



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Infrared absorption cross sections for propane (C₃H₈) in the 3 μm region

Jeremy J. Harrison*, Peter F. Bernath

Department of Chemistry, University of York, Heslington, York YO10 5DD, UK

ARTICLE INFO

Article history:

Received 3 October 2009

Received in revised form

20 November 2009

Accepted 28 November 2009

Keywords:

C₃H₈

Propane

High-resolution Fourier transform spectroscopy

Infrared absorption cross sections

Remote-sensing

Atmospheric chemistry

ABSTRACT

Infrared absorption cross sections for propane have been measured in the 3 μm spectral region from spectra recorded using a high-resolution FTIR spectrometer (Bruker IFS 125 HR). The spectra of mixtures of propane with dry synthetic air were recorded at 0.015 cm⁻¹ resolution (calculated as 0.9/MOPD using the Bruker definition of resolution), at a number of temperatures and pressures appropriate for atmospheric conditions. Intensities were calibrated using two propane spectra (recorded at 278 and 293 K) taken from the Pacific Northwest National Laboratory (PNNL) IR database.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Propane was first identified in 1910 as the main volatile component in petrol by W. Snelling of the US Bureau of Mines [1]. It now has many uses, e.g. as domestic, industrial, and vehicle fuels.

After ethane, propane is the most abundant non-methane hydrocarbon (NMHC) in the atmosphere. Propane has a relatively long atmospheric lifetime of about 10 days and is lost primarily by reaction with OH to produce acetone in 80% yield [2,3]. Sources are highly uncertain and include leakage of natural gas and liquefied petroleum gas (LPG). Biomass burning and biogenic emissions are relatively small. According to Etiope and Ciccioli [4], researchers have been overlooking an important source of light hydrocarbons to the atmosphere: Earth's natural degassing from geological processes. This

degassing accounts for at least 10 percent of total propane emissions. Estimates of global propane emissions have varied extensively over the years. Recent estimates are 24–60 [5], 23 [6], 15–20 [2], 12 [3], and 10.6–12 Tg yr⁻¹ [4].

Propane has only a negligible direct radiative forcing effect; however, like many VOCs (volatile organic compounds) it has a significant impact on air quality. Its oxidation by OH leads to the production of tropospheric ozone, which is toxic and a strong greenhouse gas. The 2007 IPCC report [7] lists tropospheric ozone as the third most important anthropogenic factor (after methane and carbon dioxide) in driving climate change.

Propane is a key precursor in the formation of acetone which in turn produces peroxyacetyl nitrate (PAN), a reservoir for NO_x [8]. The lifetime of PAN in the troposphere increases with altitude, due to its greater thermal stability at lower temperatures, increasing from a few hours at the Earth's surface to several months at the tropopause. The relatively long lifetime in the middle and upper troposphere allows it to be transported over long distances, equivalent to a long-distance transport of NO_x.

* Corresponding author. Tel.: +44 1904 434589;

fax: +44 1904 432516.

E-mail address: jjh506@york.ac.uk (J.J. Harrison).

Nearly all tropospheric ozone results from the photolysis of NO_2 , so for this reason the sources of pollutant emission may in fact be long distances from the regions of resulting elevated ozone [9].

Surface measurements by Singh and Salas [10] along the US eastern Pacific coast reveal a significant north-south gradient for propane, with average northern concentrations up to 10 times higher than found in the southern hemisphere. Furthermore, there is a significant seasonal trend in propane abundance, which is greatest in the winter months.

Ground based measurements have also been made in clean marine air at remote southern-hemisphere locations, for example Baring Head (New Zealand) and Scott Base (Antarctica) [11]. These observations reinforce the relative lack of propane sources in the southern hemisphere compared to the northern hemisphere. Arctic measurements at Barrow (Alaska) [12] again reveal the presence of propane. The hydrocarbon distributions in background arctic air (March 1989) resemble aged urban air more closely than urban air. This observation provides evidence that the source of arctic haze may be anthropogenic emissions from mid-latitude industrialised locations.

A number of airborne flask-measurement campaigns have also been carried out, such as TROPOZ II [13]. In this study a latitudinal gradient in propane mixing ratios was observed, decreasing from 2 ppbv in the north to 0.07 ppbv in the south, as well as a seasonal variability, both of these consistent with Singh and Salas [10].

