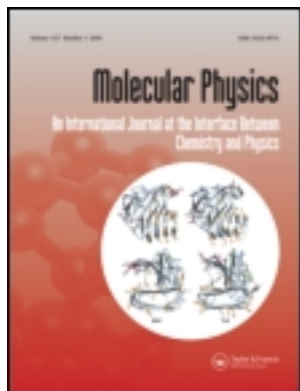


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RESEARCH ARTICLE

High resolution study of the $\nu_5 + \nu_{12}$ band of C_2H_4

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The combination band $\nu_5 + \nu_{12}$ of ethylene, C_2H_4 , has been recorded for the first time with a high resolution Fourier transform spectrometer Bruker IFS 125HR. Assignments of transitions and preliminary rotational analysis are made. Two models (Hamiltonian of the isolated vibrational state and Hamiltonian that takes into account resonance interactions) are used. Influence of the local resonance interactions on the parameters and reproduction power of the models is discussed.

Keywords: ethylene; high-resolution spectra; spectroscopic parameters

1. Introduction

Ethylene is a naturally occurring compound in ambient air that affects atmospheric chemistry and the global climate. Ethylene acts as a hormone in plants and its role in plant biochemistry, physiology, mammals' metabolism, and ecology is the subject of extensive research. Due to its high reactivity towards hydroxyl (OH) radicals, ethylene plays a significant role in troposphere chemistry and ozone generation. This contribution to atmospheric chemistry makes ethylene a climate-relevant trace gas and its air concentration, sources and sinks are of interest to atmospheric science. Ethylene is also important as a prototype example in the development of our understanding of relating spectra, dynamics, and potential hypersurfaces of many organic molecules. Therefore, for many years, the ethylene molecule has been the subject of both extensive experimental (see, e.g. review in [1,2]), and theoretical (see e.g. [3,4] and references cited therein) studies. Unfortunately, the presence of twelve vibrational modes, on the one hand, and of numerous local resonance interactions, on the other hand, leads to such complicated structures of ro-vibrational spectra of ethylene, that up to the present a high resolution analysis has been made only for the low energy vibrational bands.

In the present contribution we present the results of the first high resolution analysis of the combinational band, $\nu_5 + \nu_{12}$, that have been recorded with a high resolution Fourier transform spectrometer Bruker IFS 125HR in the Institute of Atmospheric Optics (Tomsk, Russia). Section 2 presents the experimental details.

Description of the recorded spectrum, assignments of transitions, and determination of upper ro-vibrational energies are presented in Section 3. Section 4 gives theoretical background for further analysis of obtained upper ro-vibrational energies and determination of spectroscopic parameters. The final Section 5 presents results of analysis and discussion of the results.

2. Experimental details

Absorption spectra of a commercial sample of ethylene (99.9% stated purity, used without further purification) in the spectral region of $4250\text{--}4650\text{ cm}^{-1}$ were recorded at the Institute of Atmospheric Optics (Tomsk, Russia) using a Bruker IFS 125HR high-resolution Fourier transform spectrometer. The spectrometer was equipped with a CaF_2 beam splitter, an InSb detector, operating at liquid nitrogen temperature, and a tungsten halogen lamp as the light source. The measurements were performed using Thermo Electron gas multi-pass absorption cells with CaF_2 windows and with gold-coated mirrors. This cell was located inside the evacuated sample compartment and was fitted with the light beam of the spectrometer. The records of ethylene absorption spectra were made at room temperature with an optical path length of 10 m and a pressure sample of 5 mbar. The spectrometer resolution was 0.005 cm^{-1} and no numerical apodisation was applied (Boxcar function). The signal-to-noise ratio (expressed as the maximum signal amplitude divided by twice the RMS noise amplitude) was about 1000. It was obtained by the coaddition of

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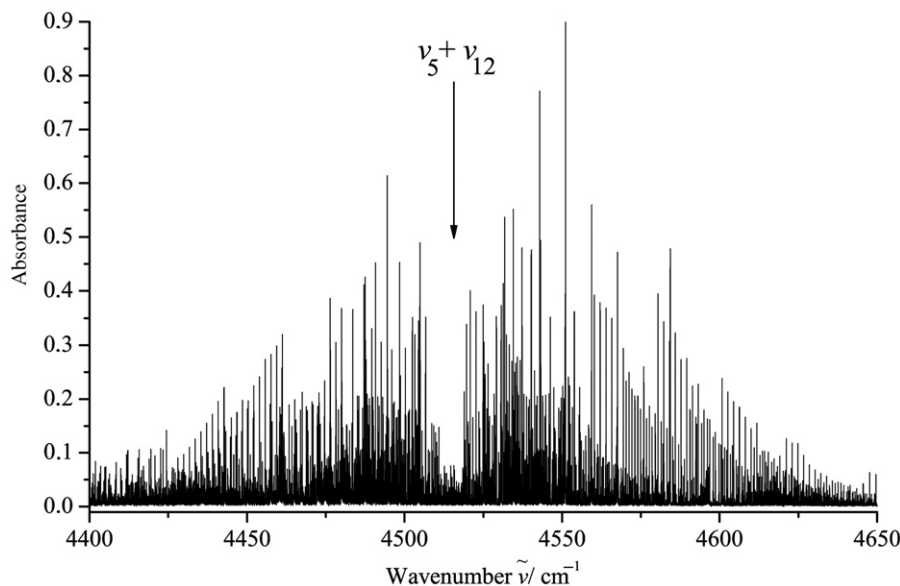


Figure 1. Survey spectrum of C_2H_4 in the region of $4350\text{--}4650\text{ cm}^{-1}$. Experimental conditions: room temperature; pressure and absorption path length are 6 mbar and 10 m, respectively.

1600 interferograms. Calibration was done using H_2O lines in the $4350\text{--}4650\text{ cm}^{-1}$ region as quoted in [5].

3. Description of the spectrum and assignment of transitions

The survey spectrum in the region of $4350\text{--}4650\text{ cm}^{-1}$, where the $\nu_5 + \nu_{12}$ of the C_2H_4 molecule is located, is shown in Figure 1 (for illustration of the quality of the experiment, Figure 2 presents a small part of the high resolution spectrum). Both the strong Q-branch (their two parts are clearly pronounced near 4490 and 4530 cm^{-1}), and P- and R-branches can be seen on Figure 1. A set of very strong lines in the region of the R-branch (4551.10 cm^{-1} , 4559.39 cm^{-1} , 4567.63 cm^{-1} , 4575.97 cm^{-1} , 4584.33 cm^{-1} , 4592.75 cm^{-1} , and sets of considerably weaker red-shifted lines), with the distances between them about $8.2\text{--}8.4\text{ cm}^{-1}$, also belong to the Q-transitions of the type ($J' = JK'_a = 5K'_c = K_c - 1 \leftarrow JK_a = 4K_c$), ($J' = JK'_a = 6K'_c = K_c - 1 \leftarrow JK_a = 5K_c$), ($J' = JK'_a = 7K'_c = K_c - 1 \leftarrow JK_a = 6K_c$), ($J' = JK'_a = 8K'_c = K_c - 1 \leftarrow JK_a = 7K_c$), ($J' = JK'_a = 9K'_c = K_c - 1 \leftarrow JK_a = 8K_c$), and ($J' = JK'_a = 10K'_c = K_c - 1 \leftarrow JK_a = 9K_c$), respectively. In this case, one can see that the strength of transitions, ($J' = JK'_a = 8K'_c = K_c - 1 \leftarrow JK_a = 7K_c$), are anomalously small in comparison with the neighbouring sets of transitions, ($J' = JK'_a = 7K'_c = K_c - 1 \leftarrow JK_a = 6K_c$) and ($J' = JK'_a = 9K'_c = K_c - 1 \leftarrow JK_a = 8K_c$). This fact indicates the presence of strong resonance interactions for the upper states ($J' K'_a = 8 K'_c$) that appears in the

borrowing of intensity from transitions ($J' = JK'_a = 8K'_c = K_c - 1 \leftarrow JK_a = 7K_c$).

