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First high resolution study of the interacting $\nu_8+\nu_{10}$, $\nu_6+\nu_{10}$, $\nu_6+\nu_7$ bands and re-analysis of the $\nu_7+\nu_8$ band of trans-d$_2$-ethylene

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ABSTRACT

The high resolution IR spectrum of the trans-d$_2$-ethylene (trans-$C_2H_2D_2$) was recorded and analyzed in the region of 1450–1750 cm^{-1}, where the strongly interacting bands $\nu_8+\nu_{10}$, $\nu_7+\nu_8$, $\nu_6+\nu_{10}$, and $\nu_6+\nu_7$ are located (one of the sub-bands of the hybrid $\nu_7+\nu_8$ band was analyzed earlier; transitions belonging to the three other bands were experimentally recorded and assigned in the present study for the first time). For description of the upper ro-vibrational energy levels obtained from the assigned transitions, the used Hamiltonian takes into account resonance interactions both between four studied vibrational states, $(v_8=v_{10}=1)$, $(v_7=v_8=1)$, $(v_6=v_{10}=1)$, $(v_6=v_7=1)$, and between the state $(v_6=v_7=1)$ and the additional fifth state $(v_4=v_8=1)$ which is considered in the present study as a "dark" state. About 2360, 2150, 2020 and 1700 transitions with the values $J^{max.}/K_a^{max.}=31/21$, 44/18, 28/18 and 27/17 were assigned to the bands $\nu_8+\nu_{10}$, $\nu_7+\nu_8$, $\nu_6+\nu_{10}$, and $\nu_6+\nu_7$, respectively. A set of 103 spectroscopic parameters was obtained from a weighted least square fit procedure. This reproduces the 550, 656, 441 and 435 upper ro-vibrational energies of the vibrational states $(v_8=v_{10}=1)$, $(v_7=v_8=1)$, $(v_6=v_{10}=1)$ and $(v_6=v_7=1)$ used in the fit with a $d_{rms}=2.5\times10^{-4}$ cm^{-1}, which is close to the value of the mean experimental uncertainty (in this case, only upper energies obtained from unblended and nonsaturated transitions of relatively high intensities have been taken into account).

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, mammal's 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 [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., Refs. [2,3]), and it has been detected as a trace component in the atmospheres of the outer planets Jupiter, Saturn, Neptune, [4–7], and the satellite Titan [8–13]. 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

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organic molecules. Therefore, for many years, the ethylene molecule and its different isotopomers have been a subject of both extensive experimental (see, e.g., reviews in Refs. [14,15]) and theoretical (see, e.g., Ref. [16] 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, that up to the present a high resolution spectroscopic analysis of different ethylene species has been made only for the low energy vibrational bands.

In the present paper we continue our recent investigation of the high resolution ro-vibrational spectra of ethylene, $^{12}C_2H_4$, and its different isotopologues, Refs. [17–27], with the study of the trans-$C_2H_2D_2$ molecule. The infrared spectra of trans-$C_2H_2D_2$ were discussed in the spectroscopic literature some times (see Refs. [28–35]). The first experimentally recorded spectra of trans-$C_2H_2D_2$ have been mentioned in Ref. [28] by Charette and coworkers. In 1969 Di Lauro and Panunzi, Ref. [29], published the results of the experimental recording with a Beckman IR-9 grating spectrometer and theoretical analysis of three infrared active bands, ν_4, ν_9 and ν_{12}. The same ν_4 and ν_{12}, as well as the ν_7 and ν_{10} bands, have been recorded in Ref. [30] with an about ten times higher resolution than in the preceding Ref. [29]. In 1989, Hegelund discussed high resolution spectra of two relatively strong combination bands, $\nu_7+\nu_8$ and $\nu_4+\nu_8$, see Ref. [31]. At last, Tan and coworkers presented results of high resolution reanalysis of the bands ν_4, ν_{12} and $\nu_4+\nu_8$ in Refs. [32–35].