Despite a number of ground-based and airborne measurements, so far there have been no global measurements of propane. This work will provide accurate spectroscopic measurements that will enable the retrieval of propane abundances from atmospheric limb spectra recorded by the Atmospheric Chemistry Experiment (ACE), on board the satellite SCISAT-1. ACE uses a high-resolution Fourier transform spectrometer that covers the spectral region from 750 to 4400 cm^{-1} [14]. Due to this extended spectral coverage, it is possible to carry out retrievals in the strong $3\text{ }\mu\text{m}$ region, where all aliphatic hydrocarbons have their strongest-intensity modes (C–H stretch) and where there are relatively few spectral interferers.

Retrievals of concentration profiles from satellite data require accurate laboratory spectroscopic measurements in the form of either line parameters or absorption cross sections. The HITRAN database [15] is a good source of such spectroscopic data; however, it does not contain propane. The GEISA database [16] on the other hand does contain limited propane data, but these do not extend to the $3\text{ }\mu\text{m}$ region: 8983 lines in the $700\text{--}800\text{ cm}^{-1}$ range (unpublished data by Bjoraker [17]), and an absorption cross section recorded at 296 K and 700 Torr in the $200\text{--}2000\text{ cm}^{-1}$ range. Propane data are also contained in the Pacific Northwest National Laboratory (PNNL) IR database (<http://nwir.pnl.gov>) [18], however, these are not suitable for remote sensing of the upper troposphere for a number of reasons. All PNNL spectra are recorded at relatively low resolution (0.112 cm^{-1}) as mixtures with pure nitrogen gas, not synthetic air, at pressures of 760 Torr and temperatures of 278, 293, or 323 K.

Propane will likely be retrieved from ACE spectra using the Q branch at 2968 cm^{-1} . This region of ACE limb spectra is dominated by ethane, a very strong absorber in the troposphere. We have recently determined a set of high resolution infrared absorption cross sections in the $3\text{ }\mu\text{m}$ region for ethane/synthetic air over the pressure and temperature ranges 50–760 Torr and 194–297 K to accurately model the ethane contribution to ACE spectra [19]. In a similar manner, we have recorded a set of high resolution (0.015 cm^{-1}) infrared spectra of propane/synthetic air over a range of pressures and temperatures (40–760 Torr and 195–296 K) appropriate for atmospheric retrievals, and used these to determine a set of absorption cross sections between 2540 and 3300 cm^{-1} .

In terms of extraterrestrial remote sensing, propane is a species of significant interest to astronomers, having been identified in the atmospheres of Saturn and its moon, Titan. Propane was first detected in Saturn's stratosphere by Greathouse et al. [20] from observations taken at NASA's IRTF (Infrared Telescope Facility) atop Mauna Kea in Hawaii using TEXES (Texas Echelon Cross Echelle Spectrograph). The spectra show multiple emission lines due to the 748 cm^{-1} ν_{26} band of propane. Using limb-viewing geometry data from the Cassini/CIRS instrument, Guerlet et al. [21] have determined the temperature and abundance profiles of propane in Saturn's stratosphere in the latitudinal range 80°S to 70°N . It was found that the propane abundance globally increases from north to south by a factor of 1.9. Their retrieval scheme is sensitive to propane at about 2–3 pressure levels, centred at 1 hPa. Propane was first detected in the atmosphere of Titan by the Voyager 1 IRIS infrared spectrometer in 1980 [22]. Obtaining accurate abundances has been difficult because of a lack of reliable laboratory spectroscopic data. Using data from the Cassini/CIRS instrument obtained in limb-viewing mode at low latitudes (30°S – 30°N), Nixon et al. [23] identified at least six infrared bands of propane in Titan's atmosphere, including two for the first time. Using improved spectroscopy, they were able to retrieve propane abundances from two bands at 748 cm^{-1} (ν_{26}) and 1376 cm^{-1} (ν_{18}). This study points to the need for further accurate laboratory spectroscopic data for propane.

