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# The ethylene absorption spectrum between 6075 and 8050 $\text{cm}^{-1}$ : Empirical line list and rovibrational assignments

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## ABSTRACT

The highly congested absorption spectrum of ethylene ( $\text{C}_2\text{H}_4$ ) is analyzed between 6075 and 8050  $\text{cm}^{-1}$ . In the 6200–8050  $\text{cm}^{-1}$  range, a list of about 32,650 lines is retrieved from a room temperature spectrum recorded by Fourier transform spectroscopy ( $P = 15.72$  mbar,  $L = 45$  m). This dataset was merged with a set of about 3460 lines available in the literature in the region of the strong  $\nu_5 + \nu_9$  band near 6150  $\text{cm}^{-1}$ . In addition, two FTS spectra at 130 K provide complementary information in the 6020–6320  $\text{cm}^{-1}$  range (about 7570 lines).

Relying on the position and intensity agreements with a line list of  $^{12}\text{C}_2\text{H}_4$  transitions calculated by the variational method, a total of 4090 transitions is assigned to eighteen bands, ten of them being newly reported. All the reported assignments are confirmed by Lower State Combination Difference (LSCD) relations *i.e.* all the upper states (1749 in total) have coinciding determinations of their energies through several transitions (up to 6). The obtained empirical energy values are given and compared to their variational counterpart. As an additional validation test of the lower state assignments, the room temperature intensities are extrapolated at 130 K and compared to their experimental values. Overall, a large fraction of the strong lines of the region is assigned and the total intensity of the assigned transitions represents 46 and 55% of the total variational and experimental intensities at 296 K, respectively. In the considered range, variational positions deviate from measurements by a few  $\text{cm}^{-1}$  and the total variational absorption is underestimated by 40 %.

## 1. Introduction

We have recently undertaken a systematic study of the absorption spectrum of ethylene in the near-infrared in order to complete spectroscopic databases which lack line parameters in this region. For instance, no data are provided in the HITRAN database [1] above the 3  $\mu\text{m}$  range while the near-infrared range, at higher energy, is well suited for trace detection.

In addition to extensive empirical line lists with reasonably accurate positions and intensities, atmospheric and planetary applications require the knowledge of the lower state energy ( $E_{low}$ ) of the transitions which rules the temperature dependence of the line intensities. A pragmatic way to determine empirical  $E_{low}$  values is to retrieve line intensities of the same transition at two distinct temperatures and derive the corresponding empirical  $E_{low}$  value from the measured intensity ratio. This 2T-method which has been extensively applied to methane [2–5], is a purely experimental approach with no need of theoretical interpretation. Obviously, a better accuracy on the retrieved  $E_{low}$  values is ob-

tained applying the 2T-method to intensity sets corresponding to a large temperature gap. The case of methane is particularly favorable because the vapor pressure at liquid nitrogen temperature (77 K) is relatively high (about 10 Torr). In the case of ethylene, the same vapor pressure corresponds to about 120 K which makes the 2T-method applicable, although somewhat less accurate (in addition, the spectral congestion is higher which decreases the accuracy of the intensity retrieval).

Recently, high resolution ethylene spectra were recorded by Fourier transform spectroscopy (FTS) at four temperatures (130, 201, 240 and 297 K) providing solid experimental material for the application of the 2T-method. In a first contribution [6], we applied the 2T-method to the spectra at 130 and 297 K in the 7120–7260  $\text{cm}^{-1}$  region and could derive the empirical  $E_{low}$  values of 1249 transitions.

In fact,  $\text{C}_2\text{H}_4$  is an intermediate-size molecule tractable for high-level variational calculations. In the above study [6], we showed that rovibrational assignments of many strong lines of the (less congested) 130 K spectrum can be directly obtained by position and intensity com-

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parison to variational calculations. Nevertheless, as the differences between measured and variational positions can reach several  $\text{cm}^{-1}$ , the assignments had to be secured by applying Lower State Combination Difference (LSCD) relations: the assignment of a given upper level was validated only in case of various coincident determinations through different transitions. By this way, about 650 transitions could be rovibrationally assigned to seven vibrational bands observed at 130 K in the  $6700\text{--}7260\text{ cm}^{-1}$  region [6]. The consistency of the empirical and exact  $E_{low}$  values provided by the assignment was checked.

The quality of the  $\text{C}_2\text{H}_4$  variational calculations being sufficient to reliably assign the near infrared spectrum of ethylene at 130 K, we have recently used the same approach to assign 1674 transitions in the room temperature spectrum in the  $5800\text{--}6200\text{ cm}^{-1}$  region [7] (see Fig. 1). This region is of particular interest for trace detection as it corresponds to the first overtone of the C—H stretching and includes the strong  $\nu_5 + \nu_9$  band near  $6149\text{ cm}^{-1}$ . The used experimental list of about 12,200 lines relied on a high resolution FTS spectrum recorded at 294 K with a small pressure value of 0.47 mbar [8].

In the current work, we consider the large  $6200\text{--}8050\text{ cm}^{-1}$  region at room temperature including the  $7120\text{--}7260\text{ cm}^{-1}$  interval studied at 297 K by Mraidi et al. [6] (see Fig. 1). Line intensities of the region are about two orders of magnitude smaller than those of the  $\nu_5 + \nu_9$  band. The FTS spectrum at 297 K recorded by Mraidi et al. with a pressure of 15.7 mbar was used to construct the experimental line list. For most of the bands of the region, the assignments presented below will rely on the position and frequency matchings between theory and experiment thoroughly validated by LSCD relations. In addition, in the  $6020\text{--}6320\text{ cm}^{-1}$  interval, to help for the assignments, we will also consider the 130 K spectrum with reduced spectral congestion. As main output of the present contribution, we propose an empirical line list with assignments for many strong lines of the entire  $6075\text{--}8050\text{ cm}^{-1}$  region, thus including the  $6075\text{--}6200\text{ cm}^{-1}$  interval of the  $\nu_5 + \nu_9$  band for which the rovibrational assignments of Ref. [7] have been slightly extended.

The remaining part of the paper is organized as follows. In the next section, we recall the experimental conditions of the analyzed spectra

and present the line parameters retrieval. The rovibrational assignments in the 297 K and 130 K spectra are described in Section 3 before a discussion about the level of agreement between experiment and theory (Section 4).