In accordance with the selection rules (see, Section 4, for details), the $\nu_5 + \nu_{12}$ consists of *b*-type ro-vibrational transitions. Assignments of transitions in the present study was made with the Ground State Combination Differences method. In this case, ground state vibrational energies have been calculated with the parameters from [1] (for convenience of the reader, ground state parameters from [1] are reproduced in column 2 of Table 1). As the result of assignment, about 1600 transitions with the upper quantum numbers $J^{\text{max.}} = 27$ and $K_a^{\text{max.}} = 12$ were found for the $\nu_5 + \nu_{12}$ band. On that basis 447 upper state ro-vibrational energies were obtained. List of obtained upper energies, E , and their ‘experimental’ uncertainties, Δ , is presented in columns 2 and 3 of Table 2, respectively.

4. Theoretical background

The C_2H_4 molecule is an asymmetric top with the value of the asymmetry parameter $\kappa = (2B - A - C)/(A - C) = -0.915$ and with the symmetry isomorphic to the D_{2h} point symmetry group (see Figure 3). As a consequence, its twelve vibrational coordinates are transformed in accordance with the seven irreducible representations of the D_{2h} group (see, column 11 of Table 3, for details). Also, in accordance with the symmetry of the molecule (see, column 10 of Table 3), three $k_{z\alpha}$ -values, k_{zx} , k_{zy} , and k_{zz} , are transformed in accordance with the irreducible representations,

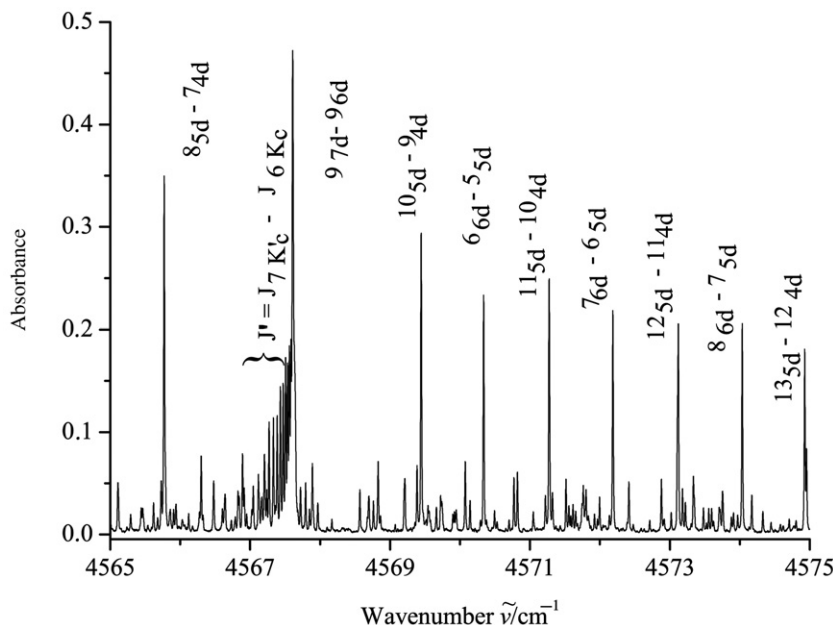


Figure 2. Small portion of the recorded high resolution spectrum of the C_2H_4 molecule. Assignments of the mostly strong transitions are shown.

B_{2g} , B_{1g} , and B_{3g} , respectively.¹ It means, that only transitions from the ground vibrational state to the upper vibrational states of the symmetry, B_{1u} (c -type transitions), B_{2u} (b -type transitions), and B_{3u} (a -type transitions), respectively, can be seen in the infrared spectra of ethylene.

The presence of twelve vibrational modes leads to a very high density of vibrational states of the C_2H_4 molecule (see, for illustration, in Table 4 part of the list of vibrational energies near the centre of the band $\nu_5 + \nu_{12}$, that have been calculated with the parameters from [3] and [4]). As a consequence, theoretical analysis of ro-vibrational spectra of that molecule requires the use of the Hamiltonian model that takes into account the presence of resonance interactions. In this case, as one can see from column 10 of Table 3, only g -type vibrational states, or only u -type vibrational states can be connected by Fermi-, or one of three Coriolis-type interactions. For that reason, because the band $\nu_5 + \nu_{12}$, considered in the present study, is one of the B_{2u} symmetry, the Hamiltonian used in our study was taken in the following form:

$$H^{v,-r} = \sum_{v,\tilde{v}} |v\rangle \langle \tilde{v}| H_{v\tilde{v}}, \quad (1)$$

where the summation extends over all interacting vibrational states of the u -type symmetry (B_{1u} , B_{2u} , B_{3u} , and/or A_u). The diagonal operators H_{vv} describe unperturbed rotational structures of the corresponding vibrational states. The nondiagonal operators $H_{v\tilde{v}}$,

($v \neq \tilde{v}$) describe different kinds of resonance interactions between the states $|v\rangle$ and $|\tilde{v}\rangle$. The diagonal block operators have the same form for all interacting vibrational states, and they have the form of Watson's Hamiltonian in the A -reduction and J' representation [6]:

$$\begin{aligned} H_{vv} = & E^v + [A^v - \frac{1}{2}(B^v + C^v)]J_z^2 + \frac{1}{2}(B^v + C^v)J^2 \\ & + \frac{1}{2}(B^v - C^v)J_{xy}^2 - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v J^4 \\ & - \delta_K^v \{J_z^2, J_{xy}^2\}_+ - 2\delta_J^v J_z^2 J_{xy}^2 + H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 \\ & + H_{JK}^v J_z^2 J^4 + H_J^v J^6 + \{J_{xy}^2, h_K^v J_z^4 + h_{JK}^v J_z^2 J^2 + h_J^v J^4\}_+ \\ & + L_K^v J_z^8 + L_{KKJ}^v J_z^6 J^2 + L_{JK}^v J_z^4 J^4 + L_{KJJ}^v J_z^2 J^6 \\ & + L_J^v J^8 + \{J_{xy}^2, l_K^v J_z^6 + l_{KJ}^v J_z^4 J^2 + l_{JK}^v J_z^2 J^4 + l_J^v J^6\}_+ \\ & + \dots, \end{aligned} \quad (2)$$

where J_α ($\alpha = x, y, z$) are the components of the angular momentum operator defined in the molecule-fixed coordinate system; $J_{xy}^2 = J_x^2 - J_y^2$; $\{\dots, \dots\}_+$ denotes the anticommutator; A^v , B^v , and C^v are the effective rotational constants connected to the vibrational states (v), and the other parameters are the differential order centrifugal distortion coefficients.

We may distinguish between four types of coupling operators $H^{v\tilde{v}}$, ($v \neq \tilde{v}$), corresponding to the four different types of resonance interactions which can occur in a set of vibrational states, B_{1u} , B_{2u} , B_{3u} , and A_u , of the D_{2h} asymmetric top molecules. If the product $\Gamma = \Gamma^v \otimes \Gamma^{\tilde{v}}$ of the symmetry species of the

Table 1. Spectroscopic parameters of the C₂H₄ molecule (in cm⁻¹).

