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High resolution analysis of C₂D₄ in the region of 600–1150 cm⁻¹



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ABSTRACT

High-accurate Fourier-transform infrared spectra of C₂D₄ were recorded and analyzed in the region of 600–1150 cm⁻¹ where the bands $\nu_7(B_{1u})$, $\nu_{10}(B_{2u})$, $\nu_{12}(B_{3u})$ are located as well as the $\nu_4(A_{1g})$ band which is forbidden by the symmetry of the molecule. The ground state rotational structure was re-analyzed by the use of ground state combination differences obtained on the basis of infrared transitions of the ν_{12} and ν_7 absorption bands. This gave us the possibility to considerably improve the rotational and centrifugal parameters of the ground vibrational state. The analysis of the experimental data and the subsequent weighted-fit procedure of the Hamiltonian parameters allowed us to reproduce the initial 4405 “experimental” ro-vibrational energy values with the $d_{rms} = 2.1 \times 10^{-4}$ cm⁻¹.

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1. Introduction

Knowledge of internal properties of the ethylene molecule is very important for numerous pure scientific and applied problems of physics, chemistry, astrophysics, planetology, atmospheric optics, biology, etc. Ethylene acts as a hormone in plants and its role in plant biochemistry, physiology, mammals metabolism, and ecology is the subject of extensive research. Ethylene is a naturally occurring compound in ambient air that affects atmospheric chemistry and the global climate. As the result of reaction with the hydroxyl (OH) radical, ethylene plays a significant role in tropospheric chemistry, Ref. [1], 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 one of the most relevant

substances of study in astrophysics (see, e.g., Ref. [2]), and it has been detected as a trace component in the atmospheres of the outer planets Jupiter, Saturn, Neptune, Refs. [3,4], and the satellite Titan, Refs. [5,6]. Ethylene plays an important role in structural chemistry as well as in other fields of chemistry; it is 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 was a subject of numerous high resolution spectroscopic studies both in the microwave and infrared spectral regions (for the laboratory high resolution studies of ethylene and its isotopologues during last five years, see Refs. [7–35], the complete, very long list is not reproduced here). As to C₂D₄, this isotopologue (as was mentioned, e.g., in Ref. [36]), as well as other deuterated ethylene species, should be always incorporated to an analysis of the Titan atmosphere. Knowledge of accurate ro-vibrational structure of spectra of the C₂D₄ molecule plays an important role in such a problem as determination of correct multi-dimension intramolecular potential

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surface of ethylene. On that reason, high resolution spectra of C_2D_4 were discussed earlier in Refs. [17,37–45]. In this case, the most studied band is the ν_{12} one which was discussed in Refs. [17,37,42,45]. The ν_7 band was analyzed in Ref. [39], and all the four fundamental bands with lowest frequency (ν_{10} , ν_7 , ν_4 , ν_{12}) were considered in Ref. [40].

In our present study, the high resolution FTIR spectra of the C_2D_4 ethylene were recorded at different experimental conditions and analyzed in the region of $600\text{--}1150\text{ cm}^{-1}$, where the strongly interacting bands ν_{10} , ν_7 , ν_4 , and ν_{12} are located. In Section 2 we discuss the conditions of our experiment. Section 3 presents the theoretical background for the studied problem (Hamiltonian model which was used in the theoretical analysis of the experimental data and estimation of the initial values of spectroscopic parameters). Description of the experimental spectra and results of assignment of transitions are given in Section 4. Section 5 presents the results of the re-analysis of the rotational structure of the ground vibrational state, and problem of the analysis of the upper vibrational states is discussed in Section 6.

2. Experimental details

Three spectra of C_2D_4 have been recorded in the wavenumber range from 600 to 1150 cm^{-1} with a Bruker IFS 120 Fourier transform infrared (FTIR) spectrometer in combination with a stainless steel White cell with a base length of 1 m . A mercury-cadmium-telluride (MCT) semiconductor detector was used. The C_2D_4 sample was purchased from EQ laboratories/CDN isotopes. The identity, chemical and isotopic purity (specified to be 99.8 atom \% D) was obvious from the spectra. The nominal instrumental resolution, defined by $1/d_{MOPD}$ (maximum optical path difference = 4.86 m), was 0.00206 cm^{-1} resulting in almost Doppler limited spectra. The pressure-induced widths (FWHM) can be estimated for C_2D_4 to be smaller than 0.0004 cm^{-1} at the highest used pressure of 200 Pa and is therefore considerably smaller compared to the Doppler widths (FWHM) which at 298 K ranges from 0.0013 cm^{-1} at $600\text{--}0.0026\text{ cm}^{-1}$ at 1150 cm^{-1} . The three experimental spectra have been recorded at the following experimental conditions for sample pressure, optical pathlength, mode of apodization, number of scans, and total line width at 600 and 1150 cm^{-1} . First spectrum I: 8 Pa , 4 m , Boxcar, 410 scans, 0.0020 and 0.0030 cm^{-1} (see also Table 1). Second spectrum II: 150 Pa , 4 m , Boxcar, 430 scans, 0.0019 and 0.0030 cm^{-1} . Third spectrum III: 200 Pa , 24 m , Norton-Beer weak, 550 scans, 0.0022 and

0.0031 cm^{-1} . For optimization of data recording and line calibration we used procedures described in Refs. [46,47] (and references therein). The spectra were calibrated with spectral lines of N_2O . The mean divergence of measured N_2O line positions from line positions published in the current Hitran data base is around 10^{-4} cm^{-1} . The divergence of single lines is below $4 \times 10^{-4}\text{ cm}^{-1}$.