## 2. Empirical line lists

In Ref. [6], eight high resolution FTS spectra of ethylene were recorded between  $5000$  and  $9000\text{ cm}^{-1}$  for four temperature values: 130 (3), 201(2), 240(1) and 297(1) K. For each temperature, two spectra were recorded at different pressures (see Table 1 of Ref. [6]). In the present work, we consider the spectrum #7 at room temperature and 15.72 mbar pressure and the two 130 K spectra (#1 and #2, at 3.37 and 0.25 mbar, respectively). The reader is referred to Ref. [6] for details about the recording conditions. Briefly, thirty passes through a cryogenic optical cell provided an absorption pathlength of 45 m. The spectral resolution of the recordings was fixed to  $0.0075\text{ cm}^{-1}$  and, depending on the spectrum, between 300 and 2400 interferograms were averaged

The ethylene spectra were accurately calibrated in frequency by recording two high resolution spectra of  $\text{N}_2\text{O}$  and accurate reference line positions provided by the HITRAN database (after calibration, the RMS deviation of the position differences was about  $3 \times 10^{-4}\text{ cm}^{-1}$ ).

In Fig. 2, we present a comparison of the spectra #7 and #1 illustrating the high spectral congestion and the important change of the appearance of the spectrum by cooling down from 297 to 130 K.

The line centres and intensities were determined using an interactive least squares multi-line fitting program (<https://fityk.nieto.pl/>, version v 1.1.1). The fit was performed assuming a simple Voigt function as line shape, thus, including in an effective way the instrument line shape. Note that, as the Doppler width (about  $0.016\text{ cm}^{-1}$  FWHM at room temperature) is larger than the spectral resolution ( $0.0075\text{ cm}^{-1}$ ), the impact of the instrument line shape is expected to be small in the considered range of weak absorption. The line intensities were obtained as the ratio of the integrated line absorbance by the product of the pathlength ( $L = 45\text{ m}$ ) and molecular density (calculated from the pressure value). An example of spectrum reproduction is presented in Fig. 3.

A list of about 32,650 lines was obtained from the 297 K spectrum between  $6197.8$  and  $8043.7\text{ cm}^{-1}$  (see Fig. 1). Due to a small increase of the instrumental noise level at high frequency, the intensity cut-off was fixed as a linear function increasing from  $1 \times 10^{-25}$  to  $2 \times 10^{-25}\text{ cm}^{-1}$  molecule between  $6500$  and  $8000\text{ cm}^{-1}$ . For comparison, the strongest lines of the region have an intensity on the order of  $2 \times 10^{-23}\text{ cm}^{-1}$  molecule. In order to extend assignments in the low energy region, in particular for a new band centred near  $6174\text{ cm}^{-1}$  (see below), we completed this list at low frequencies by adding the  $6075\text{--}6197.8\text{ cm}^{-1}$  section of the line list of Ref. [7], including the strong  $\nu_5 + \nu_9$  band near  $6150\text{ cm}^{-1}$  (about 3460 lines). The resulting room temperature list of 36,164 lines covering the  $6075\text{--}8050\text{ cm}^{-1}$  region is provided as a supplementary material.

The region near  $6200\text{ cm}^{-1}$  corresponds to the R-branch head of the  $\nu_5 + \nu_9$  band and thus includes high rotational transitions whose intensities are sharply decreased by cooling. In order to take advantage of the resulting spectral simplification and assign underlying weaker bands, we considered the 130 K spectra and elaborated a 130 K line list for the  $6075\text{--}6320\text{ cm}^{-1}$  range, based on spectra #2 (0.25 mbar) and #1 (3.37 mbar) in the  $6184\text{--}6209$  and  $6209\text{--}6320\text{ cm}^{-1}$  intervals, respectively. The resulting list of about 7570 lines between  $6020.1$  and  $6319.8\text{ cm}^{-1}$  is provided as supplementary material.

## 3. Rovibrational assignments

The rovibrational assignments were performed by comparison to the variational lists calculated in Ref. [6] up to  $9000\text{ cm}^{-1}$ . These lists extend towards higher energy the TheoReTS lists calculated up to

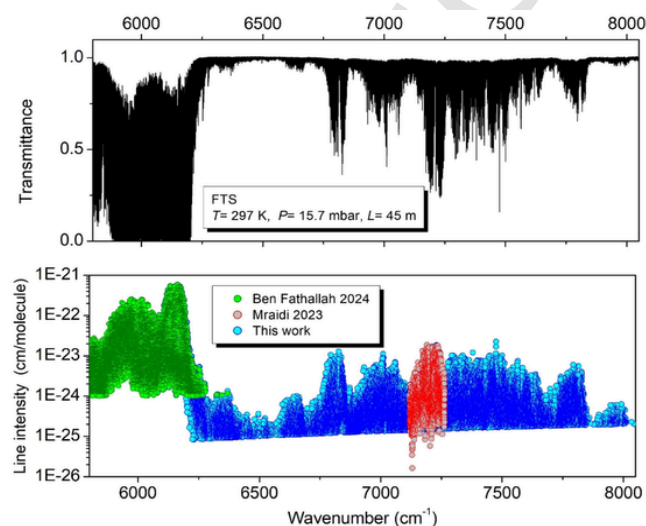


Fig. 1. Overview comparison of the ethylene spectrum at room temperature in the  $5800\text{--}8050\text{ cm}^{-1}$  interval. Upper panel: FTS spectrum recorded with a 15.72 mbar pressure and an absorption pathlength of 45 m [6], Lower panel: Empirical line list retrieved in this work in the  $6197\text{--}8050\text{ cm}^{-1}$  region (blue circles). In the  $7120\text{--}7260\text{ cm}^{-1}$  region, a list was previously derived in Ref. [6] (red circles). In the low energy region, below  $6200\text{ cm}^{-1}$ , the empirical list derived in Refs. [7,8] from a lower pressure spectrum (0.47 mbar) is included (green circles).

**Table 1**

Statistics of the transitions assigned to eighteen bands in the absorption spectrum of  $^{12}\text{C}_2\text{H}_4$  between 6075 and 8050  $\text{cm}^{-1}$  and comparison of the measured and calculated intensities.

