



Contents lists available at ScienceDirect

# Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: [www.elsevier.com/locate/jqsrt](http://www.elsevier.com/locate/jqsrt)

## First study of the ro-vibrational structure of the g-symmetry vibrational states of $C_2D_4$ from the analysis of hot bands: The $\nu_7 + \nu_{10} - \nu_{10}$ and $\nu_{10} + \nu_{12} - \nu_{10}$ bands



O.N. Ulenikov<sup>a,\*</sup>, O.V. Gromova<sup>a</sup>, E.S. Bekhtereva<sup>a</sup>, A.L. Fomchenko<sup>a</sup>, C. Sydow<sup>b</sup>, C. Maul<sup>b</sup>, S. Bauerecker<sup>b</sup>

<sup>a</sup> Institute of Physics and Technology, National Research Tomsk Polytechnic University, Tomsk, 634050, Russia

<sup>b</sup> Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38106 Braunschweig, Germany

### ARTICLE INFO

#### Article history:

Received 6 July 2016

Received in revised form

19 September 2016

Accepted 19 September 2016

Available online 28 September 2016

#### Keywords:

$C_2D_4$

High-resolution spectra

Spectroscopic parameters

Hot band

### ABSTRACT

The two strongest absorption “hot” bands of  $C_2D_4$ ,  $\nu_7 + \nu_{10} - \nu_{10}$  and  $\nu_{10} + \nu_{12} - \nu_{10}$  were analyzed for the first time on the basis of high resolution infrared spectra recorded with a Bruker high resolution Fourier transform spectrometer. About 740 and 550 transitions (233 and 174 upper state ro-vibrational energy values) with  $J^{max.} = 25$ ,  $K_a^{max.} = 18$  and  $J^{max.} = 20$ ,  $K_a^{max.} = 10$  for the bands  $\nu_7 + \nu_{10} - \nu_{10}$  and  $\nu_{10} + \nu_{12} - \nu_{10}$  were assigned. The obtained upper ro-vibrational energies were used then in the weighted fit of parameters of the effective Hamiltonian which takes into account resonance interactions between the vibrational states ( $\nu_7 = \nu_{10} = 1$ ) and ( $\nu_{10} = \nu_{12} = 1$ ), on the one hand, and eight other closely located vibrational states, on the other hand. A set of 46 varied parameters was obtained from the fit, which reproduces the initial experimental data with the rms deviation of  $2.5 \times 10^{-4} \text{ cm}^{-1}$  and which is close to experimental uncertainties.

© 2016 Elsevier Ltd. All rights reserved.

### 1. Introduction

There are many both pure basic, and applied problems in physics and chemistry where the precise information about ro-vibrational spectra of different isotopic species of a molecule is needed. In particular, one of the most important problems of physical chemistry is the precise determination of the intramolecular potential energy surface (PES) of a molecule. The knowledge of a correct PES is crucial for solving the Schrodinger equation of a molecule, which offers prospects to determine a correct set of eigenfunctions of the corresponding molecular Hamiltonian. In turn, this information allows one to solve numerous problems in physical chemistry, astrophysics,

planetology, atmospheric and environmental sciences, etc. (see, e.g., Refs. [1–13]).

One of the most efficient ways to precisely determine a molecular PES is to calculate it by *ab initio* methods with a subsequent calibration of the results on the basis of highly accurate experimental ro-vibrational data (see, e.g., Refs. [14–16]). In this case, the larger the number of experimentally recorded and analyzed ro-vibrational bands (especially, high excited bands, see, e.g. Refs. [17–21]), the more precise results one can expect to obtain. Another way to improve the quality of *abinitio* calculated PES is to exploit proper information about different isotopic modifications of the considered molecule for PES calibration, Refs. [22–25]. In this context, the present paper continues our recent study of high resolution infrared spectra of ethylene,  $^{12}C_2H_4$ , and its different isotopic species, Refs. [26–34], with the goal to determine highly accurate spectroscopic parameters of as many as possible ro-vibrational states of different ethylene isotopologues.

\* Corresponding author.

E-mail address: [Ulenikov@mail.ru](mailto:Ulenikov@mail.ru) (O.N. Ulenikov).

