



# Absorption cross sections of *n*-butane, *n*-pentane, cyclopentane and cyclohexane

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## ABSTRACT

The infrared absorption cross sections of pure *n*-butane, *n*-pentane, cyclopentane and cyclohexane have been measured in the 3.3  $\mu\text{m}$  region (and 6.8  $\mu\text{m}$  region for cyclopentane) by high resolution Fourier transform spectroscopy. The samples had temperatures of 294 K and 230 K for *n*-butane, 294 K and 218 K for *n*-pentane, 296 K and 235 K for cyclopentane, and 294 K and 222 K for cyclohexane. These spectra are important for molecular identification in extraterrestrial environments such as Saturn's moon Titan, giant planets and exoplanets. All spectra are provided as data point files.

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## 1.1. Introduction

The oxidation of non-methane hydrocarbons plays an important role in the production of tropospheric ozone and aerosols, with these hydrocarbons largely coming from fugitive emissions of fossil fuel production [1]. Simple hydrocarbons have also been observed in the atmospheres of the giant planets [2] and Saturn's moon Titan [3] which has an organic-rich atmosphere and is considered to be like that of pre-biotic Earth [4,5]. Organic molecules are produced on Titan by dissociation and ionization of nitrogen and methane in the upper atmosphere. Reactions between two methyl radicals produce ethane and other photochemical processes form larger hydrocarbons. Organic photochemistry also produces an orange aerosol haze on Titan [3,6]. The atmospheres of giant planets are likely reservoirs of complex hydrocarbon species.

Numerous non-methane hydrocarbons ( $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{C}_2\text{H}$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_2$  and  $\text{C}_6\text{H}_6$ ) [3] have been detected in the stratosphere of Titan mainly using the CIRS (Composite Infrared Spectrometer) Fourier transform instrument on the Cassini spacecraft that was in orbit around Saturn. The most recent hydrocarbons detected on Titan are allene (propadiene,  $\text{CH}_2\text{CCH}_2$ ) from TEXES (Texas Echelon-cross-Echelle Spectrograph) on the NASA IR Telescope Facility by Lombardo *et al.* [7] and cyclopropenylidene ( $\text{c-}$

$\text{C}_3\text{H}_2$ ) found with ALMA (Atacama Large Millimeter/submillimeter Array) by Nixon *et al.* [8]. Titan's stratosphere has a temperature of about 80 to 200 K at pressure of about 10 to 0.01 Torr of mainly nitrogen [3]. Hydrocarbon fractional abundances range from 0.2 ppb for benzene ( $\text{C}_6\text{H}_6$ ) to a few percent for methane ( $\text{CH}_4$ ). None of the hydrocarbons studied in this paper have been detected on Titan yet, although they are all potentially present.

The detection of hydrocarbon species in the Earth's atmosphere and the atmospheres of planets, moons and exoplanets relies on reliable spectroscopic line lists and cross sections. Most existing spectroscopic cross sections for hydrocarbon species were collected at relatively low resolution and are often broadened by  $\text{N}_2$ . Higher resolution spectroscopic cross sections that can resolve sharper spectroscopic features are necessary in order to identify and quantify these species under conditions where pressure broadening is small. Our present work includes absorption cross sections in the  $3000\text{ cm}^{-1}$  (CH stretching) region for *n*-butane, *n*-pentane, cyclopentane and cyclohexane along with  $1460\text{ cm}^{-1}$  (6.8  $\mu\text{m}$ ) cross sections for cyclopentane.

## 1.2. *n*-butane

Butane has two isomers: isobutane and *n*-butane. Hydrocarbons like ethane and propene have been observed in Titan [9] and giant planets [10,11] and the photochemical models of Titan [12] and Saturn [13] predict butane to be as abundant as other small hydrocarbons. Curtis *et al.* [14] suggest the possibility that some of the

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haze particles in Titan's atmosphere may be coated with a layer of butane at the tropopause and it may influence cloud formation mechanisms. Navarro-Gonzalez et al. [15] have experimentally studied the corona discharge of a simulated Titan atmosphere and have identified several hydrocarbons including ethane, propane, *n*-butane, *n*-pentane, and cyclopropane. Hewett et al. [16] have estimated upper limits for the abundance of *n*-butane and isobutane on Titan.

