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# An empirical spectroscopic database for acetylene in the regions of 5850–6341 $\text{cm}^{-1}$ and 7000–9415 $\text{cm}^{-1}$

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## ABSTRACT

Six studies have been recently devoted to a systematic analysis of the high-resolution near infrared absorption spectrum of acetylene recorded by Cavity Ring Down spectroscopy (CRDS) in Grenoble and by Fourier-transform spectroscopy (FTS) in Brussels and Hefei. On the basis of these works, in the present contribution, we construct an empirical database for acetylene in the 5850–9415  $\text{cm}^{-1}$  region excluding the 6341–7000  $\text{cm}^{-1}$  interval corresponding to the very strong  $\nu_1 + \nu_3$  manifold. Our database gathers and extends information included in our CRDS and FTS studies. In particular, the intensities of about 1700 lines measured by CRDS in the 7244–7920  $\text{cm}^{-1}$  region are reported for the first time together with those of several bands of  $^{12}\text{C}^{13}\text{CH}_2$  present in natural isotopic abundance in the acetylene sample.

The Herman-Wallis coefficients of most of the bands are derived from a fit of the measured intensity values. A recommended line list is provided with positions calculated using empirical spectroscopic parameters of the lower and upper energy vibrational levels and intensities calculated using the derived Herman-Wallis coefficients. This approach allows completing the experimental list by adding missing lines and improving poorly determined positions and intensities. As a result the constructed line list includes a total of 10973 transitions belonging to 146 bands of  $^{12}\text{C}_2\text{H}_2$  and 29 bands of  $^{12}\text{C}^{13}\text{CH}_2$ . For comparison the HITRAN database in the same region includes 869 transitions of 14 bands, all belonging to  $^{12}\text{C}_2\text{H}_2$ . Our weakest lines have an intensity on the order of  $10^{-29}$  cm/molecule, about three orders of magnitude smaller than the HITRAN intensity cut off. Line profile parameters are added to the line list which is provided in HITRAN format.

The comparison of the acetylene database to the HITRAN2012 line list or to results obtained using the global effective operator approach is discussed in terms of completeness and accuracy.

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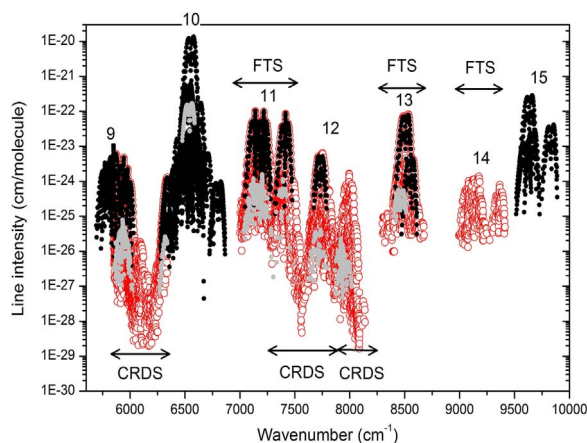
## 1. Introduction

Acetylene is probably the most studied four-atom molecule and constitutes a prototype system for molecular dynamics (see for instance Refs [1–11], and references therein). The rovibrational absorption spectrum of  $^{12}\text{C}_2\text{H}_2$  in its  $\bar{X}^1\Sigma_g^+$  ground state has been investigated in a considerable number of contributions both theoretically and experimentally up to the visible region near 25,000  $\text{cm}^{-1}$ . Different reviews and databases collecting these experimental results can be found in Refs [5,9–11]. As a result of increasing rovibrational couplings the spectrum shows an increasing complexity and congestion at high energy. In general the strongest bands keep a mostly unperturbed appearance up to very high excitation energy [6,7] and appear on a dense background of

lines which are much more difficult to interpret. Each vibrational level interacts with a limited set of vibrational levels through a set of anharmonic and Coriolis interactions [1,3,5,9]. The interacting levels belong to a same polyad characterized by the quantum number,  $P = 5V_1 + 3V_2 + 5V_3 + V_4 + V_5$ . We adopt the  $(V_1V_2V_3V_4V_5l_4l_5)$  conventional normal mode 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  $l_5$ .

The most used spectroscopic databases namely HITRAN [12] and GEISA [13] include only the strongest bands of each polyad while the review of the literature shows that many additional bands have been reported in studies mostly dedicated to rovibrational assignment and line positions analysis. The lack of intensity measurements prevents the inclusion of these observations

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**Fig. 1.** Overview of the acetylene spectrum between 5000 and 10000  $\text{cm}^{-1}$ . The HITRAN2012 line list [12] (full black circles) is superimposed to our global experimental line list based on Refs [16–21] (red open circles). The  $^{12}\text{C}^{13}\text{CH}_2$  transitions are highlighted (full grey circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

in databases. In the recent years, important efforts have been undertaken to extend the observations from different near infrared spectra recorded at room temperature by Cavity Ring Down spectroscopy (CRDS) [14–17,20] and Fourier-transform spectroscopy (FTS) [18,19,21]. The results obtained in Refs [16–21], are presented in more details below (Section 2) and illustrated in Fig. 1. Overall, they cover the wide 5850–9415  $\text{cm}^{-1}$  region at the exception of the 6341–7000  $\text{cm}^{-1}$  interval corresponding to the very strong  $\nu_1 + \nu_3$  manifold. FTS spectra recorded at ULB-Brussels [18,19] and USTC-Hefei [21] were used to study the  $\Delta P = 11, 13$  and 14 series of bands above 7000  $\text{cm}^{-1}$  (see Fig. 1). The typical sensitivity of the studied FTS spectra allows measurements of intensities larger than  $4 \times 10^{-26}$   $\text{cm/molecule}$ . As a result of the high sensitivity of the CRDS recordings (noise equivalent absorption,  $\alpha_{\text{min}}$ , ranging between  $5 \times 10^{-11}$  and  $10^{-10}$   $\text{cm}^{-1}$ ), an intensity threshold detectivity below  $10^{-28}$   $\text{cm/molecule}$  was achieved. A considerable amount of new information was retrieved in the spectral intervals studied by CRDS, in particular in the transparency window around 6000  $\text{cm}^{-1}$  [14,17] and in the range of the  $\Delta P=12$  series of bands extending from 7250 to 8250  $\text{cm}^{-1}$  [16,20].