2. Experimental

2.1. Spectrometer

All absorption spectra were recorded at the Molecular Spectroscopy Facility, Rutherford Appleton Laboratory using a high-resolution FTIR spectrometer (Bruker IFS 125 HR) with a KBr beamsplitter, indium antimonide (InSb) detector, and the internal mid-IR radiation source (globar). An optical filter restricted the optical throughput to the spectral region between 2400 and 3500 cm^{-1} . The overall intensity of infrared radiation falling on the InSb detector was therefore maximised in the region of interest without saturating the detector.

2.2. Gas cell

A 26-cm-long single-pass stainless-steel absorption cell, a double-walled cylinder with wedged ZnSe windows sealed on sprung PTFE o-rings, was used for all measurements. The wedged windows eliminate interference fringes (channel spectra) caused by reflections at the surface. The o-ring mounting of the windows is critical to prevent leaks at temperatures down to ~ 200 K. The cell was mounted inside the sample compartment of the spectrometer, which was evacuated to < 0.2 Pa in order to minimise the absorbance of impurity gases, and condensation of these gases on the cell windows at the lower measurement temperatures. Cell temperatures below room temperature were achieved by circulating ethanol from a liquid-nitrogen-cooled ethanol bath through the space between the cell walls. The temperature was controlled by regulating the liquid-nitrogen flow via a solenoid valve which was switched by the output of a comparator that compares the temperature in the ethanol bath against a user pre-set temperature. This setup allows automatic temperature control of the cell from ~ 194 K to room temperature for extended periods of time. The actual cell temperature was monitored by five platinum resistance thermometers (PRTs) in thermal contact at different points on the exterior surface of the cell.

2.3. Sample purity and preparation of gas mixtures

Propane (Sigma-Aldrich, 99.97% purity) and dry synthetic air ('Air Zero Plus', Air Products, 20.9% $O_2 \pm 0.2\%$, $H_2O \leq 0.5$ ppm, $CH_4 \leq 0.05$ ppm, $CO + CO_2 \leq 0.1$ ppm, 99.99990% overall purity) were both used 'as is' without additional purification. Mixtures were prepared using a gas line, directly attached to the absorption cell. The vacuum was maintained (baseline pressure below < 0.001 Torr) using a Pfeiffer turbomolecular pump (CompactTurbo TMH 071 P) backed by a Leybold rotary vane pump (Trivac D8B). The mixtures were prepared by introducing a small amount of propane directly into the cell and then adding dry synthetic air. Pressures were not measured

directly in the cell, but close by, further along the gas line, using full scale 10, 100 and 1000 Torr Baratron capacitance manometers (MKS). Thermal transpiration effects due to the positioning of the pressure gauges relative to the cell and the diameter of the connecting tubing relative to the mean free path of molecules can be safely neglected [24].

2.4. Recording of spectra

Details of the pressures, temperatures, and instrument parameters for all scans are contained in Table 1. Air-broadened spectra were recorded at 0.015 cm^{-1} resolution (calculated as $0.9/\text{MOPD}$ using the Bruker definition of resolution). Pre- and post-sample background (empty cell) scans were also recorded as the cell was under vacuum. All spectra were recorded in blocks of 20 scans and subsequently co-added.

2.5. Error budget

The measured average temperature variation of the (outer surface of the) cell was 0.1 K (0.03%) at room temperature and about 1 K (0.5%) at 195 K. Errors for the spanned temperature range varied more or less linearly with temperature.

The optical pathlength was determined by direct measurement, with the error estimated to be 0.1%.

The uncertainties in the pressure readings are estimated to be 0.5%. As discussed in our previous paper on ethane absorption cross sections [19], the method used to prepare the sample mixtures often results in a discrepancy between the measured propane pressure reading and the actual propane partial pressure in the cell after addition of synthetic air. For this reason the intensity scale of the cross sections derived in this work is calibrated using propane spectra from the PNNL IR database. This is discussed further in Section 3.1.

The photometric uncertainty is estimated to be 2%. Small drifts in the spectral baseline were noticed with time. It is possible that these drifts, which more or less

Table 1

Summary of the pressures, temperatures, and instrument parameters for all scans.

