was applied to all spectra. The calibrated wavenumber scale has an accuracy of about 0.0002 cm<sup>-1</sup>. No calibration was required for the spectra broadened by N<sub>2</sub>.

The spectra recorded in the 450–1250 cm<sup>-1</sup> region suffered from considerable channeling (sinusoidal fringing). The fringes were reduced using interactive software at the Canadian Light Source that first isolates the fringes in the interferogram. The fringes are then Fourier transformed to create a correction spectrum which is divided into the observed spectrum to reduce the fringing. However, the spectra for a total pressure of 10 Torr of nitrogen and propene (in particular) still have substantial residual fringing. This fringing behaves like “noise” and reduces the signal-to-noise ratio by a factor of about 5. The cross sections for pure samples were not satisfactory and are not reported.

The main target was the relatively weak band at 576 cm<sup>-1</sup> so a higher sample pressure was used to improve the spectra. As a result, a few of the spectra of the stronger band near 912 cm<sup>-1</sup> were saturated and the cross sections are not reliable. All of the spectra (except at 202 K) for 100 Torr total pressure of nitrogen and propene had saturated Q-branches near 912 cm<sup>-1</sup>. In addition, two other spectra, 10 Torr at 232 K and 265 K, were saturated in the same region, and the 10 Torr 265 K spectrum was also saturated near 893.94 cm<sup>-1</sup>. The saturated cross section points have been replaced by 0 values. The saturated regions are small ( $<1$  cm<sup>-1</sup>) and good data are available in this region from Sung et al. [5].

### 3. Results and discussion

The 28 cross section files are available from the MoLLIST (Molecular Line Lists. Intensities and SpecTra) [14] website <http://bernath.uwaterloo.ca/molecularlists.php>. The cross section values should be multiplied by  $10^{-18}$  and the units are cm<sup>2</sup>/molecule.



**Fig. 1.** Overview of the propene cross sections at low wavenumbers with 105 mTorr of propene and a pressure of 100 Torr of N<sub>2</sub> at 202 K.

**Table 2**  
Comparison of integrated areas in the region 800–1100 cm<sup>-1</sup>.

Source	Integrated area (x 10 <sup>-18</sup> cm <sup>2</sup> /molecule)
JPL <sup>a</sup> at 298 K	8.79 ± 0.47
Es-sebbar et al. <sup>b</sup> at 296 K	9.14
PNNL <sup>c</sup> at 278, 298, 323 K	9.41 ± 0.01
This work at 294.35 K	9.13 ± 0.09 <sup>d</sup>
JPL <sup>a</sup> at 270 K	8.93 ± 0.47
This work at 265.25 K	8.89
JPL <sup>a</sup> at 230 K	9.21 ± 0.49
This work at 232.05 K	9.30
This work at 201.75 K	9.38 ± 0.21 <sup>e</sup>

<sup>a</sup> JPL value based on summing pseudolines, Ref. [5].

<sup>b</sup> Ref. [11].

<sup>c</sup> Ref. [9].

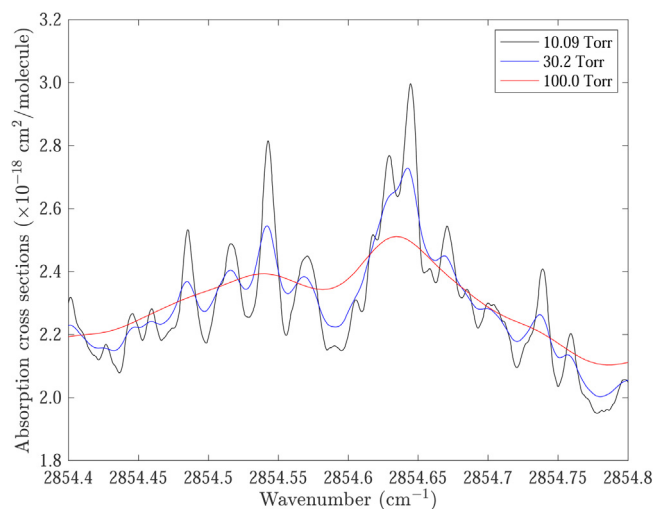
<sup>d</sup> Average integrated area of two total pressures.

<sup>e</sup> Average integrated area of three total pressures.

