



Quantitative mid-infrared spectra of allene and propyne from room to high temperatures



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ABSTRACT

Allene (a-C₃H₄; CH₂CCH₂) and propyne (p-C₃H₄; CH₃C₂H) have attracted much interest because of their relevance to the photochemistry in astrophysical environments as well as in combustion processes. Both allene and propyne have strong absorption in the infrared region. In the present work, infrared spectra of a-C₃H₄ and p-C₃H₄ are measured in the gas phase at temperatures ranging from 296 to 510 K. The spectra are measured over the 580–3400 cm⁻¹ spectral region at resolutions of 0.08 and 0.25 cm⁻¹ using Fourier Transform Infrared spectroscopy. Absolute integrated intensities of the main infrared bands are determined at room temperature and compared with values derived from literature for both molecules. Integrated band intensities are also determined as a function of temperature in various spectral regions.

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1. Introduction

Allene (a-C₃H₄; CH₂CCH₂) and propyne (p-C₃H₄; CH₃C₂H) have attracted much interest for a long time because of their relevance to the photochemistry in planetary environments [1–8]. More recently, infrared (IR) spectra at high temperatures have gained a lot of interest because of the warm atmospheres of exoplanets, known as “Hot Jupiters”, which are now being extensively studied [9,10]. Furthermore, a-C₃H₄ and p-C₃H₄ represent key intermediates in combustion processes [11–16]. They are ubiquitous and play a crucial role in the formation of propargyl radical, a key intermediate in the production of aromatic compounds and soot particles [11–13].

Both allene and propyne absorb strongly in the IR domain (see Linnett et al. [17]; Rasmussen et al. [18]; Mills et al. [19]; Stone [20]; Koga et al. [21]; Kondo and Koga [22]; Maki and Pine [23]) thus providing possibilities for sensitive detection in extraterrestrial environments for both molecules. Allene may be present in Titan and in the atmosphere of giants planets including Jupiter [24] and Saturn [8,25]. However, only propyne has so far been detected in the atmosphere of Titan [1,3,26,27]. As pointed out by Teanby et al. [7], the determined abundance of propyne in Titan's atmosphere is questionable due to the uncertainties in

the laboratory measurements. In addition, the absence of allene is difficult to explain by photochemical models since both isomers are expected to transform into each other, undergoing similar processes. It has been proposed that perhaps complete isomerization of a-C₃H₄ into p-C₃H₄ occurs.

In the mid-IR spectral domain, the strongest fundamental bands of allene are observed near 841 (ν₁₀), 999 (ν₉) and 1957 cm⁻¹ (ν₆). The strongest transitions of propyne in the mid-IR are observed near 633 (ν₉), 1452 (ν₇) and 3334 cm⁻¹ (ν₁). Over the last few decades, the spectroscopic characterization of a-C₃H₄ and p-C₃H₄ in the laboratory has been the topic of many studies using various spectroscopic diagnostics. Fourier Transform Infrared (FTIR) spectroscopy studies have been used to analyze the IR spectra and determine vibrational assignments and molecular structure (see Refs. [28–30]). High-resolution tunable diode laser spectroscopy has been used to determine line intensities and collisional broadening parameters [31–34] as well as rotational and molecular constants [35–38].

This paper is part of our studies on gas-phase spectroscopy of molecules relevant to the photochemistry in planetary atmospheres, warm exoplanetary atmospheres and combustion processes. To enable the study of allene and propyne in such environments, and in order to provide extensive information about the constituents of planetary atmospheres as well as their excitation processes, high quality IR spectra are needed. In combustion processes, IR data will be used for the development of high-tem-

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perature quantitative diagnostics to study the decomposition of allene and propyne using shock tube and rapid compression machines. In the present study, we report the IR spectra of a-C₃H₄ and p-C₃H₄ as a function of temperature (296–510 K). Section 2 presents our experimental setup used to measure absorption spectra and in Section 3 we describe briefly the procedure used to retrieve cross-sections and integrated intensities. IR spectra and band assignments are presented in Section 4 and finally, we present the integrated intensities and the influence of high temperatures.

2. Experimental method

IR spectra were measured between 580 and 3400 cm⁻¹ using a Fourier Transform Infrared (FTIR) spectrometer (Bruker Vertex 80V). The experimental setup was described previously for the investigation of 1-butene and propylene (see Es-sebbar et al. [39,40]) and only a brief description is given here. A KBr beamsplitter, a Global mid-IR source and a DLaTGS detector were used to record the spectra. Based on the maximum interferometer mirror displacement, spectral resolution up to 0.06 cm⁻¹ can be reached. Here, entrance aperture diameters of 2 and 2.5 mm and a collimating mirror of 100 mm focal length were used. These settings result in spectral resolution of 0.08 and 0.25 cm⁻¹. The interferograms were corrected with the Mertz phase function and the boxcar apodized interferograms were zero-filled to produce the final spectrum. The modulated IR light was transmitted through an optical cell, made of stainless steel and equipped with KBr windows. The cell placed inside the chamber of the FTIR instrument, has an optical path length of 10 cm. To record spectra at high temperatures, the absorption cell was heated using a heating jacket connected to a controller system. The temperature was measured continuously with five type-K (Omega) thermocouples along the length of the absorption cell with an uncertainty less than 0.5%.

