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Measurements of linestrengths, N_2-, Ar-, He- and self-broadening coefficients of acetylene in the $\nu_4+\nu_5$ combination band using a cw quantum cascade laser

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ABSTRACT

Linestrengths, N_2-, Ar-, He- and self-broadening coefficients of acetylene have been measured at 296 K in the *P* branch of the $\nu_4+\nu_5$ combination band for 25 rotational transitions. The effect of gas temperature is studied over 296–683 K for five transitions to allow the determination of the temperature dependent exponent *n* for N_2- and Ar-broadening coefficients. These measurements were performed using a continuous-wave quantum cascade laser (cw-QCL) operating over 1253–1310 cm^{-1}. Spectroscopic parameters were obtained by fitting absorption spectra using Voigt, Galatry and Rautian profiles. Linestrength and broadening results are compared with previous studies available in literature for the $\nu_4+\nu_5$ combination band and other vibrational bands of acetylene.

1. Introduction

Acetylene (C_2H_2) has been identified as an important species in a variety of applications. In combustion, acetylene is produced during the oxidation of hydrocarbon fuels and acts as a precursor for soot formation which has carcinogenic effects on human health [1,2]. Quantitative measurements of acetylene in combustion processes are critical in evaluating the environmental impact of different fuels [3]. Acetylene is also present in earth's atmosphere in trace quantities as it is formed by the burning of fossil fuels [4]. Furthermore, acetylene concentration in human breath has been identified as a biomarker for smoking [5]. Acetylene has been found as a trace constituent of the Titan atmosphere and in outer planetary atmospheres of Jupiter and Saturn [6,7]. Accurate measurements of important spectroscopic parameters such as linestrengths, collisional broadening coefficients and their temperature dependencies are crucial for precise measurements of acetylene concentration in a variety of environments.

Acetylene is a linear symmetric molecule and has five vibrational modes. Unlike other bands in near infra-red region, the $\nu_4+\nu_5$ combination band, located in mid infra-red region, is fairly strong [8]. Rotational transitions in this combination band are separated sufficiently to be identified easily for the determination of individual spectroscopic parameters. A number of studies have been performed in the past to determine linestrengths and collisional broadening coefficients for the acetylene spectral region 1240–1390 cm^{-1}. Podolske et al. [9] used a diode laser spectrometer to measure linestrengths for 17 transitions in the *R*-branch of the $\nu_4+\nu_5$ combination band. In the same study, collisional broadening coefficients of acetylene perturbed by H_2 and N_2 were reported for three lines. From measurements made with tunable diode lasers, Devi et al. [10] derived N_2- and air-broadening coefficients for a total of 29 lines between 1250 and 1380 cm^{-1} in the *P* and *R* branches. Individual line intensities of acetylene in

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the P and R branches of the $\nu_4+\nu_5$ combination band have been measured at room temperature using Fourier Transform Infrared (FTIR) Spectroscopy in a number of studies [11–14]. Among recent measurements of spectroscopic parameters of acetylene in the $\nu_4+\nu_5$ combination band, one should note the studies performed by Lepère's group [15–20]. Room temperature linestrengths and self-broadening coefficients have been measured for 30 lines in P and R branches over 1275–1390 cm^{-1} spectral region using a tunable diode laser spectrometer [15]. Temperature dependent exponents of self-broadening coefficients of 7 transitions was measured in the temperature range of 173–273 K [18]. Room temperature N_2-broadening coefficients were measured for 12 transitions in the R branch of $\nu_4+\nu_5$ band [19]. A similar study was carried out for 15 transitions in the temperature range of 173–273 K to determine temperature dependent exponents of N_2-broadening coefficients [16,17]. Room temperature CO_2–broadening coefficients have also been reported for 24 transitions in the spectral range of 1270–1400 cm^{-1} [20].

