



First high resolution ro–vibrational analysis of C₂HD₃ in the region of the ν_{12} band

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ARTICLE INFO

Article history:

Received 24 May 2018

Revised 4 July 2018

Accepted 4 July 2018

Available online 5 July 2018

Keywords:

C₂HD₃ ethylene

High-resolution spectra

Spectroscopic parameters

ABSTRACT

The high-resolution infrared spectra of C₂HD₃ ethylene was analyzed for the first time in the region of 1230–1340 cm⁻¹, where the strong ν_{12} band is located. The 1748 transitions with the maximum values of the upper quantum numbers $J^{max.} = 43$ and $K_a^{max.} = 14$ were assigned to the ν_{12} band. The 14 transitions have been assigned to the $2\nu_{10}$ band whose appearance is caused by the strong resonance interaction with the ν_{12} one. For description of the assigned transitions (upper ro-vibrational energy levels), the effective Hamiltonian was used which takes resonance interactions between the vibrational state ($\nu_{12} = 1$) and three other closely located states, ($\nu_{10} = 2$), ($\nu_7 = \nu_{10} = 1$) and ($\nu_4 = \nu_{10} = 1$) into account. A set of 70 spectroscopic parameters obtained from a weighted least square fit reproduces the initial experimental data (593 upper energy values, 1762 transitions) with the $d_{rms} = 1.3 \times 10^{-3}$ cm⁻¹. Finally, the strengths of 106 ro-vibrational lines of the ν_{12} band were roughly estimated.

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1. Introduction

Ethylene is an important chemical species in many fields such as synthetic and analytical chemistry, astrophysics and astrobiology, laser techniques and planetology, etc. 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]). 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, over the years numerous both theoretical and laboratory spectroscopic studies of the ethylene molecule and its different isotopologues have been performed. Without having the opportunity to refer all the “ethylene” studies, we mention here only a few of them, namely, studies which have been per-

formed during the last ten years (see Refs. [15–54] and references cited therein).

The subject of the present study is the ν_{12} band of the C₂HD₃ species. Earlier the high resolution spectra of C₂HD₃ have been discussed only in a few papers, Refs. [55–63]. The first three papers are devoted to the theoretical *ab initio* estimations of the intramolecular force field parameters, and estimations of the fundamental band centers of the C₂HD₃ molecule can be found there. In the fourth, Ref. [58], the local mode model (see, e.g., Refs. [64–68]) is applied for analysis of the CH and CD stretching vibrational manifolds of C₂H₃D and C₂HD₃. In a set of papers by Tan with co-authors, Refs. [59–63], the high resolution spectra of the ν_8 and $2\nu_8$ bands of ¹²C₂HD₃ and ¹³C₂HD₃ are discussed.

In this paper we present the results of the first analysis of the high resolution Fourier transformed spectra of ¹²C₂HD₃ in the region of 1230–1340 cm⁻¹ where the ν_{12} band is located. The experimental details are given in Section 2. Section 3 presents briefly the theoretical background of our study. A description of the experimental spectra and assignment of transitions are given in Section 4. Section 5 is devoted to the analysis of the ro–vibrational energy structure of the ($\nu_{12} = 1$) vibrational state and discussion. Estimation of individual line strengths is discussed in Section 6.

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Table 1
Experimental setup for the regions 1060–2050 cm^{-1} of the infrared spectrum of C_2HD_3 .

Spectr.	Resolution / cm^{-1}	No. of scans	Detector	Beam- splitter	Opt. path- length/m	Aperture /mm	Temp. / $^\circ\text{C}$	Pressure /Pa	Calibr. gas
I	0.0021	350	MCT	KBr	4	1.3	25 ± 1	100	H_2O , N_2O
II	0.0021	300	MCT	KBr	24	1.3	25 ± 1	500	H_2O , N_2O

2. Experimental details

In the Braunschweig infrared laboratory two spectra in the 1060–2050 cm^{-1} region have been recorded using an IFS120HR Fourier transform infrared spectrometer (FTIR) combined with a stainless steel White cell with a base length of one meter and a maximum path-length of up to 50 m. A Globar IR source, a KBr beamsplitter, a mercury–cadmium–telluride (MCT) semiconductor detector have been used.

