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Ethylene-1-^{13}C ($^{13}C^{12}CH_4$): First analysis of the ν_2, ν_3 and $2\nu_{10}$ bands and re–analysis of the ν_{12} band and of the ground vibrational state

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ABSTRACT

High-resolution FTIR ro-vibrational spectra of the $^{13}C^{12}CH_4$ molecule in the region of 600–1700 cm^{-1}, where the bands ν_3, ν_{12} and ν_2 are located, were recorded and analyzed with the Hamiltonian model. This model takes resonance interactions between these three bands as well as strong interactions with six neighboring bands, ν_{10}, ν_8, ν_7, ν_4, ν_6, and $2\nu_{10}$ into account. More than 3800 ro-vibrational transitions belonging to the bands ν_3, ν_{12}, ν_2 and $2\nu_{10}$ were assigned (for the first time for the ν_2, ν_3 and $2\nu_{10}$ bands) with the maximum values of quantum numbers $J^{max.}/K_a^{max.}$ equal to 22/8, 52/18, 30/11 and 27/12, respectively. On this basis, a set of 62 vibrational, rotational, centrifugal distortion and resonance interaction parameters was obtained from the weighted fit. These parameters reproduce 1562 initial "experimental" ro-vibrational energy levels obtained from unblended lines with the *rms* error $d_{rms} = 2.6 \times 10^{-4}$ cm^{-1}. Furthermore, ground state parameters of the $^{13}C^{12}CH_4$ molecule were improved.

1. Introduction

Ethylene (C_2H_4) is an important chemical species in many research fields such as chemistry, interstellar space, planetary nebulae, study of the atmospheres of the Earth and other planets, etc. Ethylene has been observed in the terrestrial atmosphere as a tropospheric pollutant, Refs. [1,2]. Beyond the earth's atmosphere, ethylene exists as a product of methane photochemistry in other planetary atmospheres, Refs. [3,4], and it has been observed in the atmospheres of the outer planets such as Jupiter, Saturn, and Neptune, Refs. [5–8], as well as in the atmosphere of Saturn's biggest moon Titan, Refs. [9–11]. As a consequence, the most abundant isotopic species $^{12}C_2H_4$ has been the subject of a number of studies involving line positions as well as line intensities (see, e.g., Refs. [12–14], and Refs. therein). On the other hand, the ethylene-1-^{13}C isotopologue has seldom been discussed, Refs. [3,15–20], despite the fact that it is the most abundant isotopic impurity (2.2%) in normal samples (the $^{13}C_2H_4$ and C_2H_3D isotopic species are indeed about 100 times less abundant), and, as a consequence, one can expect to observe it in the spectra of the atmospheres of the outer planetary bodies (in particular, Titan) among the other ^{13}C isotopologues as $^{13}CH_4$, $^{13}C^{12}CH_2$, $H^{13}CN$, $^{13}CH_3D$, etc. (see, e.g., Refs. [21,22]). As mentioned in Ref. [16], knowledge of the high-resolution ro-vibrational spectra of $^{13}C^{12}CH_4$ is very important for understanding the optical pumping process in ethylene.

The present work on the $^{13}C^{12}CH_4$ is a continuation of our recent study of the high resolution spectra of ethylene and its different isotopologues in the infrared region, Refs. [23–33], with the $^{13}C^{12}CH_4$ molecule. As was mentioned above, $^{13}C^{12}CH_4$ was studied before only in a few articles, Refs. [15–20]. The first high resolution analysis of IR spectra of $^{13}C^{12}CH_4$ was made by De Vleeschouwer and co-authors in 1981, Ref. [15] where the $\nu_5 + \nu_{12}$ band (band center near 4503 cm^{-1}) has been analyzed. One year later, the same authors reported the analysis of the $^{13}C^{12}CH_4$ IR spectra in the 10 μm spectral region where the ν_7, ν_8, ν_4, ν_6, and ν_{10} strongly interacting fundamentals are located. The next investigation of the transitions of the $^{13}C^{12}CH_4$ isotopologue was made 20 years later in Ref. [3] where 88 transitions of $^{13}C^{12}CH_4$ were recorded by infrared heterodyne spectroscopy, but not assigned. In 2010, one of us (see Ref. [17]) presented an analysis of the FTIR spectra of $^{13}C^{12}CH_4$ in the region of the ν_{12} band (1360–1520 cm^{-1}), which was considered to be isolated. Later the ν_{12} band was re-analyzed in Ref. [18] again as an isolated band. Also in 2010, Flaud with coauthors, Ref. [19], made an analysis of the FTIR spectra of $^{13}C^{12}CH_4$ in the 700–1190 cm^{-1} region (transitions belonging to the ν_{10}, ν_8, ν_7 and ν_4 bands have been assigned, and the ν_6 band has been considered as "dark" band). In 2011, absolute line intensities and self-broadened half-width coefficients of transitions were analyzed in the same spectral region and discussed in Ref. [20].