Subject of the present study is the totally deuterated isotopologue of ethylene, the  $C_2D_4$  molecule. Earlier, only the ground vibrational state and the  $\nu_{10}$ ,  $\nu_7$ ,  $\nu_4$ ,  $\nu_{12}$  fundamentals have been analyzed with a high resolution, Refs. [35–44]. In this paper we present results of the rotational analysis of two *g*-type vibrational states ( $\nu_7 = \nu_{10} = 1$ ) and ( $\nu_{10} = \nu_{12} = 1$ ) (transitions from the ground vibrational state to these states are totally forbidden by the symmetry of the  $C_2D_4$  molecule). We analyzed the weak “hot” bands,  $\nu_7 + \nu_{10} - \nu_{10}$  and  $\nu_{10} + \nu_{12} - \nu_{10}$ , and this gave us the possibility to obtain the rotational structure of the ( $\nu_7 = \nu_{10} = 1$ ) and ( $\nu_{10} = \nu_{12} = 1$ ) vibrational states. The structure of this paper is as follows. Section 2 describes the experimental conditions of the recorded spectra. Section 3 briefly gives the theoretical background (Hamiltonian model) used in the present study. Estimation of the initial values of spectroscopic parameters is discussed in Section 4. Assignment of transitions and of the further fit of the Hamiltonian parameters on the basis of the recorded experimental data are presented in Section 5.

## 2. Experimental details

The experimental details have been described in a related article recently Ref. [44], compare also Table 1. Using a Bruker IFS 120 Fourier transform infrared (FTIR) spectrometer in combination with a stainless-steel White cell (base length 1 m) three spectra of  $C_2D_4$  have been recorded in the wavenumber range from 600 to 1200  $cm^{-1}$ . A mercury-cadmium-telluride (MCT) semiconductor detector was used. The  $C_2D_4$  sample was purchased from EQ laboratories/CDN isotopes and was specified with a purity of 99.8 atom %. 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 are therefore considerably smaller compared to the Doppler widths (FWHM) which at 298 K ranges from 0.0013  $cm^{-1}$  at 600  $cm^{-1}$  to 0.0026  $cm^{-1}$  at 1200  $cm^{-1}$ . 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 1200  $cm^{-1}$ . First spectrum: 8 Pa, 4 m, Boxcar/self-apodization, 410 scans, 0.0020 and 0.0030  $cm^{-1}$ . Second spectrum: 150 Pa, 4 m, Boxcar/self-apodization, 430 scans, 0.0019 and 0.0030  $cm^{-1}$ . Third spectrum: 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. [45,46]. 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  $10^{-4} cm^{-1}$  with a divergence of single lines below  $4 \times 10^{-4} cm^{-1}$ .

## 3. Theoretical background

Analogous studies of hot bands in the ethylene  $D_{2h}$ -symmetry species have been made earlier in Refs. [47,48]. The present study of the  $C_2D_4$  molecule is motivated by the fact that different shifts of band centers can lead to considerably different pictures of resonance interactions in comparison with the main,  $^{12}C_2H_4$ , molecule (see columns 2 and 3 of Table 2 where the values of estimated band center shifts for studied bands are presented for the  $C_2D_4$  species, as well as for the  $^{13}C_2H_4$  one).

The upper states ( $\nu_7 = \nu_{10} = 1$ ) and ( $\nu_{10} = \nu_{12} = 1$ ) of the  $C_2D_4$  molecule are *g*-type states, and, for this reason, transitions in absorption from the ground vibrational state to the ( $\nu_7 = \nu_{10} = 1$ ) and ( $\nu_{10} = \nu_{12} = 1$ ) states are forbidden by the symmetry of the molecule. At the same time, the “hot” transitions from the *u*-type vibrational state ( $\nu_{10} = 1$ ) are allowed, and, as a consequence, the ro-vibrational energies of the upper states ( $\nu_7 = \nu_{10} = 1$ ) and ( $\nu_{10} = \nu_{12} = 1$ ) can be determined from the “hot” transitions. Of course, such “hot” transitions are considerably weaker than transitions belonging to the “cold”  $\nu_7$  and  $\nu_{12}$  bands which are located in the same spectral regions. The top parts of Figs. 1 and 2 show overview spectra of the  $\nu_7/\nu_7 + \nu_{10} - \nu_{10}$  and  $\nu_{12}/\nu_{10} + \nu_{12} - \nu_{10}$  bands. Small fragments of the Q-branches of the  $\nu_7 + \nu_{10} - \nu_{10}$  and  $\nu_{10} + \nu_{12} - \nu_{10}$  bands are presented in the bottom parts of Figs. 1 and 2.

