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Re-analysis of the high resolution FTIR spectrum of $C_2H_2D_2$ -cis in the region of 1280–1400 cm⁻¹



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ABSTRACT

The high-resolution infrared spectrum of $C_2H_2D_2$ -cis ethylene was analyzed in the region of 1280–1400 cm⁻¹, where the strong ν_{12} band is located. More than 2000 transitions (about three times more than it was made in the preceding studies) were assigned with the maximum values of the upper quantum numbers $J^{max} = 45$ and $K_a^{max} = 19$ ($J^{max} = 31$ and $K_a^{max} = 13$ in the preceding studies). For the first time, 22 transitions belonging to the $2\nu_{10}$ weak band were assigned. For description of the assigned transitions (upper rovibrational energy levels), the Hamiltonian model was used which takes into account resonance interactions between the vibrational state ($\nu_{12} = 1$) and three other closely located states: ($\nu_{10} = 2$), ($\nu_8 = \nu_{10} = 1$), and ($\nu_3 = 1$). A set of 43 spectroscopic parameters obtained from a weighted least square fit reproduces the initial experimental data (817 upper energy values and more than 2000 transitions) with the $d_{mns} = 2.2 \times 10^{-4}$ cm⁻¹ which is close to experimental uncertainties and considerably better than in prior studies. Ground state rotational and centrifugal distortion parameters were improved on the basis of the IR experimental data of the present study and microwave data from the earlier literature.

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1. Introduction

Ethylene is a naturally occurring compound in ambient air that affects atmospheric chemistry and the global climate. Due to its high reactivity towards hydroxyl (OH) radicals, ethylene plays a significant role in tropospheric chemistry and ozone generation, Ref. [1]. Ethylene is one of the most relevant substances of study in astrophysics [2–13]. It acts as a hormone in plants and its role in plant biochemistry, physiology, mammals metabolism, and ecology is the subject of extensive research (see, *e.g.*, [14]).

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http://dx.doi.org/10.1016/j.jqsrt.2015.10.011 0022-4073/© 2015 Elsevier Ltd. All rights reserved. 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, both the ethylene molecules and its different isotopologs have been the subject of extensive studies (as an illustration, we mention here some last years publications, Refs. [15–19]).

In the present paper we continue our study of high resolution spectra of the ethylene molecule and its different isotopologs, Refs. [20–27], and focus on the study of the $C_2H_2D_2$ -cis ethylene. This molecule was discussed earlier in Refs. [28–36]. The low resolution spectrum of $C_2H_2D_2$ -cis in a mixture with the $C_2H_2D_2$ -trans isotopomer was recorded in [28]. In Ref. [29] already high resolution microwave (MW) spectra of $C_2H_2D_2$ -cis and a few other

ethylene isotopic species were recorded with the goal to analyze dipole moment and r_z structure. Regular high resolution studies of C₂H₂D₂-cis were made by Hegelund and Nicolaisen, Refs. [30–32] and Tan with co-authors, Refs. [33–36]. Hegelund and Nicolaisen analyzed nine rovibrational bands, ν_5 , ν_6 , ν_7 , ν_9 , ν_{12} , $\nu_2 + \nu_{12}$, $\nu_3 + \nu_6$, $\nu_4 + \nu_7$, and $\nu_7 + \nu_8$. Tan with co-authors re-analyzed the bands ν_6 , ν_7 , ν_{12} , and $\nu_7 + \nu_8$ on the basis of IR spectra, which have been recorded with a higher resolution than in the works of Hegelund and Nicolaisen. In this case, for the ν_{12} band the resonance interaction with the $2\nu_{10}$ band was taken into account that allowed authors of Ref. [33] to reproduce the initial experimental transitions of the ν_{12} band with the $d_{rms} = 0.00075$ cm⁻¹.

