Absorption cross sections for neopentane broadened by nitrogen in the 3.3 μm region

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ABSTRACT

Infrared absorption spectra of neopentane, 2,2-dimethylpropane, $C(CH_3)_4$, were recorded in the 2550-3350 cm^{-1} region by high resolution Fourier transform spectroscopy at the Canadian Light Source (CLS). Absorption cross sections were obtained for pure samples and with nitrogen as a broadening gas for 4 temperatures (202, 232, 265, 297 K).

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1. Introduction

Neopentane (2,2-dimethylpropane, C_5H_{12}) is an unusual hydrocarbon with tetrahedral symmetry like methane. Hydrocarbons are present in the Earth's atmosphere, typically from fugitive emission from fossil fuel production [e.g., 1]. They are also present in the atmospheres of the Giant Planets [e.g., 2] and Titan [3], the largest moon of Saturn, where they originate from the photolysis of methane. Cold planetary atmospheres are likely to be reservoirs of highly complex hydrocarbons, in both gaseous and condensed states.

Titan has a thick atmosphere (1.5 atm at the surface) composed of 95% N_2 and 5% CH_4 at a temperature of 94 K near the surface [3]. Most of the hydrocarbons are produced by photolysis and ion molecule chemistry in the stratosphere and mesosphere [4]. So far 9 hydrocarbon molecules including benzene have been detected by infrared spectroscopy using the Composite Infrared Spectrometer (CIRS) on the Cassini mission or using ground-based telescopes [3,5]. Neopentane could form by the radical-radical recombination reaction of CH_3 with the relatively stable tertiary butyl radical, $C(CH_3)_3$. Neopentane may be detectable in Titan's atmosphere by infrared spectroscopy, but there are no high resolution laboratory spectra available.

Many infrared and Raman measurements have been made on neopentane [6–10], and inelastic neutron scattering data are also available [11]. Force field calculations, e.g., by Schachtschneider and Snyder [12], and *ab initio* calculations, e.g., by Mirkin and Krimm [13], and Bernath et al. [14] have been carried out. Bernath et al. [14] also carried out anharmonic and local mode calculations focusing on the 800–1800 cm^{-1} spectral region. They recorded high resolution spectra at room temperature and 232 K, and rotationally analyzed two bands.

Neopentane has 45 normal modes and 19 fundamental frequencies of vibration, 3 of a_1 symmetry (v_1-v_3), 1 a_2 (v_4), 4 e (v_5-v_8), 4 t_1 (v_9-v_{12}) and 7 t_2 (v_{13}-v_{19}), of which only the t_2 modes are infrared active [13,14]. The a_1, e and t_2 modes are Raman active, and the a_2 and t_1 modes are inactive. In the C–H stretching region, the 12 C–H bonds lead to 5 fundamental vibrational frequencies in the 2800–3000 cm^{-1} region: $v_1(a_1)$, 2909 cm^{-1}; $v_4(e)$, 2955 cm^{-1}; $v_9(t_1)$, (2942) cm^{-1}; $v_{13}(t_2)$, 2959.6 cm^{-1}; $v_{14}(t_2)$, 2876.2 cm^{-1}. Only the $v_9(t_1)$ mode has not been measured in the laboratory and is estimated to be at 2942 cm^{-1} from a VPT2-B3LYP calculation [14].