In the present study we follow the analogous analysis of the  $\nu_7 + \nu_{10} - \nu_{10}$  and  $\nu_{10} + \nu_{12} - \nu_{10}$  bands of  $^{12}C_2H_4$ , Ref. [47]. Taking resonance interactions in the four lowest vibrational states into account (see, Ref. [44]), one can draw the conclusion that the physically reasonable description of experimental data is possible only if resonance interactions of the vibrational state ( $\nu_7 = \nu_{10} = 1$ ) with the states ( $\nu_{10} = 2$ ), ( $\nu_7 = 2$ ), ( $\nu_4 = 2$ ), ( $\nu_4 = \nu_{10} = 1$ ), and ( $\nu_4 = \nu_7 = 1$ ) are considered. On the other hand, interactions of the vibrational state ( $\nu_{10} = \nu_{12} = 1$ ) with the states ( $\nu_{12} = 2$ ), ( $\nu_7 = \nu_{12} = 1$ ), ( $\nu_4 = \nu_{12} = 1$ ) also have to be considered. In general, we include 10 interacting vibrational states in the present study. As a consequence, for a theoretical analysis we employ a method of effective rotational operators in the form (see, e.g., Refs. [49–51])

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

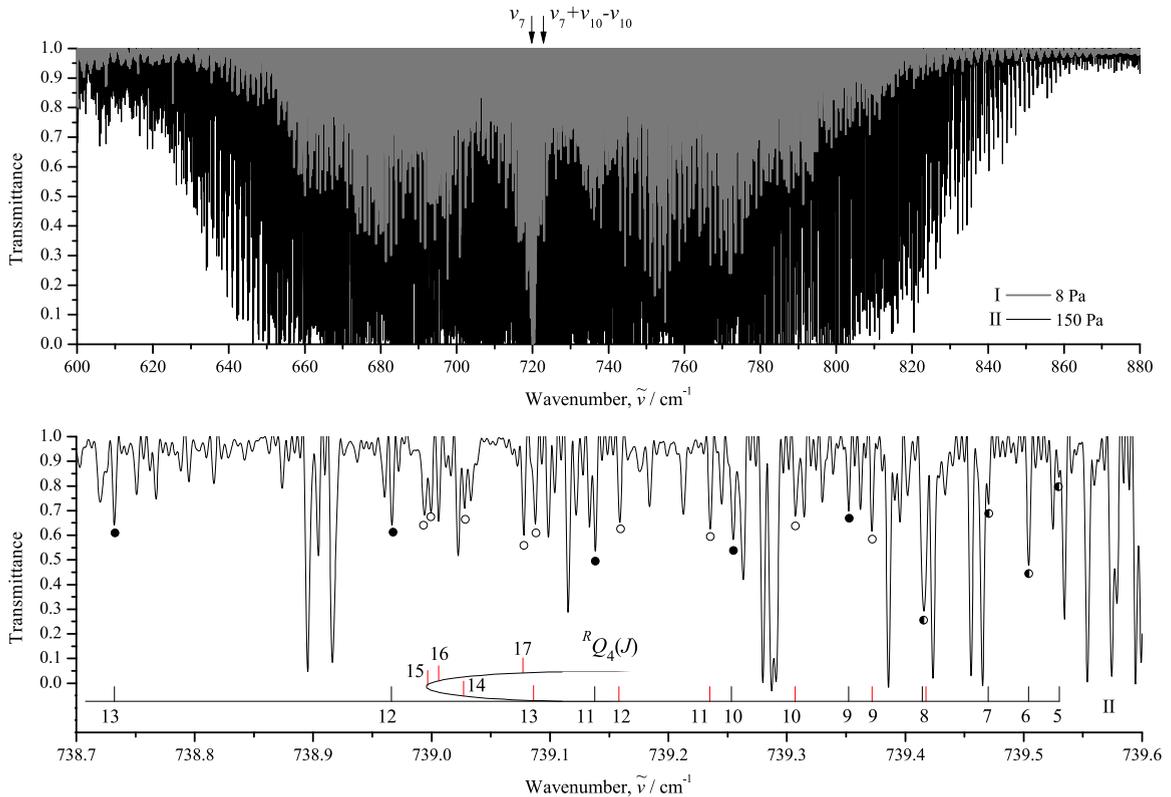
**Table 1**

Experimental setup for the 600–1200  $cm^{-1}$  region 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./ $^{\circ}C$	Pressure /Pa	Calibr. gas
I	600–1200	0.0021	410	Globar	MCT	KBr	4	1.5	$25 \pm 0.5$	8.0	$N_2O$
II	600–1200	0.0021	430	Globar	MCT	KBr	4	1.5	$25 \pm 0.5$	150	$N_2O$
III	600–1200	0.0021	550	Globar	MCT	KBr	24	1.5	$25 \pm 0.5$	200	$N_2O$

