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Infrared absorption cross sections for hot isobutane in the CH stretching region

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ABSTRACT

Spectra of pure isobutane were recorded at high temperature in the C-H stretching region (2750–3050 cm^{-1}) with a high resolution Fourier transform spectrometer. Isobutane absorption cross sections were determined for six temperatures from 295 K to 739 K. These data may be useful for simulations of hot Jupiter exoplanets and brown dwarfs. Integrated cross sections were compared with adjusted cross section data from the Pacific Northwest National Laboratory (PNNL) database.

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Introduction

Hydrocarbons are found in planetary and exoplanetary atmospheres [1,2]. Butane is a hydrocarbon that exists in the Earth's atmosphere mainly from fossil fuel combustion and fugitive emissions from oil and gas production [3,4]. Titan is a moon of Saturn with a dense atmosphere of N_2 and CH_4 capable of forming hydrocarbons including potentially butane through photochemical reactions [5]. Propane has already been detected on Titan [6] and also on Saturn [7]. The detection of methane, ethane and propane in the atmospheres of Jupiter and Saturn, and the detection methane in brown dwarfs and exoplanets suggests that hydrocarbons such as butane might also be found in hot Jupiter exoplanets. Hot hydrocarbons have already been detected in the auroral regions of Jupiter [8].

Butane (C_4H_{10}) has two isomers, *n*-butane with C_{2h} symmetry and isobutane with C_{3v} symmetry at equilibrium [9,10]. Isobutane has 24 fundamental vibrational frequencies, 8 with a_1 symmetry (ν_1 – ν_8), 4 optically forbidden a_2 modes (ν_9 – ν_{12}) and 12 doubly degenerate e modes (ν_{13} – ν_{24}). In the C-H stretching region there are 6 allowed fundamental frequencies (ν_1 – ν_3 , ν_{13} – ν_{15}) [11]. We have recorded high resolution spectra of pure hot isobutane at 6 temperatures in the 2500–3500 cm^{-1} spectral region to provide absorption cross sections to aid in the detection of isobutane in hot Jupiters and brown dwarfs. This work is the fourth in a series of

papers on hot hydrocarbon absorption cross sections and uses the same methods as for ethane [12], propane [13] and propene [14].

Isobutane spectroscopy has been the subject of several papers and the older literature has been reviewed in them. Hewett et al. [15] measured infrared absorption cross sections of isobutane broadened by N_2 and H_2 in the 1050–1900 cm^{-1} spectral range for 210–296 K. Although *n*-butane and isobutane were not detected on Titan, upper abundance limits were determined [15]. Similar cross section measurements were made in the 3 μm region for 202–294 K samples [16]. Bernath et al. [11] rotationally analyzed two infrared bands and were able to assign the bands in the 3 μm region with the help of anharmonic local mode calculations.

Experimental

The experimental method used was similar to previous work on hot ethane [12], propane [13] and propene [14] so only a summary is provided here. Transmission spectra of isobutane were recorded for six nominal temperatures, 295 K, 373 K, 473 K, 573 K, 673 K and 723 K using a sealed quartz cell, a tube furnace and a Bruker IFS 120/125HR (120 bench with 125 electronics) Fourier transform spectrometer. At each temperature (except 295 K) 4 spectra were recorded. With the infrared glower on, the first spectrum was recorded with isobutane in the cell (A_{ab}) at 1 Torr pressure and the second spectrum was without isobutane in the cell (A_{ref}). In order to correct for the sample and cell emission, the glower was turned off and the third spectrum was recorded with isobutane in the cell (B_{em}) and the fourth spectrum was the emission spectrum of the empty cell (B_{ref}). The cell transmission τ was calculated as:

