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Research paper

The high-resolution infrared spectrum of the $\nu_3 + \nu_5$ combination band of jet-cooled propyne

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ABSTRACT

We present the first detection of the high-resolution ro-vibrational spectrum of the $\nu_3 + \nu_5$ combination band of propyne around 3070 cm^{-1}. The fully resolved spectrum is recorded for supersonically jet-cooled propyne using continuous wave cavity ring-down spectroscopy (cw-CRDS). The assignments are supported with the help of accurate *ab initio* vibration-rotation interaction constants (α_i) and anharmonic frequencies. A detailed analysis of the rotationally cold spectrum is given.

1. Introduction

Propyne, also known as methylacetylene ($H_3C{-}C{\equiv}CH$), is a small unsaturated hydrocarbon of astrophysical importance. It is believed to play a role in the chemistry of a number of hydrocarbon-rich astronomical objects, including the atmosphere of Titan [1], the dark cloud TMC-1 [2], the circumstellar shell of the AGB star IRC+10216 [3], and two protoplanetary nebulae CRL 618 [4] and SMP LMC 11 [5], where it has been observed in the infrared (IR) through the ν_9 ($H{-}C{\equiv}C$ bending) mode, and by radio astronomy through pure rotational transitions. In addition, the close spacing of the rotational transitions of different K' subbands, and the relatively low dipole moment ($\mu = 0.78$ D) [6] make propyne an ideal probe of the interstellar medium's kinetic temperature; since the excitation temperature increases as K' increases [7–9].

From a pure spectroscopic point of view this molecule is also interesting. As a prolate symmetric top the aliphatic (CH_3) and acetylenic (CH) stretches are suitably decoupled from each other that the strong acetylenic CH stretch mode (ν_1) is not strongly perturbed [10]. Studies of spectra that are perturbed through weak near-resonant couplings to background vibrational states, as seen in other transitions of propyne, make it of interest for studying intramolecular vibrational relaxation (IVR) [11–13,10,14–17]. Moreover, comparison between high-resolution measurements as presented here for propyne and *ab initio* methods offers a good test of the accuracy of the Hamiltonians used to describe the involved molecular energy levels.

Propyne has been extensively studied in the electronic ground state (X^1A_1) through a number of microwave and IR experimental studies and *ab initio* calculations (Ref. [18], and references therein). In fact, all of the fundamental bands and a substantial number of combination bands involving either ν_3 ($C{\equiv}C$ stretch) or ν_5 ($C{-}C$ stretch) excitations have been studied at high-resolution [19–23,10,14,16,24,9,18,25,26]. The spectroscopic identification of the $\nu_3 + \nu_5$ combination band has not yet been reported. Based on the published band origins for ν_3 [20] and ν_5 [25], the $\nu_3 + \nu_5$ combination band is expected at ~ 3068 cm^{-1}.

The results of a survey around this wavelength are presented here. The experimental and theoretical details are given in Section 2. The spectroscopic analysis and discussion are presented in Section 3. Line positions are available from the supplementary material.

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2. Methods

2.1. Experimental

The experimental setup has been described in detail in Ref. [27], and has recently been used to measure the $\nu_3 + \nu_8$ combination band, involving the CH_3 rocking mode of jet-cooled propyne around 3175 cm^{-1} [26]. The main difference with the present experiment is that a different single-mode continuous-wave optical parametric oscillator (cw-OPO) had to be used; the Aculight, Argos 2400-SF-C module that covers 3.2–3.9 μm is used, instead of the B module, which covers 2.5–3.2 μm.

A gas mixture of 0.05% propyne in 1:1 argon:helium is used as the precursor gas. The gas is then supersonically expanded with a 4 bar backing pressure through a long (0.3×30 mm) slit nozzle connected to a pulsed valve (General valve, serial 9) [28] into a vacuum chamber with a stagnation pressure of $\sim 1.5 \times 10^{-2}$ mbar, realized by a large roots blower system with a total pumping capacity of 4800 m^3/hr. The valve runs at 10 Hz, and the typical gas pulse has a duration of about 800 μs. The pulsed gas flow is used to create a high pressure jet expansion, increasing the local number density of propyne molecules at the nozzle slit.

The absorption spectrum is recorded using cw-CRDS, with the IR laser path intersecting the expansion roughly 1 cm downstream from the nozzle body. The optical cavity is comprised of two highly reflective plano-concave mirrors ($R \sim 99.98\%$, centered at 3300 cm^{-1}). Typical empty cavity ring-down times (τ_0) are about 9 μs. The hardware (boxcar integrator) based multi-trigger and timing scheme described in detail in Ref. [27] is used to coincide the laser light and gas pulse. This guarantees that the trigger scheme compensates for the low duty cycle when combining a cw laser with a pulsed gas expansion. For this experiment the optical cavity length is modulated at ~ 26 Hz, using a piezo crystal mounted on the back of one of the cavity mirrors.