In our present study, the high resolution FTIR spectra of the trans-$C_2H_2D_2$ ethylene were recorded at different experimental conditions and analyzed in the region of 1450–1750 cm^{-1}, where the strongly interacting bands $\nu_8+\nu_{10}$, $\nu_7+\nu_8$, $\nu_6+\nu_{10}$, and $\nu_6+\nu_7$ are located (only one of them, namely $\nu_7+\nu_8$, was analyzed earlier; three other bands are discussed in the present study for the first time). In Section 2 we discuss the conditions of our experiment. Description of the experimental spectra and results of assignment of transitions are given in Section 3. Section 4 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 on the basis of the isotopic substitution theory). The problem of the analysis of the upper vibrational states, $(v_8=v_{10}=1)$, $(v_7=v_8=1)$, $(v_6=v_{10}=1)$ and $(v_6=v_7=1)$, is discussed in Section 5.

2. Experimental details

In the Braunschweig Infrared Laboratory three spectra of trans-$C_2H_2D_2$ have been recorded in the wavenumber region from 1100 to 2000 cm^{-1} with a Bruker IFS 120 Fourier transform infrared (FTIR) spectrometer in combination with a multiple-path White cell made from stainless steel with a base length of 1 m. A mercury–cadmium–telluride (MCT) semiconductor detector was used, combined with a Globar light source, a KBr beamsplitter, and an aperture with a diameter of 1.3 mm. The $C_2H_2D_2$ sample was purchased from Cambridge Isotope Laboratories and was specified to be 98 at%. The nominal instrumental resolution was 0.0025 cm^{-1} resulting in almost Doppler limited spectra. The apodization mode was Norton–Beer weak. The pressure-induced widths (FWHM) can be estimated for trans-$C_2H_2D_2$ 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 is 0.0040 cm^{-1} at 298 K and 1750 cm^{-1}. The sample pressure was measured by certified MKS Baratron absolute capacitance pressure gauges. The three experimental spectra have been recorded at the following experimental conditions for sample pressure, optical pathlength, number of scans, and total line width at 1750 cm^{-1}. First spectrum (not shown in the paper): 20 Pa, 4 m, 600 scans, and 0.0044 cm^{-1}. Second spectrum: 62 Pa, 16 m, 430 scans, 0.0045 cm^{-1}. Third spectrum: 200 Pa, 24 m, 700 scans, 0.0045 cm^{-1}. The spectra were calibrated with spectral lines of N_2O, Ref. [36] and references therein.

3. Description of the spectrum and assignment of transitions

The survey spectra II and III in the regions of 1450–1750 cm^{-1}, where the $\nu_8+\nu_{10}$, $\nu_7+\nu_8$, $\nu_6+\nu_{10}$ and $\nu_6+\nu_7$ bands of the trans-$C_2H_2D_2$ ethylene molecule are located, are shown in Fig. 1. In the central part of Fig. 1 one can see the strong $\nu_7+\nu_8$ band with the clearly pronounced P-, R-branches and Q-branch near 1590 cm^{-1}. Three other bands, $\nu_8+\nu_{10}$, $\nu_6+\nu_{10}$ and $\nu_6+\nu_7$, are considerably weaker. However, the P-branch of the $\nu_8+\nu_{10}$ band and the P-branch and a part of the R-branch of the $\nu_6+\nu_7$ band can be clearly seen in spectrum III near 1500 and 1725 cm^{-1}, respectively. The $\nu_6+\nu_{10}$ band is overlapped by the $\nu_7+\nu_8$ and $\nu_6+\nu_7$ bands and is not pronounced in Fig. 1. Small parts of the high resolution spectra in the region of the Q-branch of the $\nu_8+\nu_{10}(A_u)$ and $\nu_6+\nu_7(A_u)$ bands are shown in Figs. 2 and 3, respectively. These types of transitions are forbidden by the symmetry of the trans-d_2-ethylene molecule and appear in spectra only because of intensity