Parameter	(ground)	(ν ₅ = ν ₁₂ = 1)	
		J' ≤ 27	J' ≤ 12
1	2	3	4
<i>E</i>		4514.665(14)	4514.6691(58)
<i>A</i>	4.86462016	4.90615(252)	4.90502(146)
<i>B</i>	1.00105650	1.0043096(926)	1.006238(961)
<i>C</i>	0.82804599	0.825056(862)	0.82347(116)
Δ _{<i>K</i>} × 10 ⁶	86.4798	433.(145)	259.7(797)
Δ _{<i>JK</i>} × 10 ⁶	10.23214	-87.4(107)	40.6(383)
Δ _{<i>J</i>} × 10 ⁶	1.470224	1.0591(136)	-
δ _{<i>K</i>} × 10 ⁶	10.1590	-21.01(778)	636.(403)
δ _{<i>J</i>} × 10 ⁶	0.281684	-	10.24(852)
<i>H_K</i> × 10 ⁹	6.196	5287.(2886)	8755.(1663)
<i>H_{KJ}</i> × 10 ⁹	-0.424	-4721.(552)	-9003.(1974)
<i>H_{JK}</i> × 10 ⁹	0.1845	-	3165.(1221)
<i>H_J</i> × 10 ⁹	0.002501	-	-
<i>h_K</i> × 10 ⁹	3.46	-	83873.(8027)
<i>h_{JK}</i> × 10 ⁹	0.1138	-	5719.(5044)
<i>h_J</i> × 10 ⁹	0.001098	-	65.2(384)
<i>L_K</i> × 10 ⁹		-34.77(2335)	244.6(477)
<i>L_{KKJ}</i> × 10 ⁹		78.0(106)	-415.3(715)
<i>L_{JK}</i> × 10 ⁹		0.585(234)	166.9(323)
<i>L_{JJK}</i> × 10 ⁹		-	-13.23(554)
<i>l_K</i> × 10 ⁹		133.1(249)	-397.9(431)
<i>l_{KJ}</i> × 10 ⁹		-	-134.1(244)
<i>l_{JK}</i> × 10 ⁹		-	-34.2(216)
<i>P_K</i> × 10 ¹¹		9.53(667)	-169.7(317)
<i>P_{KKJ}</i> × 10 ¹¹		-58.53(786)	203.3(376)
<i>P_{KJ}</i> × 10 ¹¹		0.728(349)	-
<i>S_K</i> × 10 ¹³		-560.1(760)	-3232.(888)
<i>S_{KKJ}</i> × 10 ¹³		14.41(220)	-243.1(376)
<i>rms</i>		0.043	0.014
<i>N^a</i>		447	162
<i>n^a</i>		19	25

Note: ^a*N* is the number of experimental upper energies; *n* is the number of fitted parameters.

states *v* and \tilde{v} is equal to *A_g* (i.e. $\Gamma^v = \Gamma^{\tilde{v}}$), then the states *v* and \tilde{v} are connected by an anharmonic resonance interaction, and the corresponding interaction operator has the form:

$$\begin{aligned}
 H_{v\tilde{v}} = & \tilde{v}^v F_0 + \tilde{v}^v F_K J_z^2 + \tilde{v}^v F_J J^2 + \tilde{v}^v F_{KK} J_z^4 + \tilde{v}^v F_{KJ} J_z^2 J^2 \\
 & + \tilde{v}^v F_{JJ} J^4 + \dots + \tilde{v}^v F_{xy} (J_x^2 - J_y^2) \\
 & + \tilde{v}^v F_{Kxy} \{J_z^2, (J_x^2 - J_y^2)\}_+ + \tilde{v}^v F_{Jxy} J^2 (J_x^2 - J_y^2) + \dots
 \end{aligned}
 \tag{3}$$

If the product is $\Gamma = B_{3g}$, then the states *v* and \tilde{v} are connected by a Coriolis resonance interaction of the form:

$$\begin{aligned}
 H_{v\tilde{v}} = & iJ_z H_{v\tilde{v}}^{(1)} + \{J_x, J_y\}_+ H_{v\tilde{v}}^{(2)} + H_{v\tilde{v}}^{(2)} \{J_x, J_y\}_+ \\
 & + \{iJ_z, (J_x^2 - J_y^2)\}_+ H_{v\tilde{v}}^{(3)} + H_{v\tilde{v}}^{(3)} \{iJ_z, (J_x^2 - J_y^2)\}_+ + \dots
 \end{aligned}
 \tag{4}$$

When $\Gamma = B_{1g}$, then the following Coriolis interaction is allowed:

$$\begin{aligned}
 H_{v\tilde{v}} = & iJ_y H_{v\tilde{v}}^{(1)} + H_{v\tilde{v}}^{(1)} iJ_y + \{J_x, J_z\}_+ H_{v\tilde{v}}^{(2)} + H_{v\tilde{v}}^{(2)} \{J_x, J_z\}_+ \\
 & + \{iJ_y, (J_x^2 - J_y^2)\}_+ H_{v\tilde{v}}^{(3)} + H_{v\tilde{v}}^{(3)} \{iJ_y, (J_x^2 - J_y^2)\}_+ + \dots
 \end{aligned}
 \tag{5}$$

Finally, when $\Gamma = B_{2g}$, a Coriolis interaction of the following type is possible:

$$\begin{aligned}
 H_{v\tilde{v}} = & iJ_x H_{v\tilde{v}}^{(1)} + H_{v\tilde{v}}^{(1)} iJ_x + \{J_y, J_z\}_+ H_{v\tilde{v}}^{(2)} + H_{v\tilde{v}}^{(2)} \{J_y, J_z\}_+ \\
 & + \{iJ_x, (J_x^2 - J_y^2)\}_+ H_{v\tilde{v}}^{(3)} + H_{v\tilde{v}}^{(3)} \{iJ_x, (J_x^2 - J_y^2)\}_+ + \dots
 \end{aligned}
 \tag{6}$$

The operators $H_{v\tilde{v}}^{(i)}$, $i = 1, 2, 3, \dots$ in Equations (4)–(6) have the form:

$$\begin{aligned}
 H_{v\tilde{v}}^{(i)} = & \frac{1}{2} \tilde{v}^v C^i + \tilde{v}^v C_{K^i}^i J_z^2 + \frac{1}{2} \tilde{v}^v C_{J^i}^i J^2 + \tilde{v}^v C_{KK^i}^i J_z^4 \\
 & + \tilde{v}^v C_{KJ^i}^i J_z^2 J^2 + \frac{1}{2} \tilde{v}^v C_{JJ^i}^i J^4 + \tilde{v}^v C_{KKK^i}^i J_z^6 \\
 & + \tilde{v}^v C_{KKJ^i}^i J_z^4 J^2 + \tilde{v}^v C_{KJJ^i}^i J_z^2 J^4 + \frac{1}{2} \tilde{v}^v C_{JJJ^i}^i J^6 + \dots
 \end{aligned}
 \tag{7}$$

To prevent confusion in the label notations used, we should mention that we use two sets of axis notation in the C₂H₄ molecule. Firstly, the *x*, *y* and *z* axes are used for labelling of the rotational operators *J_α* ($\alpha = x, y$ or *z*). However, for the point group symmetry assignment of normal modes we use the standard convention in accordance with [7].

5. Ro-vibrational analysis and discussion

Theoretical analysis (fit of the Hamiltonian parameters with experimental ro-vibrational energies) of high resolution spectra of the C₂H₄ molecule is a very complicated problem. First of all, as was mentioned above, the high density of the vibrational states leads to the necessity of using the large dimension effective Hamiltonian matrix, Equation (1). In particular, in our case, as is seen from Table 4, even if one limits consideration to the vibrational states located in the region, plus/minus 100 cm⁻¹ from the centre of the band, ν₅ + ν₁₂ (it is marked by a double asterisk in Table 4), then 24 vibrational states of the *u*-type symmetry (remember, that, in accordance with the theoretical background, only *u*-type bands can interact with the studied, ν₅ + ν₁₂, band) can be found in that region. On the one hand, large number of closely located vibrational states can lead to very complicated picture of resonance interactions. On the other hand, only a few of states may be seen in an experiment under

Table 2. Experimental ro-vibrational term values for the $\nu_5 + \nu_{12}$ vibrational band of the C_2H_4 molecule (in cm^{-1})^a.

