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The absorption spectrum of acetylene near 1 μm (9280–10740 cm^{-1}) (I): Line positions

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ABSTRACT

The high-resolution absorption spectrum of acetylene is studied by Fourier-transform spectroscopy (FTS) in the 9280–10740 cm^{-1} region dominated by the $3\nu_3$ band near 9640 cm^{-1} . Line positions and intensities of 1899 $^{12}\text{C}_2\text{H}_2$ and 151 $^{12}\text{C}^{13}\text{CH}_2$ absorption lines are retrieved from a spectrum recorded at room temperature (298.5 K) with a pressure of 87.6 hPa and a path length of 105 m. The measured $^{12}\text{C}_2\text{H}_2$ lines belong to thirty-three bands, twelve of them being newly assigned. The lines of $^{12}\text{C}^{13}\text{CH}_2$ in normal abundance (2.2%) belong to seven bands. For comparison the HITRAN database in the same region includes 301 lines of four $^{12}\text{C}_2\text{H}_2$ bands. Spectroscopic parameters of the upper vibrational levels are derived from band-by-band fits of the line positions (typical *rms* values are on the order of 0.002 cm^{-1}). The comparison to the HITRAN line list and to results obtained using the global effective operator approach reveals a number of significant deviations. The occurrence of local rovibrational perturbations affecting a number of the analyzed bands is illustrated by the case of the strong $3\nu_3$ band.

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1. Introduction

In spite of being the most studied four-atoms molecule and of increasing needs for planetary applications, the status of the spectroscopic databases of acetylene (C_2H_2) in the near infrared is not satisfactory in terms of completeness and accuracy. Two major reasons explain this matter of fact: the lack of intensity information and the increasing difficulty in assigning the spectrum at high energy. While a number of studies have been devoted to rovibrational assignment and line positions analysis, intensity information is generally missing. Due to the number and strength of rovibrational interactions, if we except the strong bands dominating the spectrum, the rovibrational assignment of many overlapping perturbed bands is not straightforward and a significant fraction of acetylene lines remains.

The present contribution takes part in a long standing project aiming at constructing an empirical database for acetylene in the near infrared. We have recently released a line list for the wide 5850–9415 cm^{-1} region (excluding the 6341–7000 cm^{-1} interval)

[1] by gathering results of six studies by Fourier-transform spectroscopy (FTS) in the region of the strong bands [2–4] and Cavity Ring Down spectroscopy (CRDS) in the region of weak absorption windows between the bands [5–7]. Compared to the HITRAN [8] and GEISA [9] databases in the region, the number of bands (146) and lines (about 11000) was increased by one order of magnitude. In the present work, we follow a similar approach to extend our empirical database towards higher energy by revisiting the FTS spectrum in the 9280–10740 cm^{-1} interval.

In our preceding studies, the rovibrational analysis benefited from the predictions of the effective Hamiltonian (EH) model developed at IAO-Tomsk [10,11] which allowed identifying additional bands in previously recorded spectra. This model is a polyad model. Vibrational states in strong resonance interaction form polyads characterized by the polyad quantum number, $P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5$. [The $(V_1 V_2 V_3 V_4 V_5 l_4 l_5)$ conventional normal modes are used for the vibrational labelling where V_i are the vibrational normal modes quantum numbers, and $i = 1-5$ correspond to the symmetric CH and CC stretching modes, the antisymmetric CH stretch, and the *trans*- and *cis*-degenerate bending modes, respectively. The latter are characterized by the bending angular momentum quantum numbers, l_4 and l_5]. Using

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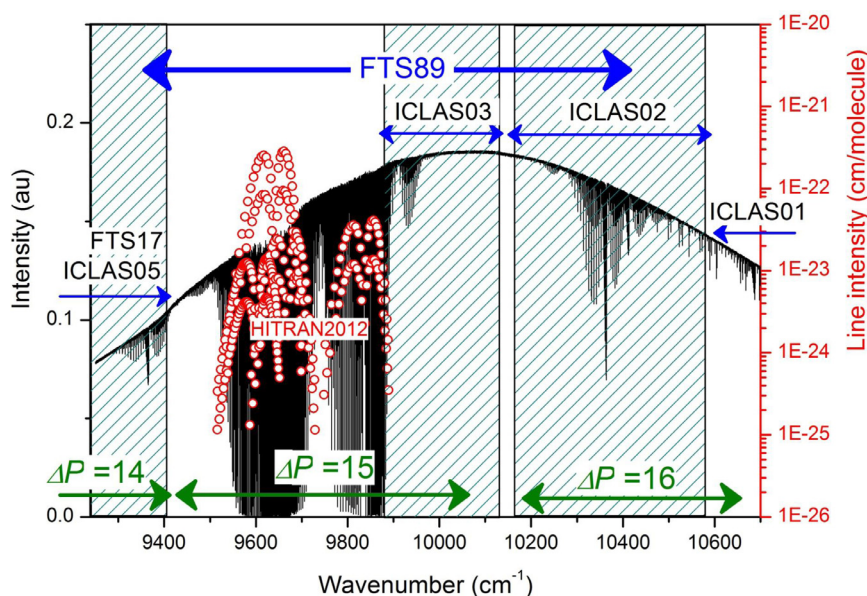