**Table 2**Some parameters of the studied vibrational states (in  $\text{cm}^{-1}$ ).

Coeff., $x_{\lambda\mu}$	Value, <sup>a</sup> $\text{C}_2\text{H}_4$	Value, <sup>b</sup> $\text{C}_2\text{D}_4$	State	Shift, <sup>c</sup> $^{13}\text{C}_2\text{H}_4$	Shift, <sup>d</sup> $\text{C}_2\text{D}_4$	Energy, <sup>e</sup> $\text{C}_2\text{D}_4$
1	2	3	4	5	6	7
$x_{44}$	-1.395	-0.698	$(\nu_{10} = 2)$	-2.023	-469.769	1191.279
$x_{47}$	-8.059	-4.030	$(\nu_7 = \nu_{10} = 1)$	-6.020	-464.699	1316.223
$x_{410}$	1.740	0.870	$(\nu_4 = \nu_{10} = 1)$	-0.796	-529.179	1324.078
$x_{412}$	2.234	1.117	$(\nu_7 = 2)$	-10.017	-458.979	1440.517
$x_{77}$	0.977	0.489	$(\nu_4 = \nu_7 = 1)$	-4.793	-520.694	1445.608
$x_{710}$	6.224	3.112	$(\nu_4 = 2)$	0.430	-590.051	1458.339
$x_{712}$	-4.716	-2.358	$(\nu_{10} = \nu_{12} = 1)$	-6.803	-596.344	1668.624
$x_{1010}$	4.597	2.299	$(\nu_7 = \nu_{12} = 1)$	-10.800	-592.102	1794.395
$x_{1012}$	-3.401	1.701	$(\nu_4 = \nu_{12} = 1)$	-5.576	-662.299	1807.967
$x_{1212}$	-3.832	-1.916	$(\nu_{12} = 2)$	-11.583	-727.089	2150.134

<sup>a</sup> Reproduced from Ref. [70].<sup>b</sup> Estimated theoretically on the basis of Eq. (10).<sup>c</sup> Reproduced from Ref. [53].<sup>d</sup> Estimated theoretically on the basis of formulas analogous to Eqs. (7) and (8). In this case, energy values  $E^{(\nu_i = 1)}$  have been taken from Ref. [31], and values of the  $x_{\lambda\lambda}$  and  $x_{\lambda\mu}$  coefficients have been taken from Ref. [70] (reproduced in column 2 of the present paper).<sup>e</sup> Estimated theoretically on the basis of Eqs. (11) and (12).

**Fig. 1.** Survey spectra of  $\text{C}_2\text{D}_4$  in the region of the  $\nu_7 + \nu_{10} - \nu_{10}$  “hot” band. Experimental conditions: sample pressure is 8 Pa, absorption path length is 4 m; room temperature; number of scans is 410 for the spectrum I, and sample pressure is 150 Pa, absorption path length is 4 m; room temperature; number of scans is 430 for the spectrum II. A small part of the high resolution spectrum II in the Q-branch region is presented in the bottom part. The marked lines belong to the “hot” band.

where the summation is taken from 1 to 10 for both  $\nu$  and  $\tilde{\nu}$ , which represent the ten vibrational states mentioned above:

$A_g$ -symmetry: |1) =  $(\nu_{10} = 2)$ , |2) =  $(\nu_7 = 2)$ , |3) =  $(\nu_4 = 2)$ ,  
|4) =  $(\nu_{12} = 2)$

$B_{2g}$ -symmetry: |5) =  $(\nu_4 = \nu_{10} = 1)$ , |6) =  $(\nu_7 = \nu_{12} = 1)$

$B_{3g}$ -symmetry: |7) =  $(\nu_7 = \nu_{10} = 1)$ , |8) =  $(\nu_4 = \nu_{12} = 1)$

$B_{1g}$ -symmetry: |9) =  $(\nu_4 = \nu_7 = 1)$ , |10) =  $(\nu_{10} = \nu_{12} = 1)$ .

any of the diagonal blocks  $H^{VV}$ , Eq. (1), describes the unperturbed rotational structure of the vibrational state