Diethyl or *n*-butane ( $C_4H_{10}$ ) has two main conformations: *s*-trans and *gauche* which have  $C_{2h}$  and  $C_2$  symmetry, respectively, with 36 fundamental vibrational frequencies. The *s*-trans and *gauche* conformers have 11 and 21 allowed Raman modes and 10 and 21 infrared active modes, respectively [17]. The lowest energy *s*-trans conformer and the higher energy (by  $234\text{ cm}^{-1}$ ) *gauche* conformations are observed in the infrared spectra of this molecule. In CH stretching region there are 10 vibrational modes.  $C_{2h}$  symmetry includes  $\nu_1$ - $\nu_3$  ( $a_g$ ),  $\nu_{12}$ - $\nu_{13}$  ( $a_u$ ),  $\nu_{20}$ - $\nu_{21}$  ( $b_g$ ), and  $\nu_{27}$ - $\nu_{29}$  ( $b_u$ ), while  $C_2$  symmetry has  $\nu_1$ - $\nu_3$ ,  $\nu_{12}$ , and  $\nu_{13}$  ( $a$ ) and  $\nu_{20}$ ,  $\nu_{21}$ ,  $\nu_{27}$ - $\nu_{29}$  ( $b$ ) modes in the  $3.3\text{ }\mu\text{m}$  region.

Absorption cross sections for isobutane have been studied extensively [16,18,19]. Grosch et al. [20] have measured absorption cross sections of *n*-butane in the CH stretching region at temperatures of 298, 373, and 473 K with nitrogen as a broadening gas. Cross sections of *n*-butane in the mid infrared region ( $7$ – $15\text{ }\mu\text{m}$ ) with nitrogen as a broadening gas at temperatures of 180–298 K were obtained by Sung et al. [21]. Jolly et al. [22] have recorded absorption cross sections of *n*-butane at 150 K and 297 K focusing on the bands centered at  $733\text{ cm}^{-1}$  and  $966\text{ cm}^{-1}$ .

This work provides the cross sections of pure *n*-butane in the  $3000\text{ cm}^{-1}$  region obtained at 296 K and 230.3 K without a broadening gas.

### 1.3. *n*-Pentane

*n*-Pentane ( $C_5H_{12}$ ) is a straight chain alkane that is an example of a volatile organic compound present in Earth's atmosphere, specifically from rapid increase in natural gas production in recent decades. Studies from Swarthout et al. [23] have looked at the environmental impacts of these volatile organic compounds, including *n*-pentane, at the Boulder Atmospheric Observatory.

*n*-Pentane has a number of *trans* and *gauche* conformations that are observed in the infrared spectra with the *trans*,  $C_{2v}$  conformation being the lowest in energy. It contains 45 fundamental vibrational frequencies, 35 being infrared active modes, and all of them being Raman active. This  $C_{2v}$  conformation includes modes of  $a_1$  ( $\nu_1 - \nu_{13}$ ),  $a_2$  ( $\nu_{14} - \nu_{23}$ ),  $b_1$  ( $\nu_{24} - \nu_{32}$ ), and  $b_2$  ( $\nu_{33} - \nu_{45}$ ) symmetry. Vibrational spectra of *n*-pentane have been studied by LaPlante et al. [24], and Raman spectra have also been studied by Kuznetsov et al. [25].

This work provides cross sections of pure *n*-pentane in the  $3000\text{ cm}^{-1}$  region obtained at 218 K and 292 K.

### 1.4. Cyclopentane

Cyclopentane ( $C_5H_{10}$ ) is a fascinating molecule due to its unusual structure and vibrations. It has 10 equivalent bent conformations of  $C_5$  symmetry and another 10 equivalent twist conformations of  $C_2$  symmetry. These 20 conformations have such small energy barriers between them that they can readily interconvert in a process known as pseudorotation [26,27]. Additionally there is also a  $D_{5h}$  planar conformation that lies approximately  $2100\text{ cm}^{-1}$  above the bent and twist conformations [27]. It is difficult to conduct a traditional analysis of the 39 vibrational modes for cyclopentane as has been previously discussed for *n*-butane and *n*-pentane in Sections 1.2 and 1.3 above because of the effects of pseudorotation. We refer the reader to the work of Ocola et al. for

a more traditional normal mode analysis [26]. We also would like to note that a more complete vibrational analysis that includes the coupling of the normal modes with the pseudorotation has just appeared [28].

This present work includes high resolution cross sections of pure cyclopentane in the CH stretching region at  $3000\text{ cm}^{-1}$  and for the  $CH_2$  scissors bend at  $1460\text{ cm}^{-1}$ .

