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Line intensities of acetylene: Measurements in the 2.5-μm spectral region and global modeling in the $\Delta p = 4$ and 6 series

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Abstract

More than 670 line intensities of nine perpendicular bands of acetylene are measured in the 2.5-μm spectral region using a step-by-step interferometer. Absolute values of line intensities are obtained with an average accuracy of 5%. Vibrational transition dipole moment and Herman–Wallis coefficients are determined for each studied band. These measured line intensities, and those previously measured in the 3.8-μm region [Jacquemart D, Lacome N, Mandin JY, Dana V, Lyulin OM, Perevalov VI. Multispectrum fitting of line parameters for $^{12}C_2H_2$ in the 3.8-μm spectral region. JQSRT, submitted for publication], are treated simultaneously within the framework of the effective operators approach. The sets of effective dipole moment parameters obtained reproduce the observed line intensities within the experimental uncertainty. The good predictive ability of the modele is demonstrated.

Keywords: Acetylene; Infrared spectroscopy; Vibro-rotational transitions; Line intensities; Transition dipole moment; Effective operators; Global treatment

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1. Introduction

This paper is aimed to pursue and improve the modelling of the line intensities of the acetylene molecule, within the framework of the method of effective operators [1–3] on the basis of the observed line intensities. To do that, substantial and accurate sets of individual line intensities are needed. In a recent work [4], about 250 line intensities were measured in the 3.8-μm spectral region, enriching noticeably our knowledge of acetylene

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intensities. According to notations adapted to a global treatment [1–3], this spectral domain concerns the series of vibrational transitions $\Delta P = 4$, with P the pseudo-quantum number $P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5$, where the V_i's are the usual vibrational quantum numbers. This series involved interacting vibrational states belonging to the polyads $\{4\nu_5\}$ through two cold bands, and $\{5\nu_5\}$ through three hot bands. To extend the knowledge of line intensities, we have studied the acetylene spectrum between 3750 and 4200 cm^{-1}. About 670 line intensities, from nine bands, were measured in this spectral region, with an average accuracy of 5%. The concerned transitions belong to the series $\Delta P = 6$, involving the polyads $\{6\nu_5\}$ through four cold bands, and $\{7\nu_5\}$ through five hot bands.

In the first part of the paper, the spectra and the methodology used to retrieve line positions and intensities will be presented, and the vibrational transition dipole moments and empirical Herman–Wallis coefficients, deduced from the usual empirical data reduction, will be reported. In the second part of the paper, the results of the simultaneous fittings of the newly measured line intensities in the series $\Delta P = 6$ and those in the series $\Delta P = 4$, performed within the framework of the method of effective operators, will be presented.

2. Line intensity measurements in the 2.5-μm spectral region of acetylene

2.1. The acetylene spectrum at 2.5 μm and experimental details

To have an idea of the spectrum of acetylene around 2.5 μm, we have gathered the main spectroscopic information in Table 1. In this part of the paper, the vibrational notations of Plíva [5,6] are used, in order to facilitate comparisons with previous works who also used the same notations. Thus, vibrational levels are noted $V_1\ V_2\ V_3\ (V_4\ V_5)^{\ell}_{\pm}r$, 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 ($r = \text{I}$ for the highest energy level), inside the set of states having the same vibrational symmetry, and coupled by ℓ-type resonances. In Table 1, we have recalled the upper vibrational state of each band, and the polyad of interacting states to which it belongs. The nine bands studied in this work are particularly interesting for practical applications (see, e.g., [7]), since they are perpendicular bands exhibiting strong Q-branches. Note that two of the observed hot bands are of the $\Delta \leftarrow \Pi$ type, and therefore are ℓ-type doubled.

Original information on the 2.5-μm bands of acetylene comes from the Wiggins et al.'s paper [8] in 1961. Later on, Palmer et al. [9] gave vibro-rotational assignments in the main bands $\nu_2+(2\nu_4+\nu_5)^1$ II and $\nu_3+\nu_4^1$. (Note that their original vibrational assignments have been interchanged in the present work according to the principle values of the expansion coefficients of the eigenfunctions obtained using our set of effective Hamiltonian parameters [2].) The seven remaining bands were studied by D'Cunha et al. [10]. As far as line intensities are concerned, to our knowledge only integrated intensities of Q-branches or band systems were published by Rinsland et al. [7] and Koops et al. [11]. As Q-branches are observed in the present work, let us

Table 1
Bands of acetylene $^{12}C_2H_2$ studied around 2.5 μm ($\Delta P = 6$ series of vibrational transitions)

Band	Center[a]	Ref.[b]	Upper level	Upper level polyad	Symmetry
$\nu_2+(2\nu_4+\nu_5)^1$ II[c]	3882.41	Palmer et al. [9]	$010(21)^1$ II	$\{6\nu_5\}$	$\Pi_u \leftarrow \Sigma^+_g$
$\nu_3+\nu_4^{1}$[c]	3898.34	Palmer et al. [9]	$001(10)^1$	$\{6\nu_5\}$	$\Pi_u \leftarrow \Sigma^+_g$
$\nu_1+\nu_5^1$	4092.35	D'Cunha et al. [10]	$100(01)^1$	$\{6\nu_5\}$	$\Pi_u \leftarrow \Sigma^+_g$
$\nu_2+3\nu_5^1$	4140.06	D'Cunha et al. [10]	$010(03)^1$	$\{6\nu_5\}$	$\Pi_u \leftarrow \Sigma^+_g$
$\nu_1+2\nu_5^0-\nu_5^1$	4069.80	D'Cunha et al. [10]	$100(02)^0_+$	$\{7\nu_5\}$	$\Sigma^+_g \leftarrow \Pi_u$
$\nu_1+2\nu_5^2-\nu_5^1$	4083.87	D'Cunha et al. [10]	$100(02)^2$	$\{7\nu_5\}$	$\Delta_g \leftarrow \Pi_u$
$\nu_1+(\nu_4+\nu_5)^0_+-\nu_4^1$	4060.76	D'Cunha et al. [10]	$100(11)^0_+$	$\{7\nu_5\}$	$\Sigma^+_u \leftarrow \Pi_g$
$\nu_1+(\nu_4+\nu_5)^0_--\nu_4^1$	4075.97	D'Cunha et al. [10]	$100(11)^0_-$	$\{7\nu_5\}$	$\Sigma^-_u \leftarrow \Pi_g$
$\nu_1+(\nu_4+\nu_5)^2-\nu_4^1$	4079.19	D'Cunha et al. [10]	$100(11)^2$	$\{7\nu_5\}$	$\Delta_u \leftarrow \Pi_g$

[a] Rough values of band centers (in cm^{-1}) are reported only as a guide.
[b] Main references giving vibro–rotational assignments and experimental line positions.
[c] The Palmer et al.'s [9] original vibrational assignments have been interchanged for these two bands.