Voigt profile is the most extensively used line profile to simulate absorption spectra for the determination of spectroscopic parameters. This profile is a convolution of Doppler broadening (Gaussian) and pressure broadening (Lorentzian). However, Voigt profile does not take into account collisional narrowing effect which arises from velocity-changing collisions. Hence, spectroscopic parameters derived from the Voigt profile can result in systematic errors of several percent when Doppler broadening is important [21–23]. More elaborate line-fitting profiles, i.e. Galatry [24] and Rautian [25] have been established which include the effect of collisional narrowing. These lineshape profiles account for the reduction in Doppler broadening due to velocity-changing collisions and resulting lineshape profile is narrower than the one modeled by Voigt profile [26]. Collisional narrowing effect can be modeled on the basis of either hard collision or soft collision theory. Soft collision model assumes that velocity after collision is strongly dependent on the velocity before collision, while hard collision model presumes that velocity after collision is unrelated to the velocity before collision. Hard collision model simulated by Rautian and Sobel'man [25] profile is generally believed to be applicable in the limit when $M_1 \ll M_2$, while soft collision model simulated by Galatry profile [24] holds when $M_1 \gg M_2$, where M_1 and M_2 are the molecular weights of absorber and perturber, respectively. In both hard and soft collisional models, a narrowing parameter (β) based on frequency of velocity-changing collisions is introduced to account for reduction in Doppler broadening [22]. Furthermore, the soft collision model can be applied in more general cases when M_1 and M_2 are not very different. This is because of the fact that small change in velocity can also result from small angle scattering of the long-range part of the intermolecular potential [22]. However, hard collision model is more difficult to apply in general situations as it explicitly assumes velocities after collision are unrelated to velocities before collisions [26]. Recently, more general line-fitting profiles taking into account velocity changes due to intermolecular collisions and speed dependence of collisional width have been developed for both soft collisional [27–29] and hard collisional models [30,31]. These speed dependent line profiles incorporate in-depth treatment of underlying physical phenomena and show better agreement with experimentally measured line profiles than soft and hard collisional models which do not account for speed dependence of broadening coefficients [32,33]. Ciurylo et al. [33] have also shown that the hard collisional model is not strictly valid in the limit $M_1 \ll M_2$.

The primary emphasis of the present study is to obtain precise linestrengths, N_2-, Ar-, He- and self-broadening coefficients of C_2H_2 for a total of 25 lines, $P(8)$–$P(33)$, in the $\nu_4+\nu_5$ combination band. To our knowledge, the current study provides first measurement of Ar- and He-broadening coefficients for the selected transitions. In addition, we report measurements of the influence of gas temperature on N_2- and Ar-broadening coefficients in the temperature range of 296–683 K for five transitions. Studies were performed using continuous-wave external cavity quantum cascade laser (cw EC-QCL) operating over 1253–1310 cm^{-1} to cover the target transitions. Spectroscopic parameters are derived by fitting measured absorption spectra using Voigt, Galatry and Rautian profiles.

2. Experimental setup

A cw EC-QCL manufactured by Daylight solutions (model: 21077 MHF) has been used in this study as the tunable mid-IR light source. The laser has a tunable range of 1217–1328 cm^{-1} and covers the entire P branch of the $\nu_4+\nu_5$ combination band of acetylene. The laser head is connected to a control box which displays centerline frequency and allows operating the laser under different settings. The laser frequency, temperature and injection current can be set using the laser control box. The highly collimated laser light can reach an energy output of 120 mW. The laser is expected to have a line-width of less than 0.001 cm^{-1}. The laser chip was maintained at 16 °C with the help of thermoelectric cooling and recirculating chiller. Depending on the nature of the application, the laser can be operated in three different frequency modes. These include fixed wavelength, coarse modulation and fast modulation modes [34]. Fast modulation can provide a fine tuning range of approximately 0.1 cm^{-1} with a sinusoidal repetition rate of 10 kHz–2 MHz, while coarse modulation provides wider tuning range of nearly 1 cm^{-1} at a maximum sinusoidal repetition rate of 100 Hz. In the current study, we have used the coarse modulation mode which provides sufficient tuning range to scan over an individual acetylene transition at the target temperature and pressure conditions. Coarse modulation is achieved by using a piezoelectric transducer (PZT) which mechanically modulates the external cavity grating. The laser PZT is driven by an external piezo-driver (Thorlabs MDT694A) which receives sinusoidal wave (100 Hz and 0–10V_{DC}) from a standard function generator (Stanford Research Systems DS 345).

Fig. 1 shows the experimental setup used in the present work. The stainless steel gas cell (Reflex Inc.), mounted with parallel ZnSe windows, has a path length of 10 cm and is designed to operate at relatively high pressure and temperature, up to 20 bar and 770 K, respectively. Temperature