Line intensities of $^{12}C_2H_2$ in the 7.7 μm spectral region

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ABSTRACT

Absolute intensities of 414 lines are measured in eight bands of the 7.7 μm spectral region of the $^{12}C_2H_2$ molecule, with an average accuracy of 5%. Vibrational transition dipole moment squared values and empirical Herman–Wallis coefficients are obtained in order to model the rotational dependence of the transition dipole moment squared, except for some forbidden bands for which smoothed values are given. These data are used to calculate a line list for atmospheric or astrophysical applications.

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1. Introduction

The 7.7 μm spectral region of acetylene $^{12}C_2H_2$ corresponds to the $\Delta P = 2$ sequence of vibrational transitions [1], P being a pseudo-quantum number equals $5v_1+3v_2+5v_3+v_4+v_5$, where v_1, v_2, v_3, v_4, and v_5 are the quantum numbers associated with the normal modes of vibration of the molecule in the ground electronic state. More extensive work on this spectral region can be found in Kabbadj et al. [2], where vibro-rotational lines are assigned in 16 bands around the $(v_4+v_5)_+^0$ strong cold band at 1328 cm⁻¹. These 16 bands are hot bands, except for $(v_4+v_5)^2$ at 1343 cm⁻¹. Among them, four "forbidden" bands were observed by Kabbadj et al., i.e., two $\Delta \leftarrow \Sigma$ bands and one $\Sigma \leftarrow \Delta$ band, as also one $\Phi \leftarrow \Pi$ band. Recently, Robert et al. [3] performed a global vibration–rotation analysis on states up to 3000 cm⁻¹, thus including the 7.7 μm spectral region.

The integrated intensity of the band at 1328 cm⁻¹ was first measured by Kelly et al. [4], and later more accurately by Varanasi and Bangaru [5], and by Koops et al. [6]. Theoretical calculation of this band intensity was performed by Abbouti Temsamani et al. [7]. Intensities of a few lines of the R-branch of $(v_4+v_5)_+^0$ were obtained by Podolske et al. [8]. A few years ago, an accurate set of absolute line intensities was obtained by Vander Auwera [9] for the cold bands $(v_4+v_5)_+^0$ and $(v_4+v_5)^2$, the accuracy being estimated better than 2%. Intensities of some lines of $(v_4+v_5)_+^0$ were measured again by Jacquemart et al. [10] and Lepère et al. [11], confirming the announced accuracy. Furthermore, collisional widths of $(v_4+v_5)_+^0$ were studied by Varanasi et al. [12] (N₂-broadening at 153 and 200 K), then by Podolske et al. [8] (N₂- and He-broadening at room temperature) and by Devi et al. [13] (N₂- and air-broadening at room temperature), whereas self-broadening coefficients

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Table 1
List of the bands observed by Kabbadj et al. [2] in the $\Delta P = 2$ series of transitions of $^{12}C_2H_2$ around 7.7 μm.

Band	Center [a]	Upper level [b]	Polyad [b]	Symmetry
$\nu_2-\nu_5^1$	1245.140	$010(00)_+^0$	$\{3\nu_5\}$	$\Sigma_g^+ \leftarrow \Pi_u$
$(\nu_4+3\nu_5)_+^0-2\nu_5^0$	1308.686	$000(13)_+^0$	$\{4\nu_5\}$	$\Sigma_u^+ \leftarrow \Sigma_g^+$
$(\nu_4+3\nu_5)^2-2\nu_5^2$	1310.182	$000(13)^2$	$\{4\nu_5\}$	$\Delta_u \leftarrow \Delta_g$
$(2\nu_4+2\nu_5)_-^0-(\nu_4+\nu_5)^2$	1311.308	$000(22)_-^0\ f$	$\{4\nu_5\}$	$\Sigma_g^- \leftarrow \Delta_u$
$(2\nu_4+2\nu_5)^2\ II-(\nu_4+\nu_5)^2$	1318.652	$000(22)^2\ II$	$\{4\nu_5\}$	$\Delta_g \leftarrow \Delta_u$
$(\nu_4+2\nu_5)^1\ II-\nu_5^1$	1318.730	$000(12)^1\ II$	$\{3\nu_5\}$	$\Pi_g \leftarrow \Pi_u$
$(2\nu_4+2\nu_5)_+^0-(\nu_4+\nu_5)_+^0$	1319.942	$000(22)_+^0$	$\{4\nu_5\}$	$\Sigma_g^+ \leftarrow \Sigma_u^+$
$(2\nu_4+2\nu_5)_-^0-(\nu_4+\nu_5)_-^0$	1320.638	$000(22)_-^0$	$\{\{4\nu_5\}$	$\Sigma_g^- \leftarrow \Sigma_u^-$
$(2\nu_4+2\nu_5)^2\ II-(\nu_4+\nu_5)_-^0$	1320.908	$000(22)^2\ II\ f$	$\{4\nu_5\}$	$\Delta_g \leftarrow \Sigma_u^-$
$(3\nu_4+\nu_5)^2-2\nu_4^2$	1328.019	$000(31)^2$	$\{4\nu_5\}$	$\Delta_u \leftarrow \Delta_g$
$(\nu_4+\nu_5)_+^0$	1328.081	$000(11)_+^0$	$\{2\nu_5\}$	$\Sigma_u^+ \leftarrow \Sigma_g^+$
$(2\nu_4+\nu_5)^1\ II-\nu_4^1$	1328.314	$000(21)^1\ II$	$\{3\nu_5\}$	$\Pi_u \leftarrow \Pi_g$
$(3\nu_4+\nu_5)_+^0-2\nu_4^0$	1330.206	$000(31)_+^0$	$\{4\nu_5\}$	$\Sigma_u^+ \leftarrow \Sigma_g^+$
$(\nu_4+2\nu_5)^1\ I-\nu_5^1$	1336.644	$000(12)^1\ I$	$\{3\nu_5\}$	$\Pi_g \leftarrow \Pi_u$
$(\nu_4+\nu_5)^2$	1342.821	$000(11)^2\ e$	$\{2\nu_5\}$	$\Delta_u \leftarrow \Sigma_g^+$
$(2\nu_4+\nu_5)^1\ I-\nu_4^1$	1348.006	$000(21)^1 I$	$\{3\nu_5\}$	$\Pi_u \leftarrow \Pi_g$
$(2\nu_4+\nu_5)^3-\nu_4^1$	1350.273	$000(21)^3 f$	$\{3\nu_5\}$	$\Phi_u \leftarrow \Pi_g$

