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Quantitative characteristics of high-resolution spectra to the benefit of astrophysics: The case of an ethylene molecule and its isotopologues

Yu V Konova, N V Kashirina, A G Ziatkova

National Research Tomsk Polytechnic, Tomsk, Russia

E-mail: ch-yuliya28@mail.ru

Abstract. Study of deuterated isotopologues is significant for the expansion of information quantity about "mother" modification of molecule. The spectra of cis-ethylene-d_2 ($C_2H_2D_2$-cis) and ethylene-d_3 (C_2HD_3) molecules have been recorded with a Bruker IFS 120 HR Fourier spectrometer in the region of the ν_3 bands location with spectral resolution of 0.0021 cm^{-1}. As a result of the experimental spectrum analysis, more than 1200 and 1000 transitions have been assigned for the ν_3 bands of $C_2H_2D_2$-cis and C_2HD_3, respectively. Study of these bands for both investigated molecules was made at first time.

1. Introduction

For the first time, the composition of the atmosphere of Titan was remotely studied by the Voyager missions in the 1980s [1], then studies were carried out by the Infrared Space Observatory in 1998 and 2004 [2, 3]. Currently, there is actual information obtained from ground-based observatories and from the Cassini-Huygens mission [4]. The mentioned above and many other studies have shown that the atmosphere of Titan not only demonstrates the rich content of organic molecules and a peculiar thermal structure, but also shows impressive new meteorological phenomena.

The first studies in the field of infrared spectroscopy made it possible to obtain information only about the temperatures and chemical structures of the studied planets (for example, for the planet Titan [1]; the spectral resolution was 4.3 cm^{-1}). Further studies, which were carried out already from the surface of the Earth, made it possible to register and determine the lines of methane in the spectrum, first to detect the mesosphere on Titan in the infrared range [5], and also to register the high-resolution spectra of ethylene on Titan (with spectral resolution is equal to 0.53 cm^{-1}) [6].

As a result of the previous remote missions and research of the obtained data, the study of the spectral characteristics of the C_2H_4 molecule is in demand, due to the fact that it is included in the list of molecules found in the atmosphere of the giant - planets. In addition, the presence of deuterated modifications of the detected molecules was shown in [7], which leads to the need for researching the spectra of isotopologues for the completion of databases (such as HITRAN and GEISA).

The study of different ethylene isotopologues is of great interest as in the spectra of such kinds of molecules there are additional transitions, which are forbidden in the basic modification. This is because it has a lower symmetry as compared with molecule of ethylene, which symmetry group is isomorphic to D_{2h} point symmetry group and has 8 irreducible representations. For comparing, C_{2v} point symmetry group has 2 times less irreducible representations (namely, 4).

This paper is devoted to the study of the ν_3 fundamental bands for the two different isotopologues of ethylene: $C_2H_2D_2$-cis and C_2HD_3.

2. Experimental details

The experimental spectra have been recorded in the Braunschweig Infrared Laboratory (Germany) using IFS120HR Fourier transform infrared (FTIR) spectrometer based on the principle of the Michelson interferometer in combination with stainless steel White cell with a base length of 1 m.

The gas $C_2H_2D_2$-cis sample was purchased from the Cambridge Isotope Laboratories. The chemical and isotopic purity of the sample was estimated to be 99.9%.

The gas sample of the C_2HD_3 molecule was obtained via the exchange reaction between C_2D_4 and H_2 on a nickel-wire catalyst which was electrically heated to the temperature range of 120–180°C. As the result of this procedure, seven different isotopologues have been registered: C_2H_4, C_2H_3D, $C_2H_2D_2$ (include the –trans, -as and -cis variants), C_2HD_3 and C_2D_4. The ratio of these components is presented in Table 1.

Table 1. Maximum concentration of different isotopologues listed on the gas sample.

Name of isotopolog	Max. concentration, %
C_2HD_3	42.2
C_2H_4	0.4
C_2H_3D	4.7
$C_2H_2D_2$	21.1
C_2D_4	31.6

For FTIR spectrometer a Globar IR source, a KBr beamsplitter, a mercury – cadmium – telluride semiconductor detectors have been used. In total four spectra have been analyzed for the $C_2H_2D_2$-cis and C_2HD_3 molecules. More experimental details are presented in Table 2. Survey spectra of both investigated molecules in the region of the ν_3 bands centers location are demonstrated in the left parts of Figures 1 and 2.

