

Laser detection of nuclear spin isomers of ethylene molecules

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Abstract. We report the making of a double-beam laser spectrometer to measure absorption spectra in the $\nu_5 + \nu_9$ combination vibrational band of ethylene in the region of $\lambda = 1.6 \mu\text{m}$. The spectrometer is used to find a portion of the spectrum that has well-resolved absorption lines of all four nuclear spin isomers of ethylene molecules. The rotational quantum numbers of these absorption lines and the nuclear spin isomers of ethylene molecules responsible for them are identified.

Keywords: spectroscopy of ethylene molecules, nuclear spin isomers of molecules, laser spectroscopy.

1. Introduction

Symmetric molecules with identical nuclei exist in nature in the form of nuclear spin isomers, differing in spin wave functions of identical nuclei [1]. This is a consequence of the laws of quantum statistics of systems with identical particles, bosons, or fermions. Nuclear spin isomers of molecules are unique and scarcely studied objects of molecular physics. The most known are the spin isomers of hydrogen molecules: ortho- and parahydrogen with a total spin of two protons equal to 1 and 0, respectively. Hydrogen isomers, in fact the quantum states of the same molecule, are characterised by an enormous lifetime, equal to months at atmospheric pressure. Polyatomic symmetric molecules also exist in the form of spin isomers. For example, water molecules and CH_3F molecules, like hydrogen, have two spin modifications (ortho and para-modifications), and methane (CH_4) has three modifications.

The properties of spin isomers of polyatomic molecules, primarily the processes of their conversion, are in fact only now beginning to be studied (see review [2]). This is explained by the complexity of enrichment of spin isomers in the gas phase due to the almost identical physical and chemical properties of spin isomers belonging to the same molecule. The study of spin isomers is of fundamental importance for molecular physics. Isomers are used in astrophysics to investigate the state of the space environment with the help of molecular spectra and to enhance nuclear magnetic resonance signals.

This paper is devoted to laser detection of ethylene molecules (C_2H_4) and its nuclear spin isomers. Ethylene is an

organic chemical compound that plays an important role in biology, being a gaseous phytohormone. The global industrial production of ethylene exceeds 100 million tons per year. Ethylene molecules are used in many areas of industry and science, particularly in astrophysics to study the state of the interstellar medium and exoplanets.

Ethylene molecules have spin isomers of four types: two with positive spatial parity and two with negative parity. For ethylene, the possibility of producing spin-isomer-enriched samples using the light-induced drift effect [3, 4] and the catalytic reaction of acetylene molecules with parahydrogen [5] has recently been experimentally demonstrated. Sun et al. [3] measured the time of conversion of isomers of one parity (2×10^3 s at a pressure of 1 Torr) and showed that isomers of different parity did not convert between themselves [3, 6].

Further progress in the study of ethylene spin isomers requires the development of an efficient technique for optical detection of isomer concentrations. This detection could be performed using the absorption spectra in the fundamental ν_7 band, which has well-resolved absorption lines of all four ethylene spin isomers. However, the vibrational ν_7 band is located in the wavelength range $\lambda = 10 \mu\text{m}$, for which continuously frequency-tuned lasers are not yet well developed. An attractive alternative for detecting the spin isomers of ethylene is the use of the absorption spectra in the $\nu_5 + \nu_9$ combination vibrational band in the region of $\lambda = 1.6 \mu\text{m}$. Recently performed studies of the absorption spectra in the $\nu_5 + \nu_9$ band [7, 8] show the presence of spectral regions with well-resolved rotation lines. However, in the specified spectral region there are many vibrational bands of the ethylene molecule, which complicates the identification of spectral lines. The authors of Refs [7, 8] present the spectra without identifying the belonging of the absorption lines to specific spin isomers of ethylene molecules. For ethylene cooled in a molecular beam to 35 K, Vaernewijck et al. [9] identified the absorption lines in the region of $\lambda = 1.6 \mu\text{m}$. However, a complex technique for detecting spectra did not allow Vaernewijck et al. [9] to reach an agreement of amplitudes of experimentally measured absorption lines with amplitudes of lines of theoretical spectra.