[a] Band centers, in cm^{-1}, have been compiled from Ref. [2].
[b] For each band, the upper vibrational level and the polyad to which it belongs have been quoted. For the 4 forbidden bands, the sub-level (e or f) observed in Ref. [2] is mentioned. Levels are noted as explained in Section 1.

were obtained recently by Lepère et al. [11], as well as some N_2-broadening coefficients by Fissiaux et al. [14] and by Dyne et al. [15].

The aim of this work is to initiate absolute line intensity measurements in bands for which no result has been reported in the literature. Line intensities are known for the $(\nu_4+\nu_5)_+^0$ and $(\nu_4+\nu_5)^2$ bands [9], but they are unknown for the numerous other bands observed and assigned by Kabbadj et al. [2]. These bands are gathered in Table 1. In this table, a given value of P is assigned to a given set of interacting vibrational states, named polyad or cluster. Then, polyads are noted $\{P\nu_5\}$. Vibrational levels are noted $\nu_1\ \nu_2\ \nu_3\ (\nu_4\ \nu_5)_\pm^{\ell_t}r$, with $\ell = |\ell_4+\ell_5|$, ℓ_t being the vibrational angular momentum quantum number associated with the degenerate bending mode t, $\pm$ being the symmetry type for Σ vibrational states ($\ell = 0$), and r a roman numeral indicating the rank of the level, by decreasing energy value ($r = $ I for the highest energy level), inside the set of states having the same vibrational symmetry, and coupled by ℓ-type resonances.

Intensity measurements were undertaken because the knowledge of C_2H_2 line intensities in the 7.7 μm spectral region is important for several applications, especially for astrophysical ones. For example, the acetylene molecule has been observed in the circumstellar envelopes of carbon-rich stars. Using the Infrared Spectrograph (IRS) on board the Spitzer Space Telescope (SST), Matsuura et al. [16] detected acetylene bands at 7 and 14 μm in carbon-rich asymptotic giant branch stars in the Large Magellanic Cloud. Around 7 μm, spectroscopic databases as HITRAN [17] and GEISA [18] only contain line positions and intensities that Vander Auwera calculated from his absolute measurements in the $(\nu_4+\nu_5)_+^0$ band [9], for the rotational quantum number J up to 35. But intensities measured in Ref. [9] for some lines of the $(\nu_4+\nu_5)^2$ band are not reported in the databases. The temperature of interest for applications being around 500 K [16], the knowledge of intensities in the remaining hot bands is also important. In the quoted paper [16], Matsuura et al. could not reproduce the shapes they observed in their IRS-SST spectra around 7 μm because of the lack of data in databases.

The acetylene spectrum being very crowded around $1300\ cm^{-1}$, we first focused our work on 8 bands, which include the strongest allowed bands and the forbidden ones for their interest. To perform intensity measurements, several spectra have been recorded with a Fourier transform spectrometer. A set of 414 absolute line intensities has been obtained with an average accuracy of 5%. Section 2 of the paper will be devoted to the experimental conditions and to the measurements. The results and their analysis will be given in Section 3. The last section explains how we have proceeded to set up a line list for databases.

2. Experimental details and measurements

Six spectra have been recorded with the rapid scan Bruker IFS 120 HR interferometer of the LADIR (LAboratoire de Dynamique, Interactions et Réactivité, Paris). Experimental conditions are gathered in Table 2. This interferometer was equipped with a Globar source, a Ge/KBr beam splitter, and a photovoltaic MCT (Mercury-Cadmium-Telluride) detector. An optical filter covering the spectral region between 800 and $2000\ cm^{-1}$ has been used. The whole optical path was under vacuum and a multipass cell of 1-m base length was used. The cell was equipped with KCl windows. The temperature of the gas in the cell was recorded via four platinum probes at different places inside the cell. The uncertainty on the temperature measurements has been estimated to be ± 0.5 K. Pressures were measured using two full-scale ranges MKS