



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Infrared absorption cross sections of isobutane with hydrogen and nitrogen as broadening gases

D.M. Hewett^{a,*}, P.F. Bernath^a, B.B. Billingham^b^a Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA^b Canadian Light Source Far-Infrared Beamline, 44 Innovation Blvd, Saskatoon, SK S7N 2V3, Canada

ARTICLE INFO

Article history:

Received 9 October 2018

Revised 4 February 2019

Accepted 4 February 2019

Available online 8 February 2019

Keywords:

Infrared absorption

Cross sections

Isobutane

Planetary atmospheres

Synchrotron

H₂ broadeningN₂ Broadening

ABSTRACT

Infrared absorption spectra of isobutane (C₄H₁₀) were recorded in the CH stretching spectral region (2500–3280 cm⁻¹) by high resolution Fourier transform spectroscopy (Bruker IFS 125 HR). These spectra were taken at temperatures and pressures appropriate for the gas giant planets Jupiter and Saturn, as well as for Saturn's moon Titan. Absorption cross sections were obtained for pure samples and with broadening gases relevant in those atmospheres, hydrogen and nitrogen, to further simulate the astronomical environments. Corrections to the cross sections were made using data from the Pacific Northwest National Laboratory (PNNL) infrared database.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

The atmospheres of the Gas Giant planets, Jupiter and Saturn, as well as the atmospheres of their moons, are of great interest. The composition of Saturn's moon Titan is believed to be similar to that of pre-biotic Earth [1]. Properly identifying the molecules and systems present in these atmospheres will allow scientists to model the climate and environment predicted for pre-biotic Earth, and direct observation of a similar system will allow for better modeling and more insight into the origins of life on Earth [2]. There is even the possibility of life on Titan [3].

The first step to fully understanding these systems is having accurate chemical compositions: knowing which chemicals are present and in what concentrations is essential for reliable modeling. Unfortunately full knowledge of the chemical compositions of these atmospheres has yet to be achieved. A major hurdle is the difficulty in obtaining the complex line-by-line spectroscopic data commonly used to determine molecular abundances. A way around this problem is to utilize absorption cross sections instead of molecular line parameters. Absorption cross sections depend only on the environment of the target molecule, such as temperature, pressure and composition. Absorption cross sections can also be converted to absorption coefficients and then to k-distribution

parameters for fast radiative transfer calculations [4]. The composition and physical properties of planetary atmospheres are encoded in their spectra, but suitable laboratory spectra are required for their interpretation. This work continues to build the absorption cross section catalog for molecules relevant for these atmospheres, specifically small hydrocarbons.

Recording infrared absorption cross sections at relevant temperatures and pressures, as well as with appropriate broadening gases (hydrogen, nitrogen, and helium) to simulate the molecular environment is important to provide accurate data for analysis of astronomical spectra. This study focuses on isobutane, a small hydrocarbon predicted to be present in the atmospheres of Titan and Saturn. Photochemical models of Titan [5,6] and Saturn [7] predict that C₄H₁₀ is as abundant as other small hydrocarbons such as propane (C₃H₈), which has already been detected [8,9]. These models do not distinguish between the two C₄H₁₀ structural isomers, *n*-butane and isobutane. However, in the recent modeling paper by Vuitton et al. [10], the mechanism presented favors the production of isobutane. Our isobutane data were recorded at low temperatures, and with N₂ and H₂ broadening gases, in an effort to replicate the atmospheres of the target systems.

Titan's atmosphere has a surface temperature of about 95 K at pressure of 1.4 atm [11] made of 95% N₂. Saturn's atmosphere has a temperature of about 140 K at an altitude where the pressure is 1 atm and is 96% H₂. Jupiter is similar to Saturn with a temperature of about 160 K at a pressure of 1 atm and 86% H₂ [12].

* Corresponding author.

E-mail address: dhewett@odu.edu (D.M. Hewett).

Table 1

Experimentally measured pressures and temperatures for each spectrum, with isobutane pressure (IB), broadening gas pressure (H_2/N_2), and temperature (K), along with the correction factors for each spectrum (CF).