The purpose of this work is to develop a technique for optical detection of ethylene molecules and its nuclear spin isomers from the absorption spectra in the $\nu_5 + \nu_9$ combination vibrational band of ethylene in the region of $\lambda = 1.6 \mu\text{m}$.

2. Laser spectrometer

The ethylene molecule C_2H_4 (Fig. 1) is an elongated asymmetric top with rotational constants $A \gg B \approx C$. The symmetry properties of the molecule are such that all four nuclear

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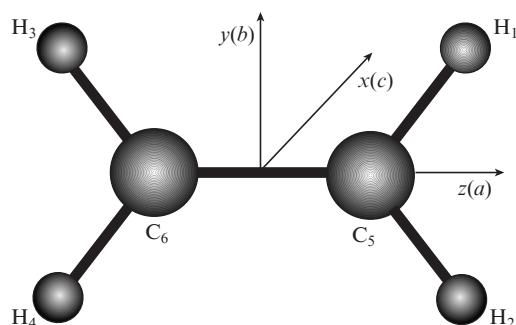


Figure 1. Ethylene molecule C_2H_4 and the orientation of the molecular coordinate system relative to the principal axes a , b and c of inertia of the molecules.

spin isomers of ethylene have different rotational quantum numbers and different absorption lines in the vibrational–rotational spectrum, which is the basis of the method for optical detection of the spin isomers of the ethylene molecule.

Ethylene has quite intense absorption lines in the $\nu_5 + \nu_9$ combination vibrational band in the region of $\lambda = 1.6 \mu\text{m}$. For such lines, the absorption cross section reaches $10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ [7, 8]. The rotational absorption lines in the $\nu_5 + \nu_9$ band are sufficiently well-resolved and, if they are successfully identified, the spectra of this band can serve as a basis for developing convenient laser diagnostics of ethylene and its nuclear spin isomers.

The scheme of the developed laser spectrometer is shown in Fig. 2. The radiation source is a TEC 500 tunable diode laser (Sacher Laserertechnik Group, Germany) with a small radiation power (10 mW), but unique spectral parameters. The modified Littrow external resonator has a diffraction grating, in which the grating rotates around a specially selected rotation axis and performs a consistent change in the length of the laser resonator. In this way, the TEC 500 laser radiation frequency is tuned in the range of $5722\text{--}6252 \text{ cm}^{-1}$ without jumps over the longitudinal modes of the resonator. In a small (up to 3 cm^{-1} wide) range, the radiation frequency can be smoothly tuned using piezoelectric ceramics, which rotates the diffraction grating and consistently changes the length of the laser resonator. The laser radiation line width is about 1 MHz.

The laser frequency is measured in a spectrometer using a lambda-meter (WS-6 model, Angstrom Co. Ltd., Russia),

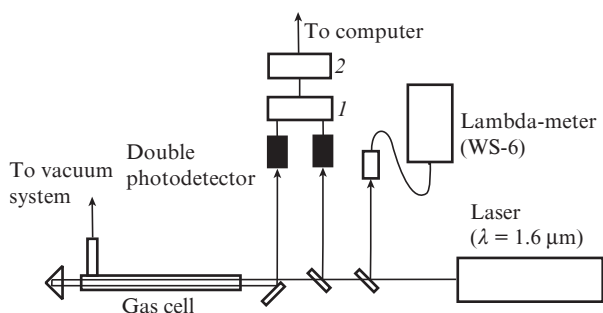


Figure 2. Schematic of a laser spectrometer for detecting ethylene molecules and its nuclear spin isomers in the region of $\lambda = 1.6 \mu\text{m}$: (1) system for subtracting and amplifying signals from photodetectors; (2) analogue-to-digital converter (NI USB 6351).

which contains a built-in calibration system for the instrument's frequency scale, providing an absolute error in measuring the emission frequency less than 200 MHz. The measurement frequency-interval error important for registering small spectral regions is less than 140 MHz. Such a conclusion can be made on the basis of the ethylene absorption lines experimentally recorded by the spectrometer, which had a half-width of 300 MHz at the $1/e$ level, with a Doppler width of the absorption line of 260 MHz. Note that using diode lasers, it is possible to implement, if necessary, a significantly higher spectral resolution in the detection of molecular gases (see, for example, [10]).