In this work described below, we provide a set of high resolution infrared absorption cross sections of cold neopentane with N_2 as a broadening gas in the 3.3 μm (3000 cm^{-1}) spectral region. These data are aimed at infrared remote sensing of neopentane particularly in Titan's atmosphere.
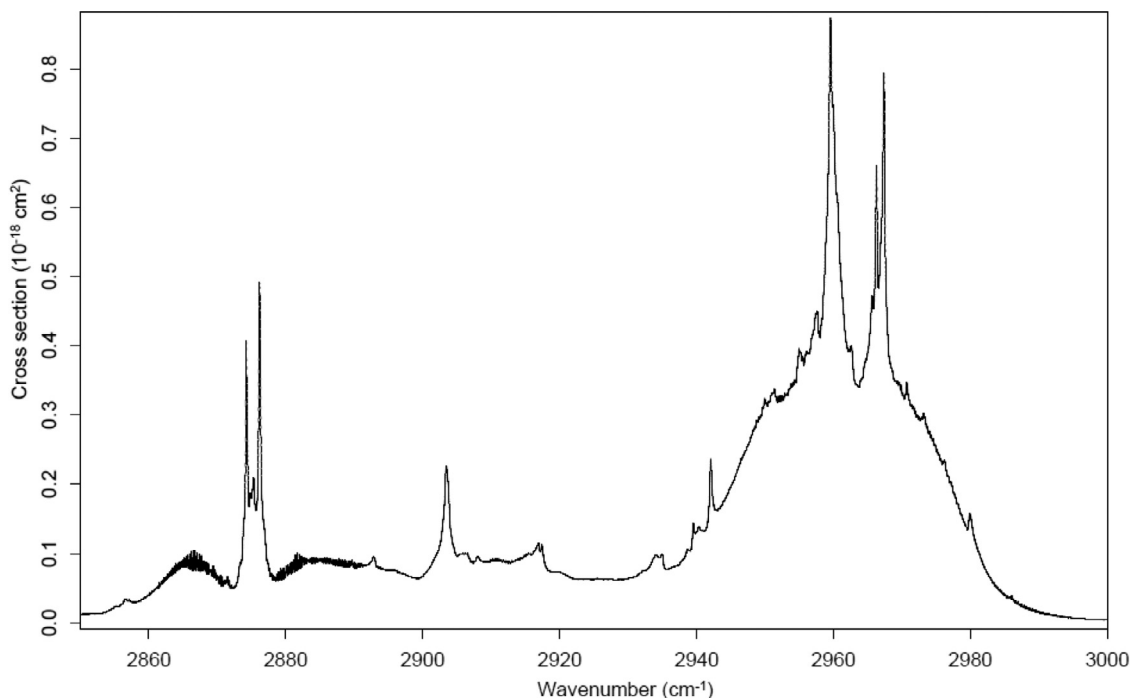
Fig. 1. Overview absorption cross sections of neopentane (32.1 mTorr of neopentane in 100 Torr total pressure of neopentane and N_2) at 202 K.

Table 1
Experimental conditions for each spectrum.

Temp (K)	Neopentane (mTorr)	Total (Torr)	Temp (K)	Neopentane (mTorr)	Total (Torr)
202.15	30.0	0.0300	265.05	44.7	0.0447
202.15	30.3	10.1	265.05	44.9	10
202.15	28.6	30.1	265.05	42.1	30
202.15	32.1	100	265.05	51.6	100.1
Temp (K)	Neopentane (mTorr)	Total (mTorr)	Temp (K)	Neopentane (mTorr)	Total (Torr)
232.15	39.8	0.0398	297.25	46.2	0.0462
232.15	39.8	10	297.25	46.2	10.05
232.15	41.4	30.2	297.25	68.6	30.2
232.15	43.6	100.1	297.25	70.4	100.4

2. Experimental method

High resolution infrared spectra of neopentane, pure and broadened by nitrogen, were recorded at the Canadian Light Source (CLS) Far Infrared Beamline with a Fourier transform spectrometer, similar to work carried out on ethane [15], propane [16] and isobutane [17]. An overview spectrum of neopentane at 202 K broadened by 100 Torr of N_2 is presented in Fig. 1. The samples were held in a 2-m base-path White-type cell set to a nominal path length of 8 m at 4 temperatures and 3 N_2 broadening gas pressures (plus the pure sample), at 202 K, 232 K, 265 K and 297 K, and 10, 30 and 100 Torr (total pressures). The samples were prepared by adding a small amount of neopentane (29–68 mTorr) to the cell, then adding the broadening gas and recording the total pressure. The pressure-path length was chosen to give a strong absorption (typically 90%) for the feature at 2960 cm^{-1} (Fig. 1). 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). As discussed below, for these low pressures the 1 Torr Baratron readings were too low by a factor of 3.0; thus, a path of 24 m was used in the calculations to compensate. 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

was uniformly cooled but uncooled windows were attached using bellows.

The spectrometer was a Bruker IFS 125 HR Fourier transform spectrometer fitted with a CaF$_2$ beamsplitter, internal globar source, a 2500–3400 cm^{-1} band pass filter and a liquid N_2-cooled InSb detector. The spectral resolution varied depending on the total pressure: 0.003 cm^{-1} (pure sample), 0.003 cm^{-1} (10 Torr), 0.01 cm^{-1} (30 Torr), and 0.04 cm^{-1} (100 Torr). The background spectra were recorded at 0.05 cm^{-1} resolution and Fourier interpolated to match the higher resolution spectra. The parameters used for recording spectra are shown in Table 1. The cell was evacuated and refilled for each spectrum. For each spectrum a minimum of 400 interferograms (200 forward and 200 backward) were co-added and boxcar apodization was used with a zero-filling factor of 8.

