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Temperature-dependent high resolution absorption cross sections of propane

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ABSTRACT

High resolution (0.005 cm^{-1}) absorption cross sections have been measured for pure propane (C_3H_8). These cross sections cover the 2550–3500 cm^{-1} region at five temperatures (from 296 to 700 K) and were measured using a Fourier transform spectrometer and a quartz cell heated by a tube furnace. Calibrations were made by comparison to the integrated cross sections of propane from the Pacific Northwest National Laboratory. These are the first high resolution absorption cross sections of propane for the 3 μm region at elevated temperatures. The cross sections provided may be used to monitor propane in combustion environments and in astronomical sources such as the auroral regions of Jupiter, brown dwarfs and exoplanets.

1. Introduction

Propane (C_3H_8) is the second most abundant non-methane hydrocarbon (NMHC) in the Earth's atmosphere after ethane (C_2H_6) [1]. Propane and the other NMHCs only have a small radiative forcing effect on the Earth's atmosphere, nevertheless the chemistry of these molecules has a significant impact on the troposphere through the reaction with the hydroxyl radical (OH), which leads to the formation of acetone. This reaction also leads to the production of peroxyacetyl nitrate (PAN) [2], which has a relatively long lifetime in the upper troposphere where it acts as a reservoir for NO_x, a catalyst for the production of ozone [3].

Propane has been identified in a number of Solar System objects. These include the atmospheres of Jupiter, from observations with the Galileo Probe Neutral Mass Spectrometer [4], and Saturn, using the TEXES instrument on NASA's Infrared Telescope Facility [5]. For both planets, emission lines from the ν_{21} band (748 cm^{-1}) were detected [5,6]. Propane has also been detected on Titan, first in the stratosphere with infrared spectra from Voyager 1 [7–9] and more recently with TEXES [10] and the CIRS instrument onboard Cassini [11,12]. Efforts to accurately quantify the propane concentration on Jupiter, Saturn and Titan have suffered from a lack of reliable spectroscopic data [11,13] or laboratory spectra of sufficient resolution [5] for the regions covered by these instruments.

On board NASA's Juno mission [14] is the Jovian Infrared Auroral Mapper (JIRAM) [15], which is due to arrive at Jupiter in July 2016. The JIRAM spectrometer covers the 2–5 μm range and will be used to study hot emission in Jupiter's auroral regions that has been assigned to H_3^+ and a number of hydrocarbon species [16]. Although the JIRAM spectrometer has a relatively low spectral resolution, it has previously been shown [11] that recent high resolution propane spectra in the 7–15 μm regions [13] were crucial

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to accurately modeling the propane contribution in low resolution spectra of Titan, and thus enabling the detection of propene (C_3H_6) [17].

The existence of propane and other hydrocarbons in the atmosphere of Jupiter, Saturn, Titan and other Solar System objects indicates the possibility of such molecules existing in the atmosphere of cool brown dwarfs and exoplanets. Methane (CH_4) has already been detected in exoplanet atmospheres [18,19] and a number of additional hydrocarbons, including propane, are predicted to exist in the atmospheres of such objects [20,21]. The relatively cool temperatures of brown dwarf atmospheres result in their spectra being dominated by molecular features. Models have predicted brown dwarf atmospheres may include propane, although at much lower concentrations than methane or ethane [21]. The atmospheres of hot Jupiters and brown dwarfs provide environments at elevated temperatures that could contain complex hydrocarbons such as propane. However, the laboratory data on which spectral models for these objects rely are incomplete or not recorded under the appropriate temperatures or pressures.

Propane, an asymmetric top molecule with C_{2v} symmetry [22], has been the subject of a number of spectroscopic studies. Of the 27 fundamental modes of propane detailed in Shimanouchi [23], several have been studied at high resolution, including the ν_4 (a_1, 1476 cm^{-1}), ν_{18} (b_1, 1378 cm^{-1}), ν_{19} (b_1, 1338 cm^{-1}), ν_{24} (b_2, 1472 cm^{-1}) bands [24], the ν_9 band (a_1, 369 cm^{-1}) [25], the ν_{21} band (b_1, 748 cm^{-1}) [26], the ν_{26} (b_2, 748 cm^{-1}), $2\nu_{19}$ (a_1)-ν_{19} (b_1) (1338 cm^{-1}). High resolution absorption cross sections of the 690–1550 cm^{-1} [13] and 2550–3300 cm^{-1} [2] regions have also been measured. In the 3 μm region there are 8 C–H stretching modes (ν_1 (a_1), ν_2 (a_1), ν_3 (a_1), ν_{10} (a_2), ν_{15} (b_1), ν_{16} (b_1), ν_{22} (b_2) and ν_{23} (b_2)) of which 7 modes are allowed, with only the ν_{10} mode being forbidden [23], as such the spectrum of propane is extremely congested in this region.