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
1		2	3	4		1		2	3	4		1		2	3	4	
1	0	1	4516.4978	0	-12	7	4	3	4629.7400	3	-11	10	7	4	4810.3561	5	-6
1	1	1	4520.3947	1	-15	7	5	3	4665.5458	4	0	10	7	3	4810.3561	5	-6
1	1	0	4520.5750	2	-10	7	5	2	4665.5458	4	0	10	8	3	4869.9261	2	-8
2	0	2	4520.1539	1	7	7	6	2	4709.2978	6	-16	10	8	2	4869.9261	2	-8
2	1	2	4523.8743		-21	7	6	1	4709.2978	6	-16	10	9	2	4937.3488	1	5
2	1	1	4524.4157	3	-5	7	7	1	4760.9505	1	6	10	9	1	4937.3488	1	5
2	2	1	4536.1068	2	3	7	7	0	4760.9505	1	6	10	10	1	5012.6045	6	13
2	2	0	4536.1130	2	4	8	0	8	4579.2818	3	32	10	10	0	5012.6045	6	13
3	0	3	4525.6233	1	39	8	1	8	4581.0184	2	-20	11	0	11	4631.7782	2	-21
3	1	3	4529.0894	1	-32	8	1	7	4587.4259	2	3	11	1	11	4632.6034	16	-14
3	1	2	4530.1734		9	8	2	7	4596.3258	2	30	11	1	10	4644.0720	4	-12
3	2	2	4541.5966	1	-2	8	2	6	4597.5238	16	16	11	2	10	4650.7380	2	23
3	2	1	4541.6276	2	5	8	3	6	4616.5850	2	-13	11	2	9	4654.3594	4	-8
3	3	1	4561.5306	7	17	8	3	5	4616.6442	1	-4	11	3	9	4671.7376	1	6
3	3	0	4561.5304		13	8	4	5	4644.4194	9	-5	11	3	8	4672.1085	2	19
4	0	4	4532.8889	3	69	8	4	4	4644.4224	10	16	11	4	8			
4	1	4	4536.0363	1	-39	8	5	4	4680.2128	2	6	11	4	7			
4	1	3	4537.8375	4	-23	8	5	3	4680.2128	2	6	11	5	7	4735.2503	8	-6
4	2	3	4548.9118	2	-4	8	6	3	4723.9653	1	2	11	5	6	4735.2503	8	-9
4	2	2	4549.0030	3	3	8	6	2	4723.9653	1	2	11	6	6	4778.9926	2	8
4	3	2	4568.8621	6	11	8	7	2	4775.5873	1	14	11	6	5	4778.9926	2	8
4	3	1	4568.8626	2	9	8	7	1	4775.5873	1	14	11	7	5	4830.4906	3	23
4	4	1	4596.7387	2	7	8	8	1	4835.1537	5	-7	11	7	4	4830.4906	3	23
4	4	0	4596.7387	2	7	8	8	0	4835.1537	5	-7	11	8	4	4890.0610	2	-3
5	0	5	4541.9291	2	73	9	0	9	4595.1506	3	-18	11	8	3	4890.0610	2	-3
5	1	5	4544.7096	2	-44	9	1	9	4596.5262	2	-1	11	9	3	4957.4772	1	-8
5	1	4	4547.4075	5	-26	9	1	8	4604.4861	10	18	11	9	2	4957.4772	1	-8
5	2	4	4558.0480	4	-2	9	2	8	4612.6785	7	-4	11	10	2	5032.7173	5	-8
5	2	3	4558.2591	1	4	9	2	7	4614.5049	2	-27	11	10	1	5032.7173	5	-8
5	3	3	4578.0306	2	2	9	3	7	4633.1246	3	-16	11	11	1	5115.7906	2	-1
5	3	2	4578.0337	7	3	9	3	6	4633.2419	1	11	11	11	0	5115.7906	2	-1
5	4	2	4605.9017	3	0	9	4	6	4660.9441	15	19	12	0	12	4652.5361	1	19
5	4	1	4605.9017	3	0	9	4	5	4660.9441	15	-7	12	1	12	4653.1625	6	-5
5	5	1	4641.7225	2	-7	9	5	5	4696.7185	7	-1	12	1	11	4666.7118	2	-1
5	5	0	4641.7225	2	-7	9	5	4	4696.7185	7	-1	12	2	11	4672.4205	6	33
6	0	6	4552.7296	3	30	9	6	4	4740.4689	1	2	12	2	10	4677.2213	7	-20
6	1	6	4555.1024	1	-43	9	6	3	4740.4689	1	2	12	3	10	4693.8067	1	-13
6	1	5	4558.8707	1	-27	9	7	3	4792.0547	2	-7	12	3	9	4694.4132	2	-4
6	2	5	4568.9992	8	-5	9	7	2	4792.0547	2	-7	12	4	9	4721.6068	2	44
6	2	4	4569.4168	1	2	9	8	2	4851.6239	1	0	12	4	8	4721.6254	3	-43
6	3	4	4589.0402	10	5	9	8	1	4851.6239	1	0	12	5	8	4757.2914	5	8
6	3	3	4589.0498	4	6	9	9	1	4919.0522	1	-1	12	5	7	4757.2914	5	2
6	4	3	4616.9009	7	11	9	9	0	4919.0522	1	-1	12	6	7	4801.0145	3	-2
6	4	2	4616.9009	7	11	10	0	10	4612.6493	3	-24	12	6	6	4801.0145	3	-2
6	5	2	4652.7165	3	-9	10	1	10	4613.7241	2	8	12	7	6	4852.4606	1	-8
6	5	1	4652.7165	3	-9	10	1	9	4623.3766	1	14	12	7	5	4852.4606	1	-8
6	6	1	4696.4663	2	-3	10	2	9	4630.8209	5	11	12	8	5	4912.0293	1	-1
6	6	0	4696.4663	2	-3	10	2	8	4633.4509	1	-17	12	8	4	4912.0293	1	-1
7	0	7	4565.3891	3	-7	10	3	8	4651.5094	2	-7	12	9	4	4979.4373	2	9
7	1	7	4567.2081	4	-36	10	3	7	4651.7251	5	19	12	9	3	4979.4373	2	9
7	1	6	4572.2148	2	-18	10	4	7	4679.3152	3	-29	12	10	3			
7	2	6	4581.7605	5	2	10	4	6				12	10	2			
7	2	5	4582.4986	2	3	10	5	6	4715.0628	3	-9	12	11	2	5137.7276	1	1
7	3	5	4601.8903	4	-8	10	5	5	4715.0628	3	-9	12	11	1	5137.7276	1	1
7	3	4	4601.9173	1	12	10	6	5	4758.8115	1	5	12	12	1	5228.5081		0
7	4	4	4629.7400	3	-9	10	6	4	4758.8115	1	5	12	12	0	5228.5081		0

(continued)

Table 2. Continued.