203 K											
H_2				N_2				Pure			
IB P (Torr)	P (Torr)	T (K)	CF	IB P (Torr)	N_2 P (Torr)	T(K)	CF	IB P (Torr)	T (K)	CF	
0.02	10	202.55	1.342	0.021	10.3	202.75	1.394	0.017	202.45	1.369	
0.027	30.1	202.65	1.406	0.031	30.1	202.65	1.419				
0.029	100.1	202.75	1.509	0.028	100	202.75	1.377				
233 K											
0.035	10	232.55	1.405	0.034	10.4	232.65	1.381	0.03	232.65	1.369	
0.039	30.3	232.65	1.382	0.04	29.9	232.65	1.423				
0.04	100.5	232.65	1.381	0.044	100.4	232.65	1.4				
264 K											
0.04	10	263.45	1.414	0.044	10.1	263.45	1.406	0.039	263.65	1.264	
0.042	30.3	263.45	1.439	0.042	30.1	263.45	1.432				
0.05	100.3	263.45	1.43	0.057	100.6	263.45	1.391				
295 K											
0.045	10.3	294.65	1.47	0.042	10.1	294.55	1.4	0.041	294.55	1.41	
0.055	30.3	294.55	1.399	0.054	30	294.55	1.377				
0.063	100.1	294.35	1.406	0.068	100.1	294.35	1.491				

Hence, the temperature (about 200–300K) and pressure range of our experiment (less than 1 atm for the stratosphere) and the use of N_2 and H_2 broadeners. On Titan hydrocarbons are typically detected [13] in the stratosphere and lower mesosphere (100–500 km altitude, 10–0.001 mbar pressure); Saturn and Jupiter are similar. Sample temperatures below 200 K are desirable, but we are limited by the chiller used to cool the cell. Spectra of lower temperature samples are planned with N_2 vapor cooled by liquid N_2 .

Spectroscopic studies of isobutane began in the 1950s [14,15], with Raman spectra of liquid isobutane and infrared spectra of gaseous samples. Lide [16] proved that isobutane has C_{3v} symmetry by microwave spectroscopy of the monodeuterated compound. Having 14 atoms, isobutane has 36 fundamental modes ($3N-6$) and 24 fundamental vibrational frequencies: 8 a_1 , 4 a_2 and 12 e symmetry modes (the a_2 modes are dipole forbidden). In 1969 Weiss and Leroi [17] took infrared spectra of gaseous isobutane in the 200–800 cm^{-1} region under high pressure conditions and determined torsional vibrational frequencies of 225 cm^{-1} (a_2) and 280 cm^{-1} (e). Overtone spectra of cryogenic isobutane were recorded in 1994 by Manzanares et al. [18], as well as gas phase spectra at room temperature, from the CH stretching region through 12,000 cm^{-1} . Manzanares et al. also carried out Hartree-Fock calculations and used a C–H local mode model to interpret their observations. Theoretical calculations of the infrared spectrum of matrix-isolated isobutane were made in 1984 [19], and more recent calculations are available from Mirkin and Krimm [20]. Hilderbrandt and Wieser [21] determined the molecular structure by combining electron diffraction and microwave data; more extensive microwave and submillimeter wave spectra were recorded by Priem et al. [22].

2. Experimental

High resolution infrared spectra of isobutane, pure and broadened by hydrogen or nitrogen, were recorded at the Canadian Light Source (CLS) Far Infrared Beamline, similar to work on propane [23,24]. Isobutane (99.5%), nitrogen (99.998%) and hydrogen (99.999%) were purchased from Praxair (Canada) and used without further purification. The samples were held in a 2-m White-type multipass cell set to a path length of 8 m at 4 temperatures and 4 broadening gas pressures (H_2 or N_2), at 203, 233, 266 and 295 K, and 0, 10, 30 and 100 Torr (total pressures). The samples were prepared by adding a small amount of isobutane