Propane pressure (Torr)	Total pressure (Torr)	Temperature (K)	Resolution (cm^{-1})	Aperture size (mm)	Apodisation function ^a	No. of scans	Scan time (h) ^b
1.0032	40.10	195	0.015	2.5	NB medium	100	1
1.0030	69.22	195	0.015	2.5	NB medium	100	1
1.0030	98.30	195	0.015	2.5	NB medium	100	1
1.0005	52.01	215	0.015	2.5	NB medium	100	1
1.0030	100.25	215	0.015	2.5	NB medium	100	1
1.0055	275.35	215	0.015	2.5	NB medium	100	1
1.0234	203.23	252	0.015	2.5	NB medium	100	1
1.0146	405.63	252	0.015	2.5	NB medium	100	1
1.0065	620.72	250	0.015	2.5	NB medium	100	1
0.9998	369.30	269	0.015	2.5	NB medium	100	1
1.0110	604.45	269	0.015	2.5	NB medium	100	1
1.0018	762.67	296.4	0.015	2.5	NB medium	100	1

^a NB=Norton-Beer.

^b Approximate. Note that each sample spectrum requires a corresponding background spectrum taken with the same spectrometer settings. The scan time is effectively doubled.

varied linearly with time, were due to organic vapours (e.g. outgassing from polymers and pump oil) being deposited on the cell windows. Great care was taken to prevent the adsorption of impurities inside the cell at low temperatures by using high purity gases and pumping out the gas line before the preparation of sample mixtures. Any possible non-linear photometric response in the InSb detector was minimised by using a narrow optical filter to restrict the optical throughput to the spectral region of interest, thereby maximising the signal without saturating the detector. Background (empty cell) spectra were recorded immediately prior to and after the sample spectra. By using averaged backgrounds to calculate the propane transmittance spectra, most of these small drifts cancelled out. However, the transmission spectra still required small corrections to ensure 100% transmittance outside the propane absorption band.

Overall, the uncertainties in the absorption cross sections reported in this paper are estimated to be 3%.

3. Results and discussion

3.1. Data analysis

Transmission spectra were calculated by dividing averaged single-channel sample scans by appropriate averaged single-channel background scans. As mentioned in Section 2.5, a further correction was necessary to ensure that the baseline extended to 100% transmittance outside the absorption band. Spectral frequencies were calibrated against an archival Kitt Peak spectrum of pure propane, with a small amount of added CO. This spectrum (970507R0.091) was recorded over a 50 cm pathlength by M.A. Smith at 1.2 Torr and 27.6 °C, with a spectral resolution of 0.0055 cm⁻¹; it is freely available via ftp from <http://diglib.nso.edu>.

The y-axes of the cross sections derived in this work were calibrated using spectra from the PNNL IR database. The reason for this arises from the method used to prepare the propane/synthetic air mixtures. Propane is first added to the cell and gas-line, followed by the synthetic air, so it is not known to what extent the gases are mixed and how much, if any, propane has been lost back along the gas-line leading to the synthetic air cylinder. We prefer to shut-off the cell from the gas-line shortly after filling it to reduce the risk of impurities reaching the cell from any small leaks in the gas-line. Therefore, the small discrepancy between the measured propane pressure and the actual propane partial pressure in the cell requires us to calibrate intensities using a dataset with a well defined propane concentration. Each PNNL spectrum is a composite of multiple pathlength–concentration burdens, and great care has been taken to ensure that sample concentrations have been determined accurately. This calibration also relies on the fact that band intensities for isolated bands comprising primarily fundamentals are essentially independent of temperature.

The calibration procedure proceeded by converting transmission spectra to PNNL units (ppm⁻¹ m⁻¹), i.e. the absorbance for a sample concentration of 1 ppm over an

optical pathlength of 1 m at 296 K, using the following equation:

$$\varepsilon_{\text{ppm}^{-1}\text{m}^{-1}}(\nu, T) = -\frac{T}{296} \frac{0.101325}{Pl} \log_{10} \tau(\nu, T) \quad (1)$$

where $\tau(\nu, T)$ is the transmittance at wavenumber ν (cm⁻¹) and temperature T (K), P is the pressure of the absorbing gas (Pa), and l is the optical pathlength (m).