The spectrometer and the acquisition of experimental data are controlled using the LabVIEW programme. Mathematical processing of measurement results, for example, approximation of the absorption line contours, is performed using the Mathcad programme. The LabVIEW and Mathcad programmes work together, sharing data files in text format.

The spectrometer has a double-beam measurement configuration. The intensities of the reference radiation and the probe radiation transmitted through the gas cell are detected by two germanium photodiodes and are subtracted from each other by the analogue method using an operational amplifier. Normalisation of the signal to the intensity of the reference radiation and the calculation of the optical density of the medium are carried out programmatically. To increase the detected optical density, the probe beam passes through a gas cell (cell length of 32 cm) twice, as shown in Fig. 2.

Of the many parts of the spectrum of the $\nu_5 + \nu_9$ band, the portion shown in Fig. 3 was the most convenient. The spectrum was obtained in one scan of the laser radiation frequency using piezoelectric ceramics. The scanning time is 15 s. The pressure of pure ethylene in the cell is 10 Torr.

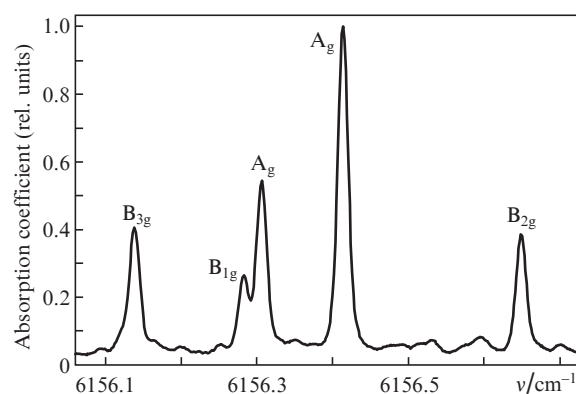


Figure 3. Fragment of the experimentally measured absorption spectrum in the $\nu_5 + \nu_9$ combination vibrational band of ethylene molecules at a pressure of 10 Torr. Shown are the symmetry types of the rotational states of ethylene molecules in the ground vibrational state.

3. Theoretical absorption spectrum model

The absorption spectra of ethylene, similar to those shown in Fig. 3, will help solve the problem posed in the work only if we can identify the spectral lines and establish their belonging to the four nuclear spin isomers of ethylene. The systematics

of rotational and nuclear spin states of ethylene molecules is quite complex and differs in the works of different authors. The systematics is based on the choice of orientation of the molecular coordinate system relative to the principal axes of inertia of the molecule and the numbered hydrogen nuclei (see Fig. 1). The numbering of nuclei allows one to relate the permutations of identical nuclei with the corresponding transformations of the Eulerian angles of the molecular coordinate system relative to the laboratory one. In the present work, we have chosen the molecular coordinate system and the systematics of states described in [11]. The choice of the quantisation axis z along the C–C bond can be easily substantiated. The ethylene molecule is an almost symmetrical top with rotational constants $B \approx C$; therefore, the decomposition of the rotational states of the asymmetric top C_2H_4 in the states of the symmetric top with a certain angular momentum projection on the C–C bond direction is the most accurate. The choice of orientation of the x and y axes is less critical and will be explained below. An ethylene molecule with numbered hydrogen atoms and a molecular coordinate system is shown in Fig. 1.