to the cell, then adding the broadening gas and recording the total pressure. The sample absorption was always less than 90% to prevent saturation and the resolution (see below) was chosen to fully resolve the sharp features. The pressures were measured with two Baratron pressure gauges (627B up to 10 Torr and 626B up to 1000 Torr). The cell was cooled with a NESLAB ULT-80DD 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 spectrometer was a Bruker IFS 125 HR Fourier transform spectrometer fitted with a CaF_2 beamsplitter, internal global source, a 2500–3280 cm^{-1} bandpass filter and a liquid N_2 -cooled InSb detector. The spectral resolution (Bruker definition of 0.9/optical path difference) was varied depending on the total pressure: 0.003 cm^{-1} (pure sample), 0.005 cm^{-1} (10 Torr), 0.01 cm^{-1} (30 Torr), and 0.04 cm^{-1} (100 Torr), and the background empty cell spectra were all recorded at 0.04 cm^{-1} resolution. The background spectra recorded at 0.04 cm^{-1} were Fourier interpolated to match the higher resolution spectra. The full set of parameters used for recording spectra is shown in Table 1. For each spectrum a minimum of 400 interferograms (200 forward and 200 backward) were co-added, boxcar apodization was used and a zero-filling factor of 8 was applied.

2.1. Calibration

Due to potential inaccuracies of the pressure gauges, a calibration is required to obtain accurate absorption cross sections. The Pacific Northwest National Laboratory (PNNL) database [25] has over four hundred vapor-phase infrared spectra which can be used to calibrate our data. The PNNL spectra are reported at 3 sample temperatures (278, 298 and 323 K) with 1 atm of N_2 broadening gas. As discussed in more detail by Harrison et al. [26], the integrated area of the absorption cross sections of isolated bands are independent of temperature and can be used for calibration. For isobutane the integrated areas from 2691.63 to 3085.26 cm^{-1} are 0.05286, 0.052853, and 0.053146 for 278, 298 and 323 K, respectively, for an average of 0.052953. The PNNL y-axis values are in units of ppm m, and conversion to the standard units of $cm^2/molecule$ requires multiplication by the constant 9.28697×10^{-16} .

The integrated area from the PNNL spectra is compared to the integrated signal from the PNNL spectra, and the CLS spectra are

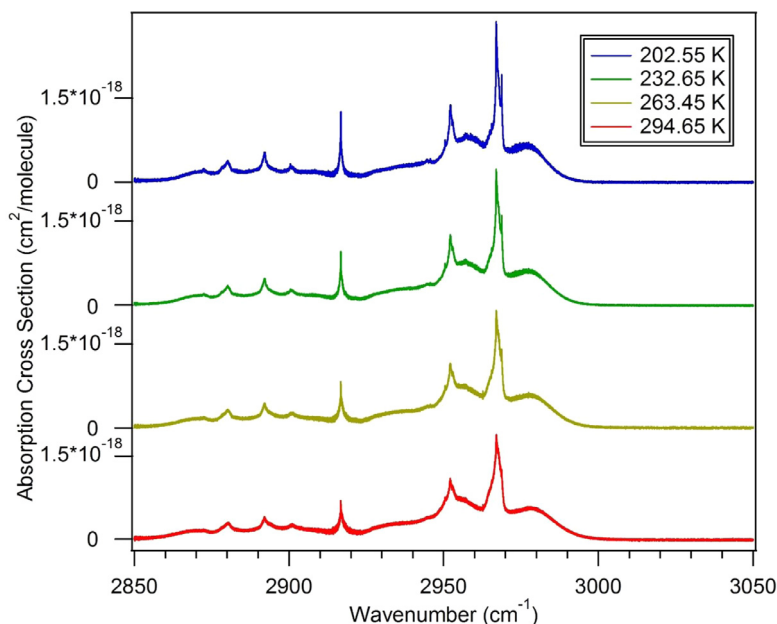


Fig. 1. Temperature series of isobutane absorption cross sections in the 3 μm region of the infrared spectrum with 100 Torr of H_2 as the broadening gas. From top to bottom: 202.55, 232.65, 263.45, and 294.65 K.

scaled accordingly to match the PNNL values. The CLS transmission spectra are converted to cross sections using Harrison et al. [26]:

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

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 ($1.3806504 \times 10^{-23}$ J/K). ξ is the correction factor used to scale each spectrum to the PNNL average value. The baselines of the cross sections were corrected with the help of the PNNL data. The correction factor ξ for each spectrum was calculated by taking the ratio between the integrated area of the PNNL absorption spectra and the integrated area of all of the CLS absorption spectra from this study, and is shown in Table 1. It should be noted that the pure spectra have a substantially lower signal to noise ratio, which affects the integration and normalization. There are also two noise spikes present in some of the spectra, the first around 2848 cm^{-1} and the second around 3013 cm^{-1} ; these are artifacts of the experiment and not signal from isobutane. The final cross section files are available in the section Appendix A. Supplementary Materials.