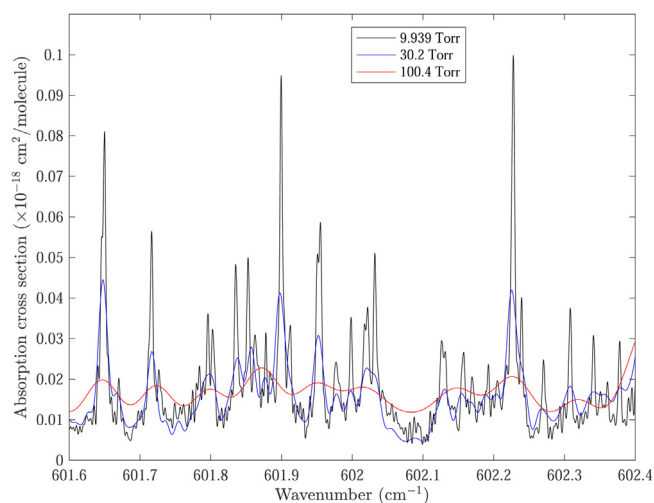
The integrated areas of strong fundamental bands in the absorption cross sections are approximately constant independent of temperature, e.g. [15,16]. Our cross sections in the CH stretching region were integrated in the 2675–3210 cm<sup>-1</sup> wavenumber region and compared with the corresponding integrated areas of the PNNL cross sections [9]. Our cross-section areas range from  $16.49 \times 10^{-18}$  to  $16.94 \times 10^{-18}$  cm<sup>2</sup>/molecule with an average value of  $16.76 \times 10^{-18}$  cm<sup>2</sup>/molecule and a standard deviation of  $0.12 \times 10^{-18}$  cm<sup>2</sup>/molecule. The PNNL database provides composite spectra at temperatures 278, 298, and 323 K [14] with areas that range from  $16.80 \times 10^{-18}$  to  $16.82 \times 10^{-18}$  cm<sup>2</sup>/molecule with an average value of  $16.82 \times 10^{-18}$  cm<sup>2</sup>/molecule. The PNNL integrated area average differs by 0.36% from our work.

Although the cross sections broadened by nitrogen are focused on the band centered around 575 cm<sup>-1</sup>, the spectra include the entire 450–1250 cm<sup>-1</sup> range (Fig. 1) and cover the 800–1100 cm<sup>-1</sup> region. Integrated areas in the 800–1100 cm<sup>-1</sup> region were compared with Sung et al. [5], Es-sebbar et al. [11] and PNNL [9], and are given in Table 2. One standard deviation on the mean area is provided, wherever possible. For our data, the cross sections with saturated points were not included in the averages. The areas and standard deviations for the JPL cross sections are based on pseudolines as reported by Sung et al. [5].

The agreement with the room temperature cross sections of Es-sebbar et al. [11] (Table 2) is very good (0.1%). The PNNL data



**Fig. 2.** Absorption cross sections of propene broadened by hydrogen at different total pressures at 297 K. (Black = 10 Torr, Blue = 30 Torr, Red = 100 Torr).



**Fig. 3.** Absorption cross sections of propene broadened by nitrogen at different total pressures at 202 K. (Green = 10 Torr, Blue = 30 Torr, Red = 100 Torr).

shows essentially no temperature dependence, while our data and that of JPL are more variable. Based on the standard deviation of our data at 202 K, our precision is about 2%; however, based on the range of our values in Table 2 our accuracy is about 5% and based on comparison with other measurements our accuracy is about 7%. Note that it is possible to carry out a detailed error analysis considering the errors in temperature, pressure, path length, gas composition and so forth as done by Harrison et al. [13], who obtained a value of about 4%, which is typical. However, more realistic error estimates (accuracy) are obtained by comparison with independent measurements, i.e., 7% is a reasonable estimate of the accuracy. These error estimates are all one standard deviation.

Fig. 2 shows the expected pressure broadening of propene lines by hydrogen near 2850 cm<sup>-1</sup>. Fig. 3 is a similar figure for broadening by N<sub>2</sub> near 600 cm<sup>-1</sup>. In the propene spectrum at 10 Torr, the vibration-rotation lines are still nearly fully resolved and only slightly broadened. At 100 Torr total pressure, the rotational structure is completely washed out by pressure broadening. The added gas induces a significant Lorentzian component to the low pressure Doppler lineshape [17]. Notice also that there is a baseline offset in both spectra due to a quasi-continuum of unresolved lines mainly from torsional hot bands from the methyl rotor.

The estimated accuracy of the PNNL cross sections is 3.2% (two standard deviations) based on a detailed error analysis and comparison with independent measurements [9]. We estimate therefore that our cross sections in the CH stretching region have similar errors of about 4% by comparison with PNNL. The cross sections, however, for the band at  $576\text{ cm}^{-1}$  are less accurate. Based on Table 2, the accuracy is a little better than about 10%.

#### 4. Conclusion

High resolution absorption cross sections of propene in the  $2680\text{--}3220\text{ cm}^{-1}$  region using hydrogen as a broadening gas and in the  $450\text{--}1250\text{ cm}^{-1}$  region using nitrogen as a broadening gas have been determined. Sample temperatures ranged from 202 K to 297 K. These low temperature cross sections are expected to be useful in the detection of propene in the atmospheres of giant planets and Titan.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRediT authorship contribution statement

**Peter F. Bernath:** Writing – original draft, Supervision. **Randika Dodangodage:** Writing – review & editing, Formal analysis, Visualization. **Jianbao Zhao:** Data curation. **Brant Billingham:** Data curation.

#### Data Availability

The data are available from the MoLLIST web site.

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