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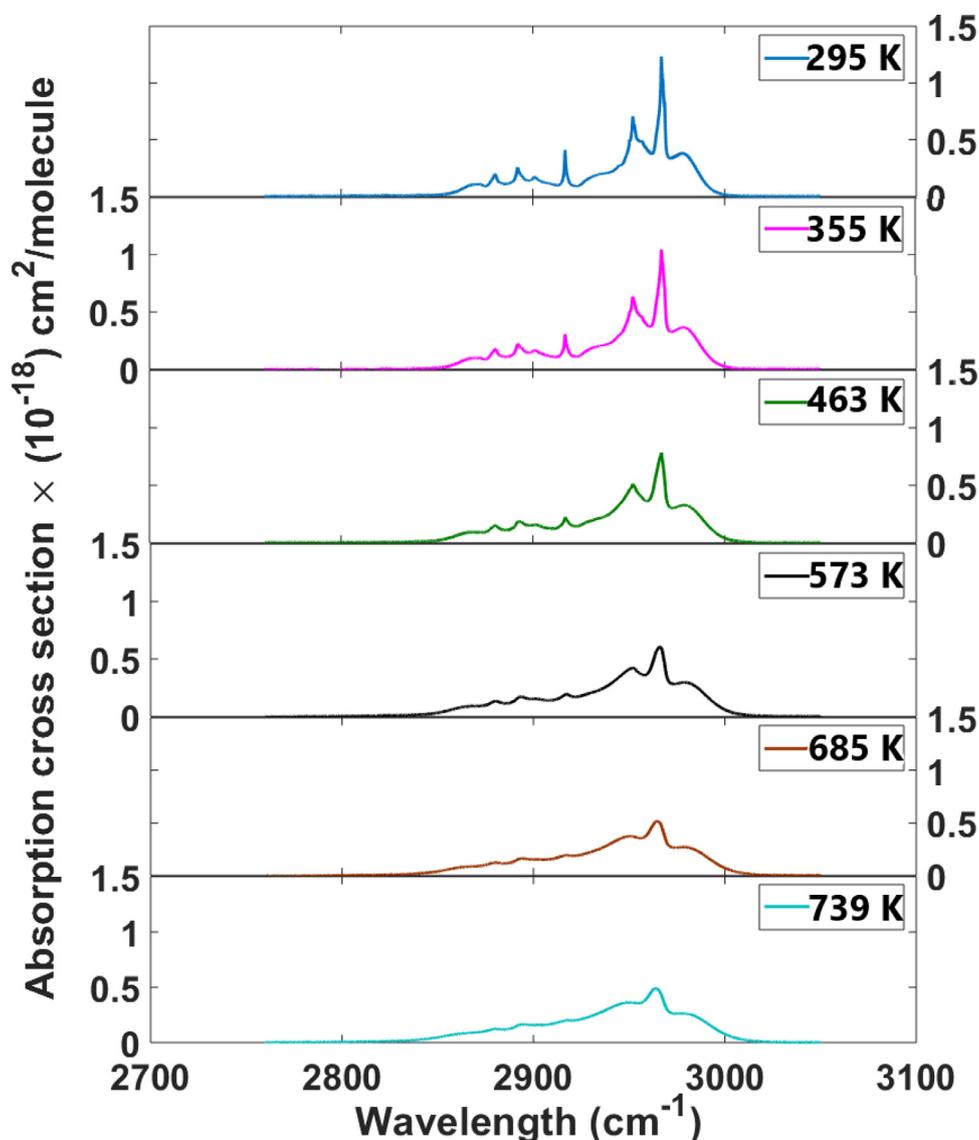


Fig. 1. Isobutane absorption cross sections at six calibrated temperatures.

Table 1
Experimental parameters.

	Value
Detector	InSb
Beamsplitter	CaF ₂
Spectrometer Window	CaF ₂
Lens	CaF ₂
Filter	Ge
Scans	128 coadds
Resolution	0.01 cm ⁻¹ (Bruker)
Zero filling factor	x16
Path length	50.8 cm

$$\tau = \frac{A_{ab} - B_{em}}{A_{ref} - B_{ref}}. \quad (1)$$

The experimental conditions are summarized in Table 1. The total spectral range covered was 2400–5400 cm⁻¹ as set by the quartz cell window and the Ge filter.

The cell pressure was not measured at the temperature of the experiment except for the room temperature sample.

Calibration and results

The nominal temperatures of the samples were obtained from the thermocouple of the tube furnace provided by the manufacturer. More accurate temperatures were determined with another thermocouple that measured the temperatures inside the quartz cell, parallel to the center of the cell. These measurements were carried out in a separate experiment with air in the cell. The temperature at the ends of the quartz cell was typically 10–20 K cooler than in the center. The calibrated temperatures at the center were 295, 355, 463, 573, 685 and 739 K corresponding to the nominal temperatures of 295, 373, 473, 573, 673 and 723 K, respectively. The calibrated temperatures have an error of about 2 K.

