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Study of resonance interactions in polyatomic molecules on the basis of highly accurate experimental data: Set of strongly interacting Bands $\nu_{10}(B_1)$, $\nu_7(B_2)$, $\nu_4(A_2)$, $\nu_8(B_2)$, $\nu_3(A_1)$ and $\nu_6(B_1)$ of $\text{CH}_2=\text{CD}_2$



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ABSTRACT

The highly accurate (experimental accuracy in line positions $\sim (1-3) \times 10^{-4} \text{ cm}^{-1}$) FTIR ro-vibrational spectra of $\text{CH}_2=\text{CD}_2$ in the region of 600–1300 cm^{-1} , where the fundamental bands ν_{10} , ν_7 , ν_4 , ν_8 , ν_3 , and ν_6 are located, were recorded and analyzed with the Hamiltonian model which takes into account resonance interactions between all six studied bands. About 12 200 ro-vibrational transitions belonging to these bands (that is considerably more than it was made in the preceding studies for the bands ν_{10} , ν_7 , ν_8 , ν_3 and ν_6 ; transitions belonging to the ν_4 band were assigned for the first time) were assigned in the experimental spectra with the maximum values of quantum numbers $J^{\text{max.}}/K_a^{\text{max.}}$ equal to 31/20, 46/18, 33/11, 50/26, 44/20 and 42/21 for the bands ν_{10} , ν_7 , ν_4 , ν_8 , ν_3 , and ν_6 , respectively. On that basis, a set of 133 vibrational, rotational, centrifugal distortion and resonance interaction parameters was obtained from the weighted fit. They reproduce values of 3920 initial “experimental” ro-vibrational energy levels (positions of about 12 200 experimentally recorded and assigned transitions) with the *rms* error $d_{\text{rms}} = 2.3 \times 10^{-4} \text{ cm}^{-1}$.

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1. Introduction

One of the important problems of physical chemistry and chemical physics is the precise determination of the intramolecular potential energy surface (PES) of a molecule. The knowledge of a correct PES is the key point for solving the Schrodinger equation of a molecule, which gives the possibility to determine a correct set of eigenfunctions of the

corresponding molecular Hamiltonian. In turn, knowledge of correct eigenfunctions allows one to solve numerous both pure scientific and applied problems in physical chemistry, astrophysics, planetology, atmospheric and environmental sciences, etc.

In our days, the most efficient way to determine precisely 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. [1–4]). In this case, the larger the number of experimentally recorded and analyzed ro-vibrational bands (especially, highly excited and/or strongly interacting bands,

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see, e.g., Refs. [5–13]), the more precise results one can expect to obtain (in the ideal case, one would like to have information about the ro-vibrational structure and parameters of all vibrational states below, for example, $10\,000\text{ cm}^{-1}$).

Ethylene acts as a hormone in plants and its role in plant biochemistry, physiology, mammals metabolism, and ecology is the subject of extensive research. Ethylene is a naturally occurring compound in ambient air that affects atmospheric chemistry and the global climate. As the result of reaction with the hydroxyl (OH) radical, ethylene plays a significant role in tropospheric chemistry [14] 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 and has been detected as a trace component of the atmospheres of the outer planets Jupiter, Saturn, Neptune, [15–19], and the satellite Titan, [20–24]. Ethylene has also been observed in the circumstellar clouds IRC10216 [25] and CRL618 [26]. Furthermore, ethylene is 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, the ethylene molecule has been a subject of both extensive experimental and theoretical studies (see, e.g. reviews in Refs. [27,28]).

The present paper is a continuation of our recent study of high resolution infrared spectra of ethylene, $^{12}\text{C}_2\text{H}_4$, and its different isotopologues, Refs. [28–36], with the goal to determine high-accuracy spectroscopic parameters of as many as possible ro-vibrational states. In this case, we focus on the spectra of the $\text{CH}_2=\text{CD}_2$ molecule in the region of $600\text{--}1300\text{ cm}^{-1}$. Earlier high resolution spectra of this molecule have been a subject of study in Refs. [37–44]. As to the spectral region discussed in this study, the first analysis of ro-vibrational spectra of $\text{CH}_2=\text{CD}_2$ was made in 1972 by Duncan and co-authors, Ref. [37]. The ν_6 , ν_7 , ν_8 , and ν_{10} fundamentals were recorded with an average resolution of 0.2 cm^{-1} . In 1981 and 1990, these bands were re-analyzed with a higher resolution of 0.05 cm^{-1} and 0.004 cm^{-1} in Refs. [39,40], respectively. In the latter case, the ν_3 band and the infrared inactive ν_4 band have been taken into consideration.

