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Infrared cross-sections and integrated band intensities of propylene: Temperature-dependent studies



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ABSTRACT

Propylene, a by-product of biomass burning, thermal cracking of hydrocarbons and incomplete combustion of fossil fuels, is a ubiquitous molecule found in the environment and atmosphere. Accurate infrared (IR) cross-sections and integrated band intensities of propylene are essential for quantitative measurements and atmospheric modeling. We measured absolute IR cross-sections of propylene using Fourier Transform Infrared (FTIR) Spectroscopy over the wavenumber range of 400–6500 cm^{-1} and at gas temperatures between 296 and 460 K. We recorded these spectra at spectral resolutions ranging from 0.08 to 0.5 cm^{-1} and measured the integrated band intensities for a number of vibrational bands in certain spectral regions. We then compared the integrated band intensities measured at room temperature with values derived from the National Institute of Standards and Technology (NIST) and the Pacific Northwest National Laboratory (PNNL) databases. Our results agreed well with the results reported in the two databases with a maximum deviation of about 4%. The peak cross-sections for the primary bands decreased by about 20–54% when the temperature increased from 296 to 460 K. Moreover, we determined the integrated band intensities as a function of temperature for certain features in various spectral regions; we found no significant temperature dependence over the range of temperatures considered here. We also studied the effect of temperature on absorption cross-section using a Difference Frequency Generation (DFG) laser system. We compared the DFG results with those obtained from the FTIR study at certain wavenumbers over the 2850–2975 cm^{-1} range and found a reasonable agreement with less than 10% discrepancy.

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1. Introduction

Propylene, also called propene ($\text{CH}_2=\text{CH}-\text{CH}_3$; C_3H_6), is an unsaturated hydrocarbon with a double bond and the second alkene after ethylene. Found in the environment and atmosphere, this molecule is ubiquitous and thus its quantification is very important [1,2]. The primary sources of propylene production include biomass burning [3–9],

thermal cracking of hydrocarbons [10,11] and incomplete combustion of fossil fuels [12,13]. It is present in motor vehicle exhaust as a result of fuel-rich combustion of hydrocarbon fuels [14,15]. Propylene is widely used by a number of chemical industries in the preparation of alkylates as additives to gasoline [16] and in the production of polypropylene [17], acrylonitrile [18] and propylene oxide [19].

Recently, propylene has been detected in the interstellar medium and the Taurus Molecular Cloud (TMC-1) and it has been suggested that propylene may play an important role in interstellar chemistry [20–22]. The gas phase chemistry and the propylene production mechanism in

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cold interstellar clouds were studied by Herbst et al. [22]. Moreover, Marcelino et al. [20] reported a relative propylene abundance of 4×10^{-9} (i.e., a column density relative to H_2 of $4 \times 10^{13} / \text{cm}^2$) near TMC-1. Detection of propylene in the interstellar environment is difficult and requires good knowledge of the spectral characteristics and temperature-dependent absolute absorption cross-section data.

Furthermore, propylene plays a key role in the pyrolysis and oxidation chemistry of larger hydrocarbons. Understanding propylene formation and decay is important for predicting the concentrations of combustion emissions, soot and unburnt hydrocarbons. Propylene is one of the primary intermediate species formed during the oxidation of large alkanes and its concentration can be relatively large in many combustion environments [23]. Temperature-dependent cross-sections are required to make quantitative time-history measurements in combustion systems. Such measurements will prove very useful in the improvement and validation of chemical kinetic mechanisms of large alkanes.

