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Line intensities of acetylene: New measurements in the 1.5- μm spectral region and global modelling in the $\Delta P = 10$ series

O.M. Lyulin^a, V.I. Perevalov^{a,*}, H. Tran^{b,1}, J.-Y. Mandin^{b,c}, V. Dana^{b,c}, L. Régalia-Jarlot^d, X. Thomas^d, D. Décatore^d

^a Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Akademicheskii av., 634055 Tomsk, Russian Federation

^b UPMC Univ Paris 06, UMR 7092, Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique, Case courrier 76, 4, place Jussieu, 75252 Paris Cedex 05, France

^c CNRS, UMR 7092, Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique, Case courrier 76, 4, place Jussieu, 75252 Paris Cedex 05, France

^d Groupe de Spectrométrie Moléculaire et Atmosphérique, CNRS, UMR 6089, Université de Reims-Champagne-Ardenne, Faculté des Sciences, BP 1039, 51687 Reims Cedex 2, France

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ABSTRACT

Using the Fourier transform spectra of the acetylene molecule recorded near 1.5- μm , the intensities of 111 lines belonging to seven hot bands of the main isotopologue $^{12}\text{C}_2\text{H}_2$ have been retrieved by means of a multispectrum fitting procedure. Considering the density of lines in the spectra, and the fact that the measured bands are the weakest observed, the accuracy of the measurements is around 10%. At first stage, an empirical treatment of these data has been performed, leading to the vibrational transition dipole moment squared and some Herman–Wallis coefficients. Then the measured line intensities of this work and collected ones from the literature have been treated simultaneously within the framework of the effective operator approach.

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1. Introduction

In a previous paper [1], we published 546 measured line intensities belonging to 13 bands of the main isotopologue $^{12}\text{C}_2\text{H}_2$ of the acetylene molecule in the 1.5- μm spectral region. The transition dipole moments squared of the lines of these bands have been modelled using a Herman–Wallis factor. Our aim was to improve the knowledge of acetylene line intensities in the domain of optical communications. Because of the clustering pattern of the vibrational levels of C_2H_2 , see e.g. Refs. [2–10], the spectrum becomes very crowded when the wavenumber of the studied spectral region increases, and shows regularly spaced bunches of strongly overlapped lines. Then line parameter measurements become very difficult to perform when one is interested in very weak bands or in bands where many lines are hidden by the strongest ones. The

* Corresponding author. Tel.: +7 3822 491794; fax: +7 3822 492086.

E-mail address: vip@lts.iao.ru (V.I. Perevalov).

¹ Presently at Laboratoire Inter-Universitaire des Systèmes Atmosphériques, Universités Paris 12 et Paris 7, CNRS, UMR 7583, 61, avenue du Général-de-Gaulle, 94010 Créteil Cedex, France.

present work is dedicated to seven remaining bands, for which the measurement process was much more difficult to perform, but allowed us to obtain 111 new line intensities.

The paper is organized in the following way. In Section 2 the experimental details and the measurement procedure are presented. An empirical data reduction of the obtained line intensities is proposed using Herman–Wallis factors. Section 3 is dedicated to the simultaneous fitting of all line intensities obtained for the $\Delta P = 10$ series of transitions which has been performed within the framework of the effective operator approach.

2. Line intensity measurements and empirical data reduction

2.1. The acetylene spectrum at 1.5 μm and experimental details

Around 1.5 μm , the acetylene spectrum shows parallel bands belonging to the $\Delta P = 10$ sequence of vibrational transitions, with P the pseudo-quantum number $P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5$, the V_i 's being the usual vibrational quantum numbers. Assignment of these bands and line position measurements have been reported in several articles, most significant of these are Refs. [11–13]. In the following, vibrational states are labelled according to Pliva [14,15] as $V_1 V_2 V_3 (V_4 V_5)_{\pm}^K r$, with $K = |\ell_4 + \ell_5|$, 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 ($K = 0$), and r a roman numeral indicating the rank of the level, by decreasing energy value ($r = 1$ for the highest energy level), inside the set of states having the same vibrational symmetry, and coupled by ℓ -type resonances. The seven bands studied in this work are listed in Table 1. All are hot bands whose upper vibrational state belongs to the $\{12\nu_5\}$ polyad of interacting vibrational states, except one band whose upper level belongs to $\{11\nu_5\}$. Four of these bands are ℓ -type doubled.

