Absorption cross-section measurements of methane, ethane, ethylene and methanol at high temperatures

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Abstract

Mid-IR absorption cross-sections are measured for methane, ethane, ethylene and methanol over 2800 – 3400 cm^{-1} (2.9 - 3.6 μm) spectral region. Measurements are carried out using a Fourier-Transform-Infrared (FTIR) spectrometer with temperatures ranging 296 – 1100 K and pressures near atmospheric. As temperature increases, the peak cross-sections decrease but the wings of the bands increase as higher rotational lines appear. Integrated band intensity is also calculated over the measured spectral region and is found to be a very weak function of temperature. The absorption cross-sections of the relatively small fuels studied here show dependence on the bath gas. This effect is investigated by studying the variation of absorption cross-sections at 3.392 μm using a HeNe laser in mixtures of fuel and nitrogen, argon, or helium. Mixtures of fuel with He have the highest value of absorption cross-sections followed by Ar and N_2 . Molecules with narrow absorption lines, such as methane and methanol, show strong dependence on bath gas than molecules with relatively broader absorption features i.e. ethane and ethylene.

Keywords: Methane; Ethane; Ethylene; Methanol; Absorption cross-section; FTIR, HeNe laser

1. Introduction

Laser-based diagnostic techniques are used in a variety of fields to measure the abundance of species of interest. Spectral absorption features span different wavelength regions from ultraviolet (UV) to visible to infrared (IR) and more. The absorption strength of molecules at various wavelengths is governed by molecular structure and oscillator strengths. Chemical species containing a C-H bond have a fundamental vibrational mode, known as the C-H stretch, in the IR region near 3.3 μm . Absorption of radiation by this vibrational mode can be readily accessed by helium-neon (HeNe) lasers or difference-frequency-generation (DFG) based tunable laser systems [1, 2]. These two laser systems can be used to develop fast time-response *in-situ* diagnostics to detect various hydrocarbons. For example, MacDonald et al. [3] used HeNe laser absorption at 3.392 μm to measure fuel concentration during the pyrolysis of n-dodecane, methylcyclohexane, and iso-cetane in a heated high-pressure shock tube. The species studied in this work (methane, ethane, ethylene and methanol) represent three different chemical groups: alkanes, alkenes and alcohol. These basic species are very important in combustion, atmospheric applications and remote sensing.

Quantitative measurements of species concentration using absorption spectroscopy require knowledge of absolute absorption cross-sections. The cross-sections of various hydrocarbons near 3.3 μm have previously been measured using FTIR spectrometer and HeNe laser. Klingbeil et al. [4] used an FTIR spectrometer to measure the spectra of twelve hydrocarbons over 2500 – 3400 cm^{-1} region for temperatures ranging from 298 to 773 K. Essabbar et al. [5, 6] measured vacuum-UV and IR spectra of 1-butene and IR spectra of propylene in the temperature range of 296 – 529 K. Etzkorn et al. [7] measured UV and IR absorption cross-sections of 24 aromatic hydrocarbons at 298 K for atmospheric applications. The infrared

absorption cross-sections of ethane and methanol were reported by Harrison et al. [8, 9] at 296 K. Also, Harrison and Bernath [10] measured the infrared absorption cross-section of propane at 296 K. Furthermore, several databases have been compiled for hydrocarbon spectra, such as HITRAN [11], NIST [12] and PNNL [13]. The HITRAN database has primarily been validated at low temperatures and its high-temperature version HITEMP only contains H₂O, CO₂, CO, NO, and OH spectra. The NIST and PNNL databases provide absorption cross-sections of many species at low temperatures (up to 50 °C). For several important hydrocarbons, such as methane and ethylene, absorption cross-section data are not available at temperatures larger than 500 °C. High-temperature cross-section data are critical for developing laser-based sensors for combustion applications.