All $\varepsilon_{\text{ppm}^{-1}\text{m}^{-1}}(\nu, T)$ were integrated between 2540 and 3300 cm⁻¹; the resulting integrals agreed with each other to about 10%. The three propane spectra (recorded at 278, 293, and 323 K) contained in the PNNL database were integrated over the same range (2540–3300 cm⁻¹). The integral for the 323 K spectrum was about 2% greater than the other two, so it was decided to discard this. The integrals at 278 and 293 K agreed within 0.8%. These were averaged; all $\varepsilon_{\text{ppm}^{-1}\text{m}^{-1}}(\nu, T)$ were then calibrated by normalising their integrals against this average. It was found that the $\varepsilon_{\text{ppm}^{-1}\text{m}^{-1}}(\nu, T)$ needed to be reduced by at most 10% or increased by at most 4% to agree with the PNNL data.

Finally, the spectral absorption cross sections, $\sigma(\nu, T)$, with units cm² molecule⁻¹, were calculated by

$$\begin{aligned} \sigma(\nu, T) &= -\xi \frac{10^4 k_B T}{Pl} \ln \tau(\nu, T) \\ &= \xi \frac{296 \times 10^4 k_B \ln(10)}{0.101325} \varepsilon_{\text{ppm}^{-1}\text{m}^{-1}}(\nu, T) \end{aligned} \quad (2)$$

where k_B is the Boltzmann constant ($=1.3806504 \times 10^{-23}$ JK⁻¹) and ξ is the factor required to scale each spectrum to PNNL values. All other symbols (and corresponding units) are as defined for Eq. (1). A selection of cross sections is given in Figs. 1 and 2. The first figure gives an overview of the entire propane 3 μm band at 215 K and 52.01 Torr; whereas the second shows the pressure dependence of the main Q branch at 250–252 K. All the spectral absorption cross sections corresponding to the experimental conditions in Table 1 are available electronically upon request from the authors.

3.2. ACE Retrievals

These cross sections will enable the first ACE propane retrievals to be developed, which will ultimately lead to the first satellite data product of propane. It is worth stressing that this is a challenging problem for several reasons. Firstly, there is a spectroscopic disadvantage compared to ethane, which dominates ACE spectra in this spectral region. The peak height of the propane Q branch in the 3 μm spectral region is more than five times weaker than the strongest ethane Q branch [19]. Secondly, there is the issue of the relative atmospheric abundance of propane compared to ethane. Ethane/propane ratios have been reported as high as about 3 in the northern hemisphere [12,13], and can be substantially higher (over 15) in remote locations in the southern hemisphere [11]. Fig. 3 gives a plot of absorption cross sections for the propane Q branch (215 K and 52.01 Torr) and ethane (215 K and 49.44 Torr) over the same spectral region. It is clear from Fig. 3 that the (weak) ethane structure will