In our previous measurements of cross sections of high temperature hydrocarbons [12–14], the cross sections at each temperature were calibrated using data from the Pacific Northwest National Laboratory (PNNL) [17]. (PNNL absorption cross sections are now available from the HITRAN database [18].) PNNL cross sections are provided for 3 sample temperatures (278, 293, and 323 K) and were recorded with 1 atm of nitrogen gas at a resolution of 0.1 cm⁻¹ [17]. As discussed in more detail by Harrison et al. [18], the integrated absorption cross section of an isolated fundamental

band is approximately independent of temperature. This approximate temperature independence can be used to calibrate the y-axis of measured spectra and was necessary because reliable pressures were not available for the samples at elevated temperatures.

The situation for isobutane is more complicated because of an apparent problem with the PNNL data, as noted previously [15,16]. In the 3 μm , region, the integrated area of the PNNL data was found to be too large and had to be divided by 1.40. The correction factor was confirmed with the spectrum recorded for the isobutane sample at 295 K in this series of hot measurements. The estimated error in this new pressure measurement is about 2%. Apart from this difference in integrated cross sections, our measurements agree well with PNNL, considering the difference in resolution and pressure broadening. There is no indication of any impurities.

The PNNL cross sections for isobutane at 293 K were divided by 1.40 and then used for the calibration of the hot isobutane cross sections. The baselines of the hot spectra were also adjusted by less than 1% near 3050 cm^{-1} by comparison with the corrected PNNL data. The cross sections are provided for the 2760–3050 cm^{-1} spectral region and the integrated area for this region was set to 343.8×10^{-19} $\text{cm}^2/\text{molecule}$ for all spectra. The spectra also contained some residual H_2O lines and they were removed by hand using the Bruker OPUS software. The final cross sections are provided as supplementary data and are plotted in Fig. 1.

For the fundamental band of a harmonic oscillator, Mills and Whiffen [20] show that the integrated cross section has no temperature dependence when hot bands and stimulated emission are included. However, for more realistic anharmonic oscillators, Yao and Overend [21] show that there is a small temperature dependence for fundamental bands. Breeze et al. [22] have made actual measurements for NO , H_2O and CO_2 and find no temperature dependence in the integrated cross sections for fundamental bands from 300 to 2500 K to within their experimental accuracy of about 10%. Our assumption of temperature independence of the integrated cross sections contributes to the measurement error.

Discussion

At room temperature, no rotational structure is observed (Fig. 1) although at 202 K, some rotational features become visible on top of an unresolved band contour [11,15]. As the temperature is raised the contour becomes increasingly washed out by hot bands and highly excited rotational lines (Fig. 1) until at 739 K, even the Q-branch at 2967 cm^{-1} has almost disappeared.

Error estimates for the isobutane cross sections are difficult to obtain. A simple analysis of the errors as carried out by Harrison et al. [19] would yield values of 4–5%, but this is clearly an underestimate in this case. Errors in the cross sections for hot isobutane are dominated by systematic effects, including the temperature gradient in the cell, the assumption that the integrated cross sections are temperature independent and the spectral region chosen for integration. Changing the integration region used for calibration changes the cross sections by about 2%. The integrated areas for 2760–3050 cm^{-1} region for the PNNL cross sections at 278, 293, and 323 K are 344.1, 343.7 and 345.6×10^{-19} $\text{cm}^2/\text{molecule}$, respectively; a maximum difference of 0.6%. Estimates of the gas pressure in the cell using the ideal gas law suggest that calibration errors are in the range of 5–10%.

The assumption of temperature independent integrated cross sections is therefore the largest source of systematic error and increases with increasing temperature. Overall, the errors are therefore estimated to be the range of 10–15%, with the largest error at 739 K.

Conclusion

High resolution pure isobutane spectra were recorded at Old Dominion University for samples at 295, 355, 463, 573, 685 and 739 K in the C–H stretching region. Six transmission spectra were obtained by correcting for background emission and then converted to absorption cross sections. The PNNL cross sections for isobutane should be adjusted by dividing by a factor of 1.40. The cross sections for hot isobutane can be used to simulate atmospheric spectra of astronomical objects such as exoplanets and brown dwarfs that are expected to contain hydrocarbons.

Note

The PNNL cross sections for isobutane are correct. Therefore, the cross sections reported in this paper need to be multiplied by 1.40.

Credit author statement

P.F. Bernath: Methodology, Supervision, Writing - original draft.
A. Fernando: Formal analysis, Visualization, Investigation, Writing - review & editing.

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.

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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.2021.107644](https://doi.org/10.1016/j.jqsrt.2021.107644).

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