J	K_a	K_c	E	Δ	J	K_a	K_c	E	Δ	J	K_a	K_c	E	Δ
	1		2	3		1		2	3		1		2	3
13	0	13	4674.9225	1	15	6	9	4878.1393	11	17	12	5	5365.5355	
13	1	13	4675.3904	3	15	7	9	4929.3919	3	18	0	18	4811.3613	1
13	1	12	4690.8142	1	15	7	8	4929.3919	3	18	1	18	4811.4398	5
13	2	12	4695.8572	2	15	8	8	4988.9415	2	18	1	17	4837.0501	1
13	2	11	4702.0246	1	15	8	7	4988.9415	2	18	2	17	4838.9716	1
13	3	11	4717.7123	5	15	9	7	5056.3132	3	18	2	16	4854.3615	2
13	3	10	4718.6549	5	15	9	6	5056.3132	3	18	3	16	4864.5750	2
13	4	10	4745.5354	3	15	10	6	5131.5561	1	18	3	15	4869.6005	2
13	4	9	4745.5784	3	15	10	5	5131.5561	1	18	4	15	4893.0723	1
13	5	9	4781.1750	8	15	11	5	5214.5255	1	18	4	14	4893.6978	2
13	5	8	4781.1750	8	15	11	4	5214.5255	1	18	5	14	4928.4051	3
13	6	8	4824.8780	3	15	12	4	5305.2374		18	5	13	4928.4463	3
13	6	7	4824.8780	3	15	12	3	5305.2374		18	6	13	4971.8985	8
13	7	7	4876.2664	2	16	0	16	4751.8702	3	18	6	12	4971.8985	8
13	7	6	4876.2664	2	16	1	16	4752.0520	2	18	7	12	5022.8855	7
13	8	6	4935.8318	2	16	1	15	4773.7481	3	18	7	11	5022.8855	7
13	8	5	4935.8318	2	16	2	15	4776.5826	2	18	8	11	5082.3903	3
13	9	5	5003.2297	2	16	2	14	4787.8676	3	18	8	10	5082.3903	3
13	9	4	5003.2297	2	16	3	14	4800.4000	1	18	9	10	5149.7002	6
13	10	4	5078.4922	2	16	3	13	4803.2363	1	18	9	9	5149.7002	6
13	10	3	5078.4922	2	16	4	13	4828.4679	2	18	10	9	5224.9050	1
13	11	3	5161.4890	5	16	4	12	4828.7203	1	18	10	8	5224.9050	1
13	11	2	5161.4890	5	16	5	12	4863.9383	2	18	11	8	5307.7807	2
13	12	2	5252.2725	4	16	5	11	4863.9512	2	18	11	7	5307.7807	2
13	12	1	5252.2725	4	16	6	11	4907.5518	6	18	12	7	5398.4154	
14	0	14	4698.9388	1	16	6	10	4907.5518	6	18	12	6	5398.4154	
14	1	14	4699.2840	1	16	7	10	4958.7137	2	19	0	19	4843.5065	2
14	1	13	4716.7547	1	16	7	9	4958.7137	2	19	1	19	4843.6121	2
14	2	13	4721.0368	4	16	8	9	5018.2561	3	19	1	18	4871.2092	3
14	2	12	4728.7481	1	16	8	8	5018.2561	3	19	2	18	4872.7075	5
14	3	12	4743.4435	4	16	9	8	5085.6150	4	19	2	17	4890.3421	1
14	3	11	4744.8674	2	16	9	7	5085.6150	4	19	3	17	4899.3310	2
14	4	11	4771.3210	1	16	10	7	5160.8389	2	19	3	16	4905.7676	1
14	4	10	4771.4055	5	16	10	6	5160.8389	2	19	4	16	4928.1483	1
14	5	10	4806.9078	2	16	11	6	5243.7805	2	19	4	15	4929.0914	2
14	5	9	4806.9106	6	16	11	5	5243.7805	2	19	5	15	4963.4325	2
14	6	9	4850.5900	2	16	12	5	5334.4675		19	5	14	4963.5031	1
14	6	8	4850.5900	2	16	12	4	5334.4675		19	6	14	5006.8553	11
14	7	8	4901.9097	1	17	0	17	4780.7922	2	19	6	13	5006.8553	11
14	7	7	4901.9097	1	17	1	17	4780.9199	8	19	7	13	5057.7353	6
14	8	7	4961.4691	3	17	1	16	4804.4884	5	19	7	12	5057.7353	6
14	8	6	4961.4691	3	17	2	16	4806.9266	1	19	8	12	5117.2123	3
14	9	6	5028.8553	1	17	2	15	4820.2096	2	19	8	11	5117.2123	3
14	9	5	5028.8553	1	17	3	15	4831.5931	1	19	9	11	5184.4990	2
14	10	5	5104.1067	2	17	3	14	4835.4175	2	19	9	10	5184.4990	2
14	10	4	5104.1067	2	17	4	14	4859.7934	1	19	10	10	5259.6890	1
14	11	4	5187.1039	6	17	4	13	4860.2551	1	19	10	9	5259.6890	1
14	11	3	5187.1039	6	17	5	13	4895.2410	2	19	11	9	5342.5265	3
14	12	3	5277.8351		17	5	12	4895.2640	16	19	11	8	5342.5265	3
14	12	2	5277.8351		17	6	12	4938.7955	9	19	12	8	5433.1168	
15	0	15	4724.5872	2	17	6	11	4938.7955	9	19	12	7	5433.1168	
15	1	15	4724.8389	5	17	7	11	4989.8771	5	20	0	20	4877.3690	2
15	1	14	4744.3975	2	17	7	10	4958.8771	5	20	1	20	4877.4345	9
15	2	14	4747.9594	3	17	8	10	5049.4020	2	20	1	19	4906.9687	1
15	2	13	4757.3705	4	17	8	9	5049.4020	2	20	2	19	4908.1271	3
15	3	13	4771.0313	1	17	9	9	5116.7365	3	20	2	18	4928.0233	3

Table 2. Continued.

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ
	1	2	3		1	2	3			1	2	3		
15	3	12	4773.0552	2	17	9	8	5116.7365	3	20	3	17	4943.9105	2
15	4	12	4798.9655	2	17	10	8	5191.9555	4	20	4	17	4965.0787	1
15	4	11	4799.1164	2	17	10	7	5191.9555	4	20	4	16	4966.4512	6
15	5	11	4834.4951	2	17	11	7	5274.8658	1	20	5	16	5000.3180	5
15	5	10	4834.5034	14	17	11	6	5274.8658	1	20	5	15	5000.4426	4
15	6	10	4878.1393	11	17	12	6	5365.5355		20	6	15	5043.6699	7
20	6	14	5043.6721	2	22	1	22	4949.9946	2	23	10	14	5417.1741	2
20	7	14	5094.4333	18	22	1	21	4983.3093	4	23	10	13	5417.1741	2
20	7	13	5094.4333	18	22	2	21	4983.9867	2	23	11	13	5499.8098	7
20	8	13	5153.8814	3	22	2	20	5008.5207	5	23	11	12	5499.8098	7
20	8	12	5153.8814	3	22	3	20	5014.2234	4	24	0	24	5029.1497	1
20	9	12	5221.1349	4	22	3	19	5026.3268	9	24	1	24	5029.1628	2
20	9	11	5221.1349	4	22	4	18	5047.1561	8	24	1	23	5066.1093	2
20	10	11	5296.3073	4	22	5	17	5080.0104	3	24	2	23	5066.5094	3
20	10	10	5296.3073	4	22	6	17	5122.8776	5	24	7	18	5259.7307	3
20	11	10	5379.1022	1	22	6	16	5122.8905	4	24	7	17	5259.7307	3
20	11	9	5379.1022	1	22	7	16	5173.3769	3	24	8	17	5318.9919	5
20	12	9	5469.6410		22	7	15	5173.3769	3	24	8	16	5318.9919	5
20	12	8	5469.6410		22	8	14	5232.7465	2	24	9	16	5386.0668	4
21	0	21	4912.8521	6	22	8	14	5232.7465	2	24	9	15	5386.0668	4
21	1	21	4913.0447	2	22	9	15	5299.9216	3	24	10	15	5461.1345	14
21	2	20	4945.2220	7	22	9	15	5299.9216	3	24	10	14	5461.1345	14
21	2	19	4967.4304	4	22	10	16	5375.0489	2	24	11	14	5543.7061	2
21	3	19	4974.1744	1	22	10	16	5375.0489	2	24	11	13	5543.7061	2
21	3	18	4984.2006	4	22	11	17	5457.7435	5	25	0	25	5071.1992	2
21	4	17	5005.8034	4	22	11	17	5457.7435	5	25	1	25	5071.2063	1
21	5	17	5039.1391	1	23	0	23	4988.7419	3	25	1	24	5109.9410	5
21	5	16	5039.2762	2	23	1	23	4988.7574	1	25	2	24	5110.3186	3
21	7	15	5132.9800	5	23	1	22	5023.8996	3	25	7	19	5305.6907	8
21	7	14	5132.9800	5	23	2	22	5025.4081	7	25	7	18	5305.6907	8
21	8	14	5192.3916	3	23	2	21	5051.2496	7	25	8	18	5364.8869	7
21	8	13	5192.3916	3	23	3	21	5056.0079	5	25	8	17	5364.8869	7
21	9	13	5259.6092	2	23	5	18	5122.6605	5	25	9	17	5431.9004	2
21	9	12	5259.6092	2	23	7	17	5215.6263	2	25	9	16	5431.9004	2
21	10	12	5334.7601	4	23	7	16	5215.6263	2	25	11	15	5589.4320	1
21	10	11	5334.7601	4	23	8	16	5274.9460	4	25	11	14	5589.4320	1
21	11	11	5417.5077	4	23	8	15	5274.9460	4	26	9	18	5479.5770	2
21	11	10	5417.5077	4	23	9	15	5342.0744	3	26	9	17	5479.5770	2
22	0	22	4949.9758	3	23	9	14	5342.0744	3					