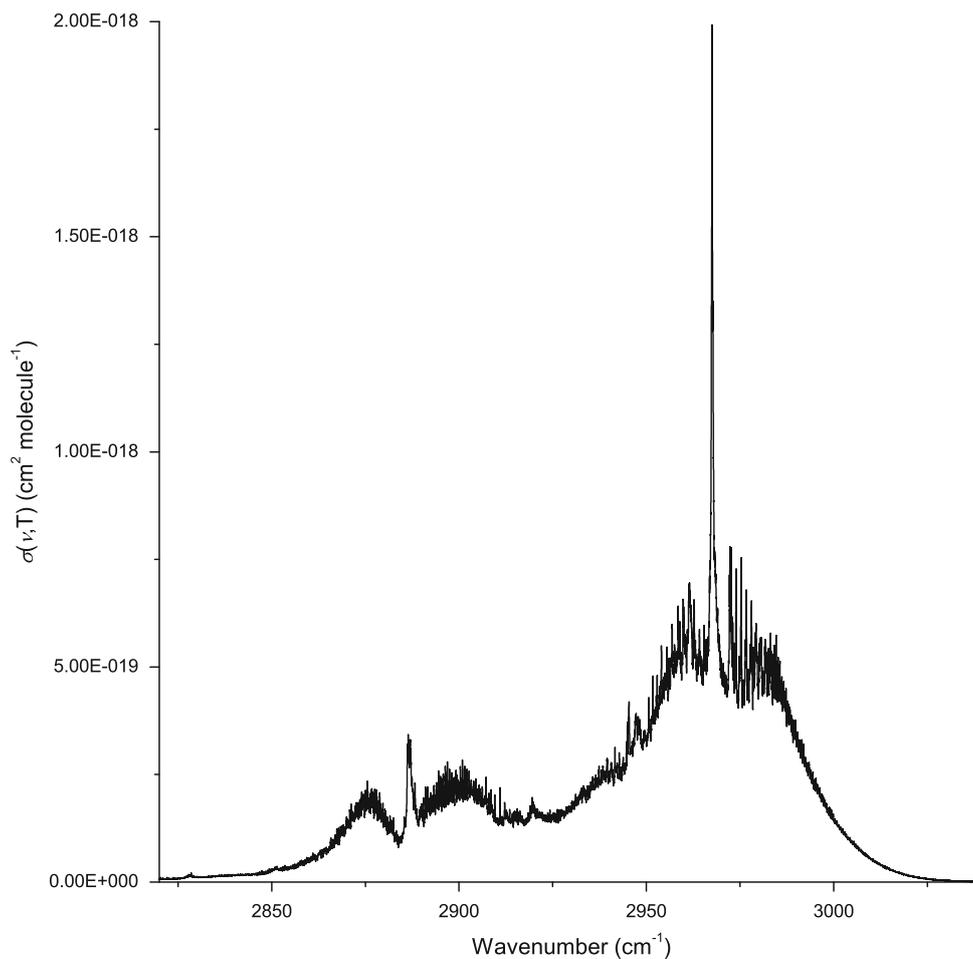


Fig. 1. Absorption cross section for the 3 μm band of propane at 215 K and 52.01 Torr.

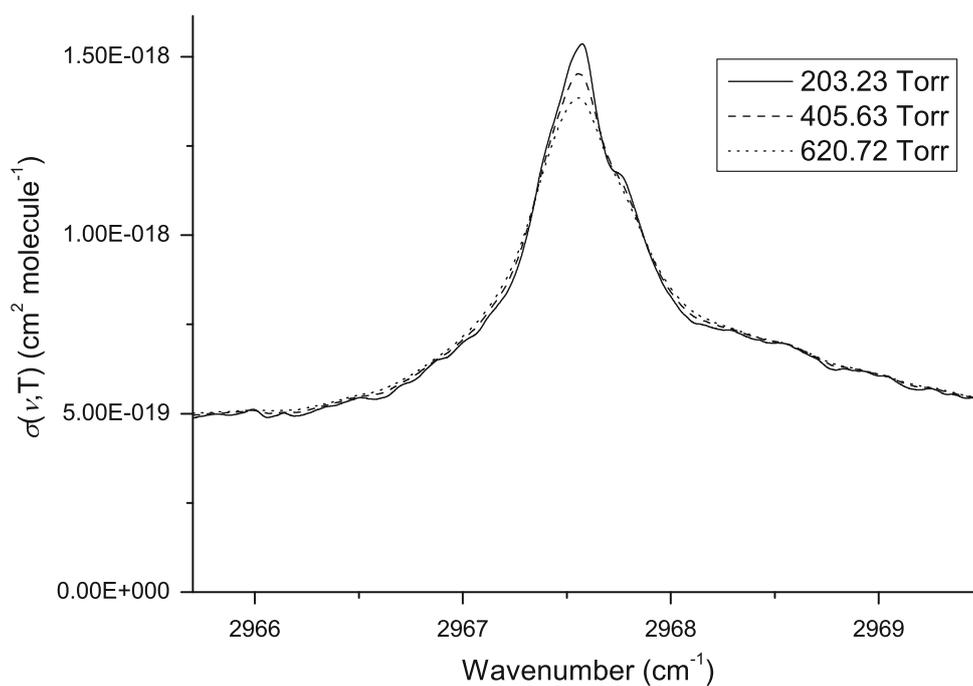


Fig. 2. Absorption cross sections showing the pressure dependence of the main Q branch of the 3 μm band of propane at 250–252 K.