### 1.5. Cyclohexane

Cyclohexane ( $C_6H_{12}$ ) is a ring of 6 carbon atoms with multiple conformations. Of these, the "chair" is the minimum energy conformation with its 6 axial and 6 equatorial hydrogen atoms. Local minima occur in the "twist boat" conformation, about  $5.5\text{ kcal/mol}$  higher than the "chair conformation." [29,30] Cyclohexane is almost completely in the chair conformation at room temperature, where less than 0.1% of the molecules are in the twist-boat conformation. Volatile organic compounds including cyclohexane are found in the Earth's atmosphere, produced by biogenic and anthropogenic means [31]. Hydrocarbons such as cyclohexane may also be found in the atmospheres of gas giant planets such as Saturn as well as its moon Titan where it is formed by organic photochemistry and ion chemistry [13,32].

The chair form of cyclohexane has  $D_{3d}$  symmetry, and the twist boat form has  $D_2$  symmetry. There are 48 normal modes and 32 fundamental vibration frequencies, listed here grouped by symmetry and using numbering of the vibrational modes from the order of irreducible representations in Herzberg's character tables: [33]  $a_{1g}$  ( $\nu_1 - \nu_6$ ),  $a_{1u}$  ( $\nu_7 - \nu_9$ ),  $a_{2g}$  ( $\nu_{10} - \nu_{11}$ ),  $a_{2u}$  ( $\nu_{12} - \nu_{16}$ ),  $e_g$  ( $\nu_{17} - \nu_{24}$ ) and  $e_u$  ( $\nu_{25} - \nu_{32}$ ). Only the 3  $a_{1u}$  and 8  $e_u$  modes are infrared active [34]. The  $a_{1g}$  and  $e_g$  modes are Raman active. There have been many previous efforts to make infrared and Raman measurements of cyclohexane in its different phases with accompanying calculations to assist with vibrational assignments [35–41]. This work builds on the previous investigation into the high-resolution infrared spectra of cyclohexane published by Bernath and Sibert [42].

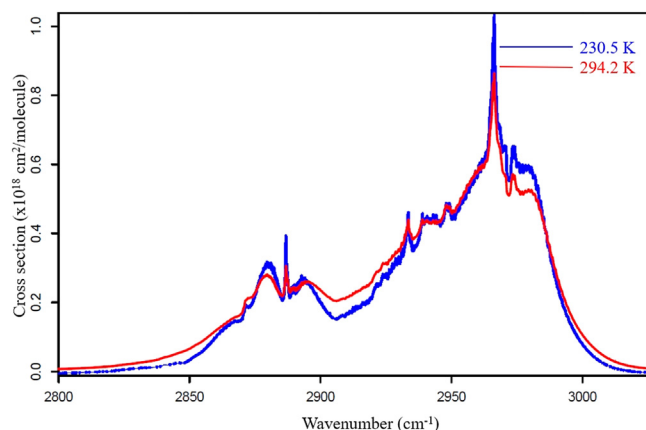
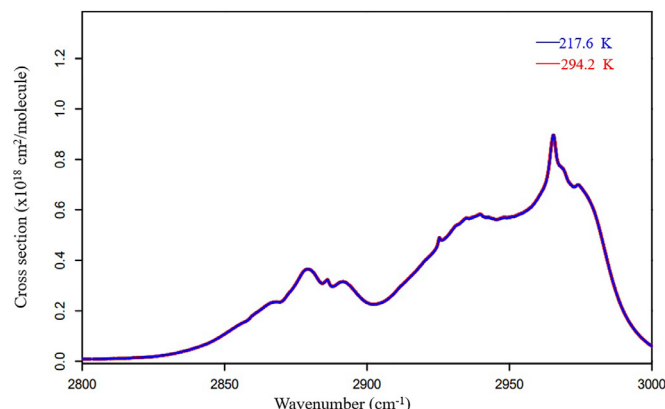
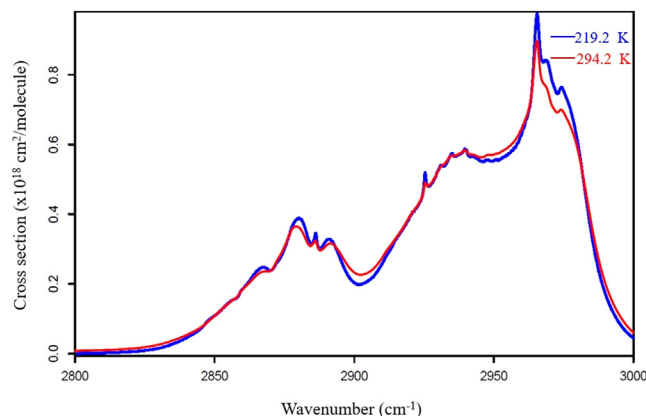
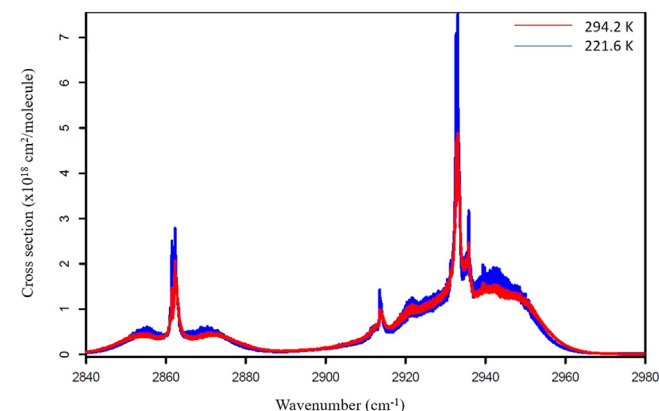
## 2.0. Method and results