The CLS transmission spectra are converted to cross sections using [18]:

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

in which $\tau(\nu, T)$ 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 optical path length (m), and k_B is the Boltzmann constant (1.380649×10^{-23} J/K). The path length used to calculate the
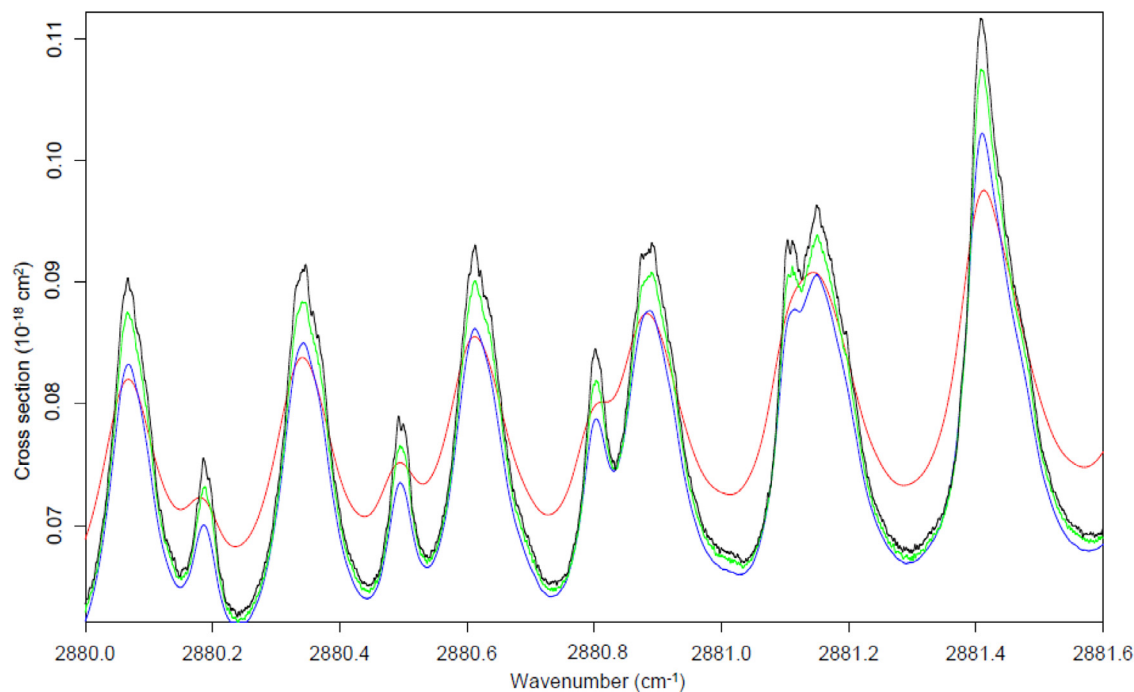
Fig. 2. Effect of N_2 broadening gas on rotational features in neopentane cross sections at 202 K. Black trace is for pure neopentane, green is 10 Torr, blue is 30 Torr and red is 100 Torr total pressure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cross sections was 24.63 m (including the total distance of 63 cm from the cell windows to the White cell mirrors).

The wavenumber and pressure-path length calibration was checked by comparison with another room temperature neopentane spectrum (10.1 Torr neopentane, 19.99 cm path length, 22.5 °C) recorded at Old Dominion University (ODU) covering a wider spectral range, and that included residual ν_3 band CO_2 lines. The spectral resolution was 0.01 cm^{-1} and a 10 Torr Baratron gage with an accuracy of about 1% was used to measure the pressure. A wavenumber calibration factor of 0.99999893(54) was applied to all of the CLS spectra. After calibration, the wavenumber scale is accurate to better than 0.001 cm^{-1}.

The ODU spectrum proved that there was an error in the pressure-path length of a factor of 3.0 because the CLS pressure measurements were a factor of 3.0 too low. The path length was changed from 8 m to 24 m in the analysis to compensate for the error in the pressures reported in Table 1.

3. Results and discussion

The 16 infrared absorption cross section files for neopentane are available as Supplementary Information and from the MoLLIST (Molecular Line Lists, Intensities and SpecTra) [19] web site http://bernath.uwaterloo.ca/molecularlists.php. The data volume is 96 MB in total (zipped) and each cross section value (in cm^2/molecule) needs to be multiplied by 10^{-18}.

