Relative high-resolution absorption cross sections of $\text{C}_2\text{H}_6$ at low temperatures

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**A B S T R A C T**

Synchrotron radiation has been used to record absorption cross sections of ethane, $\text{C}_2\text{H}_6$, in the far-infrared with very high spectral resolution (up to 0.00096 cm$^{-1}$). $\text{C}_2\text{H}_6$ is present in the atmospheres of the Gas Giant planets and Titan but the vapor pressure at relevant atmospheric temperatures (i.e., between 70 and 200 K) is low. This makes laboratory measurements difficult. We demonstrate the effectiveness of a unique “enclosive flow” cold cell, located at the Australian Synchrotron, that enables high-resolution absorption cross sections of gaseous $\text{C}_2\text{H}_6$ to be recorded at 90 K.

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1. Introduction

Remote sensing can be used to determine the physical and chemical properties of the outer planets and their satellites. Current instruments, such as the Composite Infrared Spectrometer (CIRS) aboard the Cassini space probe [1], make use of spectroscopic databases for retrievals. This is done by matching an observed planetary spectrum to a calculated spectrum from a forward radiative transfer model with assumed parameters as a function of altitude (e.g., temperature, pressure and composition). Thus, remote sensing is entirely dependent on the availability of suitable spectroscopic data.

The spectroscopic data are generally available as either line parameters or absorption cross sections. Line parameters for small molecular species (e.g., $\text{H}_2\text{O}$) can be found in spectroscopic databases, such as HITRAN [2], which have been compiled for the study of the Earth’s atmosphere. However, line parameters are not available for all molecules over the complete spectral range of remote sensing instruments (e.g., CIRS covers 10–1400 cm$^{-1}$), and for larger molecular species (e.g., benzene) it is typically more appropriate to use absorption cross sections due to the blended nature of the infrared spectrum.

Ethane ($\text{C}_2\text{H}_6$) is responsible for prominent features in the spectra of the outer planets, comets and Titan. $\text{C}_2\text{H}_6$ has 12 vibrational modes, of which only 5 are infrared active ($D_{3h}$ symmetry). Complete line assignments are difficult to obtain partly due to the low-lying torsional mode ($v_3$) near 35 μm (290 cm$^{-1}$) [3–6]. This leads to a large number of low frequency hot bands, extensive perturbations and a very dense line structure. To date, the $v_9$ mode near 12 μm (830 cm$^{-1}$) contains the most complete assignments due to extensive work reported in references [7–9]. Recent line parameters and partial assignments have also been provided for the $v_8$ band near 6.8 μm (1470 cm$^{-1}$) [10,11] as well as the 3.3 μm (3000 cm$^{-1}$) region that contains the $v_5$ and $v_7$ modes [12,13]. Although considerable progress has been made in these recent studies, high-resolution analyses generally still fail to match laboratory observations precisely.

The Pacific Northwest National Laboratory (PNNL) has recorded infrared absorption cross sections for a large number of species, including $\text{C}_2\text{H}_6$ (see http://nwir.pnl.gov and [14]). These spectra cover the 600–6500 cm$^{-1}$ spectral range; however, these data are not always suitable for remote sensing of planetary atmospheres because of the temperature (278, 293 and 323 K), pressure (760 Torr of $\text{N}_2$) and resolution (0.112 cm$^{-1}$) at which the data were recorded. The main problem with using relatively low resolution absorption cross sections is that spectroscopic features (e.g., sharp Q-branches) are under-resolved and give incorrect radiative transfer. Due to these issues, Harrison et al. [15] have provided high-resolution infrared cross sections of the 3.3 μm band intended for retrievals of terrestrial $\text{C}_2\text{H}_6$ from atmospheric observations. Whilst these measurements extend the absorption
cross sections of C₂H₆ to lower temperatures, the air-broadened spectra are unsuitable for planetary retrievals. Nixon et al. [16] highlighted the importance of reliable high-resolution spectroscopic data for planetary retrievals by observing propane (C₃H₈) in the atmosphere of Titan. This was made possible after the removal of propane (C₃H₈) by using the latest absorption cross sections obtained from a series of N₂-broadened spectra at temperatures as low as 145 K [17].