Although FTIR spectrometer can measure cross-section data over a range of wavelengths, HeNe laser has the advantages of narrow line-width, low cost and ease of operation. Olson et al. [14] reported the absorption coefficient of 7 hydrocarbon fuels in the temperature range of 300-2000 K using a shock tube. Mallard and Gardiner [15] studied the absorption cross-section of methane from 300 to 2400 K using a shock tube. Tsuboi et al. [16] used a shock tube facility to measure the molar extinction coefficients of different hydrocarbons over 292-1100 K. Perrin and Hartmann [17] measured the absorption of methane in the temperature range of 290 - 800 K and then reported the calculated absorptivity up to 3000 K. Drallmeier measured room-temperature (296 K) absorption coefficient of different hydrocarbon species; paraffins, olefins and aromatics [18]. The dependence of absorption cross-sections on temperature (298 to 673 K) and pressure (500 to 2000 Torr) at 3.39 μm for different gaseous hydrocarbons was investigated by Klingbeil et al. [19]. Mevel et al. [20] reported the gas phase absorption cross-sections of 21 liquid hydrocarbons in the temperature range of 303- 413 K and suggested a correlation to calculate the

absorption cross-section based on the chemical structure of species. The dependence of the cross-sections on bath gas has not been studied well before. Therefore, the cross-sections dependence on the argon, helium and nitrogen are studied in this work.

In this work, we report the spectra of methane, ethane, ethylene and methanol at high temperatures (296 – 1120 K) over 2800 to 3400 cm^{-1} (2.9 – 3.6 μm) region. This wavelength region is important due to relatively high absorption strengths and is accessible by HeNe laser (3.392 μm) or tunable difference-frequency-generation (DFG) laser systems. Therefore, these measured high-temperature spectra are needed to design interference-free quantitative absorption diagnostics for combustion applications. Effect of instrument broadening is considered by comparing measurements performed by FTIR spectrometer with HeNe laser. Additionally, the effect of bath gases on absorption cross-sections is analyzed by performing measurements in argon, helium and nitrogen.

2. Experimental Setup

Experimental setup used in this work is shown in Fig. 1. Fourier Transform Infrared (FTIR) spectrometer is a valuable device to measure absorption cross-sections over a wide range of wavelengths. The FTIR spectrometer used is Bruker VERTEX 80v and its broadband beam is modulated through the Michelson interferometer. This modulated beam passes through a heated cell and is detected by the detector. The FTIR can operate over 700 to 8000 cm^{-1} with a minimum spectral resolution of 0.08 cm^{-1} . Table 1 lists the operating conditions of the FTIR used in this work. In all measurements, a reference/baseline signal is recorded when the cell is evacuated and the transmitted signal is recorded after sample is introduced in the cell. Another reference/baseline signal is recorded after pumping out the sample from the cell. The difference

between the baseline before and after the sample measurement is generally quite small. In this work, the FTIR wavelength was calibrated for each hydrocarbon with the corresponding spectra from Sharpe et al. [13] at 298 K.

Fixed-wavelength measurements were carried out using a helium-neon (HeNe) laser (2.0 mW, Newport, R-32172). Its center wavenumber was measured by Bristol Spectrum Analyzer and found to be at 2947.909 cm^{-1} , as suggested by Mallard and Gardiner [15]. Spectral resolution of the HeNe laser is approximately 0.01 cm^{-1} (FWHM). Common-mode-rejection (CMR) scheme is used to account for laser intensity fluctuations. A calcium-fluoride beam splitter is used to direct part of the beam to the reference detector 1 (Vigo Systems, PVMI-3TE-10.6, 2 mm x 2 mm active area) while the rest of the beam is transmitted to detector 2 which is identical to detector 1. An iris is used before each detector to minimize broadband emission from the furnace.

