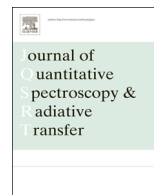




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The Fourier transform absorption spectrum of acetylene between 7000 and 7500 cm⁻¹

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ABSTRACT

High resolution (0.011 cm⁻¹) room temperature (295 K) Fourier transform absorption spectra (FTS) of acetylene have been recorded between 7000 and 7500 cm⁻¹. Line parameters (positions, intensities and self broadening coefficients) have been measured using a multispectrum treatment of three FTS spectra, recorded at 3.84, 8.04 and 56.6 hPa. As a result, a list of 3788 lines was constructed with intensities ranging between about 10⁻²⁶ and 10⁻²² cm/molecule. Comparison with accurate predictions provided by a global effective operator model (Lyulin OM, Perevalov VI, Teffo JL, Proc. SPIE 2004;5311:134–43) led to the assignment of 2471 of these lines to ¹²C₂H₂. The assigned lines belong to 29 ¹²C₂H₂ bands, 12 of them being newly reported. Spectroscopic parameters of the upper vibrational levels were derived from band-by-band fits of the line positions (typical *rms* values are on the order of 0.001 cm⁻¹). About half of the analyzed bands were found to be affected by rovibrational perturbations. Line parameters obtained in this work were compared with those available for about 350 transitions in the HITRAN 2012 database. The large set of new data will be valuable to refine the parameters of the global effective Hamiltonian and dipole moments of ¹²C₂H₂.

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1. Introduction

An overview of the absorption spectrum of acetylene recorded between 6900 and 8800 cm⁻¹ using Fourier transform spectroscopy (FTS) is displayed in Fig. 1. The spectrum shows strong absorbing regions separated by mostly transparent spectral windows. In general, the strong band systems are associated with combination bands with upper levels (of *u* symmetry) involving the

CH and CC stretching modes. Some of the strongest bands are indicated in Fig. 1. The conventional normal mode numbering in acetylene is used throughout this paper, with 1–5 corresponding to the symmetric CH σ_g^+ (ν_1) and CC σ_g^+ (ν_2) stretchings, the antisymmetric CH stretch σ_u^+ (ν_3), and the *trans*- π_g (ν_4) and *cis*- π_u (ν_5) degenerate bendings with corresponding zero order harmonic frequencies equal to 3398, 1981, 3316, 608 and 729 cm⁻¹, respectively [1]. The latter are characterized by the usual bending angular momentum quantum numbers, l_4 and l_5 , with $k=l_4+l_5$. In general, the bright levels are involved in a set of strong vibrational anharmonic couplings. The resulting intensity transfers lead to the observation of side bands superimposed to hot band transitions. As a

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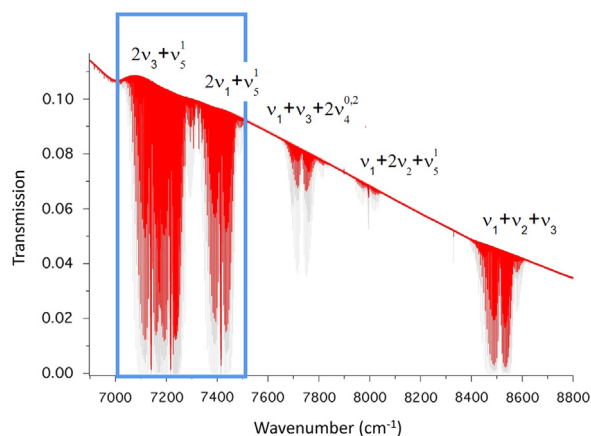


Fig. 1. Overview of the room temperature FTS spectrum of acetylene between 6900 and 8800 cm^{-1} . The spectra recorded at 3.84 and 56.6 hPa are displayed in red and grey, respectively. The region presently investigated together with some of the dominant bands observed is indicated. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

consequence of the resulting spectral congestion and of the occurrence of frequent perturbations, rovibrational assignments become more and more difficult with increasing wavenumber.