Band	Variational [6]			Assigned lines			
	Band center <sup>a</sup> ( $\text{cm}^{-1}$ )	Nb.	Int. sum <sup>b</sup> (cm/molecule)	Nb.	Int. sum (cm/molecule)		
					Exp.	Var.	Exp./Var
1 $\nu_5 + \nu_9$ <sup>b</sup>	6150.46	2701	$7.76 \times 10^{-20}$	688	$7.84 \times 10^{-20}$	$5.97 \times 10^{-20}$	1.31
		<i>1353</i>	<i><math>8.71 \times 10^{-20}</math></i>	<i>492</i>	<i><math>9.37 \times 10^{-20}</math></i>	<i><math>7.80 \times 10^{-20}</math></i>	1.2
2 $\nu_2 + \nu_5 + \nu_{12}$ <sup>b</sup>	6173.60	1612	$9.71 \times 10^{-22}$	149	$5.24 \times 10^{-22}$	$2.18 \times 10^{-22}$	2.4
		<i>813</i>	<i><math>8.94 \times 10^{-22}</math></i>	<i>222</i>	<i><math>1.09 \times 10^{-21}</math></i>	<i><math>4.71 \times 10^{-22}</math></i>	2.31
3 $3\nu_2 + \nu_{12}$	6363.39	504	$1.42 \times 10^{-22}$	214	$7.44 \times 10^{-23}$	$8.30 \times 10^{-23}$	0.90
4 $\nu_1 + \nu_2 + \nu_6 + \nu_{10}$ <sup>b</sup>	6639.29	399	$1.08 \times 10^{-22}$	141	$5.04 \times 10^{-23}$	$5.87 \times 10^{-23}$	0.86
		<i>384</i>	<i><math>2.03 \times 10^{-22}</math></i>	<i>221</i>	<i><math>1.26 \times 10^{-22}</math></i>	<i><math>1.66 \times 10^{-22}</math></i>	0.76
5 $\nu_5 + \nu_{10} + 2\nu_{12}$	6754.05	415	$1.02 \times 10^{-22}$	164	$6.29 \times 10^{-23}$	$5.58 \times 10^{-23}$	1.13
6 $\nu_9 + \nu_{10} + \nu_{11}$	6815.91	539	$6.40 \times 10^{-22}$	223	$6.13 \times 10^{-22}$	$4.43 \times 10^{-22}$	1.38
7 $2\nu_5 + \nu_{10}$	6953.83	948	$3.57 \times 10^{-22}$	293	$2.88 \times 10^{-22}$	$1.85 \times 10^{-22}$	1.56
8 $\nu_4 + \nu_9 + \nu_{11}$	7011.44	914	$4.10 \times 10^{-22}$	176	$3.37 \times 10^{-22}$	$1.47 \times 10^{-22}$	2.29
9 $2\nu_5 + \nu_7$	7059.25	230	$6.04 \times 10^{-23}$	59	$7.06 \times 10^{-23}$	$2.40 \times 10^{-23}$	2.94
10 $\nu_6 + \nu_9 + 2\nu_{12}$	7169.24	1070	$5.28 \times 10^{-22}$	441	$5.07 \times 10^{-22}$	$3.40 \times 10^{-22}$	1.49
11 $\nu_5 + \nu_6 + \nu_{11}$	7212.44	622	$1.09 \times 10^{-21}$	305	$1.39 \times 10^{-21}$	$8.60 \times 10^{-22}$	1.62
12 $\nu_3 + \nu_5 + \nu_{11}$	7324.02	1514	$1.10 \times 10^{-21}$	258	$6.70 \times 10^{-22}$	$4.73 \times 10^{-22}$	1.42
13 $\nu_9 + \nu_{11} + \nu_{12}$	7424.73	937	$8.00 \times 10^{-22}$	181	$4.32 \times 10^{-22}$	$3.79 \times 10^{-22}$	1.14
14 $\nu_3 + \nu_5 + \nu_9$	7477.11	1375	$1.04 \times 10^{-21}$	235	$5.40 \times 10^{-22}$	$4.78 \times 10^{-22}$	1.13
15 $2\nu_5 + \nu_{12}$	7561.58	1219	$6.61 \times 10^{-22}$	208	$2.61 \times 10^{-22}$	$2.12 \times 10^{-22}$	1.23
16 $2\nu_9 + \nu_{12}$	7618.46	734	$2.23 \times 10^{-22}$	148	$1.84 \times 10^{-22}$	$9.39 \times 10^{-23}$	1.96
17 $\nu_2 + \nu_5 + \nu_9$	7774.57	743	$3.43 \times 10^{-22}$	179	$2.08 \times 10^{-22}$	$1.51 \times 10^{-22}$	1.38
18 $\nu_5 + 2\nu_8 + \nu_9$	7973.84	131	$2.97 \times 10^{-23}$	28	$1.30 \times 10^{-23}$	$9.85 \times 10^{-24}$	1.32
	<b>Total <sup>c</sup></b>	<b>12,294</b>	<b><math>7.63 \times 10^{-21}</math></b>	<b>3253</b>	<b><math>5.70 \times 10^{-21}</math></b>	<b><math>3.99 \times 10^{-21}</math></b>	<b>1.43</b>
		<b>/16,607</b>	<b><math>/8.62 \times 10^{-20}</math></b>	<b>/4090</b>	<b><math>/8.46 \times 10^{-20}</math></b>	<b><math>/6.39 \times 10^{-20}</math></b>	<b>/1.32</b>

Notes.

<sup>a</sup> Variational value of the band center [6].

<sup>b</sup> For the bands #1, #2 and #4, the second row of values (in italics) corresponds to the 130 K spectrum.

<sup>c</sup> The first values correspond to bands from #3 to #18, thus excluding the strong  $\nu_5 + \nu_9$  band (#1) which has an overwhelming weight (see Text). The second values correspond to the 18 bands of the table. For comparison, the sum of the variational line intensities for all the 88,680 transitions predicted between 6075 and 8050  $\text{cm}^{-1}$  is  $1.40 \times 10^{-19}$  cm/molecule. The corresponding sum of all the line intensities measured in the same region is  $1.54 \times 10^{-19}$  cm/molecule. The assigned lines represent thus about 46 % and 55 % of the total variational and experimental absorption, respectively.

6400  $\text{cm}^{-1}$  from extensive first-principle calculations using accurate *ab initio* potential and dipole moment surfaces [9-11]. Note that the intensity cutoff was fixed to  $1 \times 10^{-25}$  cm/molecule which is on the same order than that of the experimental intensity values.

### 3.1. Room temperature spectrum

The overview comparison between the experimental and variational lists presented on the upper panels of Fig. 4 shows that at the large frequency scale of the plots and with a logarithmic scale for the line intensities the agreement is very good. This is less the case at a larger scale of a few  $\text{cm}^{-1}$  (lower panels of Fig. 4) where the one-to-one correspondence between the experimental and calculated transitions is far to be obvious. The uncertainties on the variational positions and intensities combined with a high spectral congestion make rovibrational assignments mostly impossible without the help of LSCD relations. In practice, in each spectral region, the dominant band was first identified in the variational list. Over the entire region, eighteen bands predicted by theory were considered in decreasing order of their intensity. They are listed in Table 1. In Fig. 5, transitions of the five dominant bands predicted between 7160 and 7600  $\text{cm}^{-1}$  have been highlighted. The assignment procedure consisted in considering the dominant band of a given region and assigning experimental lines of the region in decreasing order of their intensities. Once the assignment to the dominant band was completed, the second dominant band was considered to assign the remaining unassigned experimental lines.