In the present study we make a new analysis of the high resolution spectrum of $\text{CH}_2=\text{CD}_2$ in the region of $600\text{--}1300\text{ cm}^{-1}$ on the basis of the more accurate experimental data and the physically more reasonable Hamiltonian model (see, e.g., Refs. [45–49]). The structure of the paper is as follows. Section 2 describes the experimental conditions of the recorded spectra. Section 3 gives briefly the theoretical background for the present study. Description of the experimental spectra and results of assignment of transitions are given in Section 4. Section 5 presents the results of the fit of the Hamiltonian parameters on the basis of recorded experimental data and discussion.

2. Experimental details

The spectrum of $\text{CH}_2=\text{CD}_2$ in the $950\text{--}1300\text{ cm}^{-1}$ region was recorded 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 $\text{CH}_2=\text{CD}_2$ 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 $296 \pm 0.5\text{ K}$ 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 about 800 Pa in the gas cell. A multiple-pass absorption cell with a total absorption length of 0.80 m was used. A total of 970 scans with scanning time of about 16 h were co-added to produce the final spectrum. The absorption lines of N_2O in the $1238\text{--}1322\text{ cm}^{-1}$ range, Ref. [50], were used to calibrate the $\text{CH}_2=\text{CD}_2$ spectrum. The spectrum of N_2O was collected just before that of $\text{CH}_2=\text{CD}_2$. With systematic errors arising from the limitation due to the resolution of 0.0063 cm^{-1} of the spectra recorded, calibration and the noise level in the spectrum, the absolute accuracy of the measured $\text{CH}_2=\text{CD}_2$ lines can be approximated to be 0.00065 cm^{-1} .

In the Braunschweig Infrared Laboratory two spectra in the $600\text{--}1200\text{ cm}^{-1}$ region have been recorded using an IFS 120HR Fourier Transform infrared spectrometer (FTIR) in 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 semiconductor detector and the sample, ethylene-1,1- d_2 (gas) with a chemical purity of better than 99% purchased from CDN Isotopes have been used. While the resolution of 0.0021 cm^{-1} was constant for all spectra, measuring time (14.8 and 19 h), number of scans (310 and 400), optical path-length (4 m) and sample gas pressure (7 and 150 Pa) have been varied to get lines with stronger and weaker line intensities. The sample temperature was $296 \pm 0.5\text{ K}$. For details compare Table 1. The final spectral resolution was mainly limited by Doppler broadening and resulted in 0.0022 cm^{-1} at 600 cm^{-1} and 0.0032 cm^{-1} at 1200 cm^{-1} . The contribution of the pressure broadening to the final spectral resolution is marginal for sample pressures up to a few hundred Pa.

3. Theoretical background

3.1. Effective hamiltonian

The $\text{CH}_2=\text{CD}_2$ molecule is an asymmetric top with the value of the asymmetry parameter $\kappa = (2B - A - C)/(A - C) \approx -0.860$ and with the symmetry isomorphic to the C_{2v} point symmetry group (the symmetry properties of the $\text{CH}_2=\text{CD}_2$ molecule are shown in Table 2 of Ref. [32], and we do not reproduce them here). From analysis of Table 2, Ref. [32], it is possible to see that transitions in absorption are forbidden between vibrational states (νI) and ($\nu I'$)

Table 1
Experimental setup for the regions 600–1300 cm⁻¹ of the infrared spectrum of CH₂ = CD₂.

Spectr. Region/cm ⁻¹	Institute	Resolution/cm ⁻¹	Measuring time/h	No. of scans	Source	Detector	Beam-splitter	Opt. path-length/m	Aperture/mm	Temp./°C	Pressure/Pa	Calibr.gas
I 600–1200	Braunsch.	0.0021	14.8	310	Globar	MCT	KBr	4	1.5	23 ± 0.5	7.0	N ₂ O, H ₂ O
II 600–1200	Braunsch.	0.0021	19.0	400	Globar	MCT	KBr	4	1.5	23 ± 0.5	150	N ₂ O, H ₂ O
III 950–1300	Nanyang	0.0063	16.0	970	Globar	Hg–Cd–Te	KBr	0.8	1.5	23 ± 0.5	800	N ₂ O

when $(\nu\Gamma) \otimes (\nu'\Gamma') = A_2$ (here \otimes denotes the direct product). For the allowed band, the following applies:

