# Infrared absorption cross sections for propene

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## Abstract

Propene ($C_3H_6$) 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 $cm^{-1}$ and 450-1250 $cm^{-1}$ regions by high-resolution Fourier transform spectroscopy with $H_2$ and $N_2$, respectively, as broadening gases. Samples of propene were held at 202, 232, 265, 297 K.

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

## 1. Introduction

Propylene or propene ($C_3H_6$) is an important small alkene that is found in the Earth's atmosphere [1]. Hydrocarbon ion-molecule and photochemistry chemistry 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 $cm^{-1}$ [3]. The atmosphere of Titan is about 95% nitrogen and 5% methane near the surface. Sung et al. [4], therefore, 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.

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/$H_2$ abundance ratio of 0.08 ($H_2$ abundance of 93% and He abundance of 7%) and a $CH_4$ abundance of about 0.5% [5]. Propane has been detected in Saturn's atmosphere [6] and propene is expected to be formed by photochemistry [7]. 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. [4] 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 [8] that are now available in HITRAN [9]. Es-sebbar et al. [10] have published cross sections in the 400 - 6500 $cm^{-1}$ range. Very recently, we obtained high resolution propene cross sections [11] 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 $cm^{-1}$). We report here on the corresponding data for propene broadened by hydrogen [11], and on propene broadened by nitrogen in the 500-650 $cm^{-1}$ region, a spectral region not covered by Sung et al. [4].

## 2. Experimental Method

The experimental procedure used near 3000 $cm^{-1}$ is identical to our previous propene measurements in the same spectral region [11]. 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 ($\pm$0.02 m) and at four different temperatures (nominally 202, 232, 266, 293 K) with nominal broadening gas pressures of 10, 30, 100 Torr.

Absorption spectra in this CH stretching region of propene were obtained using a high-resolution Fourier transform spectrometer (Bruker IFS 125HR) with a $CaF_2$ beamsplitter, an InSb detector and a bandpass filter to cover the 2500-3280 $cm^{-1}$ region. The spectral resolutions were as reported previously [11].

Spectra for the band centered around 575 $cm^{-1}$ were obtained using a KBr beamsplitter, a Ge:Cu detector in a QMC Instruments cryostat at about 4 K. The 450-1250 $cm^{-1}$ 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 $N_2$ broadening gas were the same as for the $H_2$-broadened measurements. For different total pressures, the spectral resolution was varied: 0.00096 $cm^{-1}$ 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. 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.

Propene was added to the cell, and then hydrogen or nitrogen was added until the desired total pressure was obtained. The transmission spectra were converted to cross sections using [12]:

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

where, $\tau(\nu,T)$ is the transmittance at wavenumber $\nu$ ($cm^{-1}$) and temperature $T$ (K), $P$ is the pressure of the absorbing gas in pascals (Pa), $l$ is the path length in meters (m) and $k_B$ ($1.380649 \times 10^{-23}$ J $K^{-1}$) 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 [11] and a calibration factor of 0.999999380 (corresponding to a shift of about -0.0018 $cm^{-1}$) was applied to all spectra. The

calibrated wavenumber scale has an accuracy of about 0.0002 $cm^{-1}$. No calibration was required for the spectra broadened by $N_2$.

The spectra recorded in the 450-1250 $cm^{-1}$ 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. The cross sections for pure samples were not satisfactory and are not reported.

The main target was the relatively weak band at 576 $cm^{-1}$ so a high pressure was used to improve the spectra. As a result, a few of the spectra of the stronger band near 912 $cm^{-1}$ were saturated and the cross sections are not reliable. All of the spectra for 100 Torr total pressure of nitrogen and propene had saturated Q-branches near 912 $cm^{-1}$. 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 $cm^{-1}$.

89 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 |

## Results and discussion

The 28 cross section files are available as supplementary data and can also be obtained from MoLLIST (Molecular Line Lists. Intensities and SpecTra) [13] website http://bernath.uwaterloo.ca/molecularlists.php. The cross section values 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. [14]. Our cross sections in the CH stretching region were integrated in the 2675 - 3210 $cm^{-1}$ wavenumber region and compared with the corresponding integrated areas of the PNNL cross sections [8]. Our cross-sections range from $16.49 \times 10^{-18}$ to $16.94 \times 10^{-18}$ cm/molecule with an average value of $16.76 \times 10^{-18}$ cm/molecule and a standard deviation of $0.12 \times 10^{-18}$ cm/molecule. The PNNL database provides composite spectra at temperatures 278, 298, and 323 K [13] with areas that range from $16.80 \times 10^{-18}$ to $16.82 \times 10^{-18}$ cm/molecule with an average value of $16.82 \times 10^{-18}$ cm/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 $cm^{-1}$, the spectra include the entire 450-1250 $cm^{-1}$ range (Figure 1) and cover the 800-1100 $cm^{-1}$ region. Integrated areas in the 800-1100 $cm^{-1}$ region were compared with Sung et al. [4] and PNNL, and are given in Table 2.