The nominal instrumental resolution defined as $1/d_{MOPD}$ (maximum optical path difference) was 0.0021 cm^{-1} for all spectra. The spectra were calibrated by using spectral lines of the N_2O and H_2O molecules.

Table 2. Experimental setup.

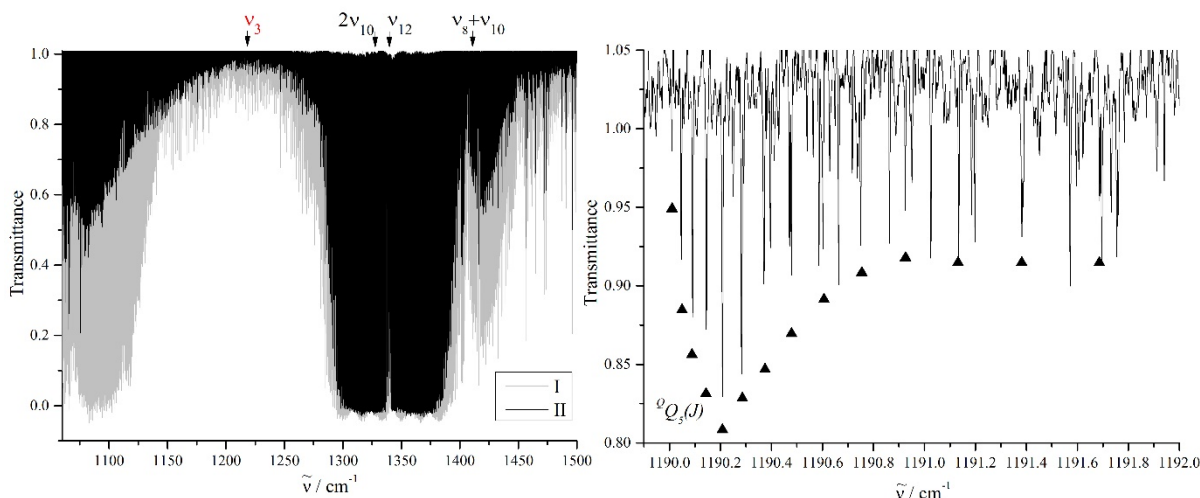| Molecule name	No. of spectr.	Region, cm^{-1}	Resolution, cm^{-1}	No. of scans	Optical path length, cm^{-1}	T, K	P, mbar
$C_2H_2D_2$-cis	I	1060-	0.0021	400	4	300	2
	II	2000		470	16		
C_2HD_3	III	640-	0.0021	320	4	300	2
	IV	1150		500			0.2

Figure 1. The survey spectra of $C_2H_2D_2$-cis in region 1060–1500 cm^{-1} (left);
a part of of its Q – branch (right).
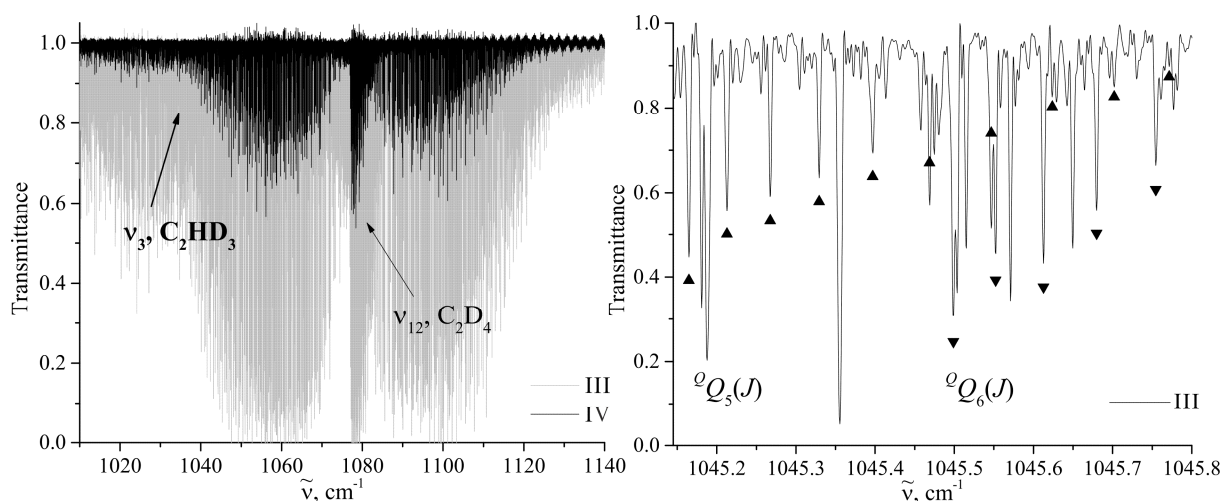

Figure 2. Experimental spectra of the C_2HD_3 molecule in the region of the ν_3 band (left) and part
of its Q - branch (right).