The accuracy of PNNL cross sections is estimated as $\pm 3.2\%$ (2 standard deviations) based on a comparison of independent measurements carried out at PNNL and NIST [25]. Based on a previous work [27], we estimate an error of about 5% (one sigma) for the cross sections, which agrees approximately with the standard deviation of the individual calibration factors.

2.2. Effects of varying temperature and pressure

The temperature dependence of the infrared spectra of isobutane is shown in Fig. 1, where an overall broadening and loss of resolution is observed as the temperature is increased from 203 K to 295 K. This trend is similar to that observed when comparing spectra from various broadening gas pressures at a constant temperature, where an increase in the broadening gas pressure re-

sults in a decrease in overall peak intensity and resolution and an increase in the width of the spectral features. These trends are less notable in the pressure series than the temperature series because the features in the spectra are each composed of many rovibrational lines and are much wider than the pressure-broadened widths.

3. Conclusions

High resolution infrared transmission spectra of isobutane, pure and with N_2 and H_2 broadening gases, were recorded at the Canadian Light Source synchrotron facility. These spectra were recorded in the 3 μm region of the infrared spectrum, ranged in temperature from 203 K to 295 K, and varied in broadening gas pressure from 0 Torr to 100 Torr. These ranges are necessary to replicate the conditions found in the astronomic atmospheres of interest: the atmospheres of the Giant Planets and their moons. These transmission spectra were then converted into absorption cross sections which can be used to interpret astronomical spectra. Based on previous work, the error in these cross sections is about 5%. The next projects in this series include publication of high resolution cross sections based on isobutane CLS spectra already recorded in the $1050\text{--}1900 \text{ cm}^{-1}$ region, spectra of hot isobutane in the 3 μm region and an improved vibrational analysis.

Acknowledgments

The NASA Outer Planets Research and Planetary Data Archiving and Restoration Tools program (PDART) provided funding (Grant number NNX16AG44G). We thank A. Wong, M. Pokhrel and J. Zhao for their help with the isobutane project. Research described in this paper was performed at the Canadian Light Source, which is supported by the Canada Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jqsrt.2019.02.008](https://doi.org/10.1016/j.jqsrt.2019.02.008).