All spectra were recorded with a Bruker IFS 120/125HR Fourier transform spectrometer at a resolution of  $0.04\text{ cm}^{-1}$ . An internal glowbar source, KBr beamsplitter and a liquid  $N_2$  cooled InSb detector were used in the setup (liquid  $N_2$  cooled HgCdTe detector for the  $1460\text{ cm}^{-1}$  band of cyclopentane). Samples of each molecular gas were prepared in a single pass  $20\text{ cm}$  cell fitted with wedged  $CaF_2$  windows. For the low temperature spectra, the cell was cooled with a liquid ethanol circulator. Table 1 displays the number of sample and background scans averaged for each molecule at the given temperature and pressure.

Figs. 1–4 show the CH stretch cross sections of pure *n*-butane, *n*-pentane, cyclopentane and cyclohexane, respectively, between  $2800$  and  $3050\text{ cm}^{-1}$ , collected at two different temperatures as indicated in Table 1. Fig. 5 shows the cross section of pure cyclopentane  $CH_2$  scissors bending mode between  $1440$  and  $1560\text{ cm}^{-1}$  at  $235.2\text{ K}$  and  $294.2\text{ K}$ . In producing Fig. 5, strong lines associated with water were removed using the straight-line generation function of the OPUS program. Fig. 6 represents a zoomed in view of *n*-butane  $CH_2$  symmetric stretch centered around  $2886\text{ cm}^{-1}$  at  $230.5\text{ K}$  where P, Q and R rotational structure is clearly seen. Similarly, Fig. 7 shows sharp P, Q and R rotational structure for cyclohexane's  $\nu_{13}$   $a_{2u}$  mode at  $2861.51\text{ cm}^{-1}$  and the  $\nu_{26}$   $e_u$  mode at  $2862.28\text{ cm}^{-1}$  measured at  $221.6\text{ K}$ . [42] All spectra are included in the supplemental data section as data point files.

**Table 1**  
Molecule specific experimental parameters.

Molecule	Number sample and background scans	Pressure (Torr)	Temperature (K)	Frequency Correction Factor
<i>n</i> -butane	512	2.047	294.2	0.999995689(16)
	512	2.560	230.5	0.999995727(14)
<i>n</i> -pentane	640	0.385	294.2	0.99999760(38)
	640	2.191	217.6	0.999998534(23)
Cyclopentane (3000 cm <sup>-1</sup> )	640	0.431	296.2	0.999995727(14)
	640	0.198	235.2	0.999995684(24)
Cyclopentane (1460 cm <sup>-1</sup> )	640	27.89	294.2	0.999994088(87)
	640	18.15	235.8	0.999994041(23)
Cyclohexane	640	1.06	294.2	0.999998539(25)
	640	0.87	221.6	0.999996739(21)

**Fig. 1.** Cross sections of pure *n*-butane in the CH stretching region. Blue is at 230.5 K and red is at 294.2 K.**Fig. 3.** Cross-section of pure cyclopentane CH<sub>2</sub> symmetric stretch ( $\nu_9$ ) at 2879 cm<sup>-1</sup> and CH<sub>2</sub> antisymmetric stretch ( $\nu_{15}$ ) at 2966 cm<sup>-1</sup>. Blue trace was collected at 235.2 K and red trace collected at 296.2 K.**Fig. 2.** Cross sections of pure *n*-pentane in the CH stretching region. Blue is at 217.6 K and red is at 294.2 K.**Fig. 4.** Cross-section of pure cyclohexane C-H stretching region blue plot is 221.6 K; the red plot is at 294.2 K.