3. Theoretical background

3.1. Effective Hamiltonian

The C_2D_4 molecule is an asymmetric top with the value of the asymmetry parameter $\kappa \approx (2B - A - C)/(A - C) = -0.817$ and with the symmetry isomorphic to the D_{2h} point symmetry group (see Fig. 1). For convenience of the reader, the symmetry properties in C_2D_4 are shown in Table 2: the list of irreducible representations and table of characters of the D_{2h} symmetry group are presented in columns 1–9; symmetries of rotational operators, J_α , and of direction cosines, $k_{z\alpha}$, are shown in column 10; column 11 presents a symmetry of any of twelve vibrational coordinates q_λ of the C_2D_4 molecule. From analysis of Table 2, it is possible to see that transitions in absorption are allowed only between vibrational states, (νI) and $(\nu' I')$, whose symmetries I and I' have different indexes “u” and “g”. Moreover, transitions are allowed from the

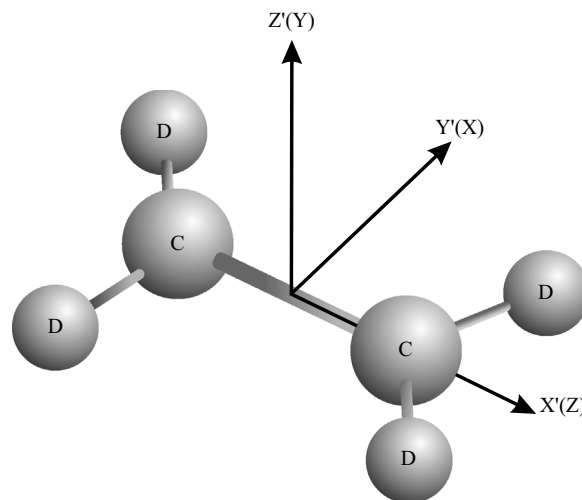


Fig. 1. Axis definitions used in the present work for the C_2D_4 molecule. The primed symbols refer to the axis definitions for the D_{2h} symmetry group used in the classification of the vibrational modes. The unprimed symbols refer to the Cartesian axis definitions of the I' representation of Watson's A -reduced effective Hamiltonian.

Table 1
Experimental setup for the regions $600\text{--}1150\text{ cm}^{-1}$ of the infrared spectrum of C_2D_4 .

Spectr.	Region/ cm^{-1}	Resolution/ cm^{-1}	No. of scans	Source	Detector	Beam- splitter	Opt. path- length/m	Aperture/mm	Temp./ $^{\circ}\text{C}$	Pressure/Pa	Calibr. gas
I	600–1150	0.0020–0.0030	410	Globar	MCT	KBr	4	1.5	25 ± 0.5	8.0	N_2O
II	600–1150	0.0019–0.0030	430	Globar	MCT	KBr	4	1.5	25 ± 0.5	150	N_2O
III	600–1150	0.0022–0.0031	550	Globar	MCT	KBr	24	1.5	25 ± 0.5	200	N_2O

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

Repr.	E	σ_{xy}	σ_{xz}	σ_{yz}	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}

ground vibrational state only to the upper vibrational states of the $B_{1u}, B_{2u},$ or B_{3u} type. Transitions to the upper vibrational state of the A_u -type are forbidden by the symmetry and can appear in the spectrum only because of Coriolis type resonance interactions. As can be also seen from column 10, transitions from the ground vibrational state to the vibrational states of the $A_g, B_{1g}, B_{2g},$ or B_{3g} types are completely forbidden by the symmetry properties and because of absence of interactions between states of the u an g types. It can be seen also from Table 2 that

1. the $B_{1u} \leftarrow A_g$ bands are the c -type ones, and the selection rules for them are: $\Delta J = 0, \pm 1$ and $\Delta K_a = odd, \Delta K_c = even$;
2. the $B_{2u} \leftarrow A_g$ bands are the b -type ones, and the selection rules for them are: $\Delta J = 0, \pm 1$ and $\Delta K_a = odd, \Delta K_c = odd$;
3. the $B_{3u} \leftarrow A_g$ bands are the a -type ones, and the selection rules for them are: $\Delta J = 0, \pm 1$ and $\Delta K_a = even, \Delta K_c = odd$.