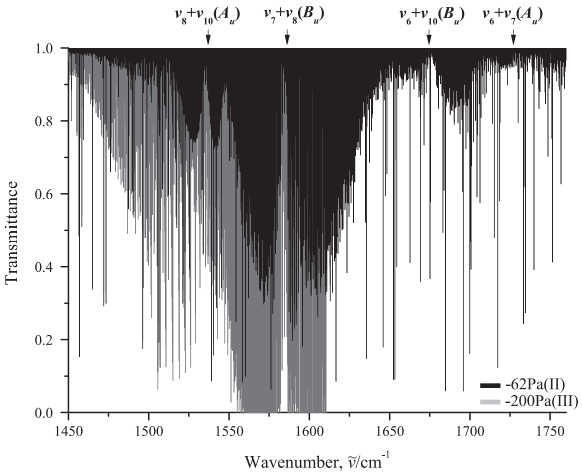

Fig. 1. Survey spectrum of trans-d_2-ethylene in the region of 1450–1750 cm^{-1}. Experimental conditions: absorption path length is 16 and 24 m; room temperature; number of scans and sample pressure is 430 and 62 Pa for the black spectrum and 700 and 200 Pa for the grey spectrum.

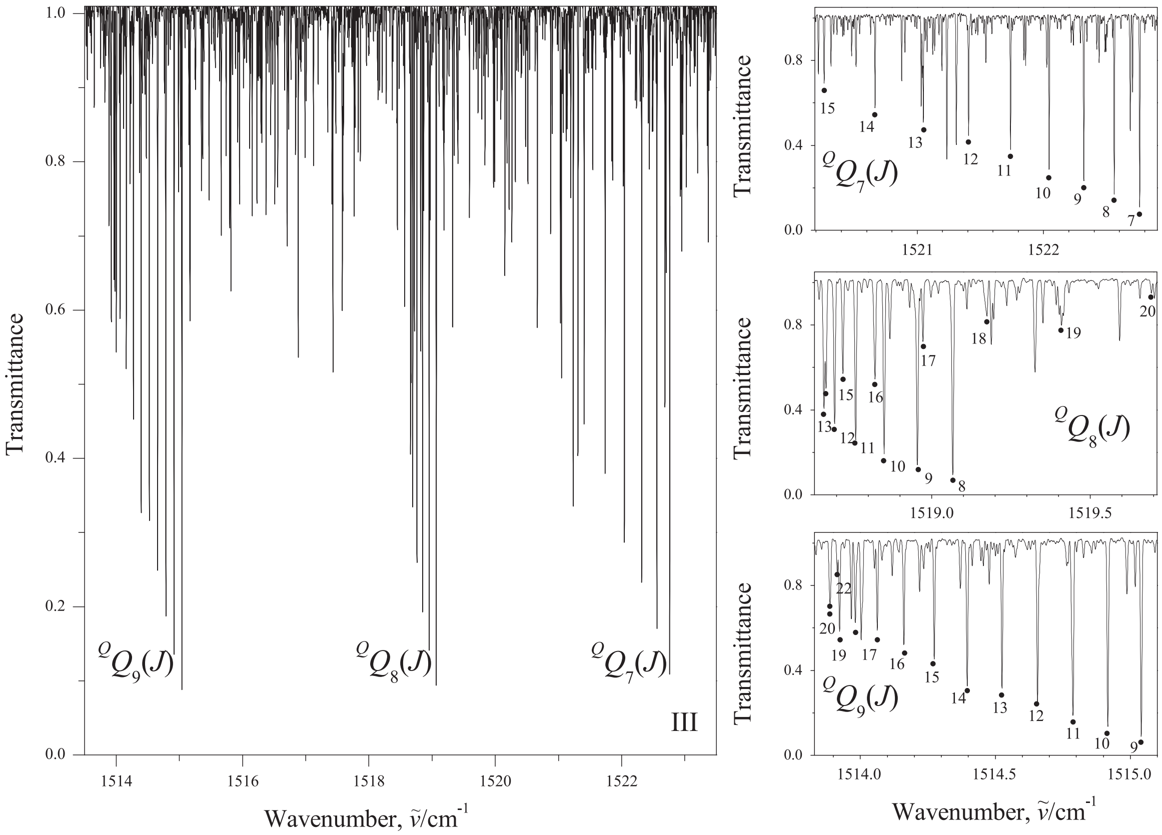

Fig. 2. Details of the high resolution experimental spectrum of trans-d$_2$-ethylene in the Q-branch region of the $\nu_8+\nu_{10}$ band. A few sets of transitions belonging to the Q-branch are marked in the spectrum. For experimental conditions, see captions of Fig. 1 and Table 1.