In our present study, we focus on the ν_{12} band. As a result of the analysis of the experimentally recorded spectrum, we were able to assign about three times more transitions with higher values of quantum numbers *J* and K_a than it was made before. In the fit of experimental data we took into account interactions of the ν_{12} band with three additional bands: $2\nu_{10}$, ν_3 and $\nu_8 + \nu_{10}$ with the band centers near 1331 cm⁻¹, 1220 cm⁻¹, and 1425 cm⁻¹, respectively. This gave us the possibility to considerably improve the *rms* deviation. In Section 2 we discuss the conditions of our experiment. Section 3 presents briefly the theoretical background for our study. Description of the experimental spectra and assignments of the



Fig. 1. Axes definitions used in the present work for the $C_2H_2D_2$ -cis molecule. The primed symbols refer to the axis definitions for the $C_{2\nu}$ symmetry group used in the classification of the vibrational modes. The unprimed symbols refer to the Cartesian axis definitions of the *I*^r representation of Watson's *A*-reduced effective Hamiltonian.

transitions are given in Section 4. Because it was found that for higher quantum numbers *J* and K_a "experimental" values of ground state combination differences (GSCD) began to differ considerably from the known values of GSCD calculated in the literature, Refs. [29,34], we reanalyzed the rotational energies of the ground vibrational state on the basis of the GSCD derived from our experimental data and from those known in the literature resulting from highly accurate MW transitions. The conclusions are also described in Section 4. The results of an analysis of the upper vibrational states are presented in Section 5.

2. Experimental details

Spectra of C₂H₂D₂-cis have been recorded in the wavenumber range from 1280 to 2000 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 C₂H₂D₂-cis sample was purchased from Cambridge Isotope Laboratories. The identity, chemical and isotopic purity (specified to be better than 99%) was obvious from the spectra. The nominal instrumental resolution, defined by $1/d_{MOPD}$ (maximum optical path difference), was 0.0025 cm⁻¹ resulting in almost Doppler limited spectra in combination with the weak Norton-Beer apodization. The experiment was performed with an optical pathlength of 16 m. at a sample pressure of 37 Pa and a scan number of 460. The pressureinduced widths (FWHM) can be estimated to be smaller than 0.0001 cm^{-1} at 37 Pa and is therefore considerably smaller compared to the Doppler widths (FWHM) which at 300 K ranges from 0.0023 cm^{-1} at 1000 cm^{-1} to 0.0046 cm^{-1} at 2000 cm⁻¹. The spectra were calibrated with spectral lines of N₂O (Ref. [37] and references therein). The absolute wavenumber accuracy of nonblended, unsaturated and not too weak lines can be estimated to be about 10^{-4} cm⁻¹.

3. Theoretical background and the Hamiltonian model

The C₂H₂D₂-cis molecule is an asymmetric top with the value of the asymmetry parameter $\kappa = (2B-A-C)/(A-C) \simeq -0.868$ and with the symmetry isomorphic to the C_{2 ν} point symmetry group (see Fig. 1). For convenience of the

Table 1				
Symmetry types and characters of irreducible re	presentations of the	$C_{2\nu}$ group	(application to	C ₂ H ₂ D ₂ -cis).

Repr.	Е	C ₂	$\sigma_{\nu}(XZ)$ 4	$\sigma_{v}(yz)$	Vibr.	Rot.	Rot. (<i>I</i> ^r)
1	2	3		5	6	7	8
$ \begin{array}{c} A_1 \\ A_2 \\ B_1 \\ B_2 \end{array} $	1 1 1 1	1 1 -1 -1	1 -1 1 -1	1 -1 -1 1	q ₁ ,q ₂ ,q ₃ ,q ₉ ,q ₁₀ q ₄ ,q ₈ q ₅ ,q ₆ ,q ₁₁ ,q ₁₂ q ₇	J_z, k_{zz} J_y, k_{zy} J_x, k_{zx}	J _x , k _{zx} J _y , k _{zy} J _z , k _{zz}



Fig. 2. Normal vibrational coordinates of the $C_2H_2D_2$ -cis molecule ($C_{2\nu}$ symmetry group).

reader, the symmetry properties of $C_2H_2D_2$ -cis are presented in Table 1: the list of irreducible representations and table of characters of the $C_{2\nu}$ symmetry group are shown in columns 1–5; symmetries of vibrational coordinates q_{λ} (see also Fig. 2), rotational operators J_{α} , and direction cosines $k_{z\alpha}$ are shown in columns 6 and 7. Column 8 presents symmetries of rotational operators J_{α} and direction cosines $k_{z\alpha}$, which correspond to the l^r representation (see, *e.g.*, Refs. [38–40]) in asymmetric top molecules.