### 3.0. Discussion

#### 3.1. Calibration

All spectra were wavenumber calibrated using CO<sub>2</sub> lines between 2323 and 2348 cm<sup>-1</sup> from the HITRAN database [43]. The frequency correction factors are included in Table 1 along with their standard deviations. These correction factors do not have associated intercepts and resulted in an average shift in frequency in the 3.3  $\mu$ m region of less than 0.01 cm<sup>-1</sup> and a shift of 0.005 cm<sup>-1</sup> in the 6.8  $\mu$ m region for cyclopentane. As we had some difficulty obtaining accurate pressure measurements, all cross sections reported in this work had the area under their respective cross section calibrated to match the area under similar, lower resolution,

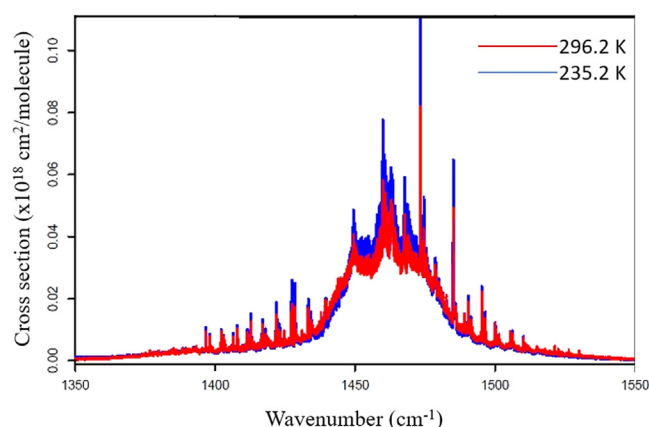
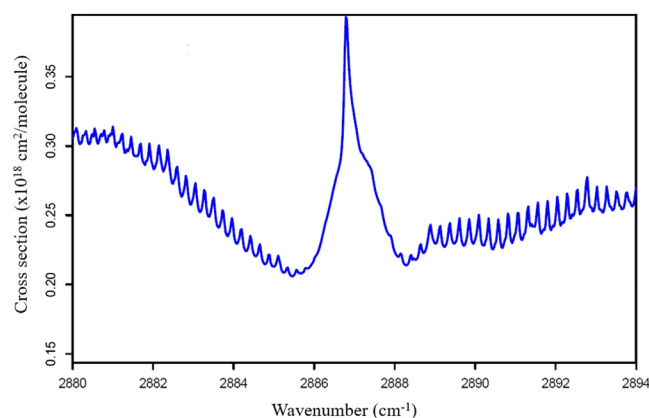
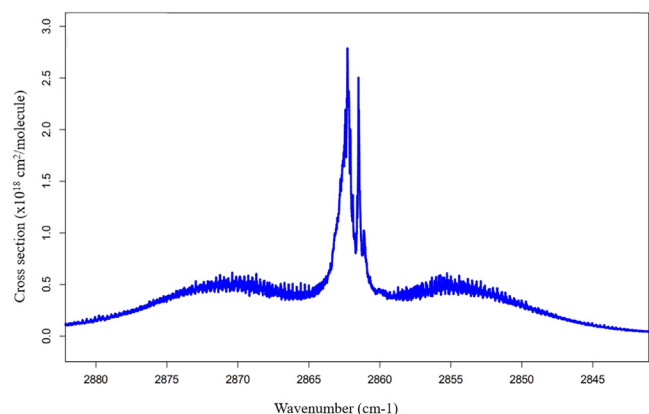
spectra obtained by Pacific Northwest National Laboratory (PNNL). [44] Table 2 shows the integrated areas of the PNNL data (at 296 K) along with the integration bounds used for each case. This correction assumes that the area under each cross section curve is independent of temperature as we have done in the past [43]. In addition, Grosch et al. [20] found that integrated cross sections of gaseous hydrocarbons do not change significantly with temperature. It is also worth noting that Grosch et al.'s cross section for *n*-butane also matched that of PNNL very closely [20].