Quartz cell is placed inside a tube furnace (Fisher Scientific, model BlueBird) where the 7.747 cm long test section is within the uniform temperature region of the furnace. The two outer sections of the quartz cell are evacuated to avoid ambient absorption by $\text{CO}_2/\text{H}_2\text{O}$ along the laser path. The temperature of the test gas is measured by four equally spaced K-type thermocouples (Omega) along the test section. All measurements at temperatures higher than 650 K are carried out using the quartz cell. Lower temperature measurements are carried out using a stainless-steel 10-cm long cell. This cell is equipped with a heating jacket and is placed inside the FTIR compartment; details of this cell can be found elsewhere [5].

Pressure of the gas mixture is monitored by two capacitance manometers with full-scale ranges of 20-Torr and 1000-Torr (Baratron MKS 620A). A magnetically-stirred mixing vessel is

used to prepare mixtures of the hydrocarbons with bath gas. The optical cell is evacuated using a vacuum pump to pressures less than 0.001 Torr, with outgassing rate of less than 0.005 Torr/min. Three measurements of the cross-section are taken at each temperature and then averaged. All spectra presented in this work are measured at a pressure of 760 Torr (1 atm). All bath gases (argon, nitrogen and helium) have a purity of 99.999%, while methane, ethane and ethylene have purities of 99.999%, 99.9995% and 99.95%, respectively. All gases were supplied by AHG Gases. Methanol is supplied by Sigma-Aldrich with a purity of 99.8%.

When measuring the absorption cross-section of hydrocarbons at high temperatures, thermal decomposition must be taken into consideration. Chemkin-Pro commercial software with detailed chemical kinetic mechanism of Marinov et al. [21] was used to simulate thermal decomposition of methane, ethane, ethylene, and methanol as a function of temperature. At high temperatures where decomposition of the fuel can occur, the static cell experiments were replaced with flow experiments which reduced the residence time of the gas sample inside the heated quartz cell thereby avoiding the decomposition of fuel. The flow rates were controlled by a combination of inlet and outlet metering valves. Flow experiments were used during the measurements of methane, ethane, ethylene and methanol spectra at temperatures higher than 900 K.

3. Data Analysis

Beer-Lambert law describes the absorption of monochromatic light passing through a uniform medium:

$$A_v = -\ln \left(\frac{I}{I_0} \right) = \sigma_v \cdot L \cdot n \quad (1)$$

where A_v is the absorbance, I_0 is the reference signal, I is the transmitted signal, σ_v is the absorption cross-section in $\text{cm}^2/\text{molecule}$, L is the optical path length in cm, and n is the concentration of the gas in cm^{-3} . Absorption cross-section can be calculated by:

$$\sigma_v = \frac{A_v kT}{PL} \quad (2)$$

where k is the Boltzmann's constant ($k = 1.38065 \times 10^{-23}$ J/K), P is the pressure and T is the temperature of the gas. Integrated band intensity is the integration of the absorption cross-sections over an entire vibrational band or over a certain wavelength region. In this work, cross-sections are integrated over $2500 - 3400 \text{ cm}^{-1}$ to calculate the integrated band intensity by:

$$S_v = \int \sigma_v dv = \frac{kT}{PL} \int A_v dv \quad (3)$$

Detailed uncertainty analysis is carried out to estimate the errors in the measured absorption cross-section and the integrated band intensity. According to equations (2) and (3), there are five sources of uncertainty: absorbance, mole fraction, temperature, pressure and path length. In this work, absorbance (A_v) values generally varied between 0.2 and 2 which resulted in relatively high signal-to-noise-ratio (SNR). The uncertainty on the absorbance is taken from the standard deviation of the recorded data. The uncertainty on the mole fraction of the fuel is due to the partial pressure of the fuel and the total pressure. The uncertainty of the two pressure gauges (Baratrons) used is $\pm 0.12\%$ of the reading. To avoid the adsorption of methanol, a liquid fuel, to the walls of the mixing vessel, the partial pressure of methanol is kept at less than half of its saturation vapor pressure at 296 K. The temperature uncertainty comes from the temperature profile in the test section and the uncertainty of the thermocouple readings. The pressure remains almost constant during the experiment and the uncertainty of the test pressure is $\pm 0.12\%$ of the

reading. The uncertainty in the path length is due to the expansion of the two optical windows with temperature and the path travelled by the laser beam. The overall uncertainty of the absorption cross-section (or the integrated band intensity) is given by:

$$\frac{d\sigma_v}{\sigma_v} \text{ (or } \frac{dS_v}{S_v} \text{)} = \sqrt{\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta x_i}{x_i}\right)^2 + \left(\frac{\Delta T}{T}\right)^2 + \left(\frac{\Delta P}{P}\right)^2 + \left(\frac{\Delta L}{L}\right)^2} \quad (5)$$