The primary constituents of the atmospheres of Jupiter and Saturn are hydrogen and helium, approximately 86% H₂ and 14% He for Jupiter and 88% H₂ and 12% He for Saturn (by mole fraction [18]). In each case, trace gases account for less than 1% of the atmosphere, of which methane is the most abundant (~ 0.3%), but C₂H₆ provides a detectable contribution (~ 0.0004%). The atmospheric profiles of Jupiter and Saturn demonstrate that the majority of C₂H₆ is found at a typical temperature range of around 70–200 K [19].

Titan is the only moon in the Solar System with an appreciable atmosphere, approximately 95% N₂ and 5% CH₄ at a total pressure of 1.5 atm at the surface [20,21]. The trace species are mainly hydrocarbons formed from the photolysis of CH₄ [22] and subsequent reactions, as is the case for C₂H₆ [23]. In Titan, the atmospheric profile indicates that the majority of C₂H₆ is found at a typical temperature of 70–180 K [19], and pressures between 0.075 and 75 Torr (~ 40–300 km) [24].

Hence, it would be appropriate to have cross-sections of C₂H₆ over a temperature range 70–200 K that are broadened by H₂ and He (Jupiter and Saturn) as well as N₂ (Titan). Absorption cross sections of C₂H₆ have not previously been provided over the complete temperature range due to the low vapor pressure at low temperatures (~ < 1 Torr below 110 K [25]). Planetary atmospheres provide extremely long effective path lengths that are difficult to obtain and often impractical for laboratory conditions. Conventional cooling of the gas typically leads to the C₂H₆ condensing on the cell walls.

The aim of this work is to provide high-resolution cross sections of C₂H₆ that includes all of the fundamental bands over the appropriate temperature ranges and conditions of the outer planets and Titan. This will be completed using a Fourier transform spectrometer (FTS), cold cell and infrared source at Old Dominion University (ODU) as well as with synchrotron sources. This paper introduces our latest experiments at the Australian Synchrotron (AS), which provides the necessary source and cell to enable high-resolution absorption cross sections to be recorded at temperatures and ranges that are difficult or excessively time consuming to obtain using the equipment available at ODU.

2. Synchrotron radiation

Synchrotron radiation has a number of advantages over a traditional radiation source (typically a glower) when recording high-resolution spectra in the far/mid infrared region using an FTS [26]. Many benefits will be discussed in this special issue, but only key improvements are mentioned here.

The narrow intense beam provided by a synchrotron allows small apertures to be used, and therefore high spectral resolutions. The signal-to-noise at wavelengths longer than 10 μm is improved by at least a factor of three when compared to a glower. Since the signal-to-noise ratio increases as the square root of integration time, this leads to a reduction in acquisition time by almost a factor of 10. Due to the large number of spectra that are required to obtain high-resolution infrared cross sections at relevant temperatures and pressures, synchrotron radiation is a valuable (and under-exploited) source for absorption cross sections of vibrational bands at wavelengths longer than 10 μm.

3. Measurements

The Far IR/THz beamline of the AS provides a Bruker IFS 125 spectrometer with a maximum optical path difference (MOPD, Δ) of 9.3 m and therefore, a maximum resolution R = 0.00096 cm⁻¹ is possible (R ~ 0.9/Δ using the Bruker definition). The AS also has unique access to a cooled gas cell that has been designed to record spectra of gases at low temperatures [27] based on a cell designed for supercooling molecular clusters [28]. The cell can be used in two operating modes depending on the temperature and gas of interest. The standard static mode is when the sample gas is sealed within the cell at fixed pressure during measurements. The second mode is known as “Enclosive Flow Cooling” (EFC) and is achieved by enclosing the sample gas within a laminar flow of buffer gas to avoid condensation on the cell walls. The enclosive conditions are created by introducing the sample gas at the center of a vertical cell with an exhaust at the base. A buffer gas is introduced to the cell from all directions as it has to pass through a cylinder with holes (the colander) before reaching the exhaust. The gases are drawn through the cell by the exhaust, thus creating a columnar laminar flow that constrains the sample gas to the center of the cylinder (see reference [27] for diagram). The EFC cell has a maximum path length of 20 m, but since the sample gas is rapidly cooled by the buffer gas without freezing out on the walls, the enclosive mode allows spectra to be acquired that are more typical of longer path lengths (e.g., planetary atmospheres) at low temperatures.