For a given experimental line, based on the position and intensity agreement, a counterpart was tentatively identified among the variational transitions of the considered variational band (the typical level of

intensity agreement is illustrated on the two lower panels of Fig. 4 which are plotted with identical intensity scales). Using a dedicated home-made program developed under LabVIEW, all the variational transitions reaching the same upper state energy were identified in the calculated line list and searched in the experimental list. Due to the LSCD relations, all variational transitions reaching a given upper level should have their positions shifted identically compared to their experimental counterparts. More precisely, taking into account the experimental position uncertainty, the position shifts must be identical within typically  $4 \times 10^{-3}$   $\text{cm}^{-1}$ . As demonstrated in Refs. [6,7], the LSCD relations combined with an acceptable intensity agreement (for instance a factor of 5 between the experimental and variational intensities) provide a stringent criterion for unambiguous assignments (for a given upper level, up to six transitions can be found fulfilling LSCD relations). Nevertheless, accidental coincidences are more probable for the weak transitions as the density of weak lines is higher both in the experimental and calculated datasets. This is the reason why, in the present work, we have used the dependence of the line intensity between 297 K and 130 K as an additional check (see below).

In the above previous works [6,7], the variational values of the ground state rotational energies were added to the experimental line positions to check the coincident value of the upper state energies but in Ref. [7], we evidenced that the variational value of the lower state energy given in Ref. [6] may differ from HITRAN values by a few  $10^{-3}$   $\text{cm}^{-1}$  for high rotational levels, thus impacting significantly the LSCD relations. This is the reason why, in the present work, we used the HITRAN values [1] of the ground state energies for checking the LSCD relations.

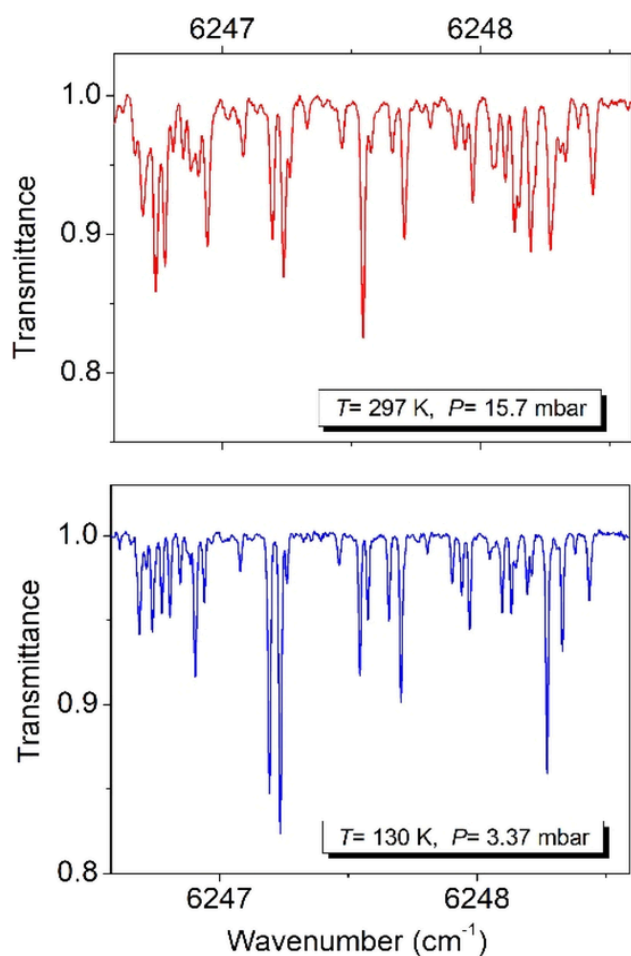


Fig. 2. Temperature dependence of the ethylene spectrum near  $6248\text{ cm}^{-1}$ . The spectrum #7 at 297 K (upper panel) is compared to the spectrum #1 at 130 K (lower panel).

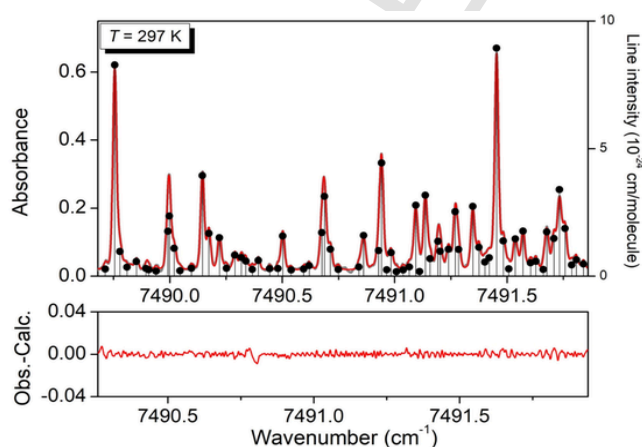


Fig. 3. Line parameter retrieval from the FTS spectrum of ethylene at 297 K ( $P = 15.72\text{ mbar}$ ) near  $7491\text{ cm}^{-1}$ . The best fit spectrum is superimposed to the measured spectrum and the corresponding residuals are displayed on the lower panel.