Notes: ^aIn Table 2 Δ is the experimental uncertainty of the energy value, equal to one standard error in units of 10^{-4} cm^{-1} ; δ is the difference $E^{\text{exp.}} - E^{\text{calc.}}$, also in units of 10^{-4} cm^{-1} ; Δ is absent for the energy values those have been obtained from a single transition.

the usual conditions. As a consequence, the problem of a fit of the Hamiltonian parameters begins to be very unstable and 'incorrect'.

As experience shows (see, e.g. [8,9]), there is only one way for the correct solution of such spectroscopic problems. This way is a theoretical prediction and further, to constrain all more or less suitable spectroscopic parameters of all 'dark' vibrational states presented in the Hamiltonians (1)–(7): both the resonance interaction parameters in Equations (3)–(7), and rotational parameters, centrifugal coefficients, and

band centres in the diagonal blocks, Equation (2). However, for the ethylene molecule, it is practically impossible to make correct estimations because of the absence of undoubted information both about vibrational spectroscopic parameters ($\omega_\lambda, x_{\lambda\mu}, \dots, F_{\text{Fermi}}, F_{\text{D.-D.}}$, etc.), and about parameters of the intramolecular potential function. For example, even centres of the bands can be estimated only very roughly, and, for analysis, the important Fermi-, and/or Coriolis type spectroscopic parameters are even more difficult to estimate. To confirm that statement we refer the

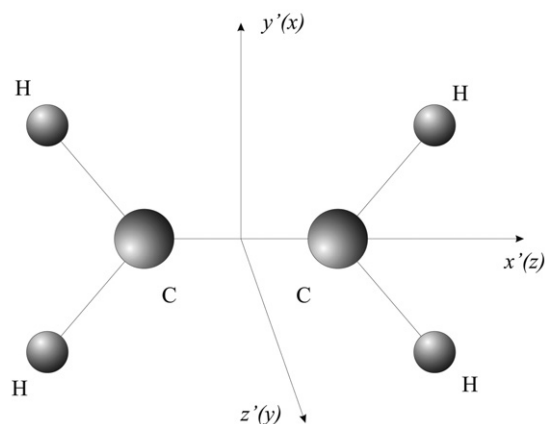


Figure 3. Axes definitions used in the present work for the ethylene, C_2H_4 , molecule. The primed symbols refer to the axis definitions for the D_{2h} symmetry group used in the classification of the vibrational modes. The unprimed symbols refer to the Cartesian axis definitions of the I' representation of Watson's A -reduced effective Hamiltonian.

Table 3. Symmetry types and characters of irreducible representations of the D_{2h} group.

Repr.	E	$\sigma_{x'y'}$	$\sigma_{x'z'}$	$\sigma_{y'z'}$	i	$C_2(z')$	$C_2(y')$	$C_2(x')$	Rot.	Vibr.
1	2	3	4	5	6	7	8	9	10	11
A_g	1	1	1	1	1	1	1	1		Q_1, Q_2, Q_3
A_u	1	-1	-1	-1	-1	1	1	1		Q_4
B_{1g}	1	1	-1	-1	1	1	-1	-1	J_y, k_{zy}	Q_5, Q_6
B_{1u}	1	-1	1	1	-1	1	-1	-1		Q_7
B_{2g}	1	-1	1	-1	1	-1	1	-1	J_x, k_{zx}	Q_8
B_{2u}	1	1	-1	1	-1	-1	1	-1		Q_9, Q_{10}
B_{3g}	1	-1	-1	1	1	-1	-1	1	J_z, k_{zz}	
B_{3u}	1	1	1	-1	-1	-1	-1	1		Q_{11}, Q_{12}

reader to [3,4] and to Table 4, where the results of calculations of the band centres in the region 4410–4620 cm^{-1} are presented. In this case, column 2 gives the results obtained with the parameters from [3], and column 3 presents results of analogous calculations with the parameters from [4]. One can see that in many cases differences between the two sets of data are too large for undoubted constraining of the band centres in a fit procedure. As a consequence, at the present time only tentative theoretical analysis of the obtained experimental ro-vibrational energies of the ($v_5=v_{12}=1$) vibrational state is possible.

As the analysis shows, the rotational structure of the ($v_5=v_{12}=1$) vibrational state is strongly perturbed by numerous resonance interactions. As an illustration, Figure 4 presents examples of local resonances in some sets of ro-vibrational states [$J' K'_a K'_c$]($v_5=v_{12}=1$) with

a fixed value of the quantum number K'_a . The ro-vibrational structure is especially strongly perturbed for the states with the value of quantum number J more than 11–12. For that reason we believe (the made calculations confirm this statement) that without correct theoretical predictions of both the resonance parameters, and parameters of all ‘dark’ states, the resonance Hamiltonian model, Equations (1)–(7), is not better than the model for the isolated vibrational state. At the same time, if using the experimental ro-vibrational energies of the states with $J \leq 12$, the results of the fit are suitable enough and can be considered as a satisfactory approximation for the real spectroscopic parameters. As a consequence of all the above, we made three different fits with the obtained ro-vibrational energies of the ($v_5=v_{12}=1$) vibrational state.

In the first fit all 447 upper energies with $J^{\max.} = 27$ and $K'_a^{\max.} = 12$, obtained from the experimental line positions, were used as the initial data in the Hamiltonian model of an isolated vibrational state, Equation (2). The parameters obtained from the fit are presented in column 3 of Table 1, and the *rms* deviation of the fit is 0.043 cm^{-1} using 19 fitted parameters (in this case, an addition of the number of fitted parameters does not improve the *rms* value). The obtained *rms* deviation is considerably larger than the uncertainties in the experimental line positions. Moreover, as is seen from column 3 of Table 3, even such an *rms* value is achieved with physically unsuitable values of the spectroscopic parameters.

The second fit was made also with the Hamiltonian model of the isolated vibrational state, but only energy levels with the value of quantum number $J \leq 12$ were used as the initial data. Results of the fit are shown in column 4 of Table 1. One can see that, in spite of the considerable reduction of the number of experimental energies, the *rms* value is considerably larger than the experimental uncertainties, and the values of the obtained parameters are physically unsuitable. This fact clearly illustrates the necessity of taking into account resonance interactions even for low ro-vibrational levels.

The third fit, as the second one, was also made using the experimental energy levels that correspond to the states with $J \leq 12$. However, the Hamiltonian that takes into account resonance interactions, Equations (1)–(7), was used. Because, as was discussed above, using all 23 ‘dark’ u -type vibrational states from Table 4 in the Hamiltonian (1)–(7) is a meaningless procedure, at the first step of analysis we tried to limit the number of states that should be entered in Equation (1). For that reason we only considered the states, ($v'_1 \dots v'_{12}$), which are marked in Table 4 by an

Table 4. Calculated band centres (in cm^{-1}) of the C_2H_4 molecule in the region of 4410–4620 cm^{-1} .