Ultra-pure (99.999%) a-C₃H₄ and p-C₃H₄, purchased from Abdullah Hashim Industrial Gases & Equipment Co. Ltd., were used for IR studies. Spectra were recorded with pure samples and also with a mixture of 4% a-C₃H₄ in N₂. Measurements were made at various temperatures ranging from 296 to 510 K. At each temperature, series of spectra were recorded between 580 and 3400 cm⁻¹ for various pressures. The pressure was monitored using three Baratron capacitance gauges (20, 100, and 1000 Torr full-scale ranges). Before and after each measurement, 120 co-added scans were recorded with the cell evacuated to take into account any drift in the background intensity. The absorption cell was evacuated to about 1 × 10⁻⁴ Torr using a turbo-molecular pump (Turbo-v 81-M Varian) backed by a rotary mechanical pump (Varian DS-102). For the room-temperature (296 K) measurements, the entire FTIR compartment was evacuated to less than 0.1 mbar to avoid absorption by CO₂ and H₂O. For high-temperature measurements, N₂ gas was used to purge the FTIR spectrometer. To calibrate the FTIR wavenumber scale and to assign the observed features with corresponding line positions, spectra of CO and CH₄ gases were recorded and compared with the corresponding lines in the HITRAN database.

3. Data analysis

The absorbance, A_v , can be written using the Beer–Lambert law:

$$A_v = \ln(I_0/I)_v = \varepsilon_v(lp) \quad (1)$$

where I_0 is the incident intensity recorded with the empty cell (background), I is the transmitted intensity measured with a-C₃H₄ or p-C₃H₄ samples, ε_v is the absorption coefficient at wavenumber

ν in cm⁻¹ atm⁻¹, l is the optical path length in cm; and p is the gas pressure in atm.

The absorption coefficient ε_v can be converted to cross-section values (cm²/molecule) using:

$$\sigma_v = (\varepsilon_v/N)(T(K)/273.15) \quad (2)$$

where $N = 2.68676 \times 10^{19}$ /cm³ is the Loschmidt number at standard values of temperature and pressure (273.15 K/1013.25 mbar).

In order to determine the integrated band intensity (S_v), given in cm⁻² atm⁻¹, the integrated absorbance ($\int A_v dv$) is first calculated as a function of gas pressure for different a-C₃H₄ and p-C₃H₄ bands. Then integrated absorbance ($\int A_v dv$) is plotted as a function of the product of the optical path length and the partial pressure of the sample (lp):

$$\int A_v dv = (lp) \int \varepsilon_v dv = (lp)S_v \quad (3)$$

The linear dependence of the integrated absorbance with lp is systematically verified and the absolute integrated intensity (S_v) is deduced from the slope of the linear fit. These integrated intensity values are compared with quantitative results taken from the PNNL database [41]. Absorbance spectra taken from PNNL database were first converted to cross-section values by combining Eqs. (1) and

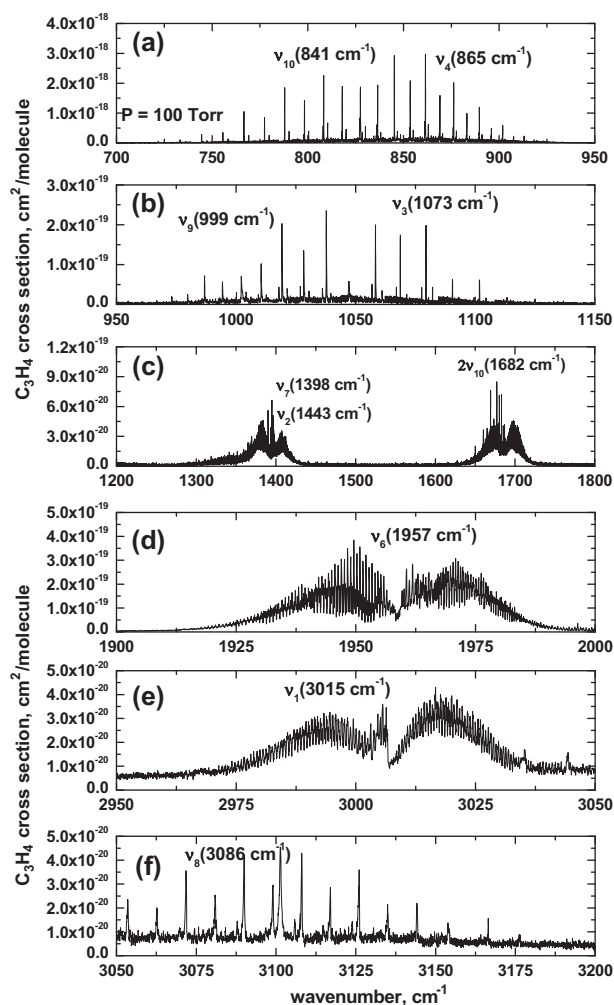


Fig. 1. Allene absorption cross-sections between 700 and 3200 cm⁻¹ at 296 K. Spectra are recorded for 4% a-C₃H₄/N₂ mixture and the total pressure is 100 Torr. The main features are identified and summarized in Table 1. Spectra between 700 and 1150 are recorded at spectral resolution of 0.08 cm⁻¹. Spectra in the 1200–3200 cm⁻¹ range are recorded at 0.25 cm⁻¹ resolution.

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