In accordance with the selection rules for the asymmetric top molecules of the $C_{2\nu}$ symmetry (see, *e.g.*, Refs. [41–48]), there are three types of vibrational bands which are allowed in absorption:

- (1) the *a*-type bands with the selection rules for them $\Delta J = 0, \pm 1$ and $\Delta K_a =$ even, $\Delta K_c =$ odd;
- (2) the *b*-type bands with the selection rules $\Delta J = 0, \pm 1$ and $\Delta K_a = \text{ odd}, \Delta K_c = \text{ odd};$
- (3) the *c*-type ones with the selection rules $\Delta J = 0, \pm 1$ and $\Delta K_a = \text{ odd}, \Delta K_c = \text{ even.}$

To choose which type of selection rules is applied to a concrete absorption band, one should consider that

- (1) the selection rules are determined by unequal-to-zero matrix elements of the $k_{z\alpha}$ values: k_{zx} , k_{zy} and k_{zz} are responsible for the appearance of the *b*-, *c* and *a*-type transitions (bands);
- (2) the following rule (see, *e.g.*, Refs. [43,49]) is valid: type of vibrational band (*a*-, *b*-, or *c*-) for an asymmetric top molecule is determined by the symmetry $\Gamma(k_{z\alpha}) = A_2 \otimes \gamma^{\nu_1} \otimes \gamma^{\nu_2}$, where $\Gamma(k_{z\alpha})$ is the symmetry of $k_{z\alpha}$ (see column 8 of Table 1), γ_1^{ν} and γ_2^{ν} are the symmetries of the lower and upper vibrational states, respectively, and \otimes denotes a direct product. In our

case of the C₂H₂D₂-cis molecule, γ_1^{ν} is A_1 (ground vibrational state). As a consequence, $(A_1 \leftarrow A_1)$ are the bands of the *b*-type, $(B_1 \leftarrow A_1)$ are the bands of the *a*-type, and $(B_2 \leftarrow A_1)$ are the bands of the *c*-type. For that reason, the $\nu_{12}(B_1)$ bands can be identified as the *a*-type band. As was mentioned in the introduction, in the further analysis we also took into account the bands $2\nu_{10}(A_1)$, $\nu_3(A_1)$, and $\nu_8 + \nu_{10}(A_2)$. The two first of them are the bands of the *b*-type, the third one is forbidden in absorption by the symmetry of the molecule.

The effective Hamiltonian model which was used for theoretical analysis of experimental data was discussed in the literature many times (see, *e.g.*, Refs. [50–52]). 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. [53–56])

$$H^{\text{vib.}-\text{rot.}} = \sum_{\nu,\bar{\nu}} |\nu\rangle \langle \tilde{\nu} | H_{\nu\bar{\nu}}, \tag{1}$$

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

$$\begin{aligned} |1\rangle &= (v_3 = 1, A_1), \quad |2\rangle = (v_{10} = 2, A_1), \\ |3\rangle &= (v_8 = v_{10} = 1, A_2) \quad \text{and} \quad |4\rangle = (v_{12} = 1, B_1). \end{aligned}$$

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^r representation (see, *e.g.*, Refs. [38,57]):

$$H_{\nu\nu} = E^{\nu} + \left[A^{\nu} - \frac{1}{2}\left(B^{\nu} + C^{\nu}\right)\right]J_{z}^{2} + \frac{1}{2}\left(B^{\nu} + C^{\nu}\right)J^{2} + \frac{1}{2}\left(B^{\nu} - C^{\nu}\right)J_{xy}^{2}$$