The rotational Hamiltonian of the asymmetric top C_2H_4 is diagonalised in [11] in the basis states

$$|\alpha, p\rangle = f_k [|\alpha\rangle + (-1)^{p+J} |\bar{\alpha}\rangle], \quad 0 \leq K \leq J, \quad (1)$$

$$f_k = \begin{cases} 1/\sqrt{2}, & K \neq 0, \\ 1/2, & K = 0. \end{cases}$$

Here $|\alpha\rangle$ and $|\bar{\alpha}\rangle$ are the states of a symmetric top with $\alpha \equiv \{J, K, M\}$ and $|\bar{\alpha}\rangle \equiv \{J, -K, M\}$; $K = |k|$; $p = 0, 1$ is the quantum number; J is the angular momentum of the molecule; and k and M are the projections of the angular momentum onto the quantisation axis of the molecular and laboratory coordinate systems, respectively. States (1) realise one-dimensional representations of the $D_{2h}(M)$ group with characters determined by the relations

$$R_z^\pi |\alpha, p\rangle = (-1)^K |\alpha, p\rangle, \quad R_y^\pi |\alpha, p\rangle = (-1)^{K+p} |\alpha, p\rangle, \quad (2)$$

$$R_x^\pi |\alpha, p\rangle = (-1)^p |\alpha, p\rangle.$$

The ethylene molecule rotation operations R_z^π , R_y^π and R_x^π , as well as the characters of the irreducible representations of the $D_{2h}(M)$ group are given in Table 1. For the operations of permutations of numbered nuclei (see Fig. 1) and permutations with inversion, Table 1 lists the abbreviated notations:

Table 1. Symmetry operations of the $D_{2h}(M)$ group and their characters [12].

Representation	E R^0	a R_z^π	b R_y^π	c R_x^π	E^* R_x^π	a^* R_y^π	b^* R_z^π	c^* R^0
A_g	1	1	1	1	1	1	1	1
A_u	1	1	1	1	-1	-1	-1	-1
B_{1g}	1	1	-1	-1	-1	-1	1	1
B_{1u}	1	1	-1	-1	1	1	-1	-1
B_{2g}	1	-1	1	-1	-1	1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1
B_{3g}	1	-1	-1	1	1	-1	-1	1
B_{3u}	1	-1	-1	1	-1	1	1	-1

Note. In the right-hand part of the table, symbols in the upper row correspond to the symmetry operations, and the symbols in the lower row correspond to equivalent rotations.

$$a = (12)(34), \quad b = (13)(24)(56), \quad c = (14)(23)(56),$$

$$a^* = E^*a, \quad b^* = E^*b, \quad c^* = E^*c, \quad (3)$$

where E^* is the inversion operation of the Cartesian coordinates of all electrons and nuclei of the molecule in the laboratory coordinate system. The data of Table 1 and relations (2) show that, depending on the parity of the quantum numbers K and p , the rotational states $|\alpha, p\rangle$ generate four irreducible representations of the $D_{2h}(M)$ group:

$$A_g(K, p - \text{even}), \quad B_{1g}(K - \text{even}, p - \text{odd}), \quad (4)$$

$$B_{2g}(K, p - \text{odd}), \quad B_{3g}(K - \text{odd}, p - \text{even}).$$

Note that the choice of basis rotational functions $|\alpha, p\rangle$ according to (1) and molecular axes, as in Fig. 1, made the association of the quantum number p with the spatial parity of states very simple: even states [the character of the inversion operation $\chi(E^*) = 1$] have $p = 0$, and odd states with $\chi(E^*) = -1$ have $p = 1$. This yields the association of the quantum numbers of the rotational states, adopted in this work, with the frequently used quantum numbers K_a and K_c (see, for example, [12]), projections of the angular momentum on the a and c axes of the molecular coordinate system, respectively, in the form

$$K = K_a, \quad p = 0.5[1 - (-1)^{K_c}]. \quad (5)$$

Thus, the quantum number K is equal to K_a , and the parities p and K_c coincide.