To study the acetylene spectrum around 1.5 μm , 10 spectra were obtained with the GSMA step-by-step interferometer [16,17]. These spectra are the same as in a previous work [1], so that detailed experimental conditions can be found in Table 2 of Ref. [1]. To summarize the main information, let us recall that the unapodized FWHM resolution is between 0.006 and 0.01 cm^{-1} , and the SNR around 1000. The absorbing path length is 24 or 32 m, and the pressure ranges between 1 and 80 hPa. The apparatus was used with a tungsten radiation source, SiO_2 splitting and mixing plates, InSb detectors, and CaF_2 cell windows. Pressures were measured with a MKS Baratron 10- and 100-Torr manometer with an accuracy of 0.5%.

2.2. Measurement procedure and results

The measurement procedure used to retrieve line parameters from the spectra is the same as in Refs. [18,19]. A Voigt profile was used to calculate the absorption coefficient of the lines, and the self-broadening coefficients were fixed to the values calculated according to Ref. [20]. As far as the self-shifting coefficients are concerned, they were fixed to zero. The main differences with respect to our previous work [1] are due to the increasing difficulty of the measurement process when the bands become very weak, or when one is interested in bands whose lines are strongly overlapped. Because of these reasons, the accuracy is between 5% and 20%, with a mean value around 10%. Finally, we were able to obtain 111 line intensities in seven hot bands, but some of these bands have sparse data. These intensities are listed in Table 2, with the 2 SD confidence intervals.

Table 1

List of the seven hot bands studied in the $\Delta P = 10$ series of transitions of $^{12}\text{C}_2\text{H}_2$ for which line intensities are measured in this paper.

Band	Centre ^a (cm^{-1})	Upper level ^b	Polyad ^c	Lower level ^b	Symmetry	Refs.
$\nu_1 + \nu_2 + (2\nu_4 + \nu_5)^1 1 - \nu_4^1$	6616.57	110(21) ¹ 1	{11 ν_5 }	(10) ¹	$\Pi_u \leftarrow \Pi_g$	d,e
$2\nu_3 + 2\nu_2^2 - (\nu_4 + \nu_5)^2$	6342.62	002(20) ²	{12 ν_5 }	(11) ²	$A_g \leftarrow A_u$	
$2\nu_3 + (\nu_4 + \nu_5)_0^+ - 2\nu_5^0$	6355.89	002(11) ⁰ ₊	{12 ν_5 }	(02) ⁰ ₊	$\Sigma_u^+ \leftarrow \Sigma_g^+$	
$\nu_1 + \nu_3 + 2\nu_5^0 - 2\nu_5^0$	6512.71	101(02) ⁰ ₊	{12 ν_5 }	(02) ⁰ ₊	$\Sigma_u^+ \leftarrow \Sigma_g^+$	d
$\nu_1 + \nu_3 + 2\nu_5^2 - 2\nu_5^2$	6513.22	101(02) ²	{12 ν_5 }	(02) ²	$A_u \leftarrow A_g$	d,e
$\nu_1 + \nu_3 + (\nu_4 + \nu_5)_0^- - (\nu_4 + \nu_5)_0^-$	6512.73	101(11) ⁰ ₋	{12 ν_5 }	(11) ⁰ ₋	$\Sigma_g^- \leftarrow \Sigma_u^-$	e
$\nu_1 + \nu_3 + (\nu_4 + \nu_5)^2 - (\nu_4 + \nu_5)^2$	6504.90	101(11) ²	{12 ν_5 }	(11) ²	$A_g \leftarrow A_u$	d,e

^a Bands are gathered according to the vibrational quantum numbers. Rough values of band centres have been compiled from Ref. [11] and are given only as a guide to locate the bands.

^b A full notation is given for the vibrational levels (only ν_4 and ν_5 are quoted for the lower level, since ν_1 , ν_2 , and ν_3 are equal to zero for this level in our case).

^c For convenience, the polyad to which the upper vibrational level belongs is also recalled.

^d Rovibrational assignments and line positions can be found in the original work of Baldacci et al. [12]. Note that all the bands quoted in this table have been assigned by Keppler et al. [11].

^e Line positions with the announced accuracy of 0.0003 cm^{-1} can be retrieved from Kou et al. [13].

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