Several molecular databases include data for propane. HITRAN [27] contains cross sections for propane, broadened by air, from Harrison and Bernath for 195–296.4 K at high resolution (0.015 cm^{-1}) in the range 2540–3300 cm^{-1} [2]. GEISA [28] includes cross sections for 220–2000 cm^{-1}, broadened by N_2, recorded at 296 K at a resolution of 0.25 cm^{-1}, as well as 8983 transitions in the range 700–800 cm^{-1}, the CH_2 rocking mode region at a resolution of 0.08 cm^{-1}. Absorption cross sections of propane broadened by N_2 are available from the Pacific Northwest National Laboratory (PNNL), recorded in the infrared at 278, 293 and 323 K, in the range 600–6500 cm^{-1} at medium resolution (0.1 cm^{-1}) [29]. Cross sections provided by Sung et al. [13] were also recorded, broadened by N_2, at various temperatures between 145–297 K, in the range 690–1550 cm^{-1} at resolutions of 0.0033–0.0056 cm^{-1}. Absorption cross sections for propane broadened by N_2 have been measured in the 3 μm region (2500–3400 cm^{-1}) at elevated temperatures [30], although at medium resolution (0.09 cm^{-1}) and relatively low temperatures (298, 373 and 473 K).

The efficiency of fuels and engines is important for industrial applications. The combustion reactions involved can be analyzed by sophisticated models, which include a large number of temperature dependent reactions from the constituents of fuels and the products of their combustion. To this end, spectra have been recorded to monitor a number hydrocarbons in combustion reactions [31–35].

Cross sections from high resolution spectra (0.1 cm^{-1} or better) of a number of hydrocarbons have been studied in the 3 μm region at elevated temperatures, including ethane [36], propylene (C_3H_6) [31,37], methane, ethane and ethylene (C_2H_4) [38]. Klingbeil et al. [31] have also obtained spectra of a number of larger hydrocarbons (12 in total) at 1 cm^{-1} resolution up to 500 °C. However there do not exist high resolution cross section measurements of propane for the 3 μm region. Such data are required to accurately model hot environments such as auroral regions on Jupiter, exoplanets or brown dwarfs. This paper addresses the lack of high resolution cross sections of propane at high temperature.

2. Experimental

High resolution (0.005 cm^{-1}) propane spectra were recorded between 2500 and 3500 cm^{-1}, at five temperatures from 296 K to 700 K using a Bruker IFS 125 Fourier transform spectrometer. This region contains the seven active C–H stretching modes [23] and a number of combinations and overtones of the various other modes. The propane gas (Airgas, 99.99% purity) is contained in an all quartz cell (i.e., with quartz windows) which is heated to the appropriate temperature using a tube furnace.

To obtain a transmission spectrum (τ) two individual spectra are recorded for each temperature and combined as,

$$\tau = \frac{A_{ab}}{A_{ref}}, \tag{1}$$

where the C_3H_8 absorption component is given by A_{ab} and A_{ref} is the background spectrum.

The conditions for the experiment are detailed in Table 1. At higher temperatures (600 and 700 K) there is an emission component which is significant enough that it must be corrected for. As a result two additional spectra were recorded for these temperatures without the infrared source, one with propane in the sample cell and one without. These emission spectra were subtracted from A_{ab} and A_{ref} respectively. The experimental setup and procedure for obtaining the transmission spectrum are

Table 1
Experimental conditions and setup of the Bruker 125 HR.

Spectral range (cm^{-1})	2500–3500
Temperature range (K)	296–700
Resolution (cm^{-1})	0.005
Cell path length (cm)	50
Detector	InSb
Filter	Germanium
Windows	CaF_2
Beamsplitter	CaF_2
Number of scans	300