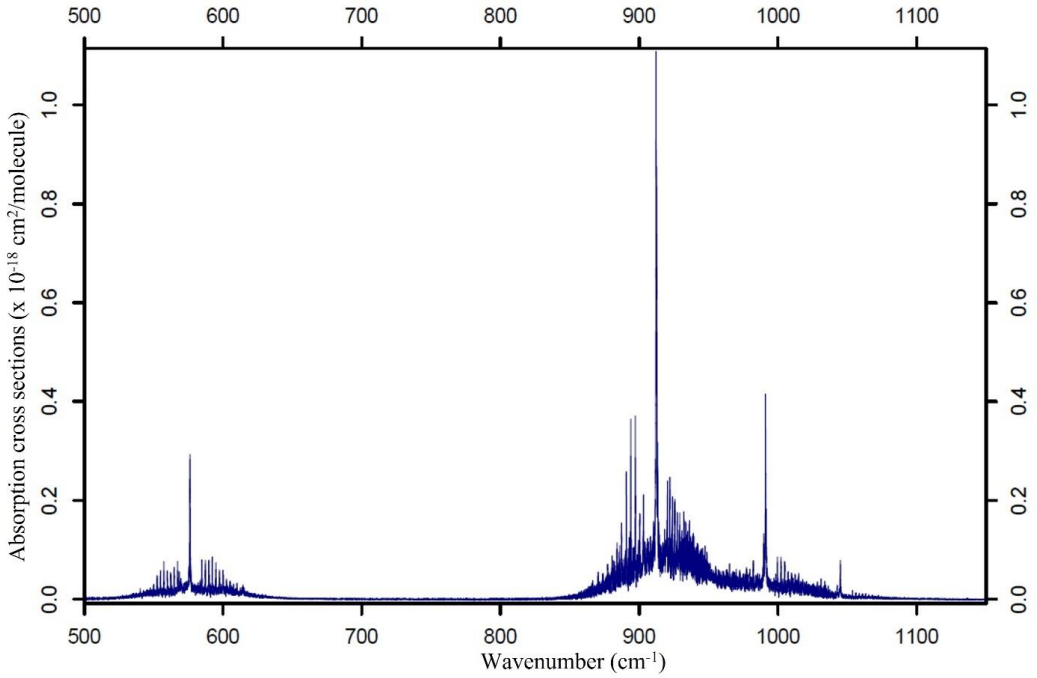


**Figure 1**. Overview of the propene cross sections at low wavenumbers with 105 mTorr of propene and a pressure of 100 Torr of $N_2$ at 202 K.

Table 2: Comparison of integrated areas in the region 800-1100 $cm^{-1}$.

| Source | Integrated area (x $10^{-18}$ cm/molecule) |
|---|---|
| JPL[a] at 298 K and 296 K | 8.79 |
| PNNL at 298 K | 9.65 |
| This work at 294.35 K | 9.12[b] |
| JPL at 270 K | 8.93 |
| This work at 265.25 K | 8.64[a] |
| JPL at 230 K | 9.21 |
| This work at 232.05 K | 9.16[a] |

[a]JPL (Ref. [4])

[b]Average integrated area of the three total pressures is given.

Fig. 2 shows the expected pressure broadening of propene lines by hydrogen near 2850 $cm^{-1}$. Figure 3 is a similar figure for broadening by $N_2$ near 600 $cm^{-1}$.

The estimated accuracy of the PNNL cross sections is 3.2% based on independent measurements [8]. 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 $cm^{-1}$ are less accurate. Based on Table 2, the accuracy is a little better than about 10 %.