The uncertainty of the measured absorption cross-section is calculated to be less than 5% for lower temperatures and about 8% for temperatures higher than 700 K.

4. Results and Discussion

Absorption cross-sections of methane, ethane, ethylene and methanol are reported here over a temperature range of 296 – 1100 K. The FTIR spectrometer is used to measure spectra over the wavelength range of 2800 – 3400 cm^{-1} . HeNe laser, operating at 3.932 μm , is used to measure the absorption cross-section at a fixed frequency. Finally, the effect of bath gas on absorption cross-sections is analyzed by making measurements in helium, argon and nitrogen as bath gases.

4.1. Temperature-dependent mid-IR spectra

Absorption cross-sections of methane, measured by the FTIR, are plotted in Figure 2 as a function of temperatures (296 - 1120 K) over 2800 – 3300 cm^{-1} region. Methane spectra in this region consist of relatively narrow absorption lines and the spectra are dominated by strong absorptions due to the ν_3 C-H stretching mode and small contribution from the $\nu_2+\nu_4$ combination band [22]. It can be observed from Fig. 2 that as temperature increases, peak transition intensity decreases while higher rotational levels get populated and the band continuum increases. As discussed earlier, to ensure methane does not undergo decomposition during high-temperature measurements (919 K, 1120 K), a flow experiment is used to reduce the

residence time. The FTIR measurements are performed with a spectral resolution of 0.16 cm^{-1} for low temperature ($T < 500\text{ K}$) and 0.6 cm^{-1} for experiments at temperature higher than 500 K . The later resolution was selected to maximize the signal-to-noise ratio for high-temperature measurements where the mid-IR beam was directed through the furnace and had relatively low transmitted intensity.

Figure 3 shows ethane spectra recorded over $2800 - 3200\text{ cm}^{-1}$ region by FTIR at five temperature values from 296 to 921 K . The absorption spectra exhibit strong absorption assigned to ν_7 C-H stretching mode together with small contribution of ν_{10} feature near 2985 cm^{-1} [22]. Similar to methane, the peak intensities decrease with increasing temperature and the band continuum increase. In the insert of the same figure, ethane spectrum obtained at 296 K with a resolution of 0.16 cm^{-1} are compared with the PNNL data measured at 0.112 cm^{-1} spectral resolution [13]. The two spectra agree very well with each other confirming that the chosen resolution of 0.16 cm^{-1} is sufficient to resolve various features of ethane spectrum.

Ethylene spectra measured between 2850 and 3250 cm^{-1} are shown in Fig. 4 as a function of temperature. The ν_{11} feature located near 2988 cm^{-1} [22] is dominant in this region. The gas temperature has the same effect as discussed above for methane and ethane. The change in the peak intensity with temperature is illustrated in the insert of the figure for the ν_{11} peak near 2988 cm^{-1} . The cross-sections of ethylene are weaker than ethane because of the replacement of the C-H bond by the C=C bond.

The measured absorption cross-sections of methanol in the spectral range of $2750 - 3400\text{ cm}^{-1}$ are presented in Fig. 5 as a function of temperature ($296 - 778\text{ K}$). Recently, high-resolution (0.015 cm^{-1}) absorption spectra of methanol were measured near $3.3\text{ }\mu\text{m}$ at low temperatures

(204 – 296 K) by Harrison et al. [9]. There are three fundamental vibrational modes in this region which are ν_2 , ν_3 and ν_9 with values of 2999, 2844 and 2970 cm^{-1} , respectively [22]. Absorption cross-sections of methanol are weaker than methane due to the replacement of the C-H bond with the C-O one. However, methanol spectrum is relatively broad due to the contribution of neighboring bands of methanol.