Fig. 1. Overview of the studied acetylene spectrum in the 9280–10740 cm^{-1} region recorded by Fourier transform spectroscopy (pressure of 87.6 hPa, path length of 105 m). The displayed region covers the entire $\Delta P = 15$ –16 series of bands and part of the $\Delta P = 14$ series. The HITRAN2016 list is superimposed (right-hand logarithmic scale for line intensities). The range of previous studies is indicated: FTS89 [14], FTS17 [4], ICLAS01 [19], ICLAS02 [18], ICLAS03 [17] and ICLAS05 [15].

the EH eigenfunctions, the effective dipole moment (EDM) parameters of each ΔP series of bands were fitted to the available measured intensity values. As a result, the Tomsk model provides not only predicted line positions but also reasonable intensity values for most of the predicted bands. This is a key advantage in the assignment process.

An overview of the spectrum under analysis is presented in Fig. 1 together with the range of the most relevant previous analysis in the region. The HITRAN2016 line list included in Fig. 1 consists of the four strongest bands dominated by the $3\nu_3$ band at 9640 cm^{-1} . The HITRAN positions and intensities were obtained by FTS by Vander Auwera et al. [12] and Jacquemart et al. [13], respectively. The most exhaustive analysis in the region (9362 – 10413 cm^{-1}) was reported by Herman et al. in 1989 by FTS with 40 m path length and 9 Torr pressure [14]. Four intervals were studied by high sensitivity Intracavity Laser Absorption Spectroscopy (ICLAS). The spectra in the region below 9410 cm^{-1} and in the 9857 – 10118 cm^{-1} interval were recorded using a Vertical External Cavity Surface Emitting Laser (VECSEL). ICLAS-VECSEL provides typical detectivity at the $\alpha_{\min} = 10^{-9} \text{ cm}^{-1}$ level [15] *i. e.* significantly beyond the FTS sensitivity. Nevertheless, due to the VECSEL laser dynamics [16], ICLAS-VECSEL can hardly be used for quantitative spectroscopy and no line intensity information was provided. The spectra in the 10160 – 10570 cm^{-1} interval [18] and above 10600 cm^{-1} [19] were investigated by high sensitivity ICLAS using a Ti: Sapphire laser. Again no intensity information was retrieved in the region. Intensity measurements of the strongest bands in the 9000 – 9420 cm^{-1} region was very recently obtained by FTS [4] and incorporated in the empirical database [1].

In the present work, we use a high resolution FTS spectrum recorded at USTC–Hefei with a path length of 105 m to construct a line list and extend the assignments in the 9280 – 10740 cm^{-1} range. The spectrum assignments, comparison with databases and discussion of the rovibrational perturbation are presented in the next section of this paper. A companion paper will be devoted to line intensities and will include the derivation of the Herman–Wallis coefficients and of the $\Delta P = 15$ and 16 EDM parameters, and the construction of a recommended line list in the region.

2. Experimental details, line list construction and rovibrational assignments

The FTS spectrum was recorded at USTC (Hefei, China) with a Bruker IFS 120 HR Fourier–transform spectrometer equipped with a multi-pass White cell adjusted to its maximum optical path length of 105 m. A tungsten source, a CaF_2 beam splitter and a Ge diode detector were used. The line positions were calibrated using the absorption lines of water (present as an impurity in the cell) given in HITRAN [8]. The unapodized resolution was 0.0142 cm^{-1} . The temperature and pressure were 298.5 K and 87.6 hPa, respectively.

A homemade multiline fitting computer code was used to derive the line positions and intensities. The line shape was modeled with the Voigt profile. The Doppler half width at half maximum was fixed to its theoretical value of about 0.011 cm^{-1} . The Lorentzian width of about 0.012 cm^{-1} , corresponding to an average pressure self broadening of $0.14 \text{ cm}^{-1}/\text{atm}$ [2], was adjusted when necessary. The typical *rms* of the (Meas.–Sim.) residuals correspond to a noise equivalent absorption $\alpha_{\min} \approx 3 \times 10^{-7} \text{ cm}^{-1}$ which leads to smallest measured line intensities on the order of a few $10^{-26} \text{ cm/molecule}$. We estimate the accuracy of the intensities reported in the present work to be about 15% for relatively strong isolated lines. Overall, line centers and intensities were derived for a set of about 3000 lines. A number of lines due to water observed in the high energy part of the spectrum were manually removed from the line list, leaving about 2500 lines to be assigned.

3. Rovibrational assignments

As mentioned above, the $^{12}\text{C}_2\text{H}_2$ rovibrational assignments relied on previous studies and on the predictions of the effective Hamiltonian model developed in Tomsk in the frame of the effective operator approach [10]. This model considers all the resonance interactions between rovibrational levels up to the ninth order of perturbation theory. Effective rovibrational parameters were adjusted to reproduce about 25,000 measured line positions collected from the literature up to 9900 cm^{-1} . The usual criteria (presence of a Q branch, observation of the 1:3 intensity alternation from even

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