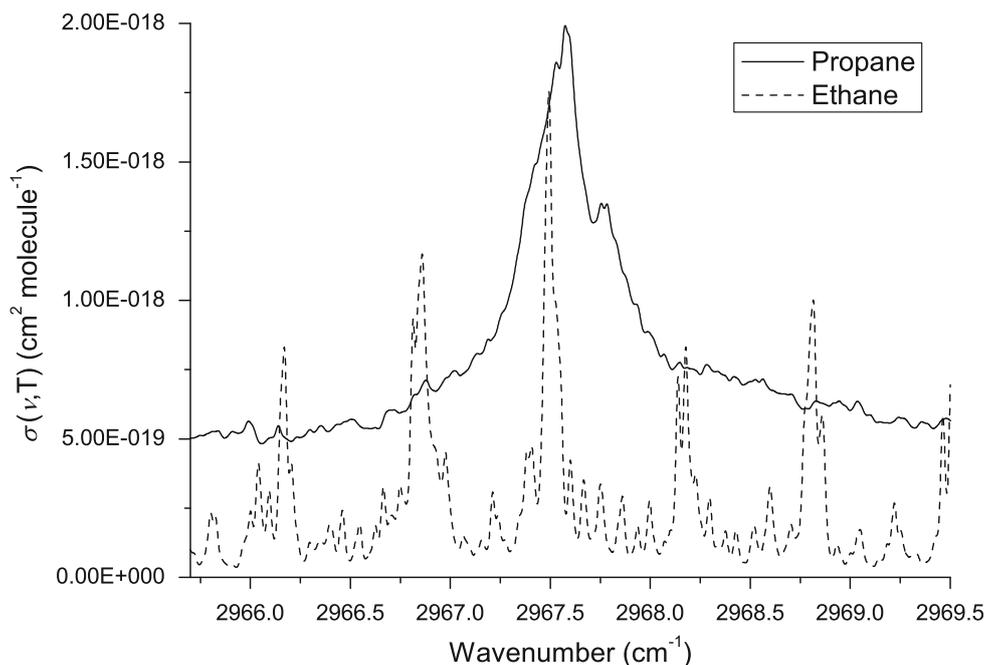


Fig. 3. Absorption cross sections for the propane Q branch (215 K and 52.01 Torr) and ethane (215 K and 49.44 Torr) over the same spectral region.

begin to dominate the propane Q-branch as the ethane/propane ratio increases.

4. Conclusions

High-resolution infrared absorption cross sections for propane (between 2540 and 3300 cm^{-1}) have been measured with an estimated uncertainty of 3%. The data were recorded for mixtures with dry synthetic air at 0.015 cm^{-1} resolution using a range of temperatures and pressures appropriate for atmospheric conditions. Intensities were calibrated against two propane spectra (recorded at 278 and 293 K) taken from the PNNL IR database. These cross sections will be used to develop a propane retrieval scheme from ACE solar occultation spectra.

Acknowledgements

The authors wish to thank the Natural Environment Research Council (NERC) for supporting J.J. Harrison through Grant NE/F002041/1, and for access to the Molecular Spectroscopy Facility (MSF) at the Rutherford Appleton Laboratory (RAL). R.G. Williams is thanked for providing technical support at the RAL. The propane data were recorded as part of a proposal to the MSF entitled “Low temperature, high resolution spectroscopy in the 3, 7 and 11.7 μm bands of ethane and propane gases” by N. Bowles, J.J. Remedios and P.F. Bernath. We also thank N.D.C. Allen and R.J. Parker for assistance with some of the early propane measurements that were ultimately not used because of leaks in the absorption cell.