The issue of reporting error in our cross sections is difficult and somewhat subjective. For the wavenumber calibration, the shift is on the order of 0.005–0.01 cm<sup>-1</sup> as stated above, but after calibration the accuracy is 0.005 cm<sup>-1</sup> or better based on the standard deviation of the calibration factor. The error in our cross sections

**Table 2**

Limits of integration along with the area under the curve for cross sections obtained from PNNL. The PNNL data used was collected at 296 K.

Molecule	Integration limits (cm <sup>-1</sup> )	Area (x 10 <sup>-18</sup> cm <sup>2</sup> /molecule)
<i>n</i> -butane	2776.298 - 3042.959	49.900
<i>n</i> -pentane	2778.116 - 3050.899	60.318
Cyclopentane (2966 cm <sup>-1</sup> )	2768.910 - 3062.819	57.843
Cyclopentane (1460 cm <sup>-1</sup> )	1350.561 - 1610.255	1.897
Cyclohexane	2833.759 - 2977.299	75.434

**Fig. 5.** Cross-section of pure cyclopentane CH<sub>2</sub> scissors bend ( $\nu_6$ ) centered around 1460 cm<sup>-1</sup>. Blue trace was collected at 235.2 K and red trace collected at 294.2 K.**Fig. 6.** A zoomed in look at the P, Q, and R branches of *n*-butane CH<sub>2</sub> symmetric stretch ( $\nu_2$ ) centered around 2886 cm<sup>-1</sup> at 230.5 K.**Fig. 7.** Illustrates the P, Q, and R branches of cyclohexane centered around 2862 cm<sup>-1</sup>; prominently visible are the  $\nu_{13}$  a<sub>2u</sub> mode at 2861.51 cm<sup>-1</sup> and the  $\nu_{26}$  e<sub>u</sub> mode at 2862.28 cm<sup>-1</sup> at 221.6 K.

comes from several sources including the PNNL data with an estimated error of  $\leq 3\%$ . [44] Our error cannot be lower than this. Based on previous experience [43], we estimate an error of about 5% for our cross sections.

### 3.2. Comments on spectra

Fig. 5 depicts the cross section of cyclopentane's CH<sub>2</sub> scissors bend ( $\nu_6$ ) centered around 1460 cm<sup>-1</sup>. Clearly seen in these spectra are sharp transitions spaced approximately 5 cm<sup>-1</sup> apart associated with the pseudorotation between the low-lying C<sub>s</sub> and C<sub>2</sub> conformations. [26,27] We have recently published an analysis of this observed structure that couples the normal modes to this pseudorotation [28].

Fig. 6 is an expanded view of the *n*-butane CH stretch centered at 2886 where clear rotational structure is observed including P, Q and R branches. Similarly, Fig. 7 depicts a zoomed in look at cyclohexane's  $\nu_{13}$  a<sub>2u</sub> mode centered at 2861.51 cm<sup>-1</sup> and its  $\nu_{26}$  e<sub>u</sub> mode centered at 2862.28 cm<sup>-1</sup>. Again, P, Q and R branches are clearly observed. Both of these spectra illustrate the importance of high resolution spectral cross sections that include sharp spectral features to molecular identification and quantitative uses.

### 4.0. Conclusion

Included in this work are high resolution spectra of pure *n*-butane, *n*-pentane, cyclopentane and cyclohexane collected at two different temperatures in the 3000 cm<sup>-1</sup> CH stretching region for each molecule. Additionally, CH scissors bending region centered at 1460 cm<sup>-1</sup> for cyclopentane is also reported. These spectra represent significant improvements in resolution to existing spectra. This improvement in resolution makes these spectra useful for molecular identification and quantitative studies in low pressure environments such as Saturn's moon Titan and other planetary systems. Spectra of lower temperature samples are desirable to more closely match conditions on Titan and the outer planets, but our measurements serve as a useful starting point. All of these spectra are provided as data point files in the supplementary section of the paper.

### 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

**Jason J. Sorensen:** Investigation, Writing – original draft, Supervision, Formal analysis. **Peter F. Bernath:** Conceptualization, Resources, Funding acquisition, Writing – review & editing. **Ryan M. Johnson:** Investigation, Formal analysis, Writing – original draft. **Randika Dodangodage:** Investigation, Formal analysis, Writing – original draft. **W. Doug Cameron:** Investigation, Formal analysis, Writing – original draft. **Keith LaBelle:** Investigation, Formal analysis, Writing – original draft.



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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.2022.108284](https://doi.org/10.1016/j.jqsrt.2022.108284).

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