4.2 . Integrated band intensities

Since absorption cross-sections are measured as a function of temperature at two spectral resolutions (0.16 and 0.6 cm^{-1}), it is interesting to discuss our results in terms of the integrated intensities. The integrated intensities of the four studied hydrocarbons over the spectral region 2500 – 3400 cm^{-1} are listed in Table 2 at 296 K. The obtained results are compared with data available in the literature. Our values are in good agreement with previous measurements of Sharpe et al. [13], Klingbeil [23], and Harrison et al. [8, 9] with a maximum difference of about 6%. The integrated band intensity of ethane is higher than methane since the band intensity for alkanes increases as the number of the C-H bonds increases [24]. Ethylene has lower integrated band intensity due to the replacement of C-H bonds with C=C double bond. Although the peak absorption cross-section of methanol is lower than methane, it has higher integrated band intensity due to the overall broader spectrum that results from additional vibrational modes.

The integrated band intensities are also calculated at higher temperatures and are presented in Table 3. Over the studied temperature range, the band intensities vary by about 10%, 12%, 7%, and 1% for methane, ethane, ethylene and methanol, respectively. It cannot be said conclusively whether the integrated band intensities exhibit slight temperature dependence or if the observed variations are the result of experimental uncertainties. It has been reported

previously [6, 25, 26] that the band intensities of fundamental vibrational bands can exhibit small temperature dependence because of the overlap from other bands.

The effect of spectral resolution on the integrated band intensities is also studied. Methane spectra at conditions similar to this work were simulated using HITRAN [11] database and a Voigt profile with spectra resolution of 0.01 cm^{-1} ; integrated band intensities are compared in Table 4. Even though the spectra from HITRAN have higher resolution (0.01 cm^{-1}) than the measurements (0.16 or 0.6 cm^{-1}) reported here, the integrated band intensities are in good agreement with a maximum difference of 8.7% at the highest temperature. This difference at the highest temperature could be because of hot band transitions not included in the HITRAN database. In another work on spectral measurements of propylene (C_3H_6), it was demonstrated that the integrated band intensities at various spectral resolutions were within 2% of each other [6].

4.3 . Bath gas dependent absorption cross-sections at $3.392\text{ }\mu\text{m}$

A helium-neon (HeNe) laser is used to measure the absorption cross-sections at $3.392\text{ }\mu\text{m}$ for methane, ethane, ethylene and methanol with three bath gases (argon, nitrogen and helium). Figure 6 shows the absorption cross-sections of methane measured over a temperature range of $296 - 1045\text{ K}$ and pressure near 760 Torr . Our measured values are compared with previous measurements by Klingbeil et al. [19] Perrin and Hartmann [17], Tsuboi et al. [16], Harrison et al. [8, 9] and Olson et al. [14] using HeNe laser at temperatures less than 600 K . As expected, the absorption cross-sections decrease with increasing temperature as the population in ground state reduces.