The AS is crucial for measurements at wavenumbers below 1000 cm⁻¹, particularly at low temperatures (~ < 110 K) since the natural vapor pressure of C₂H₆ requires long path lengths (e.g., enclosive flow measurements). Temperatures as low as 200 K can be reached at ODU using a static ethanol cooled cell with a 20 cm path length [29]. The MOPD for the Bruker spectrometer at ODU is 4.3 m, corresponding to a spectral resolution of 0.0021 cm⁻¹. For wavenumbers greater than 1000 cm⁻¹, measurements at ODU will be able to reach the sensitivity of synchrotron spectra. However, measurements at wavenumbers less than 1000 cm⁻¹ should be conducted at a synchrotron. Current work is being done at the Canadian Light Source (CLS) to provide a static liquid-N₂ cooled cell that is capable of taking measurements when the C₂H₆ vapor pressure remains relatively high (i.e., T > 110 K).

Each PNNL cross section is a composite of approximately ten pathlength concentrations, making these data suitable for calibration. Since the integrated band intensities are independent of temperature, the PNNL data will be used to calibrate our high-resolution cross sections, as done previously [15]. Combining the

### Table 1

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Source</th>
<th>C₂H₆ pressure (Torr)</th>
<th>N₂ pressure (Torr)</th>
<th>Resolution (cm⁻¹)</th>
<th>Scans</th>
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<td>0.002</td>
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</tr>
</tbody>
</table>

* Path length of 2 m.

**Enclosive conditions.
spectra from all three locations (ODU, AS and CLS) will enable the high-resolution infrared cross section of C$_2$H$_6$ to be provided for all the fundamental bands at the appropriate temperature ranges of the outer planets and Titan.

4. Proof of concept

Measurements were taken at the AS during February 2014 to test the feasibility of the low vapor pressure measurements of C$_2$H$_6$. N$_2$-broadened spectra were taken at four temperatures (200, 160, 120 and 90 K) using the synchrotron and EFC cell. The results cover the appropriate temperature range and atmospheric conditions of Titan and are summarized in Table 1.

Fig. 1 displays the N$_2$-broadened spectra of C$_2$H$_6$ at 200 K and demonstrates the reduction of spectral resolution on the $^7$Q$_3$ (near 814.5 cm$^{-1}$) and $^5$Q$_2$ (near 817.1 cm$^{-1}$) sub-bands with increasing pressure. The spectra are recorded at a higher resolution than the observed pressure-broadened linewidth (primarily due to N$_2$-broadening) and a corresponding background spectrum (i.e., empty cell) was recorded to create the transmittance spectra. Reflections in the beamline due to windows and mirrors, required to direct the beam through the EFC cell, result in a strong channeling that causes a sine-like wave to be present in the baseline due to interference. This channeling effect is partly removed by dividing by the background, but a residual effect can be seen in the fluctuating intensities of the highest resolution spectra (top two spectra of Fig. 1).

The cell is cooled and maintained at a specified temperature using the boil-off from liquid-N$_2$. Measurements at 200, 160 and 120 K demonstrated the feasibility of using the EFC cell in static mode at the temperatures appropriate for the outer planets and Titan. The same cooling method is used to reach a temperature of 90 K where the vapor pressure of C$_2$H$_6$ is approximately 0.02 Torr [25]. Fig. 2 displays the spectra of two measurements at 90 K for the $^5$Q$_1$ sub-band near 819.7 cm$^{-1}$ (described in Table 1). These two spectra demonstrate the significant improvement between enclosive and static modes when using the EFC cell.