The resulting spectrum is recorded in a series of ~1.2 cm^{-1} parts that partially overlap to guarantee that spectra can be directly compared. While the spectrum is recorded, the laser frequency is simultaneously measured using a wavelength meter (Bristol Instruments, 621A-IR). The frequency accuracy is independently calibrated by measuring known transitions of ethylene (C_2H_4) [29]. The resulting maximum frequency uncertainty of ± 0.002 cm^{-1} is dictated by the wavemeter.

2.2. Theoretical

Equilibrium geometry and second-order vibrational perturbation theory (VPT2) calculations are carried out at the CCSD(T) level of theory. The core-valence correlation-consistent quadruple-ζ basis set (cc-pCVQZ) [30] is used to determine the equilibrium geometry and rotational constants, since it has been shown to give highly accurate geometries for acetylenic molecules [31,32]. The atomic natural orbital (ANO) basis set with the truncation [4s3p2d1f] for non-hydrogen atoms and [4s2p1d] for hydrogen (hereafter known as ANO1) [33] is used to determine the anharmonic vibrational frequencies and electronic ground state spectroscopic constants of propyne. It has been shown to reproduce experimental frequencies better than the correlation-consistent basis sets [34,32]. All calculations are performed with the development version of the CFOUR program [35].

3. Results and discussion

An overview of the experimental spectrum is shown in the upper trace of Fig. 1(a). It shows a regular pattern with excellent signal-to-noise spreading over 15 cm^{-1}. A parallel band consistent with a C_{3v} symmetric top molecule A_1-A_1 transition is clearly seen with a Q-branch at ~3070.1 cm^{-1}, very close to the predicted $v_3 + v_5$ frequency of 3068 cm^{-1}. The experimental spectrum is analyzed using the PGOPHER software [36], assuming a rotational temperature of 18 K and a Gaussian linewidth of 0.004 cm^{-1}. The latter is determined by minimal residual Doppler broadening in the slit nozzle expansion. A first fit of the strongest transitions gives lower state rotational constants in good agreement with

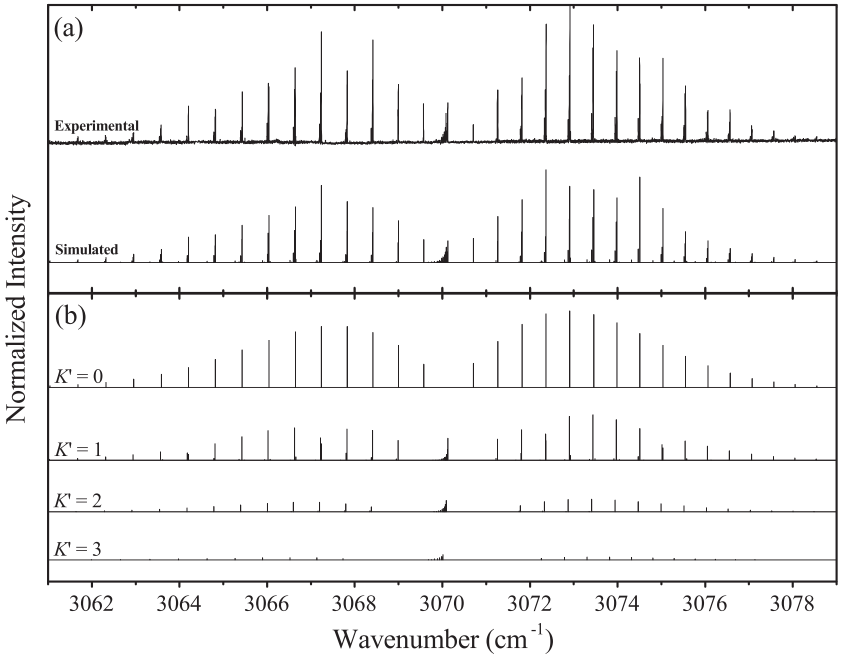

Fig. 1. (a) The experimental spectrum from 3059.5 to 3080.5 cm^{-1} (upper trace), and simulated spectrum (lower trace) of the $\nu_3 + \nu_5$ combination band comprising of different K' subbands. (b) Simulations of the K' = 0, 1, 2, and 3 subbands (including transitions to perturbing states). A rotational temperature of 18 K is used in the simulated spectra.