References

- [1] Clarke DW, Ferris JP. Chemical evolution on Titan: comparisons to the prebiotic Earth. *Orig Life Evol Biosph* 1997;27:225–48.
- [2] Trainer MG, Pavlov AA, DeWitt HL, Jimenez JL, McKay CP, Toon OB, Tolbert MA. Organic haze on Titan and the early Earth. *Proc Natl Acad Sci USA* 2006;103:18035–42.
- [3] McKay C. Titan as the abode of life. *Life* 2016;6:8.
- [4] Fu Q, Liou KN. On the correlated k-distribution method for radiative transfer in nonhomogeneous atmospheres. *J Atmos Sci* 1992;49:2139–56.
- [5] Yung YL, Allen M, Pinto JP. Photochemistry of the atmosphere of Titan: comparison between model and observations. *Astrophys J Suppl Ser* 1984;55:465–506.
- [6] Dabrijevic M, Loison JC, Hickson KM, Gronoff G. 1D-coupled photochemical model of neutrals, cations and anions in the atmosphere of Titan. *Icarus* 2016;268:313–39.
- [7] Moses JL, Bézard B, Lellouch E, Gladstone GR, Feuchtgruber H, Allen M. Photochemistry of Saturn's atmosphere: I. Hydrocarbon chemistry and comparisons with iso observations. *Icarus* 2000;143:244–98.
- [8] Nixon C, Jennings DE, Flaud JM, Bézard B, Teanby AN, Irwin P, Ansty TM, Coustenis A, Vinatier S, Flasar FM. Titan's prolific propane: the Cassini CIRS perspective. *Plan Space Sci* 2009;57:1573–85.
- [9] Greathouse TK, Lacy JH, Bézard B, Moses JL, Richter MJ, Knez C. The first detection of propane on Saturn. *Icarus* 2006;181:266–71.
- [10] Vuitton V, Yelle RV, Klippenstein SJ, Hörst SM, Lavvas P. Simulating the density of organic species in the atmosphere of Titan with a coupled ion-neutral photochemical model. *Icarus* 2019.
- [11] Mueller-Wodarg ICF, Strobel DF, Moses JL, Waite JH, Crovisier J, Yelle RV, Bougher SW, Roble RG. Neutral atmospheres. *Space Sci Rev* 2008;139:191–234.
- [12] Irwin P. Giant planets of our solar system. Heidelberg, Berlin: Springer-Verlag; 2009. p. 428.
- [13] Vinatier S, Bézard B, Nixon CA. The titan $^{14}\text{N}/^{15}\text{N}$ and $^{12}\text{C}/^{13}\text{C}$ isotopic ratios in HCN from Cassini/CIRS. *Icarus* 2007;191:712–21.
- [14] Evans JC, Bernstein HJ. The vibrational spectra of isobutane and isobutane-D1. *Can J Chem* 1956;34:1037–45.
- [15] Wilmshurst JK, Bernstein HJ. The infrared and raman spectra of $\text{HC}(\text{CD}_3)_3$ and $\text{DC}(\text{CD}_3)_3$. *Can J Chem* 1957;35:969–79.
- [16] David RL Jr. Structure of the isobutane molecule; change of dipole moment on isotopic substitution. *J Chem Phys* 1960;33:1519–22.
- [17] Weiss S, Leroi GE. Infrared spectra and internal rotation in propane, isobutane and neopentane. *Spec Acta A Mol Spec* 1969;25:1759–66.
- [18] Manzanares C, Peng J, Mina-Camilde N, Brock A. Overtone spectroscopy of isobutane at cryogenic temperatures. *Chem Phys* 1995;190:247–59.
- [19] Schrader B, Pacansky J, Pfeiffer U. Calculation of the frequencies and intensities in the infrared spectra of matrix-isolated tert-butyl radical and isobutane. *J Chem Phys* 1984;88:4069–73.
- [20] Mirkin NG, Krimm S. Ab initio analysis of the vibrational spectra of conformers of some branched alkanes. *J Mol Struct* 2000;550:551:67–91.
- [21] Hilderbrandt RL, Wieser JD. The zero point average structure of isobutane as determined by electron diffraction and microwave spectroscopy. *J Mol Struct* 1973;15:27–36.
- [22] Priem D, Colmont JM, Petitprez D, Bailleux S. The rotational spectrum of isobutane up to 640 GHz: splitting of the $|K|=3$ transitions. *J Mol Spec* 1997;184:84–7.
- [23] Wong A, Billinghamurst B, Bernath PF. Helium broadened propane absorption cross sections in the far-IR. *Mol Astrophys* 2017;8:36–9.
- [24] Wong A, Hargreaves RJ, Billinghamurst B, Bernath PF. Infrared absorption cross sections of propane broadened by hydrogen. *J Quant Spec Rad Trans* 2017;198:141–4.
- [25] Sharpe SW, Johnson TJ, Sams RL, Chu PM, Rhoderick GC, Johnson PA. Gas-phase databases for quantitative infrared spectroscopy. *App Spec* 2004;58:1452–61.
- [26] Harrison JJ, Bernath PF. Infrared absorption cross sections for propane (C_3H_8) in the 3 μm region. *J Quant Spec Rad Trans* 2010;111:1282–8.
- [27] Harrison JJ, Allen NDC, Bernath PF. Infrared absorption cross sections for ethane (C_2H_6) in the 3 μm region. *J Quant Spec Rad Trans* 2010;111:357–63.