References

- [1] Myers RL. The 100 most important chemical compounds: a reference guide. Westport, Connecticut, USA: Greenwood Press; 2007.
- [2] Singh HB, O'Hara D, Herlth D, Sachse W, Blake DR, Bradshaw JD, et al. Acetone in the atmosphere: distribution, sources, and sinks. *J Geophys Res* 1994;99(D1):1805–19.
- [3] Jacob DJ, Field BD, Jin EM, Bey I, Li Q, Logan JA, et al. Atmospheric budget of acetone. *J Geophys Res* 2002;107(D10):4100, doi:10.1029/2001JD000694.
- [4] Etiopie G, Ciccioli P. Earth's degassing: a missing ethane and propane source. *Science* 2009;323:478.
- [5] Bonsang B, Lambert G. Nonmethane hydrocarbons in an oceanic atmosphere. *J Atmos Chem* 1985;2:257–71.
- [6] Kanakidou M, Singh HB, Valentin KM, Crutzen PJ. A two-dimensional study of ethane and propane oxidation in the troposphere. *J Geophys Res* 1991;96(D8):15,395–413.
- [7] Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, et al., editors. IPCC, 2007: Climate Change 2007: The physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. See <http://www.ipcc.ch>.
- [8] Singh HB, Hanst PL. Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: an important reservoir for nitrogen oxides. *Geophys Res Lett* 1981;8(8):941–4.
- [9] Gupta ML, Cicerone RJ, Blake DR, Rowland FS, Isaksen ISA. Global atmospheric distributions and source strengths of light hydrocarbons and tetrachloroethene. *J Geophys Res* 1998;103(D21):28219–35.
- [10] Singh HB, Salas LJ. Measurements of selected light hydrocarbons over the Pacific Ocean: latitudinal and seasonal variations. *Geophys Res Lett* 1982;9:842–5.
- [11] Clarkson TS, Martin RJ, Rudolph J. Ethane and propane in the Southern marine troposphere. *Atmos Environ* 1997;31(22):3763–71.
- [12] Doskey PV, Gaffney JS. Non-methane hydrocarbons in the Arctic atmosphere at Barrow, Alaska. *Geophys Res Lett* 1992;19(4):381–4.
- [13] Boissard C, Bonsang B, Kanakidou M, Lambert G. TROPOZ II: global distributions and budgets of methane and light hydrocarbons. *J Atmos Chem* 1996;25:115–48.
- [14] Bernath PF, McElroy CT, Abrams MC, Boone CD, Butler M, Camy-Peyret C, et al. Atmospheric Chemistry Experiment (ACE): mission overview. *Geophys Res Lett* 2005;32(L15S01), doi:10.1029/2005GL022386.

- [15] Rothman LS, Gordon IE, Barbe A, Benner DC, Bernath PF, Birk M, et al. The HITRAN 2008 molecular spectroscopic database. *JQSRT* 2009;110:533–72.
- [16] Jacquinet-Husson N, Scott NA, Chedin A, Crepeau L, Armante R, Capelle V, et al. The GEISA spectroscopic database: current and future archive for Earth and planetary atmosphere studies. *JQSRT* 2008;109:1043–59.
- [17] Husson N, Bonnet B, Scott N, Chedin A. Management and study of spectroscopic information — the GEISA program. *JQSRT* 1992;48(5/6):509–18.
- [18] Sharpe S, Johnson T, Sams R, Chu P, Rhoderick G, Johnson P. Gas-phase databases for quantitative infrared spectroscopy. *Appl Spectrosc* 2004;58(12):1452–61.
- [19] Harrison JJ, Allen NDC, Bernath PF. Infrared absorption cross sections for ethane (C₂H₆) in the 3 μm region. *JQSRT* 2010;111(3):357–63.
- [20] Greathouse TK, Lacy JH, Bezard B, Moses JL, Richter MJ, Knez C. The first detection of propane on Saturn. *Icarus* 2006;181:266–271.
- [21] Guerlet S, Fouchet T, Bézard B, Simon-Miller AA, Flasar FM. Vertical and meridional distribution of ethane, acetylene and propane in Saturn's stratosphere from CIRS/Cassini limb observations. *Icarus* 2009;203:214–32.
- [22] Maguire W, Hanel R, Jennings D, Kunde V, Samuelson R. C₃H₈ and C₃H₄ in Titan's atmosphere. *Nature* 1981;292:683–6.
- [23] Nixon CA, Jennings DE, Flaud JM, Bezard B, Teanby NA, Irwin PGJ, et al. Titan's prolific propane: the Cassini CIRS perspective. *Planet Space Sci* 2009;57(13):1573–85.
- [24] Takaishi T, Sensui Y. Thermal transpiration effect of hydrogen, rare gases and methane. *Trans Faraday Soc* 1963;59:2503–14.