The rovibrational assignments of the spectra were performed on the basis of the predictions of the effective Hamiltonian (EH) model developed at IAO-Tomsk [9]. This model is a polyad model which considers all the resonance interactions between rovibrational levels up to the eighth order of perturbation theory. Using 237 effective rovibrational parameters, the Tomsk global EH reproduces with a *rms* deviation of  $3.65 \times 10^{-3}$   $\text{cm}^{-1}$ , about 25000 measured line positions collected from the literature belonging to 494 bands lying in the 50–9900  $\text{cm}^{-1}$  region [9]. This result was achieved after exclusion of about 4000 line positions. The very recent CRDS and FTS data above 7915  $\text{cm}^{-1}$  [18–20] are not yet incorporated as input data used to refine the EH parameters. The CRDS study around 8000  $\text{cm}^{-1}$  [20] indicates that the positions predicted with the EH agree with the observations within typically 0.05  $\text{cm}^{-1}$  and deviations between new observations and predictions gradually increase up to 1  $\text{cm}^{-1}$  near 9500  $\text{cm}^{-1}$  (see Section 4.2).

The rest of this report is organized as follows. In the next Section 2, we review the six data sources [16–21] used to construct the database. In order to obtain a consistent set of spectroscopic line parameters, the published experimental data had to be completed in some spectral regions. For each data source, newly reported information is detailed. In particular, line intensities in the

CRDS spectra between 7244 and 7920  $\text{cm}^{-1}$  unreported in Ref [16] are presently retrieved and additional information concerning the intensities of  $^{12}\text{C}^{13}\text{CH}_2$  lines is obtained. In Section 3, the construction of the experimental database obtained by gathering the various line lists is presented. Then, when possible, we derived the vibrational transition dipole moment squared,  $I_{\text{rot}}^2$ , and Herman-Wallis coefficients from a fit of the measured line intensities. This allows completing (or improving) the experimental database by adding (or replacing) lines with positions calculated from the empirical spectroscopic parameters of the lower and upper vibrational states and intensities calculated using the Herman-Wallis coefficients. Finally, a recommended line list is obtained by selecting for each line either the calculated or measured line parameters. Section 4 is devoted to a comparison to the HITRAN database and to the results of the effective operator approach. In the conclusion, we present some perspectives and recall that, in spite of being the most complete in the region, a high number of weak lines remain unassigned in the acetylene spectrum and are then absent from our list.

## 2. Sources of line parameters

Six experimental studies of the room temperature acetylene spectrum were used as sources of the line parameters (see Table 1):

- (i) The 5851–6341  $\text{cm}^{-1}$  spectral interval corresponding to an acetylene transparency window between the  $\Delta P=9$  and 10 band series was studied by high sensitivity CRDS in Ref [17]. The spectra was recorded at 2 and 10 Torr. As line intensities were roughly obtained from the peak heights, their uncertainty was estimated to be 20% for unblended lines. A list of about 10700 absorption features was constructed. An experimental difficulty was due to the presence of about 2500 absorption lines of ethylene present at the ppm level in the acetylene sample. A total of more than 2700  $^{12}\text{C}_2\text{H}_2$  lines were rovibrationally assigned adding about 2260 new assignments to the previous set of about 500 assigned transitions available in the literature [14,24–27]. In Ref [17], only results relative to the main isotopologue were reported. Five bands of the  $^{12}\text{C}^{13}\text{CH}_2$  isotopologue present in natural abundance (2.2%)

**Table 1**

Sources of experimental data used to construct the acetylene database in the 5851.5–6341 and 7001–9414  $\text{cm}^{-1}$  regions. The tag used to mark each source (3<sup>rd</sup> column) indicates the experimental technique and the publication year of the corresponding paper. The number of lines transferred to the global experimental list (supmat1) and new additional results obtained in this work are indicated in the two last columns.

Ref number	Spectral range ( $\text{cm}^{-1}$ )	Tag	$N^a$	New information
17	5851–6341	CRDS14	2585 <sup>b</sup>	Five $^{12}\text{C}^{13}\text{CH}_2$ bands 1011010-0000000 band of $^{12}\text{C}^{13}\text{CH}_2$
18	7000–7500	FTS15	2081	
16	7244–7918	CRDS13	1519	New intensity retrieval and nine $^{12}\text{C}^{13}\text{CH}_2$ bands
20	7915–8250	CRDS16	1220	1202101-0001010 band of $^{12}\text{C}_2\text{H}_2$ newly assigned
19	8280–8700	FTS16	649	
21	8980–9415	FTS17	345	
			Total: 8399	

Note

<sup>a</sup> Total number of lines adopted for the experimental database (supmat1).

<sup>b</sup> Including 223 strong lines transferred from the HITRAN database [12].

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