3. Theoretical background

3.1. General information about $C_2H_2D_2$-cis molecule

Cis-ethylene-d_2 is an asymmetric top molecule and the symmetry of this molecule is isomorphic to the C_{2v} point symmetry group (see Figure 3). It has 12 vibrational modes and 8 irreducible representations. One can mention from Table 3 investigated band ν_3 is A_1 symmetry. It means that ν_3 is b-type band and selection rules $\Delta J = 0; \pm 1$ and $\Delta K_a =$ odd, $\Delta K_c =$ odd.
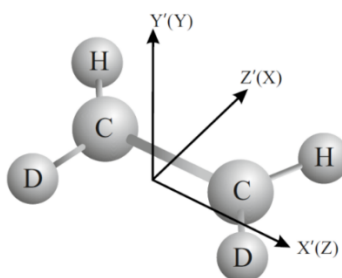
Figure 3. Axes definitions used in the present work for the $C_2H_2D_2$-cis molecule. The primed symbols refer to the axis definitions for the C_{2v} symmetry group used in the classification of the vibrational modes. The unprimed symbols refer to the Cartesian axis definitions of the I^r representation of Watson's A –reduced effective Hamiltonian.

For convenience of the reader, the symmetry properties of $C_2H_2D_2$-cis are presented in Table 3. Table 3 includes the q_λ vibrational coordinates in accordance with the list of irreducible representations and table of characters of the C_{2v} symmetry group.

Table 3. Symmetry types and characters of irreducible representations of the C_{2v} group (application to the $C_2H_2D_2$-cis molecule)

Representation	E	C_2	$\sigma_y(xz)$	$\sigma_y(yz)$	Vibrational coordinates
A_1	1	1	1	1	$q_1, q_2, q_3, q_9, q_{10}$
A_2	1	1	-1	-1	q_4, q_8
B_1	1	-1	1	-1	q_5, q_6, q_{11}, q_{12}
B_2	1	-1	-1	1	q_7

3.2 General information about C_2HD_3 molecule

C_2HD_3 molecules are asymmetric top and have 12 vibrational modes too (see Figure 4). Symmetry group of the molecule is isomorphic to C_s point symmetry group, which has only two irreducible representations (A' and A'', the symmetry properties of the molecule C_2HD_3 are presented in Table 4). As the consequence, the $A' \leftarrow A'$ bands are the hybrid bands, and transitions of both a and b – types are allowed in such bands. In the $A'' \leftarrow A'$ bands only c-type transitions are allowed. Using Table 4 one can determine, that the ν_3 investigated band can be identified as hybrid band with allowed both type of transitions – a and b - types. For such bands following selection rules corresponds: $\Delta J = 0, \pm 1$; $\Delta K_a =$ any; $\Delta K_c =$ odd.

Table 4. Symmetry types and characters of irreducible representations of the C_s group (application to C_2HD_3).

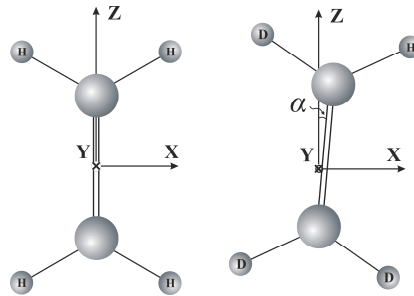| Representation	E	$\sigma_{x'z'}$	Vibrational coordinates
A'	1	1	$q_1, q_2, q_3, q_5, q_6, q_9, q_{10}, q_{11}, q_{12}$
A''	1	-1	q_4, q_7, q_8

Figure 4. Axes definitions for the C_2HD_3 molecule (right part).
For comparison, the "mother" C_2H_4 molecule is presented at the left part of the figure.