The sample C_2HD_3 was generated in our laboratory via the exchange reaction between ethylene C_2D_4 and hydrogen H_2 on a nickel–wire catalyst which was electrically heated to the temperature range of 120–180 $^\circ\text{C}$ similar as described in Ref. [69]. From this experiment it is clear that the seven isotopologues, C_2H_4 , $\text{C}_2\text{H}_3\text{D}$, $\text{C}_2\text{H}_2\text{D}_2$, C_2HD_3 and C_2D_4 , occur while the $\text{C}_2\text{H}_2\text{D}_2$ still splits into the –cis, –trans and –as variants. To get an optimum output of C_2HD_3 and a favorable concentration–ratio combination with the “neighbor isotopologues” $\text{C}_2\text{H}_2\text{D}_2$ and C_2D_4 with minimized spectral overlap, an analysis of the distribution of the five isotopologue categories dependent on the ratio of deuterium to hydrogen atoms in the gas phase of the system was performed with the following approach: each ethylene molecule has eight possibilities for its four H and D atoms to change atoms with H_2 , D_2 and HD molecules in the gas phase. In equilibrium the net inflows and outflows from the neighboring isotopologue categories are zero and therefore five balance equations can be formed. Together with the additional general balance equation for the portions of the categories being unity in sum, six equations form an overdetermined linear equation system for the five isotopologue categories which can be solved depending on the H/D atom ratio in the system. As the result, the maximum concentration forms out as a flat maximum with about 42.2 % for the C_2HD_3 portion (0.4 % for C_2H_4 , 4.7 % for $\text{C}_2\text{H}_3\text{D}$, 21.1 % for $\text{C}_2\text{H}_2\text{D}_2$ and 31.6 % for C_2D_4) at an atom ratio of $c(\text{D})/c(\text{H}) = 3$. With this atom ratio we created the mixture of isotopologues over about five hours in the heated system with the nickel wire which we used for the spectra recording. The distribution of isotopologues was checked on the one hand by the band intensities in the transmission spectra and on the other hand generally by a dynamic simulation being both in accordance with the analytical result. The fact that the bond strengths are slightly different for H and D atoms has been neglected in our calculations.

For detailed optical and recording parameters see Table 1; the optical resolution was 0.0021 cm^{-1} for both spectra, the number of scans was 350 and 300 resulting in measuring durations of 17.5 and 15 hours, the optical path-length was 4 m for both spectra and the sample gas pressure was 100 and 500 Pa to get lines with stronger and weaker line intensities. The sample temperature was $(25 \pm 1)^\circ\text{C}$. The spectral resolution at 1300 cm^{-1} was mainly dominated by Doppler broadening of 0.0029 cm^{-1} for both spectra. The pressure broadening was 0.0002 and 0.001 cm^{-1} for the used sample pressures of 100 and 500 Pa. This means that it has a secondary contribution to the total line widths which can be computed by the root sum square approximation of a convolution of Doppler, pressure and instrumental line widths resulting in 0.0032 and 0.0034 cm^{-1} for the two pressures which is in accordance with the experimental results. The spectra were calibrated with N_2O and H_2O lines which occur in the sample as an impu-

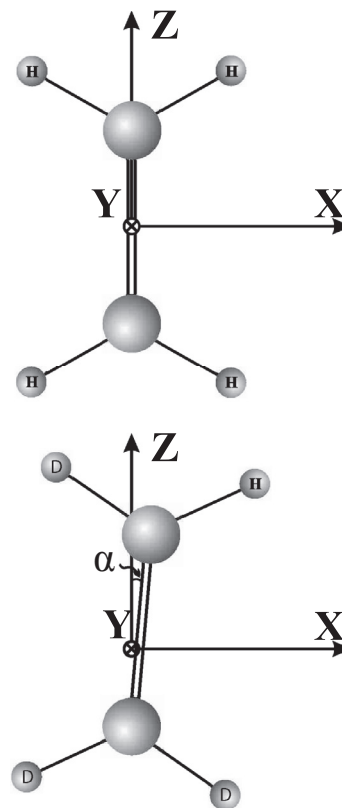


Fig. 1. Axes definitions used in the present work for the C_2HD_3 molecule (for comparison, the “mother” C_2H_4 molecule is also shown at the bottom part of the figure). The notations of axes refer to the definition of the A -reduction and I' representation of the Watson effective Hamiltonian. The angle $\alpha = 4.37^\circ$ indicates the angle between the Z axis and the $\text{C}=\text{C}$ bond, and it is the angle of a turn of the “mother” molecular-fixed coordinate system to the C_2HD_3 molecular-fixed coordinate system.

urity of small concentration. For optimization of data recording and line calibration we used data and procedures described in Refs. [34,70,71].

3. Theoretical background and the Hamiltonian model

3.1. General information

The C_2HD_3 molecule is an asymmetric top with the value of the asymmetry parameter $\kappa = (2B - A - C)/(A - C) \simeq -0.885$ and with the symmetry isomorphic to the C_s point symmetry group (see Fig. 1). For convenience of the reader, the symmetry properties of C_2HD_3 are shown in Table 2: the list of irreducible representations and table of characters of the C_s symmetry group are shown in columns 1–3; symmetries of vibrational coordinates, q_λ (see also Fig. 2), rotational operators J_α , and direction cosines $k_{z\alpha}$ are shown in column 4 and 5. Column 6 presents types of rotational operators J_α and direction cosines $k_{z\alpha}$, which correspond to the I' representation (see, e.g., Refs. [72–74]) in asymmetric top molecules.

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