- (1) if $(\nu\Gamma) \otimes (\nu'\Gamma') = A_1$, then the corresponding band is of a-type, and the selection rules are: $\Delta J = 0, \pm 1$ and $\Delta K_a = \text{even}, \Delta K_c = \text{odd}$;
- (2) if $(\nu\Gamma) \otimes (\nu'\Gamma') = B_1$, then the corresponding band is of b-type, and the following selection rules are valid: $\Delta J = 0, \pm 1$ and $\Delta K_a = \text{odd}, \Delta K_c = \text{odd}$;
- (3) for $(\nu\Gamma) \otimes (\nu'\Gamma') = B_2$, the corresponding band is of c-type, and the selection rules are: $\Delta J = 0, \pm 1$ and $\Delta K_a = \text{odd}, \Delta K_c = \text{even}$.

This means that from the bands discussed in the present study, ν_3 is a-type, ν_6 and ν_{10} are of b-type, ν_7 and ν_8 belong to the c-type bands, and ν_4 is forbidden by the symmetry of the molecule and can appear in absorption only because of resonance interactions and borrowing of intensity from other vibrational bands.

Because six vibrational states, $(\nu_{10} = 1)$, $(\nu_7 = 1)$, $(\nu_4 = 1)$, $(\nu_8 = 1)$, $(\nu_3 = 1)$ and $(\nu_6 = 1)$, which correspond to the studied bands, are located inside the region of 700–1150 cm⁻¹ (see, for illustration, Fig. 1, which is reproduced from Ref. [40]), strong resonance interactions should be expected between all of them. As the consequence, in the theoretical analysis of our experimental data the Hamiltonian model, which takes into account resonance interactions between all six mentioned vibrational states, should be used. Such a model was discussed in the literature (see, e.g., Refs. [51–55]) and is an effective Hamiltonian in the form:

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

where (in our case) the summation is taken from 1 to 6 for both ν and $\tilde{\nu}$, which represent the four above discussed vibrational states: $|1\rangle = (\nu_3 = 1, A_1)$, $|2\rangle = (\nu_7 = 1, B_2)$, $|3\rangle = (\nu_8 = 1, B_2)$, $|4\rangle = (\nu_4 = 1, A_2)$, $|5\rangle = (\nu_{10} = 1, B_1)$, and $|6\rangle = (\nu_6 = 1, B_1)$. Any diagonal block $H^{\nu\nu}$, Eq. (2), describes unperturbed rotational structure of the vibrational state $|\nu\rangle$ and has a form of reduced effective Hamiltonian in the A-reduction and I' representation (see, e.g., Refs. [56–58]):

$$\begin{aligned}
 H_{\nu\nu} = E^\nu + \left[A^\nu - \frac{1}{2}(B^\nu + C^\nu) \right] J_z^2 + \frac{1}{2}(B^\nu + C^\nu) J^2 + \frac{1}{2}(B^\nu - C^\nu) J_{xy}^2 \\
 - \Delta_K^\nu J_z^4 - \Delta_{JK}^\nu J_z^2 J^2 - \Delta_J^\nu J^4 - \delta_K^\nu J_z^2 J_{xy}^2 + 2\delta_J^\nu J^2 J_{xy}^2 + H_K^\nu J_z^6 \\
 + H_{KJ}^\nu J_z^4 J^2 + H_{JK}^\nu J_z^2 J^4 + H_J^\nu J^6 + [J_{xy}^2, h_K^\nu J_z^4 + h_{JK}^\nu J_z^2 J^2 + h_J^\nu J^4]_+ \\
 + L_K^\nu J_z^8 + L_{KJ}^\nu J_z^6 J^2 + L_{JK}^\nu J_z^4 J^4 + L_{KJ}^\nu J_z^2 J^6 + L_J^\nu J^8 + [J_{xy}^2, l_K^\nu J_z^6 \\
 + l_{KJ}^\nu J_z^4 J^2 + l_J^\nu J^6]_+ + \dots, \quad (2)
 \end{aligned}$$

where $J_{xy}^2 = J_x^2 - J_y^2$; $[\dots]_+$ denotes anticommutators; A^ν , B^ν , and C^ν are the effective rotational constants connected with the vibrational state (ν) , and the other parameters are the different order centrifugal distortion coefficients.

We may distinguish between four types of coupling operators $H^{\nu\nu}$, $(\nu \neq \tilde{\nu})$, corresponding to the four different types of resonance interactions which can occur in a set of vibrational states, A_1 , A_2 , B_1 , and B_2 , of the C_{2v} asymmetric top molecules. If the product $\Gamma = \Gamma^\nu \otimes \Gamma^{\tilde{\nu}}$ of the symmetry