We now turn to the spin functions of hydrogen nuclei in the C_2H_4 molecule. Paper [11] showed that 16 spin functions of four equivalent protons of the C_2H_4 molecule generate four irreducible representations of the $D_{2h}(M)$ molecular symmetry group:

$$A_g(7), \quad B_{3g}(3), \quad B_{1u}(3), \quad B_{2u}(3). \quad (6)$$

Here the nuclear statistical weights of the spin states are given in the parentheses. The representations of the spin states (6) have the characters of the inversion operation $\chi(E^*) = 1$, since the operation of spatial inversion does not change the spin of the particles. The total spins of the four protons of the C_2H_4 molecule in states (6) can be found using the method described in [1]. The A_g state contains one state with a total spin of four protons equal to 2, and two states with a spin equal to 0. Each of the three states, $B_{3g}(3)$, $B_{1u}(3)$ and $B_{2u}(3)$, has a total spin of four protons equal to 1.

Knowing the basis rotational and spin functions of certain symmetry in the $D_{2h}(M)$ group, it is now possible to construct full basis wave functions of the C_2H_4 molecule. Because all symmetry operations in the $D_{2h}(M)$ group perform permutations of an even number of fermion pairs in the C_2H_4 molecule, the resulting full wave function allowed by quantum statistics must have either A_g or A_u symmetry. This gives the following allowed full basis wave functions:

$$|A_g\rangle = |A_g\rangle_{\text{nuc}} |A_g\rangle_{\text{rot}}, \quad |A_g\rangle = |B_{3g}\rangle_{\text{nuc}} |B_{3g}\rangle_{\text{rot}}, \quad (7)$$

$$|A_u\rangle = |B_{1u}\rangle_{\text{nuc}} |B_{1g}\rangle_{\text{rot}}, \quad |A_u\rangle = |B_{2u}\rangle_{\text{nuc}} |B_{2g}\rangle_{\text{rot}}.$$

These relations determine the correlations of rotational and nuclear spin states in the ethylene molecule.

So far, we have considered the basis spin and rotational states. The total states $|\mu\rangle$ of the C_2H_4 molecule are the decomposition over the states of one symmetry from (7):

$$|\mu\rangle = |I, \sigma, S_{\text{spin}}\rangle |\beta, p\rangle \equiv |I, \sigma, S_{\text{spin}}\rangle \sum_K C_K |\alpha, p\rangle. \quad (8)$$

Here, I and σ are the total spin of four protons and its projection on the laboratory quantisation axis, respectively; S_{spin} is the irreducible representation of the spin state; and C_K are the decomposition coefficients. The rotational state $|\beta, p\rangle$ of the ethylene molecule has a symmetry determined by relations (7).

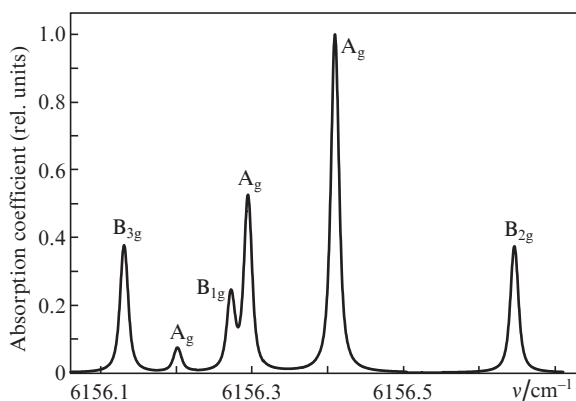


Figure 4. Fragment of the theoretical absorption spectrum in the $\nu_5 + \nu_9$ combination vibrational band of ethylene molecules. Shown are the symmetry types of the rotational states of ethylene molecules in the ground vibrational state.