Absorption cross-sections of methane show dependence on bath gas at relatively low temperatures (less than 400 K). To further investigate the effect of bath gas on methane cross-sections, series of measurements were conducted at 296 K and varying total pressure (200 – 1000 Torr). Results are shown in Fig. 7 for 1% CH₄ in He, Ar, and N₂. The measured cross-sections exhibit pressure dependence as methane has relatively narrow absorption features. For example, the cross-section decreases by a factor of 2 when increasing the pressure from 200 to 1000 Torr in CH₄/Ar mixture. At all pressures, the mixture of methane with helium has the highest cross-section, followed by CH₄/Ar and CH₄/N₂ mixtures. This trend is observed because absorption cross-section is inversely related to the collisional broadening coefficient. The HeNe laser measurements are carried out at a frequency of 2947.909 cm⁻¹ which is quite close to the line-center frequency, 2947.912 cm⁻¹, of the P(7) rotational transition of methane. For the P(7) transition, the collisional broadening coefficients (γ) of CH₄-He, CH₄-Ar and CH₄-N₂ at 296 K are 0.048 [15], 0.056 [27] and 0.063 [27] cm⁻¹/atm, respectively. This dependence of methane cross-section on bath gases was also reported by Tsuboi et al. [28] in their theoretical study. In their calculations, the absorption cross-section of CH₄-N₂ mixture is less by 35% and 10% compared to absorption cross-sections of CH₄-He and CH₄-Ar mixtures, respectively. Our experimental measurements show the corresponding decrease to be 28% and 10%.

Absorption cross-sections of methanol measured by HeNe laser are shown in Fig. 8 as a function of temperature and bath gas. Our results agree very well with the data of Tsuboi et al. [16]. The cross-section decreases with increasing temperature though the drop is much sharper at lower temperatures (< 500 K). Methanol absorption cross-sections exhibit similar dependence on bath gas as was observed for methane. At temperatures less than 600 K, methanol/He mixture has the highest cross-section followed by methanol/Ar and methanol/N₂ mixtures.

Figure 9 shows the absorption cross-sections of ethylene, measured with HeNe laser, as a function of temperature and bath gas. Relatively large ethylene concentration (10 – 40%) is used for these measurements since the ethylene absorption is relatively weak at the HeNe laser wavelength. As observed previously by Klingbeil et al. [19], the absorption cross-section of ethylene increases with temperature at the HeNe laser wavelength (2947.909 cm^{-1}). This is due to the fact that this wavelength is close to a hot band transition and its intensity increases with increasing temperatures. Ethylene shows relatively less dependence on bath gas compared to methane and methanol. However, it is clear from the high-temperature ($> 600\text{ K}$) data that the cross-section is larger for helium mixture followed by argon and nitrogen mixtures.

Absorption cross-sections of ethane, measured by HeNe laser, are shown in Fig. 10 as a function of temperature and bath gas. Our measured values agree with Harrison et al. [8] and Olson et al. [14] data but Tsuboi et al. [16] value appears to be lower by about 10%. The cross-sections show very little temperature dependence because the HeNe laser emission wavelength is close to the inflexion region (between the peak and valley) which is known to exhibit very little variation with temperature. For the same reason, the cross-sections of ethane do not exhibit appreciable dependence on the bath gas. The same phenomenon was observed in another study carried out in our laboratory for propane, propylene and ethanol (data not shown here) where their cross-sections did not show any dependence on the bath gas.

The values of the cross-sections, measured by HeNe laser, at room temperature (296 K) and atmospheric pressure (760 Torr) are summarized in Table 5 for different bath gases. As observed from Figs. 6 – 10, Table 5 also demonstrates that methane and methanol exhibit relatively strong dependence on bath gas. Since ethane and ethylene have a broad feature near the HeNe laser wavelength, their cross-sections show very little variation with bath gas.

5. Conclusions

Mid-IR absorption cross-sections were measured for methane, ethane, ethylene and methanol using an FTIR spectrometer and a fixed-wavelength HeNe laser. The studied fuels belong to three different chemical groups: alkanes, alkenes and alcohol and are very important in combustion and atmospheric kinetics. The temperature range of this study is 296 – 1120 K and the spectral region spans 2800 to 3400 cm^{-1} . The spectra of all studied fuels exhibit the expected trend of decreasing peak intensity and increasing wings of the spectrum as temperature increases. On the other hand, the integrated band intensities are found to be nearly independent of temperature. Measurements with HeNe laser are used to understand the variation of absorption cross-section at a specific wavelength with temperature and bath gas. Methane and methanol cross-sections exhibit dependence on bath gas whereas this dependence is very weak for ethane and ethylene. This work has extended the temperature range of absorption cross-sections for these fuels compared to previous works. The spectra and absorption cross-sections reported here will prove quite useful in developing high-temperature laser-based diagnostics.