In this paper we present the results of a high-resolution FTIR

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analysis of $^{13}C^{12}CH_4$ in the wave length spectral region, 1250–1700 cm^{-1}, where the bands ν_3, ν_{12} and ν_2 are located. In Section 2 we describe the conditions of our experiment. Description of the experimental spectra and results of the assignment of transitions are given in Section 3. Section 4 presents the theoretical background of the further analysis of experimental data: the use of Hamiltonian model and numerical estimation of the initial values of rotational and main resonance interaction parameters. It was found that the ground state parameters known in the literature do not allow us to correctly describe our experimental data. Therefore we re-analyzed the ground state parameters on the basis of the ground state combination differences (GSCD) derived from our experimental data. The obtained results of the ground vibrational state are presented in Section 5, whereas the outcome of the upper vibrational states analysis is discussed in Section 6.

2. Experimental details

The spectra of $^{13}C^{12}CH_4$ were recorded in the 600–1700 cm^{-1} region using the Bruker IFS 125 HR Michelson Fourier transform spectrometer located at the Nanyang Technological University in Singapore at an unapodized resolution of 0.0063 cm^{-1}. The $^{13}C^{12}CH_4$ gas samples used in the experiments were supplied by Cambridge Isotope Laboratories in Massachusetts, USA and had a chemical purity better than 98%. All spectral measurements were carried out at an ambient temperature of about 296 ± 0.5 K with a Globar infrared source, a high-sensitivity liquid–nitrogen–cooled Hg–Cd–Te detector, KBr beamsplitter, and aperture size of 1.5 mm. A capacitance pressure gauge measured the vapor pressure to be 35, 100 and about 1000 Pa in the gas cell for the three spectra depicted in Table 1. A multiple-pass absorption cell with a total absorption length of 0.80 m was used. A total of 300, 720 and 1050 scans were co-added to produce the final spectra. The absorption lines of H_2O were used to calibrate the $^{13}C^{12}CH_4$ spectra.

In the Braunschweig Infrared Laboratory four spectra in the 600–1150 cm^{-1} region and two spectra in the 1000–2000 cm^{-1} region have been recorded using an IFS 120HR 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 beamsplitters, a mercury–cadmium–telluride (MCT) semiconductor detector and the sample, $^{13}C^{12}CH_4$ (gas) with a specified chemical purity of better than 99% purchased from Sigma Aldrich have been used. For detailed optical and recording parameters see Table 1; the optical resolution was 0.0021 cm^{-1} for spectra I to IV and 0.0025 cm^{-1} for spectra V and VI, the number of scans was between 330 and 1210 resulting in measuring durations between 15.8 and 48.5 hours, the optical path-length was 4 m for all spectra apart from spectrum VI (24 m) and the sample gas pressure was varied between 0.3 and 300 Pa to get lines with stronger and weaker line intensities. The sample temperature was 296 ± 0.5 K. The final spectral resolution was mainly limited by Doppler broadening and resulted in 0.0023 cm^{-1} at 600 cm^{-1}, 0.0033 cm^{-1} at 1200 cm^{-1} and 0.0050 cm^{-1} at 2000 cm^{-1}. The pressure broadening was between 6×10^{-7} and 0.0006 cm^{-1} for the used sample pressures between 0.3 and 300 Pa. This means that it only has a minor contribution to the total line widths which were computed by the root mean square approximation of a convolution of Doppler, pressure and instrumental line widths and which is in accordance with the experimental results. The spectra were calibrated with N_2O lines recorded at a (partial) N_2O pressure of about 10 Pa with 200 and 230 scans at an optical resolution of 0.0021 cm^{-1}. The mean divergence of measured N_2O line positions (about 30 lines) from line positions published in the current HITRAN data base is around 2×10^{-4} cm^{-1} with a divergence of single lines below 4×10^{-4}. For optimization of data recording and line calibration we used data and procedures described in Refs. [34–36].

3. Description of the spectra and assignment of transitions

The survey spectra VI, VII and IX in the region of 600–1700 cm^{-1} are shown in Fig. 1. As the spectra in the spectral region between 600 and 1250 cm^{-1} have been discussed in Refs. [19,20], we focused on the region between 1250 and 1700 cm^{-1}. In this region one can see the ν_{12} band with clearly pronounced P-, Q-, and R-branches. The weak ν_3 and ν_2 bands can also be recognized at the left and right side of the ν_{12} band. Two bands, ν_6 and $2\nu_{10}$, which are located at the same region, are extremely weak and cannot be seen even in the strongest spectrum VI. The ν_1 band of N_2O is also visible in the central part of Fig. 1. Some small parts of the high–resolution spectra in the regions of the ν_{12}, ν_2, and ν_3 bands are shown in the top parts of Figs. 2, 3, and 4, respectively. One can clearly see the pronounced regular structure of separate sets of transitions of these bands.