The wave functions and energies of the rotational states of ethylene were calculated using the effective Watson Hamiltonian, which takes into account centrifugal distortion of the molecule up to sixth-order terms [13] in the expansion over the angular momentum of the molecule. The exact molecular constants of the ground electronic and vibrational states of C_2H_4 were found in [14]. Molecular constants of the $\nu_5 + \nu_9$ state are defined in [15]. The absorption spectrum in the $\nu_5 + \nu_9$ band was calculated in this work using the PGOPHER programme [16]. In this case, the equilibrium nuclear statistical weights of the spin isomers were used according to (6). The result of the calculation, the theoretical absorption spectrum in the $\nu_5 + \nu_9$ band, is presented in Fig. 4 for the wavelength region corresponding to the experimental spectrum in Fig. 3.

4. Discussion and conclusions

The PGOPHER programme calculates the frequencies and intensities of the absorption lines, as well as the energies, quantum numbers, and symmetry types of the lower and upper rotational states. The parameters of absorption lines that are important for the discussion are listed in Table 2. Very good agreement between the experimental and theoretical absorption spectra (frequencies and amplitudes of spectral lines) allows us to conclude that the lines of the measured spectrum are correctly identified. The rotational quantum numbers of the absorption lines make it possible, using relations (4), (5) and (7), to establish the symmetry of the rotational and spin states of the recorded transitions of the $\nu_5 + \nu_9$ band in the region of $\lambda = 1.6 \mu\text{m}$.

The experimental spectrum contains a number of weak absorption lines of unknown nature. However, these lines have a significantly smaller amplitude than the identified lines of the $\nu_5 + \nu_9$ band. In general, the error in detecting the concentrations of nuclear spin isomers of ethylene using the developed spectrometer and the found portion of the absorption spectrum in the $\nu_5 + \nu_9$ band can be estimated at 1%.

The disadvantages of the developed technique for detecting nuclear spin isomers of ethylene molecules include relatively high gas pressures necessary for reliable detection of the spectrum. In particular, the gas pressure during the registration of the spectrum shown in Fig. 3 was 10 Torr. This restriction is not fundamental. For example, one can use a more sensitive system of acousto-optic absorption detection, as that in [7, 8].

Thus, we have proposed and experimentally implemented a technique for laser detection of ethylene molecules and identified ethylene absorption lines in the $\nu_5 + \nu_9$ combination vibrational band. A laser spectrometer has been fabricated and a portion of the spectrum has been found in the region of $\lambda = 1.6 \mu\text{m}$, suitable for detecting all four nuclear spin isomers of ethylene molecules.

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Table 2. Parameters of the absorption lines in the spectra presented in Figs 3 and 4.

$\nu_{\text{theor}}/\text{cm}^{-1}$	A_{theor} (rel. units)	$\nu_{\text{exp}}/\text{cm}^{-1}$	A_{exp} (rel. units)	$J'_{K'_a, K'_c} \leftarrow J_{K_a, K_c}$	S_{rot}	S_{spin}
6156.130	0.38	6156.138	0.40	$3_{1,3} \leftarrow 2_{1,2}$	B_{3g}	B_{3g}
6156.201	0.069	6156.200	0.052	$13_{2,11} \leftarrow 13_{2,12}$	A_g	A_g
6156.272	0.24	6156.282	0.26	$3_{2,2} \leftarrow 2_{2,1}$	B_{1g}	B_{1u}
6156.294	0.53	6156.306	0.54	$3_{2,1} \leftarrow 2_{2,0}$	A_g	A_g
6156.409	1.00	6156.414	1.00	$3_{0,3} \leftarrow 2_{0,2}$	A_g	A_g
6156.645	0.37	6156.649	0.38	$3_{1,2} \leftarrow 2_{1,1}$	B_{2g}	B_{2u}

Note: ν_{theor} and ν_{exp} are the frequencies of the lines of the theoretical and experimental spectra; A_{theor} and A_{exp} are the amplitudes of the lines of the theoretical and experimental spectra; $J'_{K'_a, K'_c}$ and J_{K_a, K_c} are the rotational quantum numbers for the upper, $\nu_5 + \nu_9$, and ground vibrational states, respectively; S_{rot} and S_{spin} are the symmetry types of the rotational function of the ground vibrational state and the nuclear spin function, respectively.

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