Tables

Table 1. FTIR settings used to measure mid-IR spectra of methane, ethane, ethylene and methanol.

Resolution	0.16 cm ⁻¹ (T < 500K)
	0.6 cm ⁻¹ (T > 500K)
Beamsplitter	Potassium bromide (KBr)
Input aperture	2.5 mm
Detector	DigiTect DLaTGS
Light Source	Globar (Mid-infrared)
FT phase correction, zero fill	Mertz, 2 x zero-filling

Table 2. Integrated band intensities (2500 – 3400 cm⁻¹) at 296 K and comparison with previous studies. The % difference is calculated as: $\% \delta = 100 \times \left| \frac{S_{this\ work} - S_{others}}{S_{this\ work}} \right|$.

Molecule	This Work (296 K) x10 ⁻¹⁷ cm/molecule	Sharpe et al. [13] (298 K)		Klingbeil [23] (298 K)		Harrison et al. [8] (298 K)	
		x10 ⁻¹⁷ cm/molecule	% δ	x10 ⁻¹⁷ cm/molecule	% δ	x10 ⁻¹⁷ cm/molecule	% δ
Methane	1.11 (±0.06)	1.10	0.9	1.18	6.31	---	---
Ethane	2.81 (±0.14)	2.84	1.07	2.81	0.00	2.94	4.63
Ethylene	0.70 (±0.04)	0.69	1.43	0.72	2.86	---	---
Methanol	2.17 (±0.11)	2.04	5.99	---	---	---	---

Table 3. Integrated band intensities (2500 – 3400 cm⁻¹) at various temperatures.

T (K)	Methane (x10⁻¹⁷ cm/molecule)	Ethane (x10⁻¹⁷ cm/molecule)	Ethylene (x10⁻¹⁷ cm/molecule)	Methanol (x10⁻¹⁷ cm/molecule)
296	1.11 (±0.06)	2.81 (±0.14)	0.70 (±0.04)	2.17 (±0.11)
373	1.17 (±0.6)	2.98 (±0.15)	0.69 (±0.03)	2.15 (±0.11)
523	1.21 (±0.06)	3.01 (±0.15)	0.71 (±0.04)	2.16 (±0.11)
673	1.04 (±0.05)	2.99 (±0.18)	0.72 (±0.03)	2.17 (±0.13)
773	1.04 (±0.08)	3.08 (±0.25)	0.74 (±0.06)	2.17 (±0.17)
920	1.01 (±0.08)	3.15 (±0.25)	0.75 (±0.06)	---
1060	1.22 (±0.09)	---	---	---
1120	1.21 (±0.09)	---	---	---

Table 4. Comparison between the integrated band intensities (2500 – 3400 cm^{-1}) of methane from HITRAN and this work at various temperatures. The unit of the integrated band intensity is ($\times 10^{-17}$ $\text{cm}/\text{molecule}$).

T (K)	This Work	HITRAN^a (resolution 0.01 cm^{-1})	Difference, %
296	1.11 (resolution 0.16 cm^{-1})	1.11	0.0
373	1.17 (resolution 0.16 cm^{-1})	1.11	5.1
673	1.04 (resolution 0.6 cm^{-1})	1.03	1.0
773	1.04 (resolution 0.6 cm^{-1})	0.95	8.7

^a Methane spectra were obtained from HITRAN on the Web.

Table 5. Variation of the measured absorption cross-sections, using HeNe laser (3392 nm), with helium, argon and nitrogen as bath gases at 296 K and 1 atm.