The $^{13}C^{12}CH_4$ molecule is an asymmetric top of C_{2v} symmetry with the asymmetry parameter $\kappa = (2B - A - C)/(A - C) \approx -0.918$ and with the symmetry isomorphic to the C_{2v} point symmetry group. For convenience of the reader, the symmetry properties in $^{13}C^{12}CH_4$ are shown in Table 2 (reproduced from Ref. [19]): the list of irreducible representations and table of characters of the C_{2v} symmetry group are presented in columns 1–5; symmetries of vibrational coordinates q_λ, rotational operators, J_α, and of direction cosines, $k_{z\alpha}$, are shown in columns 6 and 7. In accordance with the selection rules for the asymmetric top molecules of the C_{2v} symmetry (see, e.g., Refs. [37–42]), there are three types of vibrational bands which are allowed in absorption from the ground vibrational state:

(1) the $A_1 \leftarrow A_1$ bands are the a– type ones, and the selection rules for them are $\Delta J = 0, \pm 1$ and ΔK_a= even, ΔK_c= odd;

Table 1
Experimental setup for the regions 600 - 2000 cm^{-1} of the infrared spectrum of $^{13}C^{12}CH_4$.

Spectr.	University	Region /cm^{-1}	Resolution /cm^{-1}	No. of scans	Source	Detector	Beam-splitter	Opt. path-length/m	Aperture /mm	Temp. /°C	Pressure /Pa	Calibr. gas
I	Braunschweig	600 - 1150	0.0021	330	Globar	MCT	KBr	4	1.5	23 ± 0.5	0.3	N_2O
II	Braunschweig	600 - 1150	0.0021	600	Globar	MCT	KBr	4	1.5	23 ± 0.5	3	N_2O
III	Braunschweig	600 - 1150	0.0021	350	Globar	MCT	KBr	4	1.5	23 ± 0.5	30	N_2O
IV	Braunschweig	600 - 1150	0.0021	370	Globar	MCT	KBr	4	1.5	23 ± 0.5	300	N_2O
V	Braunschweig	1000 - 2000	0.0025	1210	Globar	MCT	KBr	4	1.3	23 ± 0.5	30	N_2O
VI	Braunschweig	1000 - 2000	0.0025	480	Globar	MCT	KBr	24	1.3	23 ± 0.5	250	N_2O
VII	Singapore	600 - 1700	0.0063	300	Globar	MCT	KBr	0.8	1.3	23 ± 0.5	35	H_2O
VIII	Singapore	600 - 1700	0.0063	720	Globar	MCT	KBr	0.8	1.3	23 ± 0.5	100	H_2O
IX	Singapore	600 - 1700	0.0063	1050	Globar	MCT	KBr	0.8	1.3	23 ± 0.5	1000	H_2O

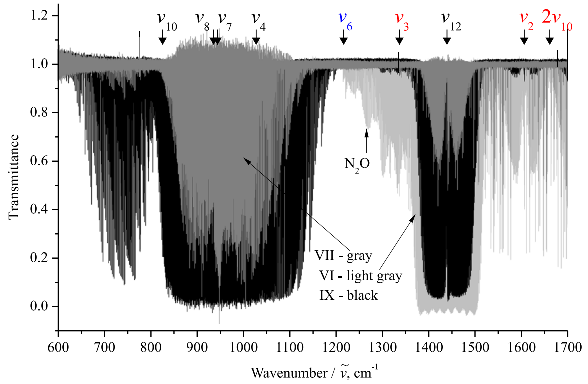

Fig. 1. Survey spectrum of $^{13}C^{12}CH_4$ in the region of 600–1700 cm^{-1}. Experimental conditions: room temperature for all spectra; absorption path length, number of scans and sample pressure are 24 m, 480 and 250 Pa for spectrum VI, 0.8 m, 300 and 35 Pa for spectrum VII, and 0.8 m, 1050 and about 1000 Pa for spectrum IX. Centers of the bands studied earlier are marked in black, centers of the ν_3, ν_2 and $2\nu_{10}$ bands studied in this paper for the first time, are marked in red in the electronic version.

(2) the $B_1 \leftarrow A_1$ bands are the b– type ones, and the selection rules for them are $\Delta J = 0, \pm 1$ and ΔK_a= odd, ΔK_c= odd;

(3) the $B_2 \leftarrow A_1$ bands are the c– type ones, and the selection rules for them are $\Delta J = 0, \pm 1$ and ΔK_a= odd, ΔK_c= even.