A number of spectroscopic experimental investigations on propylene, primarily using infrared spectroscopy, have previously been reported [24–26]. Silvi et al. [24] reported infrared spectra over 200–4000 cm^{-1} at a resolution between 0.5 and 1 cm^{-1} and assigned vibrational bands to determine the force constant parameters. Durig et al. [25] measured the far-infrared spectrum of propylene and described methyl torsional fundamental bands as well as two hot bands. Lafferty et al. [26] measured higher resolution (0.005 cm^{-1}) IR jet spectra over 911–930 cm^{-1} to resolve the fine structure of the ν_{18} and ν_{19} bands in an attempt to determine the rotational constants and to characterize the torsional splitting of propylene. Detailed IR spectra of propylene at room temperature can be found in the National Institute of Standards and Technology (NIST) database [27] and at 278, 298 and 323 K in the Pacific Northwest National Laboratory (PNNL) database [28]. Transmission spectra taken from NIST at room temperature are a composite of five combination burdens in a 25% C_3H_6/N_2 mixture and the optical path length is 5 cm [27]. The spectrum from PNNL at room temperature is an average of 10 concentration–optical path length burdens [28]. At other temperature values, the spectrum is a composite of 6 combination burdens [28]. The two databases report spectra at low to moderate spectral resolutions, 2 cm^{-1} and 0.112 cm^{-1} , respectively. However, relatively high-resolution IR absorption cross-sections of propylene and its dependence on gas temperature have not been reported in the literature or other commonly used spectral databases like HITRAN and GEISA [29,30].

Here, we used Fourier Transform Infrared Spectroscopy (FTIR) to measure the IR cross-sections of propylene and their temperature dependence over the wavenumber range of 400–6500 cm^{-1} . We recorded absorption spectra at spectral resolutions between 0.08 and 0.5 cm^{-1} and at gas temperatures ranging from 296 to 460 K. We obtained integrated band intensities for various features of propylene and compared with the values calculated from the NIST and PNNL databases [27,28]. In addition, we conducted a complementary study on the effect of temperature on cross-sections by absorption spectroscopy using the Difference Frequency Generation

(DFG) laser system operating near 3.3–3.5 μm . We compared the DFG results with the measured FTIR spectra for certain wavenumbers over 2850–2975 cm^{-1} .

2. Experimental methods

2.1. FTIR setup

Spectra were measured over 400–6500 cm^{-1} using a Fourier Transform Infrared (FTIR) spectrometer manufactured by Bruker (VERTEX 80V). The experimental setup was described previously for the investigation of 1-butene IR cross-sections and their temperature dependence [31]. The configuration and settings of the FTIR for the measurements reported here are listed in Table 1. IR light was passed through an absorption cell, which was constructed from stainless steel and KBr windows, with an optical path-length of 10 cm. The cell temperature was set using a heating jacket connected to a controller. The temperature was measured continuously with five type-K (Omega) thermocouples along the length of the absorption cell. The uncertainty on the temperature measurements was less than 0.5%. The beam spot size at the interferometer Jacquinot stop was set either 1.5 or 2.5 mm. The smaller aperture (A) allowed for higher resolution at lower wavenumbers, but for some measurements the aperture was opened to 2.5 mm (reducing the resolution) in order to obtain sufficient signal strength with the room-temperature DLaTGS detector. Based on the maximum interferometer mirror displacement, this FTIR spectrometer has a spectral resolution up to 0.06 cm^{-1} , and operates over a large wavenumber range (from 400 to 6500 cm^{-1}). The measurements presented here were collected at spectral resolutions ranging from 0.08 to 0.5 cm^{-1} , which are chosen to resolve various features of propylene with sufficient accuracy. The interferograms were corrected with the Mertz phase function. The boxcar apodized interferograms were zero-filled by a factor of 2 to produce the final spectrum. Additional spectra were zero-filled by a factor of 4 to resolve the principal features of C_3H_6 . To calibrate the FTIR wavenumber scale and to assign the observed features with corresponding line positions,

Table 1
Configuration of FTIR spectrometer for propylene spectra measurements.

FTIR spectrometer configuration	
Resolution	0.08–0.5 cm^{-1}
Beamsplitter	Potassium bromide (KBr)
FTIR input aperture	1.5 or 2.5 mm
Focal length of the collimator mirror	100 mm
Detector	DLaTGS
Light source	Global (mid-infrared)
Optical path length (reflex cell)	10 cm
FT phase correction, zero-fill	Mertz, 2 × and 4 × zero-filling
FT apodization function	Boxcar
Pressure gauges	Baratrons (20, 100 and 1000 Torr): ± 0.05% accuracy

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