The effect of pressure on the cross sections is small because the sharpest features are rotational "lines" (Fig. 2) associated with the $\nu_{14}(t_2)$ band at 2876 cm^{-1} that have a broadened width of about 0.04 to 0.07 cm^{-1}. The Doppler width of an isolated line at 202 K is about 0.0035 cm^{-1} so these asymmetric features have unresolved "cluster" splittings.

The ν_{14} band has typical P-Q-R rotational structure of an allowed t_2 mode of a molecule with T_d symmetry. However, the central Q-branch is peculiar because it is doubled and also has a weaker central feature (Fig. 3). The line spacing in the R-branch is

about 0.29 cm^{-1} and 0.27 cm^{-1} in the P-branch, which gives a ζ value of about 0.047 using the ground state B value of 0.1469 cm^{-1} [14]; in a spherical top the line spacing is about $2B(1-\zeta)$. The fits of the R or the P branch lines alone were not satisfactory, presumably because of perturbations.

The effect of lowering the temperature is illustrated in Fig. 4 for the strong $\nu_{13}(t_2)$ band. The effect of temperature is to sharpen up and intensify the spectral features as population is drained from higher energy levels into lower energy levels. Almost all of the features increase in intensity as the temperature decreases and are therefore not due to vibrational hot bands. Neopentane has two low frequency torsional modes ν_4 (a$_2$) at 218 cm^{-1} and ν_{12} (t$_1$) at 280 cm^{-1} [11], but there is little evidence of torsional hot bands in the 3 μm region, except perhaps near 2875 cm^{-1} (Fig. 3). The two small features at the center of the band are nearly constant in intensity, while the two strong Q branches on either side strengthen considerably as the temperature drops.

The simple normal mode model, which predicts two strong allowed t_2 bands, $\nu_{13}(t_2)$, 2959.6 cm^{-1} and $\nu_{14}(t_2)$, 2876.2 cm^{-1}, in the C−H stretching region [14], is clearly not satisfactory (Fig. 1). As is common for hydrocarbons [e.g., 20,21], the overtone and combination bands of the scissors modes have Fermi resonance interactions with the C−H stretching modes. A local mode model that includes these interactions (E. Sibert, personal communication about work in progress) is in much better agreement with experimental observations.