The $^{12}\text{C}_2\text{H}_2$ rovibrational assignments of the spectra studied in this work have been performed using the predictions of the polyad model developed at IAO-Tomsk [2,3]. This effective Hamiltonian (EH) considers all the resonance interactions between rovibrational levels up to the eighth order of perturbation theory. Its matrix, constructed on the Wang basis functions, has a block diagonal structure in which each block, corresponding to a subset of nearby, strongly interacting vibrational levels, is characterized by the polyad quantum number $P=5\nu_1+3\nu_2+5\nu_3+\nu_4+\nu_5$, where ν_i ($i=1-5$) are the vibrational normal modes quantum numbers, and the ef and g/u symmetry properties. The polyad structure of the EH has proved to be valid up to very high excitation [4–7]. The 265 effective rovibrational parameters presently available were determined by fitting, with a *rms* deviation of $4 \times 10^{-3} \text{ cm}^{-1}$, more than 26,000 measured line positions collected from the literature, observed up to 9900 cm^{-1} and belonging to 284 different vibrational bands [3]. The IAO-Tomsk EH is very similar to the effective Hamiltonian developed by Herman et al. at ULB [4,8–10], but the ULB-EH has more parameters. A detailed comparison of the EH parameters of the two models is however difficult because the expressions of the matrix elements often differ.

In recent years, the EH predictions were used to assign the acetylene spectrum in the weak absorbing windows investigated by Cavity Ring down Spectroscopy (CRDS), 5850–6350 cm^{-1} [10,12], 6667–7015 cm^{-1} [10,11] and 7244–7920 cm^{-1} [13]. The sensitivity of the CRDS technique combined with the accuracy of the EH predictions allowed assigning about 8000 mostly newly detected transitions. The new assignments mainly concern weak lines beyond the FTS sensitivity. However, surprisingly, we could also assign new bands of medium or even high intensity, clearly observed in FTS spectra. This fact

motivated the present work, devoted to the detailed analysis of FTS spectra recorded at ULB between 7000 and 7500 cm^{-1} . Indeed, a review of the literature indicated that many lines observed in FTS spectra were still unassigned. For instance, in the $2\nu_3+\nu_5^1$ band system near 7218 cm^{-1} , only two companion bands – $\nu_1+\nu_3+\nu_4^1$ at 7141.50 cm^{-1} and $\nu_1+\nu_2+(2\nu_4+\nu_5)^{11}$ at 7228.27 cm^{-1} – were assigned by FTS [14] (see Section 3 for the notation of the levels). As a result, the HITRAN list [15] in the 7000–7500 cm^{-1} region is limited to 347 lines (belonging to the above three bands and to the $2\nu_1+\nu_5^1$ band at 7417 cm^{-1}), with positions and intensities *stated* to originate from Jacquemart et al. [16]. In the present work, a total of 29 bands could be assigned. Note that about half of them were previously assigned in the more sensitive CRDS investigation of Ref. [13], which intersects the present study in the 7244–7500 cm^{-1} interval; however, no line intensity retrieval was performed in that latter work.

The rest of the report is organized as follows. The experimental conditions and line parameters retrieval are presented in Section 2. Sections 3, 4 and 5 are devoted to the assignment procedure, the comparison to the HITRAN line list and the band-by-band analysis, respectively.

2. Experimental details and line list construction

The spectra of acetylene were recorded at ULB between 6873 and 8925 cm^{-1} using a Bruker IFS 120 to 125 HR upgraded Fourier transform spectrometer. The spectral resolution was 0.011 cm^{-1} , corresponding to a maximum optical path difference of 81.8 cm. The instrument was fitted with a tungsten source, a 1.30 mm entrance aperture, a CaF_2 beam splitter and a 77 K InSb detector. The acetylene sample (UCAR, stated purity $\geq 99.6\%$) was used without purification. The gas was contained in a 1.72-m long white-type cell closed by CaF_2 windows and adjusted for 28 transits to provide an absorption path length of 48.3(2) m. Three spectra, recorded at 295(1) K and pressures of 3.84(2), 8.04(4) and 56.6(3) hPa (the uncertainty on the pressure is conservatively set to 0.5% of reading), were used to measure the line parameters using a multispectral fitting procedure neglecting the temperature correction. Fig. 1 shows an overview of the spectra recorded at 3.84 and 56.6 hPa.

The spectral line parameters were measured at IAO-Tomsk with a homemade multispectra fitting computer code in which a nonlinear least-squares method is applied to simultaneously fit the three spectra recorded. A few water lines most probably present in the evacuated spectrometer were also identified. Because the intensity of the water lines did not scale with the acetylene pressure, the water lines could not be included in the multispectral fitting treatment. Consequently, the nearby acetylene lines whose profile was affected by a water line could not be considered.

The line shape was modeled with the Voigt profile with Gaussian width fixed to the value calculated for $^{12}\text{C}_2\text{H}_2$ Doppler broadening. The line positions, intensities and self broadening coefficients were measured for most of the lines of strong to medium intensity. The self broadening coefficients of weak and overlapping lines were generally

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