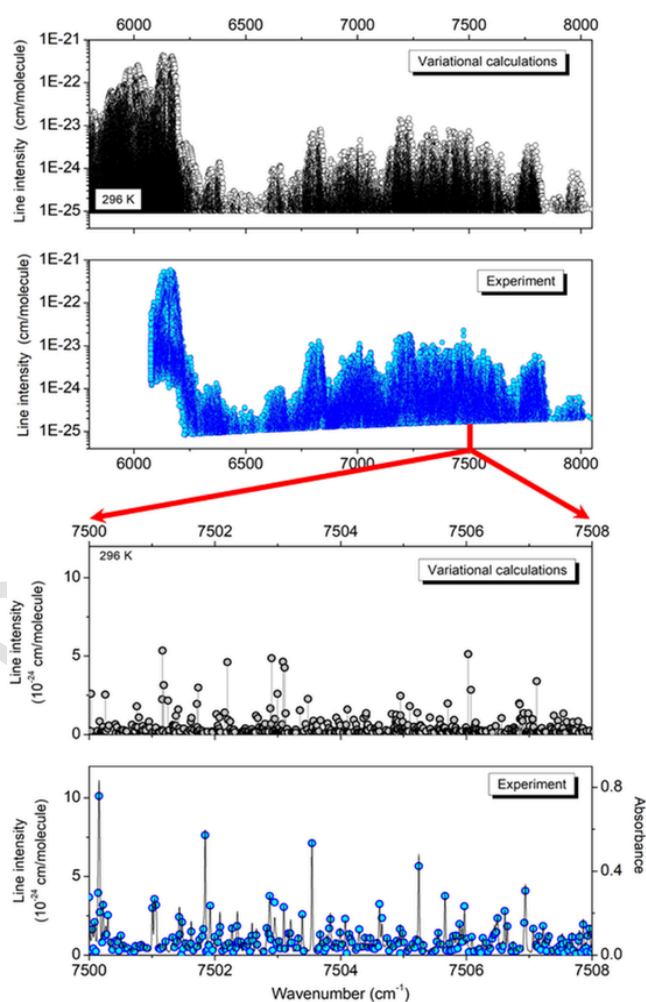
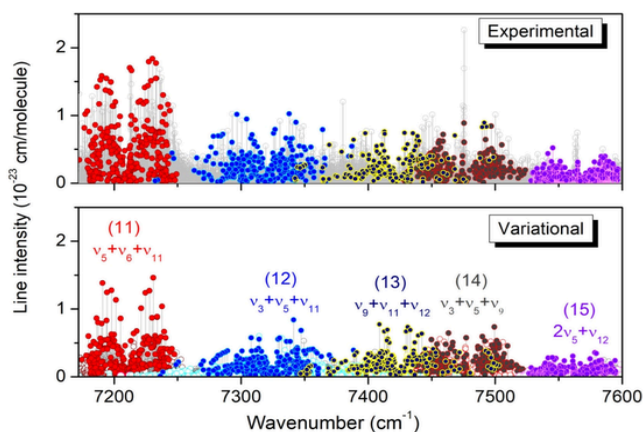


Fig. 4. Comparison of the experimental and variational spectra of ethylene at room temperature. *Upper panels*: Variational line list between  $5800$  and  $8050\text{ cm}^{-1}$  [6] and experimental list in the  $6075$ – $8050\text{ cm}^{-1}$  region (the  $6075$ – $6197.8\text{ cm}^{-1}$  section of the experimental list has been transferred from Ref. [7]), *Lower panels*: Enlargements around  $7504\text{ cm}^{-1}$  showing that the general agreement between experiment and theory observed on the upper panels is less obvious at a large frequency scale. Note that the intensities are plotted with an identical scale in order to illustrate their level of agreement.

The assigned transitions are highlighted on the experimental and variational line lists displayed in Fig. 6. Different colors are used for the eighteen assigned bands. The statistics of the assignments including intensity information is given in Table 1. For convenience, in the following, we will label the bands according to the ranking number increasing with energy given in the table. Ten of the eighteen bands are newly reported. In addition to the  $\nu_5 + \nu_9$  band (#1) analyzed in Ref. [7], the bands #5 to #11 were assigned in Ref. [6] between  $6700$  and  $7260\text{ cm}^{-1}$  but only at 130 K. Overall, the assigned room temperature line list provided as supplementary material includes 4090 assigned transitions (corresponding to 3849 lines as a number of lines corresponds to doublets). This number includes the assignments of the ten new bands and the extension of the assignments of the eight bands previously studied [6,7]. New assignments are limited for the  $\nu_5 + \nu_9$  band studied at room temperature in Ref. [7] (688 assignments instead of 653) but are more important (1665 instead of 647) for the seven bands (#5–11) assigned in the 130 K spectrum in Ref. [6]. In this case, new assignments are mostly due to the extension of the rotational structure and resulting higher number of lines observed at 297 K. The systematic



**Fig. 5.** Overview of the experimental and variational line lists at 297 K and 296 K, respectively, in the 7160–7600  $\text{cm}^{-1}$  interval. The five dominant bands predicted by variational calculations are plotted with different coloured open circles on the lower panel. For each band, the assigned transitions are highlighted with filled circles.

comparison of the 130 K and 297 K assignments of the bands #5–11 shows a coincidence for 421 of the 647 assignments of [6] and disagreement for 86 assignments, the remaining set of about 140 assignments being only reported at 130 K.

### 3.2. Spectra at 130 K

The 130 K spectra at disposal were used in two ways: as a help for the above assignments in two specific spectral intervals (6030–6320 and 6592–6682  $\text{cm}^{-1}$ ) and to check the above assignments over the entire region.

Line lists at 130 K were retrieved in the 6020–6320 and 6592–6682  $\text{cm}^{-1}$  intervals (7566 and 1589 lines, respectively). The rovibrational assignments were performed following the same procedure as described above and using the variational line list at 130 K pro-

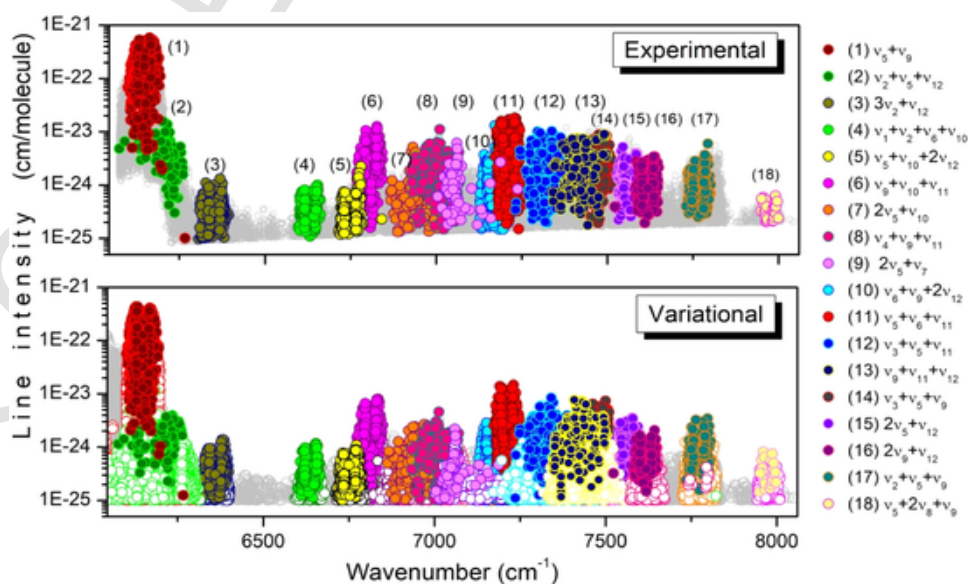
vided in Ref. [6]. The two spectral intervals were selected because the spectral congestion at room temperature hinders the assignments in those regions. The  $\nu_2 + \nu_5 + \nu_{12}$  band (#2) near 6173  $\text{cm}^{-1}$  is greatly obscured by the high rotational R-branch transitions of the  $\nu_5 + \nu_9$  band (#1) near 6149  $\text{cm}^{-1}$ . It was nevertheless possible to assign 222 transitions to this band in the 130 K spectrum. About 150 of these assigned transitions are present in the 297 K list with an intensity consistent with an extrapolation from its 130 K value. The corresponding assignments were thus transferred to the 297 K list. Note that at 130 K, 492 transitions could be assigned to the  $\nu_5 + \nu_9$  band near 6149  $\text{cm}^{-1}$ . About 40 of these assignments were absent in our 297 K list [6] and were thus transferred leading to a total number of 688 assignments for the  $\nu_5 + \nu_9$  band.