As usual, the absolute accuracy of the neopentane cross sections is difficult to determine; the various sources of error are discussed in detail by Harrison et al. [18]. All of the cross sections were integrated between 2850 cm^{-1} and 2992 cm^{-1} (Fig. 1) and this area varies by about 2%, which provides an estimate of the measurement precision. The independent measurements of cross sections for room temperature samples at Old Dominion University (not shown) and CLS differ by about 5%, which is a reasonable estimate of the absolute accuracy of the CLS cross sections.
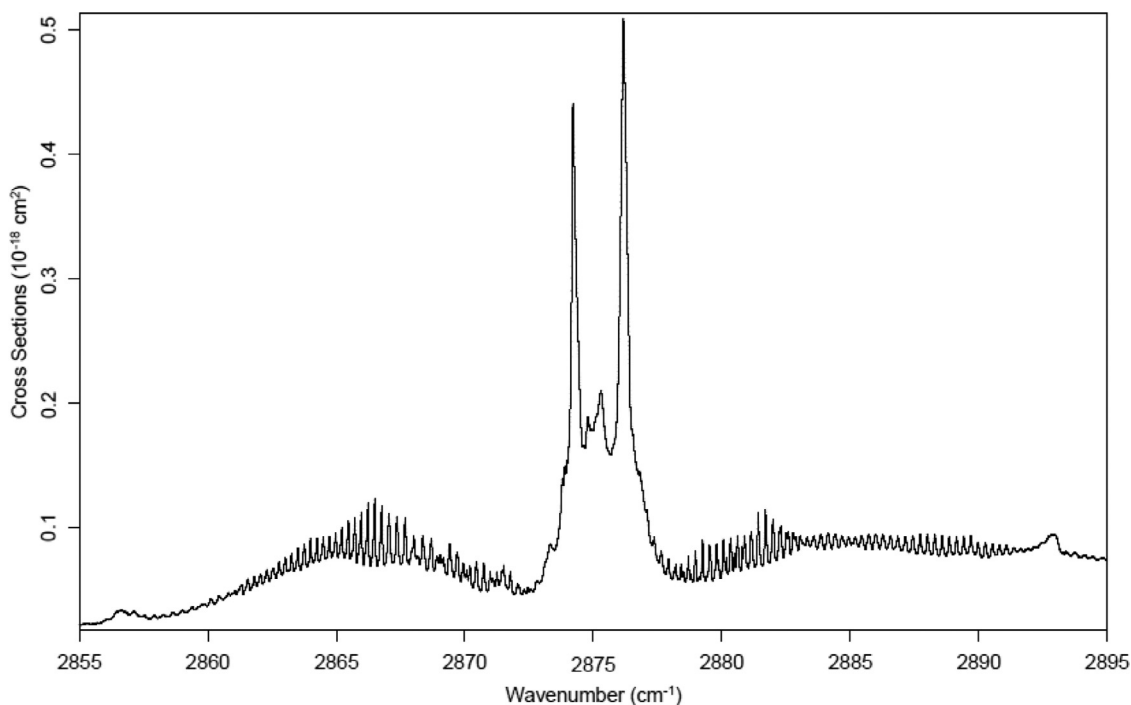
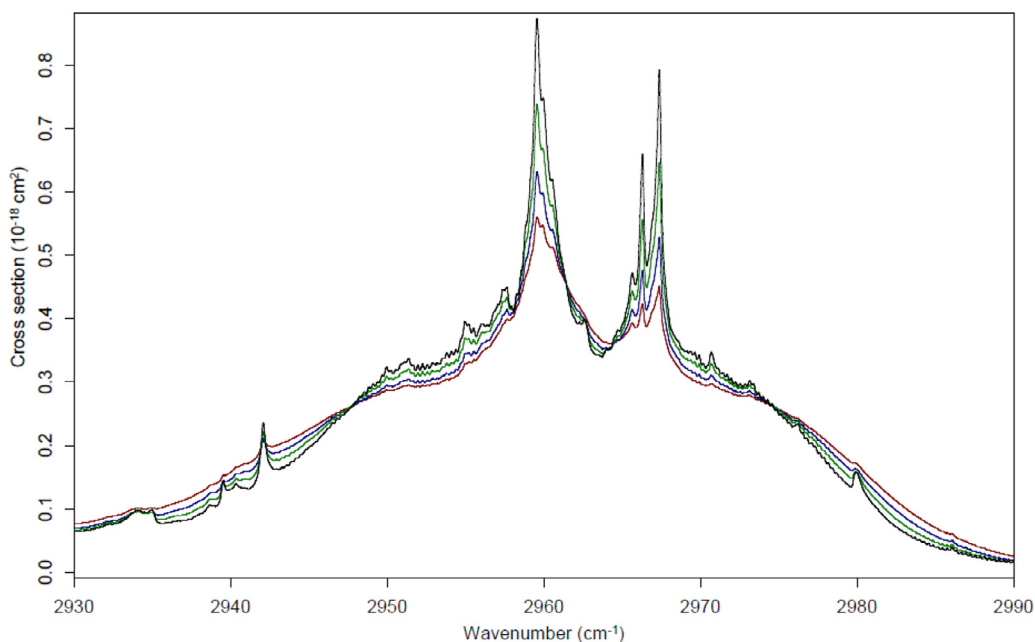**Fig. 3.** Overview of ν_{14} (t_2) band of pure neopentane at 202 K.

Fig. 4.. A series of neopentane cross sections at different temperatures for 100 Torr total pressure of N_2 and neopentane for ν_{13} (t_2) band. The red trace is 297 K, blue trace is at 265 K, green trace is 232 K and black trace is at 202 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion and future plans

High resolution absorption cross sections of neopentane have been obtained in the 2550-3350 cm^{-1} region in conditions relevant to the atmosphere of Titan. Lower temperatures (70–195 K for Titan's stratosphere [3]) are desirable but are currently unavailable due to the minimum temperature obtained with the chiller. Lower temperatures are planned by cooling the White cell with cold nitrogen vapor. Further work on the interpretation of the spectra in the C–H stretching region is underway and we plan to record additional spectra [14] to lower wavenumbers to obtain cross sections for the interpretation of CIRS spectra from the Cassini mission.

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 Bernath: Methodology, Supervision, Writing - original draft. **Randika Dodangodage:** Formal analysis. **Michael Dulick:** Validation, Investigation. **Jianbao Zhao:** Investigation. **Brant Billinghurst:** Investigation, Supervision.

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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.2020.107034.

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