For this reason the $\nu_7, \nu_{10}, \nu_{12},$ and ν_4 bands can be identified as the c -type, b -type, a -type, and forbidden one, respectively.

From the above said, one can see that a theoretical analysis of the states ($\nu_{10} = 1$), ($\nu_7 = 1$), ($\nu_4 = 1$) and the state ($\nu_{12} = 1$) which is closely located to these three ones, should be made with the Hamiltonian model which takes into account resonance interactions between different vibrational states. Such kind model was discussed in the literature many times (see, e.g., Refs. [48–50]). For that reason we will mention here only part of the Hamiltonian which is responsible for the states considered in the present study. In its general form, the effective Hamiltonian can be written as (see, e.g., Refs. [51–54])

$$H^{vib.-rot.} = \sum_{\nu, \tilde{\nu}} |\nu\rangle \langle \tilde{\nu}| H_{\nu\tilde{\nu}}, \quad (1)$$

where the summation is taken from 1 to 4 for both ν and $\tilde{\nu}$, which represent the four above discussed vibrational states:

$|1\rangle = (\nu_4 = 1, A_u), |2\rangle = (\nu_7 = 1, B_{1u}), |3\rangle = (\nu_{10} = 1, B_{2u})$ and $|4\rangle = (\nu_{12} = 1, B_{3u})$. Any diagonal block $H^{\nu\nu}$, Eq. (1), describes unperturbed rotational structure of the vibrational state $|\nu\rangle$ and has a form of reduced effective Hamiltonian in the A -

reduction and I' representation (see, e.g., Refs. [55,56]):

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

where $J_{xy}^2 = J_x^2 - J_y^2$; $[\dots, \dots]_+$ denotes anticommutators; $A^\nu, B^\nu,$ and C^ν are the effective rotational constants connected with the vibrational state (ν), and the other parameters are the different order centrifugal distortion coefficients.

Because all four considered in the present study vibrational states are the states of different symmetry, we do not discuss the Fermi-type interaction here. As to the three Coriolis-type resonance interactions, the corresponding non-diagonal blocks of the Hamiltonian (1) can be written in the following form (see, e.g., Refs. [57–59]):

1. The B -type Coriolis interaction operators H_{13} and H_{24} , which connect the vibrational state $|1\rangle = (\nu_4 = 1, A_u)$ with the state $|3\rangle = (\nu_{10} = 1, B_{2u})$ and the state $|2\rangle = (\nu_7 = 1, B_{1u})$ with the state $|4\rangle = (\nu_{12} = 1, B_{3u})$, can be written as:

$$H_{\nu\tilde{\nu}} = iJ_x H_{\nu\tilde{\nu}}^{(1)} + H_{\nu\tilde{\nu}}^{(1)} iJ_x + [J_y, J_z] + H_{\nu\tilde{\nu}}^{(2)} + H_{\nu\tilde{\nu}}^{(2)} [J_y, J_z]_+ + [iJ_x, (J_x^2 - J_y^2)]_+ + H_{\nu\tilde{\nu}}^{(3)} + H_{\nu\tilde{\nu}}^{(3)} [iJ_x, (J_x^2 - J_y^2)]_+ + \dots; \quad (3)$$

2. interaction between the states $|1\rangle = (\nu_4 = 1, A_u)$ and $|2\rangle = (\nu_7 = 1, B_{1u})$ and between the states $|3\rangle = (\nu_{10} = 1, B_{2u})$ and $|4\rangle = (\nu_{12} = 1, B_{3u})$ are described by the C -type Coriolis interaction operators H_{12} and H_{34} , respectively:

$$H_{\nu\tilde{\nu}} = iJ_y H_{\nu\tilde{\nu}}^{(1)} + H_{\nu\tilde{\nu}}^{(1)} iJ_y + [J_x, J_z] + H_{\nu\tilde{\nu}}^{(2)} + H_{\nu\tilde{\nu}}^{(2)} [J_x, J_z]_+ + [iJ_y, (J_x^2 - J_y^2)]_+ + H_{\nu\tilde{\nu}}^{(3)} + H_{\nu\tilde{\nu}}^{(3)} [iJ_y, (J_x^2 - J_y^2)]_+ + \dots; \quad (4)$$

and

3. operator describing interaction between the states $|1\rangle = (\nu_4 = 1, A_u)$ and $|4\rangle = (\nu_{12} = 1, B_{3u})$ and between the states $|2\rangle = (\nu_7 = 1, B_{1u})$ and $|3\rangle = (\nu_{10} = 1, B_{2u})$ is the A -type Coriolis interaction operator which has the form:

$$H_{\nu\tilde{\nu}} = iJ_z H_{\nu\tilde{\nu}}^{(1)} + [J_x, J_y] + H_{\nu\tilde{\nu}}^{(2)} + H_{\nu\tilde{\nu}}^{(2)} [J_x, J_y]_+ +$$