$(\nu_1\nu_2\nu_3\nu_4\nu_5\nu_6\nu_7\nu_8\nu_9\nu_{10}\nu_{11}\nu_{12})$ 1	Centre, [2] 2	Centre, [3] 3	Symmetry 4	$(\nu_1\nu_2\nu_3\nu_4\nu_5\nu_6\nu_7\nu_8\nu_9\nu_{10}\nu_{11}\nu_{12})$ 1	Centre, [2] 2	Centre, [3] 3	Symmetry 4
(0 0 0 1 0 2 1 0 0 0 0 0)	4412.06	4419.88	B_{1g}	(0 1 0 1 0 0 1 1 0 0 0 0)	4509.32	4503.38	B_{3g}
(0 0 1 0 1 0 0 0 0 0 0 0)	4415.80	4409.53	B_{1g}	(0 0 0 1 0 1 0 0 0 1 0 1)	4512.19	4501.61	$A_u(*)$
(0 0 0 2 0 0 1 0 0 0 0 1)	4416.22	4421.98	B_{2g}	(0 0 0 0 1 0 0 0 0 0 0 1)	4514.73	4504.00	$B_{2u}(**)$
(0 0 0 0 0 1 0 1 0 1 0 1)	4417.26	4404.70	B_{2g}	(0 0 0 0 0 0 0 0 2 0 2)	4519.80	4510.76	A_g
(0 0 0 0 0 0 0 0 0 0 1 1)	4420.01	4425.75	A_g	(0 1 0 1 0 0 2 0 0 0 0 0)	4520.23	4518.39	A_u
(0 0 1 1 0 1 0 0 0 1 0 0)	4427.36	4404.84	B_{3g}	(0 0 1 1 0 1 0 1 0 0 0 0)	4527.89	4516.17	B_{3u}
(0 0 0 0 0 1 1 0 0 1 0 1)	4428.57	4422.72	$B_{1u} (*)$	(0 0 1 1 0 1 1 0 0 0 0 0)	4531.30	4525.54	A_g
(0 1 0 0 0 0 0 3 0 0 0 0)	4434.48	4411.70	B_{2g}	(0 0 0 0 0 1 0 2 0 0 0 1)	4531.79	4530.51	$B_{2u} (*)$
(0 0 1 0 0 0 0 0 2 0 1)	4435.97	4424.06	$B_{3u} (*)$	(0 0 0 0 0 0 0 1 0 0 1)	4536.26	4529.15	B_{1g}
(0 0 1 0 0 0 0 0 1 0 0 0)	4437.33	4433.44	$B_{2u} (*)$	(0 0 0 0 0 1 1 1 0 0 0 1)	4536.70	4537.71	$B_{2u} (*)$
(0 1 0 0 0 0 1 2 0 0 0 0)	4442.89	4419.71	B_{1u}	(0 0 1 0 0 0 0 1 0 1 0 1)	4541.50	4517.70	B_{3g}
(0 0 1 0 0 1 0 2 0 0 0 0)	4446.46	4433.78	B_{1g}	(0 0 0 0 0 1 2 0 0 0 0 1)	4544.81	4552.22	$B_{2u} (*)$
(0 0 1 0 0 1 1 1 0 0 0 0)	4450.57	4443.45	B_{2u}	(0 0 2 1 0 0 0 0 0 1 0 0)	4547.20	4525.29	B_{2g}
(1 0 0 0 0 0 0 0 0 0 0 1)	4453.40	4452.55	$B_{3u} (*)$	(0 0 1 0 0 0 1 0 0 1 0 1)	4555.01	4542.53	$A_u (*)$
(0 1 0 0 0 0 2 1 0 0 0 0)	4454.50	4435.02	B_{2g}	(0 0 2 0 0 0 0 2 0 0 0 0)	4566.20	4528.93	A_g
(0 0 1 0 0 1 2 0 0 0 0 0)	4457.88	4460.42	B_{1g}	(0 0 2 0 0 0 1 1 0 0 0 0)	4572.51	4545.40	B_{3u}
(0 0 2 0 0 0 0 1 0 1 0 0)	4459.97	4427.99	A_u	(0 2 1 0 0 0 0 0 0 0 0 0)	4575.14	4573.31	A_g
(0 2 0 0 0 1 0 0 0 0 0 0)	4468.20	4468.20	B_{1g}	(0 1 0 2 0 0 0 1 0 0 0 0)	4579.54	4587.02	B_{2g}
(0 1 0 0 0 0 3 0 0 0 0 0)	4469.31	4444.56	B_{1u}	(0 0 2 0 0 0 2 0 0 0 0 0)	4582.02	4569.18	A_g
(0 0 2 0 0 0 1 0 0 1 0 0)	4472.68	4455.29	B_{3g}	(0 1 0 2 0 0 1 0 0 0 0 0)	4586.55	4594.42	B_{1u}
(0 1 0 2 0 0 0 0 0 1 0 0)	4481.51	4486.47	B_{2u}	(0 1 0 0 0 0 0 0 0 1 0)	4596.74	4618.34	$B_{3u} (*)$
(0 1 0 0 0 1 0 0 0 2 0 0)	4488.26	4460.40	B_{1g}	(0 1 0 0 0 1 0 1 0 1 0 0)	4601.19	4573.50	A_u
(0 0 0 0 0 3 0 0 0 1 0 0)	4492.53	4474.01	B_{3u}	(0 0 0 0 0 3 1 0 0 0 0 0)	4606.97	4624.57	A_u
(0 1 0 1 0 0 0 2 0 0 0 0)	4501.61	4495.67	A_u	(0 0 0 0 0 3 0 1 0 0 0 0)	4607.06	4621.31	B_{3g}
(0 1 0 0 0 0 0 0 0 0 0 2)	4502.74	4491.74	A_g	(0 1 1 0 0 0 0 0 0 2 0 0)	4610.90	4599.40	A_g
(0 0 0 3 0 0 0 0 0 0 0 1)	4504.84	4516.55	B_{3g}	(0 1 0 0 0 1 1 0 0 1 0 0)	4614.00	4592.73	B_{2g}
(0 0 0 2 0 2 0 0 0 0 0 0)	4507.18	4500.92	A_g	(0 0 0 1 0 1 0 1 0 0 0 1)	4616.82	4618.68	A_g

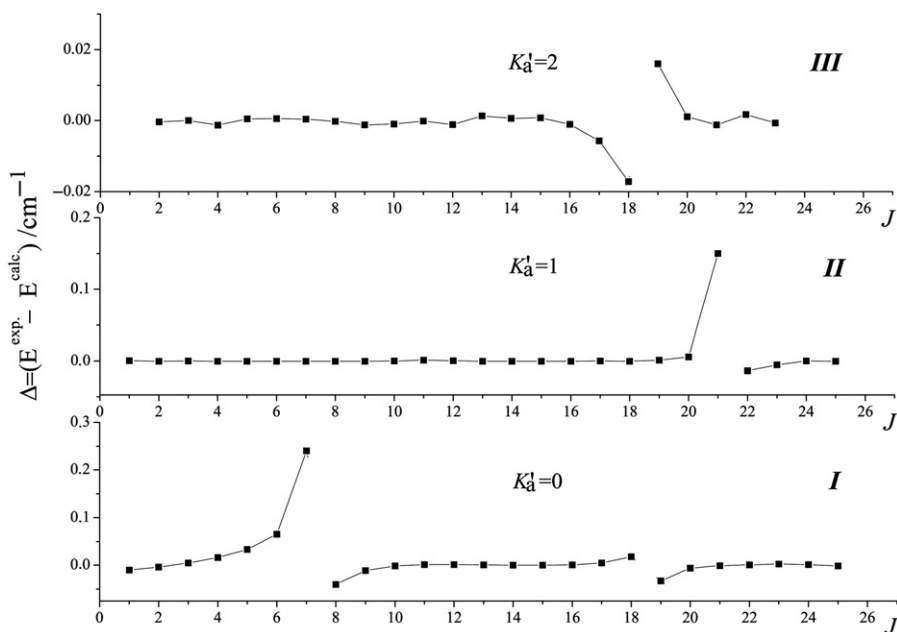
Figure 4. Illustration of local resonance interactions in the $(\nu_5 = \nu_{12} = 1)$ vibrational state (see text, for details).

