



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.

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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.

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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. Es-sebbar 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 H_2O , CO_2 , 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 (298–673 K) and pressure (500–2000 Torr) at 3.39 μm for different gaseous hydrocarbons was investigated by Klingbeil et al. [19]. Mével 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 2800–3400 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 700–8000 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 \times 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:

$$A_\nu = -\ln\left(\frac{I}{I_0}\right) = \sigma_\nu \cdot L \cdot n \quad (1)$$

where A_ν is the absorbance, I_0 is the reference signal, I is the transmitted signal, σ_ν 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:

$$\sigma_\nu = \frac{A_\nu kT}{PL} \quad (2)$$

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 cm^{-1} to calculate the integrated band intensity by:

$$S_\nu = \int \sigma_\nu d\nu = \frac{kT}{PL} \int A_\nu d\nu \quad (3)$$

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