The assigned 130 K line list is provided as a separate supplementary material and includes the assignments of the bands  $\nu_5 + \nu_9$  (#1),  $\nu_2 + \nu_5 + \nu_{12}$  (#2) and  $\nu_1 + \nu_2 + \nu_6 + \nu_{10}$  (#4). The latter band with center around 6635  $\text{cm}^{-1}$  is among the weakest assigned in the region. Its rotational assignment at 297 K was very challenging. Rotational cooling down to 130 K allows assigning 221 transitions, from which 161 could be used to newly assign or validate the 297 K assignment.

Although, we did not retrieve an empirical line list at 130 K over the entire region, the spectra at 130 K were systematically used for validating the 297 K assignments. The observed intensity change between 297 K and 130 K was compared to its value predicted using the lower state energy value provided by the assignment (The intensity of an absorption line is proportional to the population of the lower state energy and the intensity ratio is thus simply the ratio of the Boltzmann factors,  $\frac{1}{Z(T)} \exp\left(-\frac{E_{low}}{kT}\right)$ , at the two temperatures,  $Z(T)$  being the partition function tabulated for instance in the HITRAN database [1]). We present in Fig. 7 an example of agreement between the intensity values extrapolated from the assignments and the FTS spectrum at 130 K.

## 4. Discussion

Let us compare the positions and intensities provided by theory and experiment



**Fig. 6.** Overview of the experimental and variational line lists at 297 K and 296 K, respectively, in the 6045–8060  $\text{cm}^{-1}$  interval. Eighteen bands predicted by variational calculations are plotted with coloured open circles on the lower panel. For each band, the assigned transitions are highlighted with filled circles in both the experimental and variational line lists.

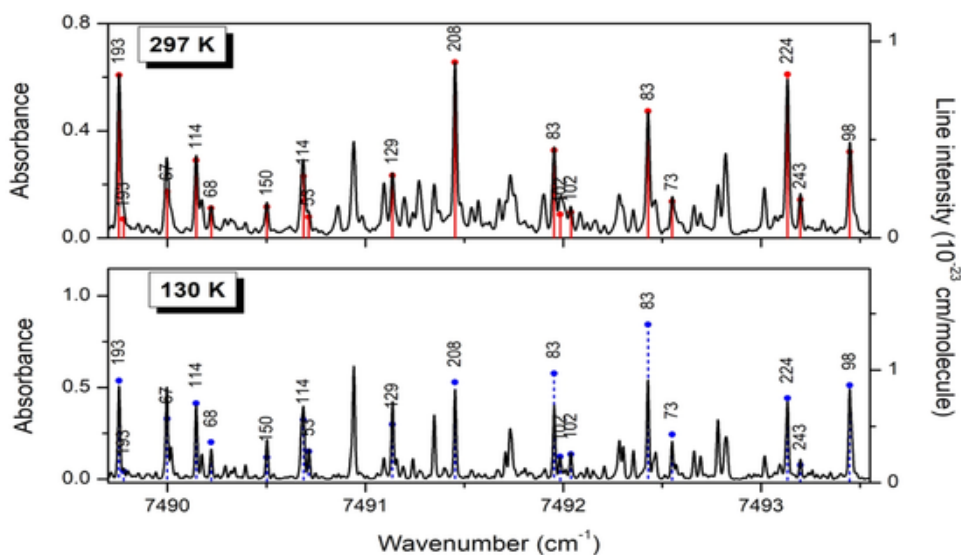


Fig. 7. Validation of the rovibrational assignments of the 297 K spectrum by comparison to the 130 K spectrum. *Upper panel:* FTS spectrum at room temperature ( $P = 15.72$  mbar) and corresponding empirical stick spectrum limited to the assigned transitions. The label attached to each transition is the lower state energy value (in  $\text{cm}^{-1}$ ) obtained from the rovibrational assignment, *Lower panel:* FTS spectrum at 130 K ( $P = 3.37$  mbar) and stick spectrum with intensities at 130 K extrapolated from the 297 K intensities using the lower state energy value.

#### 4.1. Positions and energy levels

The differences between the experimental and variational positions of the assigned lines of six of the 18 assigned bands are displayed in Fig. 8. The mostly symmetric appearance of the plots reflects the identical

deviations obtained for the  $P$  and  $R$  branch transitions (due to LSCD relations). Overall, the deviations vary between  $-8$  and  $+5$   $\text{cm}^{-1}$  which explains while there is no clear similarity between the calculated and variational spectra at the frequency scale of lower panels of Fig. 4. Let us note that in the  $5800$ – $6200$   $\text{cm}^{-1}$  region [7], better position agree-