Table 5. Spectroscopic parameters of some vibrational states of C₂H₄ (in cm⁻¹)^a.

Parameter 1	(<i>v</i> ₅ , <i>v</i> ₁₂ = 1) 2	(<i>v</i> ₃ , <i>v</i> ₉ = 1) 3	(<i>v</i> ₆ , <i>v</i> ₇ , <i>v</i> ₈ , <i>v</i> ₁₂ = 1) 4	(<i>v</i> ₆ , <i>v</i> ₁₂ = 1, <i>v</i> ₇ = 2) 5	(<i>v</i> ₁ , <i>v</i> ₁₂ = 1) 6	(<i>v</i> ₆ = 3, <i>v</i> ₁₀ = 1) 7
<i>v</i>	4513.59685(73)	4436.6275(65)	4534.3208(77)	4542.8886(83)	4459.93559(86)	4477.0094(28)
<i>A</i>	4.893889(714)	4.86462016	4.86462016	4.86462016	4.89690(231)	4.86462016
<i>B</i>	0.999950(813)	1.0010565	1.0010565	1.0010565	1.0010565	1.05273(260)
<i>C</i>	0.819630(820)	0.82804599	0.82804599	0.82804599	0.82804599	0.82804599
<i>rms</i>	0.0017					
<i>N</i> ^b	159					
<i>n</i> ^b	47					

Notes: ^aValues in parentheses are 1σ confidence intervals (in last digits). Parameters presented without confidence intervals were constrained to the values of corresponding ground state parameters from [1].

^b*N* is the number of experimental upper energies; *n* is the number of fitted parameters.

Table 6. Parameters of resonance interactions (in cm⁻¹)^{ab}.

Parameter	Value	Parameter	Value	Parameter	Value
Fermi-type interactions					
F_0^{1-2}	9.147 (786)	$F_K^{1-2} \times 10^2$	1.687 (398)	$F_J^{1-2} \times 10^2$	2.176 (329)
		$F_{JJ}^{1-2} \times 10^4$	-0.1779 (447)		
$F_K^{1-3} \times 10^2$	-2.6853 (762)	$F_{JK}^{1-3} \times 10^4$	-0.8697 (764)	$F_{KKJ}^{1-3} \times 10^6$	0.4788 (288)
F_K^{3-4}	0.4482 (186)	$F_J^{3-4} \times 10^2$	4.081 (225)	$F_{KK}^{3-4} \times 10^3$	-8.017 (411)
$F_{JK}^{3-4} \times 10^3$	-1.0243 (795)	$F_{KKK}^{3-4} \times 10^4$	0.4155 (181)		
Coriolis-type interactions					
$^{1-5}C^1$	0.13932 (888)	$^{1-5}C_{KJ}^1 \times 10^5$	-2.071 (281)	$^{1-5}C_{JJ}^1 \times 10^5$	-0.4109 (503)
$^{1-5}C_J^2 \times 10^3$	0.1298 (104)	$^{1-5}C^3 \times 10^2$	0.2366 (120)	$^{1-5}C_J^3 \times 10^4$	-0.2464 (194)
$^{1-5}C_{KK}^3 \times 10^6$	-0.2514 (442)	$^{1-5}C^3 \times 10^6$	0.07059 (811)		
$^{1-6}C_J^1 \times 10^3$	-0.4428 (818)	$^{1-6}C^3 \times 10^2$	-0.2979 (226)	$^{1-6}C_K^3 \times 10^4$	1.082 (220)
$^{1-6}C_J^3 \times 10^4$	0.4115 (346)	$^{1-6}C_{KJ}^3 \times 10^6$	-1.918 (331)	$^{1-6}C_{JJ}^3 \times 10^6$	-0.1478 (134)
		$^{1-6}C_{KKJ}^3 \times 10^8$	0.757 (125)		

Notes: ^aValues in parentheses are 1σ confidence intervals (in last digits).

^bVibrational states are denoted as: (1) = (*v*₅, *v*₁₂ = 1); (2) = (*v*₃, *v*₉ = 1); (3) = (*v*₆, *v*₇, *v*₈, *v*₁₂ = 1); (4) = (*v*₆, *v*₁₂ = 1, *v*₇ = 2); (5) = (*v*₁, *v*₁₂ = 1); (6) = (*v*₆ = 3, *v*₁₀ = 1).

asterisk, * (namely, the state (*v*₁...*v*₁₂) ≡ (*v*₅ = *v*₁₂ = 1) and the states with Δ*V* ≤ 4, where Δ*V* = ∑_{*i*=1}¹² |*v*'_{*i*} - *v*_{*i*}|), because it allows us to take into account the most important vibrational interactions of Fermi and Darling–Dennison types. Double asterisk denotes the band studied in the present paper. As is seen from Table 4, the number of such type states is 10. As a consequence, the total number of vibrational states that were used at the first step of the analysis with the Hamiltonian (1)–(7), was 11 (10 of them are ‘dark’ ones).

As further analysis shows, under the condition of absence of correct estimations both of the main resonance parameters, and centres of the ‘dark’ bands,

(a) the number of vibrational states in the Hamiltonian, Equations (1)–(7) can be

additionally reduced up to the states presented in columns 2–6 of Table 5;

(b) correct description of the sets of states [*J* 0 *J*](*v*₅ = *v*₁₂ = 1) and [*J* 1 *J*](*v*₅ = *v*₁₂ = 1) is in need of taking into account the additional state of the *B*_{3*u*} symmetry (column 7 of Table 5) which we can tentatively assign as the state (*v*₆ = 3, *v*₁₀ = 1) (see Table 4).

As the result of analysis, a set of 47 spectroscopic parameters was obtained that are presented in Tables 5 and 6 together with their 1σ statistical confidence intervals. In this case, we present in Table 5 the vibrational energies, *E*, and rotational parameters, *A*, *B*, and *C*, only. The values of all centrifugal coefficients for all vibrational states presented in Table 5 have been constrained to the values of corresponding parameters

of the ground vibrational state from column 2 of Table 1.

The obtained set of parameters reproduce 159 initial 'experimental' ro-vibrational energies (with the values of quantum number $J \leq 12$) with an *rms* deviation of 0.0017 cm^{-1} , which is already considerably more close to the experimental errors than the results of the two previous fits (also to illustrate the quality of the third fit, column 4 of Table 2 presents the values δ that are the differences $E^{\text{exp.}} - E^{\text{calc.}}$ in units of 10^{-4} cm^{-1}). The values of the obtained parameters are physically suitable and allow one to predict most of the energy levels with the value of the quantum number $J=13, 14$ with an accuracy of $0.003\text{--}0.005 \text{ cm}^{-1}$. However, for some energy levels, because of the complicated picture of the resonance interactions, accuracy of predictions is decreased up to $0.01\text{--}0.02 \text{ cm}^{-1}$. In any case, we believe that the obtained results can be considered as a good starting point for a more careful analysis in the near future.

6. Conclusion

In the present paper, we analysed for the first time the combination band $\nu_5 + \nu_{12}$ of the ethylene molecule. We used two different Hamiltonian models: isolated vibrational states and another model which takes into account resonance interactions. It is shown that the Hamiltonian model using resonance interactions allows one to reproduce the initial experimental data ($J \leq 12$) with an accuracy close to the experimental uncertainty.

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Note

1. In Table 3 characters of irreducible representations and nomenclature of the vibrational coordinates correspond to the notations of axis, x' , y' , and z' , from [7]. At the same time, belonging of the operators, J_α and/or $k_{z\alpha}$, to one or another irreducible representation of the D_{2h} group corresponds to such an orientation of the coordinate axis, x , y , and z , in the C_2H_4 molecule that provides a validity of the A -reduction and I^r -representation of a vibrational-rotational Hamiltonian.

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