3.3 Effective Hamiltonian model
Model of effective Hamiltonian is used for theoretical analysis of experimental data in following form:

$$H^{vib-rot} = \sum_{v,\tilde{v}}^{n} | v >< \tilde{v} | H^{v\tilde{v}}, \tag{1}$$

where the sum is taken over all the vibrational states. The diagonal blocks in the Hamiltonian expression $H^{v,\tilde{v}}$, describing the unperturbed rotational structure of vibrational states, have a form of reduced effective Hamiltonian (Watson's operator) [8]:

$$H^{v,\tilde{v}} = E^v + \left[A^v - \frac{1}{2}\left(B^v + C^v\right)\right]J_z^2 + \frac{1}{2}\left(B^v + C^v\right)J^2 + \frac{1}{2}\left(B^v - C^v\right)J_{xy}^2 -$$
$$- \Delta_K^v J_z^4 - \Delta_{Jk}^v J_z^4 J^2 - \Delta_J^v J^4 - \delta_K^v\left[J_z^2, J_{xy}^2\right] - 2\delta_J^v J^2 J_{xy}^2 + H_K^v J_z^6 + \tag{2}$$
$$+ H_{KJ}^v J_z^4 J^2 + H_{JK}^v J_z^2 J^4 + H_J^v J^6 + \left[J_{xy}^2, h_K^v J_z^4 + h_{JK}^v J^2 J_z^2 + h_J^v J^4\right] + ...$$

where E is the center of the band; A, B, C are rotational constants; Δ_K, Δ_{JK}, Δ_J, etc., are the different order centrifugal distortion coefficients; $J_{xy}^2 = J_x^2 - J_y^2$.

4. Results of assignment of transitions
Assignment of transitions was made on the basis of the Ground State Combination Differences (GSCD) method. To implement this method, it is required to know the exact values of the parameters of the ground state for the investigated molecules. The ground state rotational energies have been calculated with the parameters from [9] and [10] papers for $C_2H_2D_2$-cis and C_2HD_3 molecules, respectively. For convenience of the reader, these parameters are represented in the Table 5.

Table 5. Spectroscopic parameters of ground vibrational states for the $C_2H_2D_2$-cis and C_2HD_3 molecules.

Parameter	$C_2H_2D_2$-cis	C_2HD_3
A	3.32454129	2.8446778
B	0.847825953	0.78580090
C	0.673768816	0.61415904
$\Delta_K \times 10^4$	0.49105	0.31568
$\Delta_{KJ} \times 10^5$	0.36722	0.34767
$\Delta_J \times 10^5$	0.117725	0.09472
$\delta_K \times 10^5$	0.64619	0.5023
$\delta_J \times 10^6$	0.28756	0.24149
$H_K \times 10^7$	0.172	-
$H_{KJ} \times 10^9$	-0.377	-
$H_{JK} \times 10^{10}$	0.373	-
$H_J \times 10^{12}$	0.95	-

C$_2$H$_2$D$_2$-cis. As mentioned above, we have determined the energy transitions from the ground vibrational state to the upper vibrational states ($v_3 = 1$) of C$_2$H$_2$D$_2$-cis. The number of energy transitions belonging to the b - type v_3 band is about 1200. For demonstartion of spectrum analysis on the right part of Figure 1 one series of Q – branch corresponding to $K_a = 5$ is shown. The maximum values of quantum numbers J^{max}/K_a^{max} are 25/10, respectively.

C$_2$HD$_3$. As a result of the study of the experimental spectra of C$_2$HD$_3$ more than 1000 ro-vibrational transitions have been assigned for the v_3 fundamental band. In the ground of this amount of transitions, about 400 energies of upper excited state have been calculated. Obtained information corresponds to the maximum values of quantum number $J^{max}/K_a^{max} = 26/9$. By way of illustration, in Figure 2 (right part) two series for $^QQ_5(J)$ and $^QQ_6(J)$ are represented

5. Summary

In this study, we made the analysis of the high-resolution IR spectrum of the v_3 bands of the C$_2$H$_2$D$_2$-cis and C$_2$HD$_3$ molecules. Experimental spectra for investigated molecules have been recorded using FTIR spectrometer Bruker IFS 120 HR. The experimental resolution is 0.0021 cm^{-1}. More than 1200 transitions belonging to the v_3 of the C$_2$H$_2$D$_2$-cis molecule were assigned with the maximum values of the upper quantum numbers $J^{max} = 25$ and $K_a^{max} = 10$ for the first time. Also for C$_2$HD$_3$ more than 1000 transitions with $J^{max} = 26$ and $K_a^{max} = 9$ were assigned for the first time too.

Acknowledgments

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