



## Infrared absorption cross sections for propane ( $C_3H_8$ ) in the $3\ \mu m$ region

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### ABSTRACT

Infrared absorption cross sections for propane have been measured in the  $3\ \mu m$  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.

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### 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  $10.6\text{--}12\ Tg\ yr^{-1}$  [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  $NO_x$ .

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Nearly all tropospheric ozone results from the photolysis of  $\text{NO}_2$ , 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  $4400\text{ cm}^{-1}$  [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 ( $0.112\text{ cm}^{-1}$ ) 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  $2968\text{ cm}^{-1}$ . 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 ( $0.015\text{ cm}^{-1}$ ) 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  $3300\text{ cm}^{-1}$ .

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  $748\text{ cm}^{-1}$   $\nu_{26}$  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  $80^\circ\text{S}$  to  $70^\circ\text{N}$ . 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 ( $30^\circ\text{S}$ – $30^\circ\text{N}$ ), 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  $748\text{ cm}^{-1}$  ( $\nu_{26}$ ) and  $1376\text{ cm}^{-1}$  ( $\nu_{18}$ ). 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  $3500\text{ cm}^{-1}$ . The overall intensity of infrared radiation falling on the InSb detector was therefore maximised in the region of interest without saturating the detector.

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