Species	Absorption Cross-section ($\times 10^{-19} \text{ cm}^2/\text{molecule}$)			Cross-section difference $\left[\frac{N_2 - (\text{He or Ar})}{N_2} \right] \times 100$	
	Helium	Argon	Nitrogen	He-N ₂	Ar-N ₂
Methane	4.39 (± 0.22)	3.81 (± 0.18)	3.45 (± 0.17)	27.41	10.43
Methanol	1.43 (± 0.07)	1.42 (± 0.07)	1.28 (± 0.07)	12.08	10.78
Ethylene	0.075 (± 0.003)	0.073 (± 0.003)	0.073 (± 0.003)	2.27	0.00
Ethane	1.71 (± 0.10)	1.69 (± 0.08)	1.68 (± 0.08)	1.68	0.69

Figure Captions

Figure 1. Schematic of the experimental setup: a) FTIR and HeNe laser setups. b) Detailed arrangement of the quartz cell.

Figure 2. FTIR-measured spectra of methane showing the origin of the ν_3 band and the P, Q, R branches. Methane concentration ranged from 0.5 to 10% (in N_2) for different temperatures.

Figure 3. FTIR-measured spectra of ethane showing the origin of the ν_1 , ν_7 and ν_{10} bands. Ethane concentration ranged from 1 to 10% (in N_2) for different temperatures. A comparison between this work and Sharpe et al. [13] is shown the upper-right corner at 296 K.

Figure 4. FTIR-measured spectra of ethylene showing the origin of the ν_{11} and ν_9 bands. Ethylene concentration ranged from 10 to 40% (in N_2) for different temperatures. The insert shows a zoomed-in view of the temperature dependence of the ν_{11} peak.

Figure 5. FTIR-measured spectra of methanol showing the origin of the ν_2 , ν_3 and ν_9 bands. Ethylene concentration ranged from 1.5 to 6% (in N_2) for different temperatures.

Figure 6. Absorption cross-sections of methane, measured by HeNe laser (3392 nm), with different bath gases.

Figure 7. Bath gas dependent absorption cross-sections of methane with Ar, He and N_2 at 296 K. Measurements carried out with HeNe laser at 3.392 μm .

Figure 8. Absorption cross-sections of methanol, measured by HeNe laser (3392 nm), showing dependence on the bath gases (Ar, He and N_2).

Figure 9. Absorption cross-sections of ethylene, measured by HeNe laser (3392 nm), as a function of temperature and bath gas (He, Ar, N_2).

Figure 10. Absorption cross-sections of ethane, measured by HeNe laser (3392 nm), as a function of bath gases (He, Ar, N₂).

Figure 1. Schematic of the experimental setup: a) FTIR and HeNe laser setups. b) Detailed arrangement of the quartz cell.

a) FTIR and HeNe laser setup

b) Quartz cell

Figure 2. FTIR-measured spectra of methane showing the origin of the ν_3 band and the P, Q, R branches. Methane concentration ranged from 0.5 to 10% (in N_2) for different temperatures.

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Ethane concentration ranged from 1 to 10% (in N_2) for different temperatures. A comparison between this work and Sharpe et al. [13] is shown in the upper-right corner at 296 K.

Figure 4. FTIR-measured spectra of ethylene showing the origin of the ν_{11} and ν_9 bands.

Ethylene concentration ranged from 10 to 40% (in N_2) for different temperatures. The insert shows a zoomed-in view of the temperature dependence of the ν_{11} peak.

Figure 5. FTIR-measured spectra of methanol showing the origin of the ν_2 , ν_3 and ν_9 bands.

Methanol concentration ranged from 1.5 to 6% (in N_2) for different temperatures.

Figure 6. Absorption cross-sections of methane, measured by HeNe laser (3392 nm), with different bath gases.

Figure 7. Bath gas dependent absorption cross-sections of methane with Ar, He and N₂ at 296 K.

Measurements are carried out with HeNe laser at 3.392 μm .

Figure 8. Absorption cross-sections of methanol, measured by HeNe laser (3392 nm), with different bath gases (Ar, He and N₂).

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Figure 10. Absorption cross-sections of ethane, measured by HeNe laser (3392 nm), as a function of bath gases (He, Ar, N₂).

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