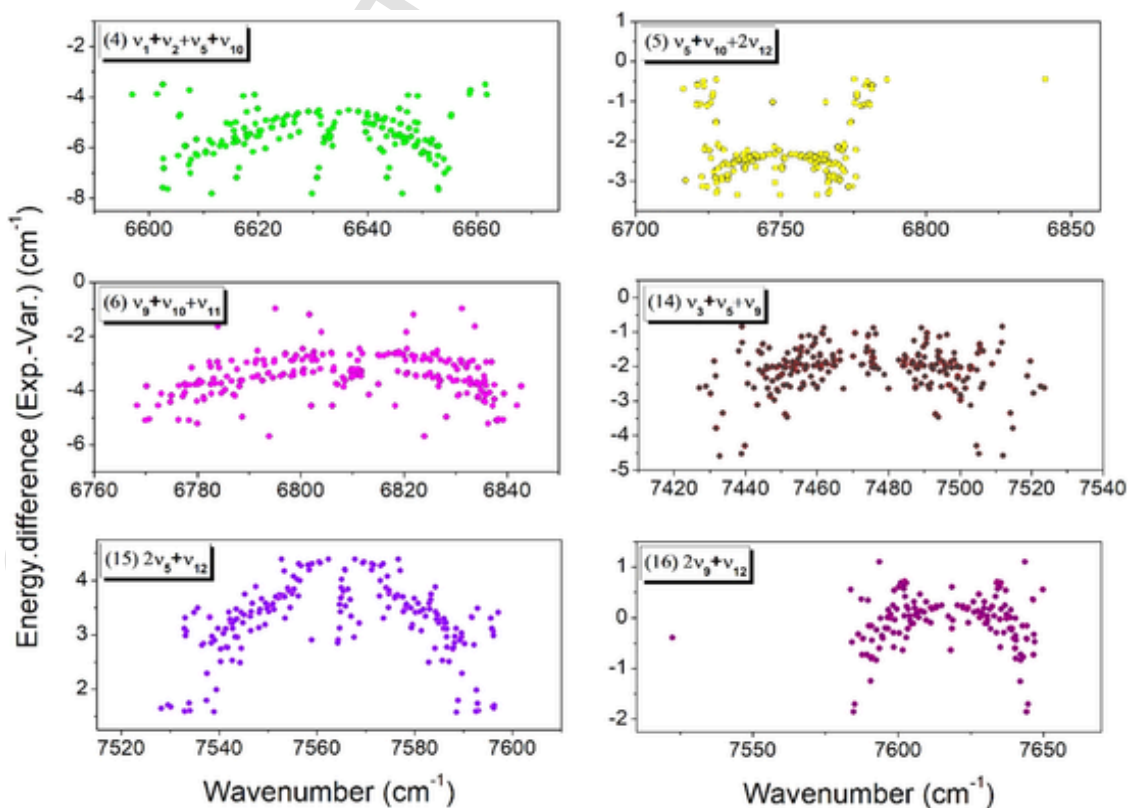


Fig. 8. Differences between the experimental and variational line positions *versus* the experimental line centers for six of the eighteen  $^{12}\text{C}_2\text{H}_4$  bands assigned between  $6075$  and  $8050$   $\text{cm}^{-1}$ .

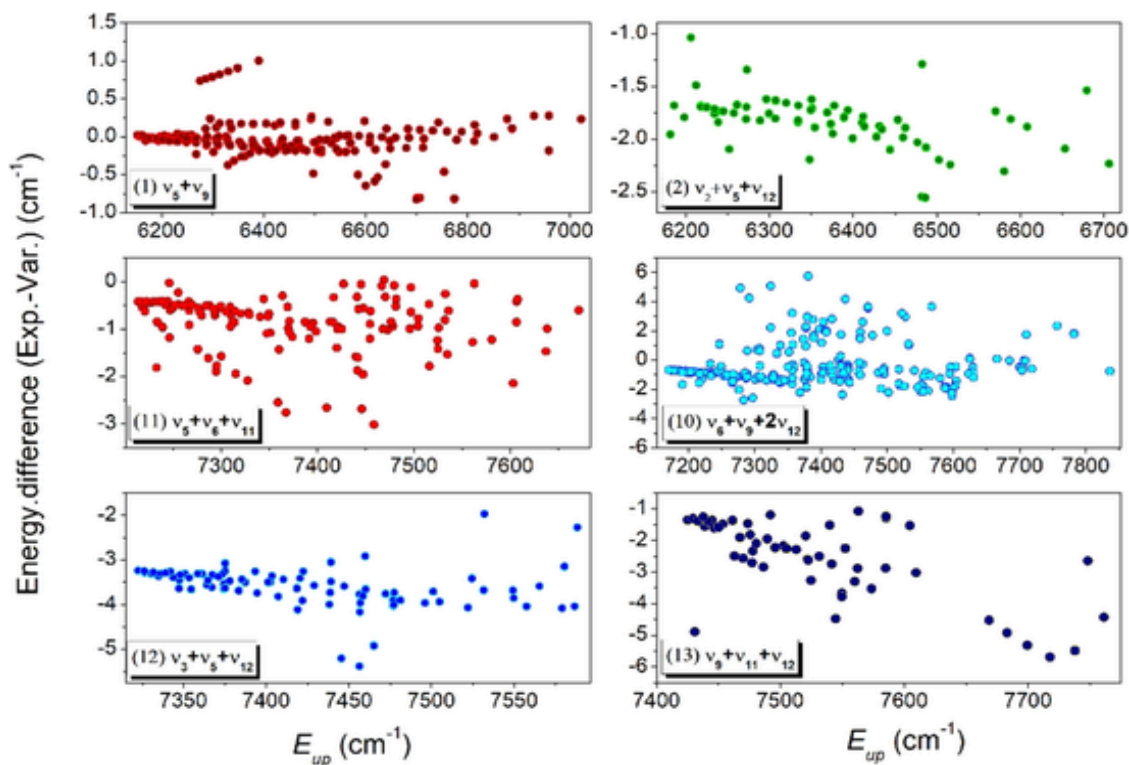


Fig. 9. Differences between the empirical and variational values of the upper energy levels *versus* the upper state empirical energy for six of the eighteen  $^{12}\text{C}_2\text{H}_4$  bands assigned between 6075 and 8050  $\text{cm}^{-1}$ .

ment was obtained with deviations of  $<1 \text{ cm}^{-1}$  for the five bands assigned in the region (see Fig. 4 of Ref. [7]).

From each assigned transition, the empirical value of the upper state energy level is obtained by adding the lower state energy to the measured line position. Due to the LSCD criterion, several determinations (up to 6) are available for each upper level. Overall, the 4090 assigned transitions yield a total of 1749 upper state energies. The average energy value and corresponding RMS of the various determinations are provided as a supplementary material, including a comparison to the variational values. For about 1300 upper energies, the RMS value is less than  $2 \times 10^{-3} \text{ cm}^{-1}$ .

Another way to illustrate the position agreement is to plot the differences between the variational and experimental energy values *versus* the energy of the upper states (Fig. 9). The average value of the various empirical determinations is used for the plots. Although a significant number of outliers is noted for each band, each plot shows a sequence of deviations decreasing with the rotational energy of the upper state. As indicated in Ref. [6], this effect may be due to the insufficient convergence of the variational calculations for  $J$  values. This rotational dependence is superimposed to a global shift reflecting the error on the vibrational energy predicted by theory.