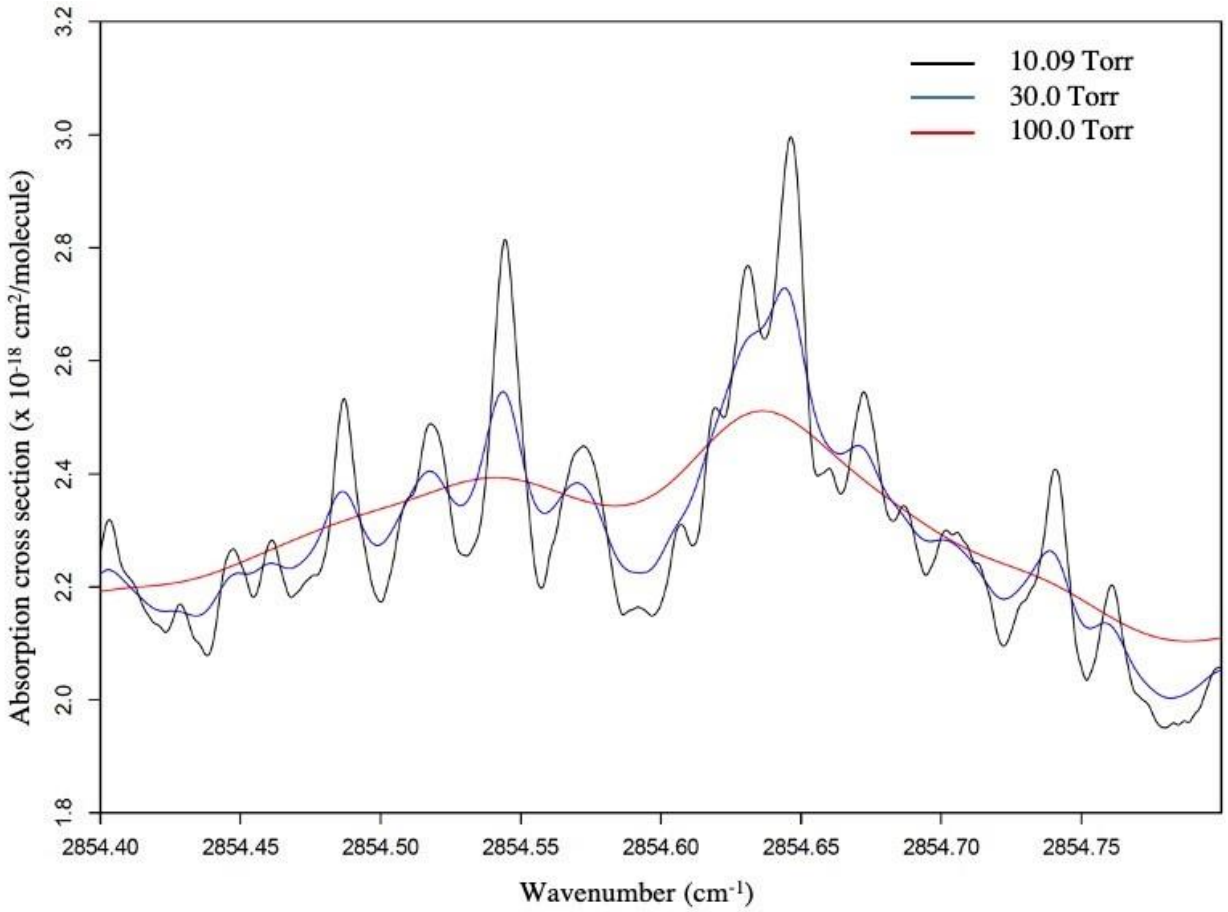


**Figure 2**. Absorption cross sections of propene broadened by hydrogen at different total pressures at 297 K. (Black = 10 Torr, Blue = 30 Torr, Red = 100 Torr)

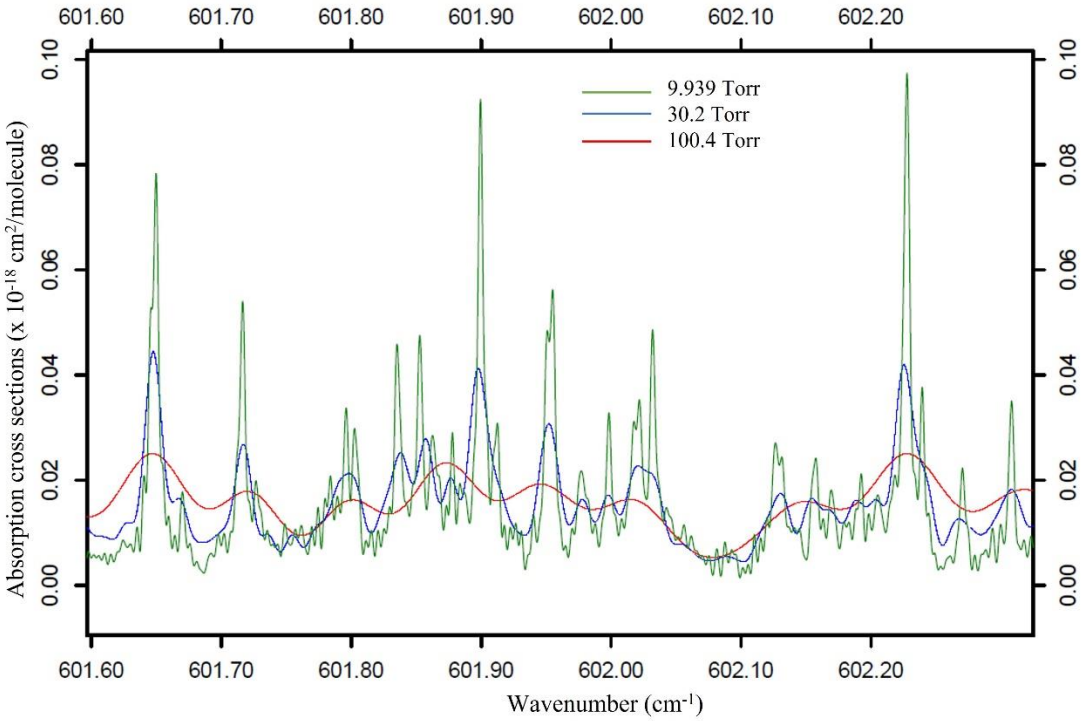


**Figure 3**. Absorption cross sections of propene broadened by nitrogen at different total pressures at 202 K. (Green = 10 Torr, Blue = 30 Torr, Red = 100 Torr)

## Conclusion

High resolution absorption cross sections of propene in the 2680 - 3220 $cm^{-1}$ region using hydrogen as a broadening gas and in the 500-650 $cm^{-1}$ 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.

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