For this reason, as it follows from Table 2, all four studied bands, $\nu_2(A_1)$, $\nu_3(A_1)$, $\nu_{12}(A_1)$ and $2\nu_{10}(A_1)$, can be identified as a– type bands.

The assignment of the transitions was made with the ground state combination differences method. Here, the rotational energies of the ground vibrational state have been calculated with two sets of parameters from Refs. [18] and [19] (for convenience of the reader, they are reproduced in columns 2 and 3 of Table 3 from Refs. [18] and [19]). As the result of the assignment, more than 3800 transitions with the maximum values of upper quantum numbers $J^{max.} = 52$ and $K_a^{max.} = 18$ have been assigned to the ν_{12} band. Additionally, for the first time we were able to assign more than 910 and 480 transitions to the weak bands ν_2 and ν_3 and 14 transitions to the very weak $2\nu_{10}$ band (for more details, see statistical information in Table 4).

It is interesting to compare the strengths of the bands, which are shown in Fig. 1 and already have been studied earlier, with the

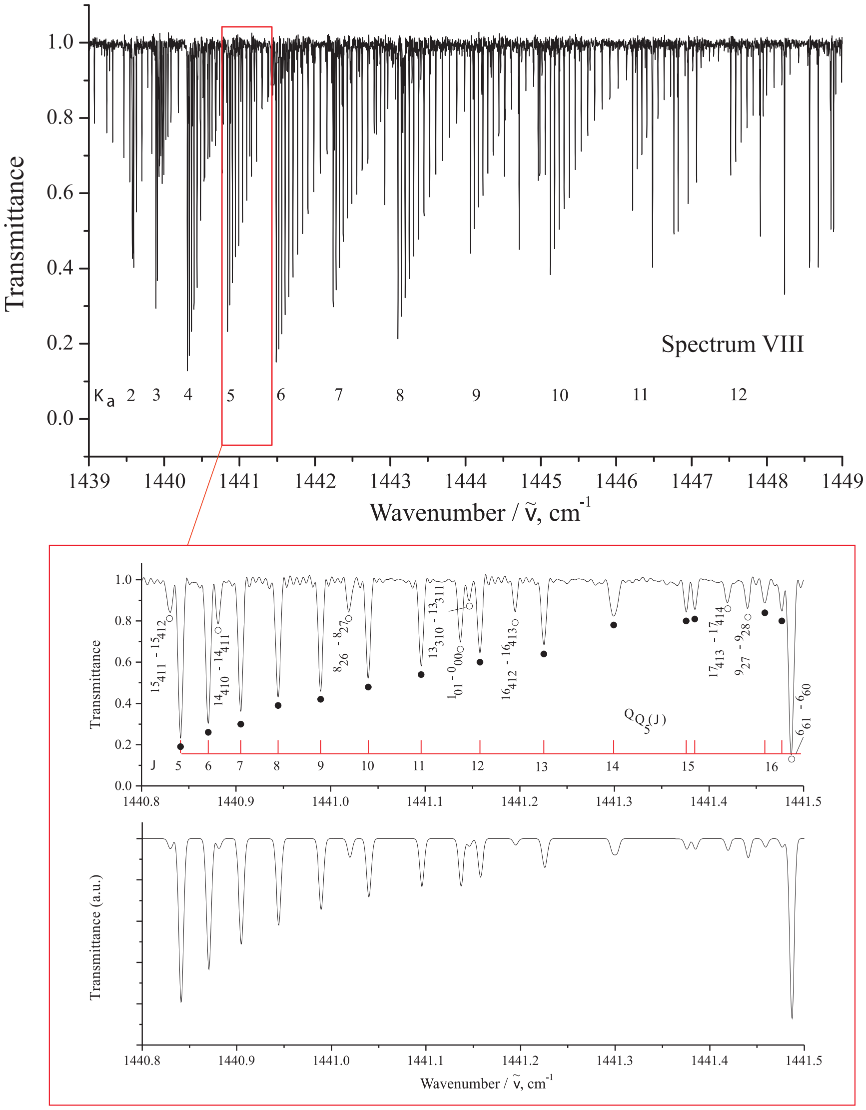

Fig. 2. A small part of the high-resolution spectrum of the $^{13}C^{12}CH_4$ molecule in the region of the Q–branch of the ν_{12} band (upper trace). Experimental conditions correspond to the spectrum VIII (see Table 1, for details). Lines belonging to the clusters of the $^QQ_{K_a}(J)$– type are marked on the top part of Fig. 2. The middle part of Fig. 2 shows a detailed structure of one separate cluster, $^QQ_5(J)$ (lines of this cluster are marked by black dots). One can see splittings for J=15 and 16. A few lines belonging to the ν_{12} band are marked by open circles. The bottom trace is the simulated spectrum (see text, for details).