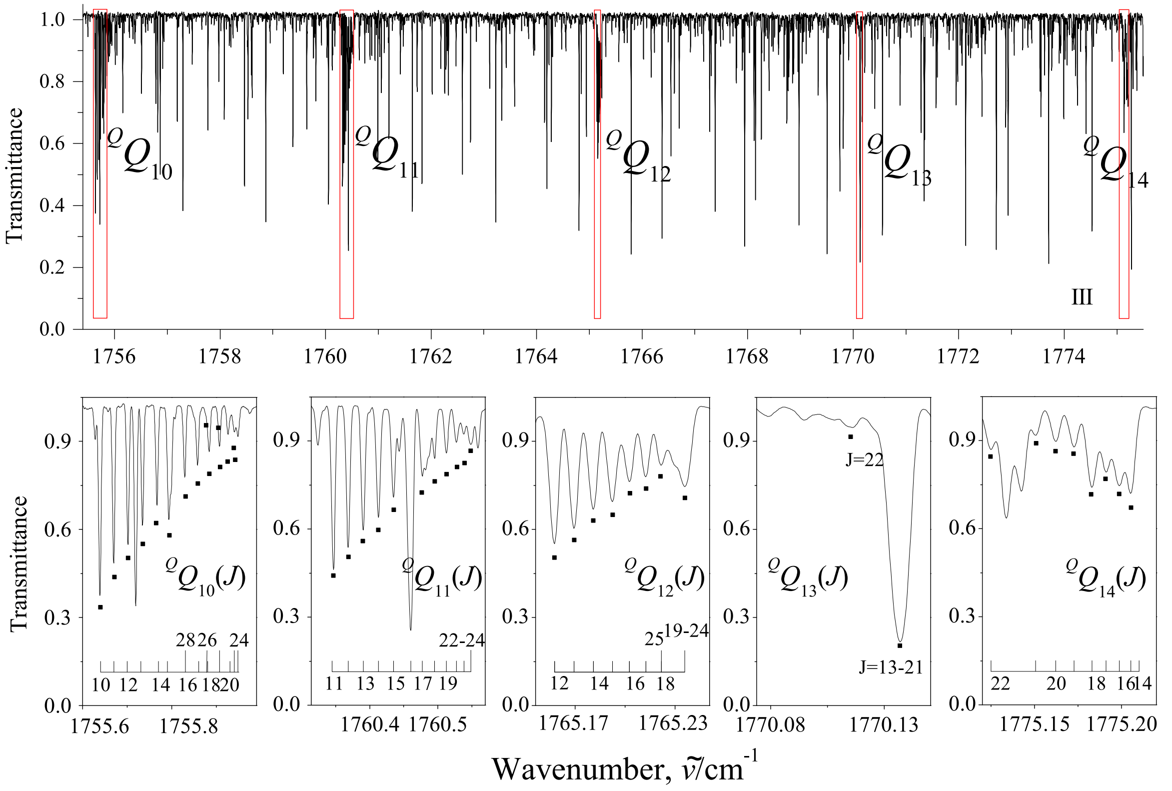

Fig. 3. Small fragments of the Q-branch of the $\nu_6+\nu_7$ band (spectrum III). Some sets of transitions belonging to the Q-branch are marked in the spectrum (see text for details). For experimental conditions, see captions of Fig. 1 and Table 1. The influence of the strong resonance interactions is seen for the sets of Q-transitions in the bottom part of Fig. 3.