#### 4.2. Intensities

Band-by-band statistics given in Table 1 include intensity information. In the following, we will limit our intensity considerations to the 6300–8050  $\text{cm}^{-1}$  region, thus excluding the  $\nu_5 + \nu_9$  (#1) band which has an overwhelming contribution compared to all the other bands. The sum of the 296 K intensities for all the transitions contributing to the ethylene spectrum over the entire 6300–8050  $\text{cm}^{-1}$  region is  $1.57 \times 10^{-20}$  and  $2.53 \times 10^{-20}$   $\text{cm}^2/\text{molecule}$  for the variational and experimental datasets, respectively (we recall that the variational intensity cut off is  $1 \times 10^{-25}$   $\text{cm}^2/\text{molecule}$  [6], similar to the detectivity

threshold of the analyzed spectra). If we consider only the assigned transitions, these numbers are reduced to  $3.99 \times 10^{-21}$  and  $5.70 \times 10^{-21}$   $\text{cm}^2/\text{molecule}$ , respectively. Thus, the assigned transitions which includes many of the strongest lines of the region, represent about 25 % and 23 % of the calculated and measured absorption of the 6300–8050  $\text{cm}^{-1}$  region, respectively.

On average, as already evidenced in Refs. [6,7], the calculated intensities are underestimated by about 40 %. In addition, large band-by-band fluctuations are observed for the average Exp./Var. intensity ratios (from 0.8 to 3.2 – see Table 1).

As illustrated in Fig. 5, part of the strong lines observed remains to be assigned. This may result from an important underestimation of the variational line intensities related to the low-order (order 4) of the normal-mode expansion used for the dipole moment [10,11] and to the lack of convergence of the high  $J$  energy levels. The spectrum is highly perturbed and our choice to support the assignments by LSCD relations may also explain that some strong lines remain unassigned due to the absence of a LSCD counterpart.

#### 5. Conclusion

The main output of the present study is a partly assigned room temperature list of 36,164 lines for ethylene between 6075 and 8050  $\text{cm}^{-1}$ . Previous extensive room temperature line lists in the region were limited to the region of the  $\nu_5 + \nu_9$  band up to 6200  $\text{cm}^{-1}$  [7] and to the 7120–7260  $\text{cm}^{-1}$  interval [6]. In spite of a considerable spectral congestion ( $> 18$  lines/ $\text{cm}^{-1}$ ) and of important differences between variational and measured line positions and line intensities, a large fraction of the strongest lines of the region could be assigned using as main criterion LSCD relations. As accidental coincidences cannot be excluded, the obtained assignments were further validated by using the intensity comparison between a FTS spectrum recorded at 130 K and room temperature intensity values extrapolated at 130 K using the lower state energy



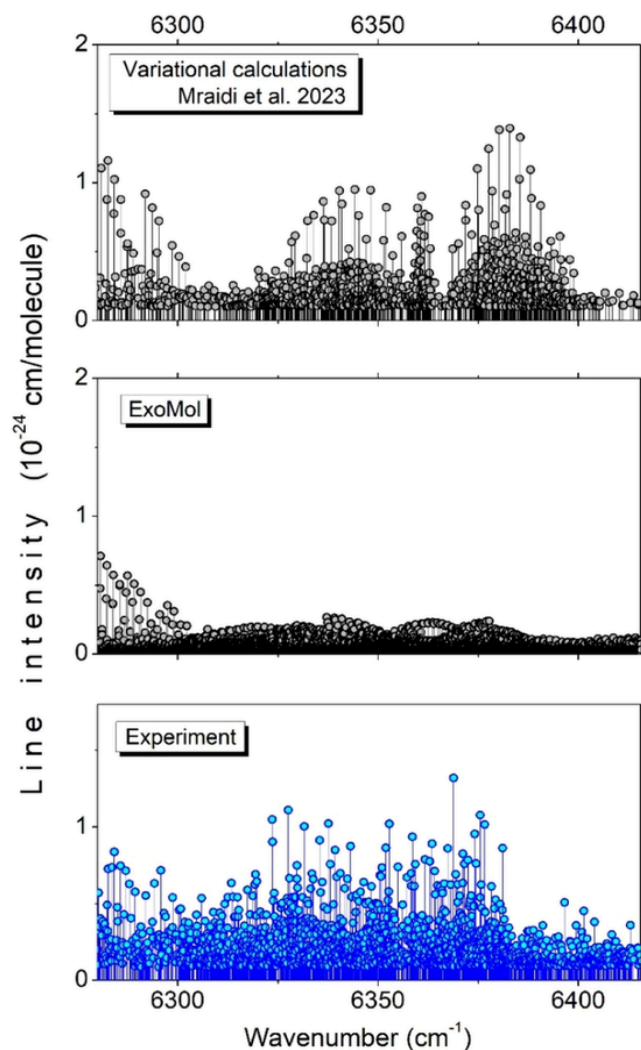


Fig. 10. Comparison of the experimental list of ethylene at 296 K to the variational list of Ref. [6] and to the ExoMol calculated lists [12] in the region of the  $3\nu_2 + \nu_{12}$  (#3) band. For a proper comparison of these stick spectra, variational doublets have been merged in single transitions with the intensity sum of the two components.

value provided by the assignments. As a result, we provide a set of 1749 empirical energy levels corresponding to 18 upper vibrational levels with vibrational term values between 6149 and 7970  $\text{cm}^{-1}$ .

Instead of the variational list of Ref. [6], which is an extension of the TheoReTS list [11], we could have tried to use the ExoMol calculated line list as basis for our assignments. The ExoMol list is an alternative variational list available up to 7000  $\text{cm}^{-1}$  [12]. In Refs. [6,7], comparisons showed similar level of agreement for both calculations compared to experiment. Note that the ExoMol vibrational labeling uses local mode quantum numbers while normal mode vibrational labelings are used in our vibrational list. It is thus not straightforward to identify corresponding transitions in the two variational lists. In Fig. 10, the various lists in the region of the weak  $3\nu_2 + \nu_{12}$  band are compared. The ExoMol intensities appear to be strongly underestimated while our vibrational band center is overestimated by about 10  $\text{cm}^{-1}$ . As already mentioned [6], the rotational structure predicted by calculations is generally more regular than observed, probably due to unaccounted rovibrational resonances.

We hope that the present experimental results will serve as a benchmark for further improvements of the variational line lists or, alterna-

tively, will help for the challenging development of an effective Hamiltonian for ethylene in the near infrared.

As a final comment, we would like to mention that the assignment of absorption spectra of intermediate size molecules based on variational line lists and LSCD relations has opened a new way to fill spectroscopic databases with assigned line lists allowing spectra simulations at various temperatures. This approach has been applied to methane [13], ammonia [14–16], ethylene etc. and could be massively extended to other species and wider spectral ranges.

#### CRedit authorship contribution statement

**O.Ben Fathallah:** Methodology, Investigation, Data curation. **S. Béguier:** Software. **M. Rey:** Investigation. **L. Manceron:** Investigation. **A. Campargue:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Data curation.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

The data are provided as Supplementary Material

#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jqsrt.2024.109175](https://doi.org/10.1016/j.jqsrt.2024.109175).

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