5. Discussion

The temperature range observed in the atmospheres of the outer planets and Titan (70–200 K) can prove difficult for some important gases (e.g., C$_2$H$_6$ and C$_3$H$_8$). When using the EFC cell at the AS in static mode, the vapor pressure of C$_2$H$_6$ at 90 K is too low to record a suitable spectrum with a 2 m path length. This paper demonstrates that when using the enclosive technique provided by the EFC cell, spectra can be recorded of C$_2$H$_6$ at 90 K. From spectra of this type, we are able to produce a set of absorption cross sections. It has previously been demonstrated that integrating an absorption cross section over an isolated band comprising primarily of fundamentals exhibits an insignificant temperature dependence [15,30–36]. For the PNNL spectra of C$_2$H$_6$ at 278, 293 and 323 K, the integrated absorption cross section between 700 and 960 cm$^{-1}$ is calculated as

$$\int_{700\text{cm}^{-1}}^{960\text{cm}^{-1}} \sigma(v, T) dv = 1.014(\pm 0.003) \times 10^{-18} \text{ cm molecule}^{-1}.$$  \hspace{1cm} (1)

with less than 0.3% change between temperatures.$^1$

Absorption cross sections can be calculated from a transmittance spectrum $\tau(v, T)$ as

$$\sigma(v, T) = -\frac{1}{\tau} \frac{10^4 k_b T}{P I} \ln \tau(v, T).$$  \hspace{1cm} (2)

$^1$ PNNL units (ppm$^{-1}$ m$^{-3}$ at 296 K) have been converted using the factor $k_b \times 296 \times \ln(10) \times 10^4 / 0.101325 = 9.28697 \times 10^{-16}$ [35].
where $v$ in the wavenumber (cm$^{-1}$), $T$ is the temperature, $k_B$ is the Boltzmann constant, $P$ is the pressure of the absorbing gas (Pa), $l$ is the optical pathlength (m) and $\zeta$ is a normalization factor [15,35]. This procedure is based on the assumption that the integrated band intensity does not vary as a function of temperature and $\zeta$ is used to account for the difficulty in determining the amount of absorbing gas with great accuracy. For the static mode observations, the pressure and temperature of the absorbing gas can be recorded and the absorption cross sections can be calculated easily using Eq. 2. However, determining the sample gas pressure for the enclosive measurements is not a simple problem, as the gas is no longer in thermal equilibrium. Therefore, only an effective pressure ($P_{\text{eff}}$) of the column can be determined. Since it is assumed that the integrated band intensity is unchanged, it is possible to calculate $P_{\text{eff}}$ for the enclosive measurement at 90 K by assuming $\zeta = 1$ and the temperature in the cell is uniform. The EFC cell has been designed to minimize temperature gradients during enclosive flow, but nevertheless a small gradient will remain over the whole path-length. Whilst this will not greatly affect the integrated absorption intensities, it is worth noting that the measured temperature will actually be an effective temperature and will also need to be considered in the error budget. Analysis of the preliminary 90 K data suggest $P_{\text{eff}}$ is greater than measured during the experiment (Table 1) thereby demonstrating the benefit of the enclosive method at temperatures when the vapor pressure is low, such as $C_2H_6$ at 90 K. These measurements are preliminary and further measurements are necessary to produce acceptable cross sections.

Another way to obtain line parameters is by using a set of pseudo-lines, which are provided on a frequency grid and are treated as if they are real transitions [38,39]. These pseudo-lines are then able to reproduce the cross sections over the temperature range as demonstrated for $C_2H_6$ [17].

The measurements presented here will be expanded to provide cross sections of the fundamental bands of $C_2H_6$ for remote sensing of the outer planets and Titan. These cross sections will cover the appropriate atmospheric temperatures (70–200 K) and will include the relevant broadening gases (H$_2$ and He for the Gas Giants, N$_2$ for Titan). We intend to continue the EFC measurements for molecules that have low vapor pressures at warmer temperatures than for $C_2H_6$. One example is $C_3H_8$, which has a vapor pressure of < 1 Torr at 140 K [25].

**References**


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