PRECISE RO-VIBRATIONAL ANALYSIS OF VIBRATIONAL BANDS IN 1100-1400 CM^{-1} REGION OF SPECTRUM OF C_2HD_3

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ТОЧНЫЙ КОЛЕБАТЕЛЬНО-ВРАЩАТЕЛЬНЫЙ АНАЛИЗ ВРАЩАТЕЛЬНЫХ ПОЛОС В ДИАПАЗОНЕ СПЕКТРА 1100-1400 $СМ^{-1}$ МОЛЕКУЛЫ C_2HD_3

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Аннотация. *В настоящей работе представляются результаты исследования колебательно-вращательных спектров молекулы C_2HD_3 в диапазоне 1100 – 1400 $см^{-1}$. Экспериментальные спектры были зарегистрированы в Техническом Университете Брауншвейга (Германия) с разрешением 0,0021 $см^{-1}$. На основе комбинационных разностей, полученных из анализа полос ν_8 и ν_{12}, улучшены параметры основного колебательного состояния. Новый набор спектроскопических параметров, позволил идентифицировать в экспериментальном спектре около 1900 переходов полосы ν_{12}. Анализ полосы ν_{12} позволяет так же найти комбинационные полосы $2\nu_{10}$, $\nu_7 + \nu_{10}$ и $\nu_4 + \nu_{10}$, проявляющиеся в спектре поглощения за счет сильных резонансных взаимодействий.*

Introduction. One of the most important problems of physical chemistry and chemical physics is the problem of precise determination of intramolecular potential energy surface (PES) of a molecule. Knowledge of a correct PES is the key point in solving the Schrodinger equation of a molecule, which gives one a possibility to determine a correct set of the corresponding molecular Hamiltonian's eigenfunctions. In turn, knowledge of correct eigenfunctions allows one to tackle numerous both purely scientific and applied problems in physical chemistry, astrophysics, planetology, atmospheric and environmental sciences, etc. For the determination of molecular PES, one needs a large amount of experimentally recorded and analyzed ro-vibrational bands. It should be noted that the larger number of experimental data, the more precise results one can expect.

Information about rotational structures of different ro-vibrational bands can be obtained from the analysis of ro-vibrational spectra. Assignment of spectral lines allows one to receive information about lower and upper states between which a transition is possible. Therefore, recording and analyzing molecular experimental spectra can provide us with the information about energies of the studied molecule. The values of energy levels, in turn, are determined by internal physical properties of a molecule. Consequently, finding out the energy levels, one

can determine the exact values of interatomic distances, vibrational frequencies, force constants, dissociation energies, and other quantities characterizing the internal properties of polyatomic molecule.

Ethylene molecule, which is broadly discussed in the scientific environment, is an important object of study from the fundamental as well as applied point of view. It should be noted that the study of this molecule is timely due to a number of reasons. Firstly, ethylene is a leading product, which is used for the production of almost half of all organic compounds. Many of these compounds are released into the atmosphere by chemical and petrochemical industrial enterprises, which leads to the generation of ozone and formation of a global climate [1, 2]. Secondly, ethylene is one of the most important objects of research in astrophysics, physics and chemistry of the planets in the solar system (in particular, it was found in the atmospheres of the giant planets and their satellites) [3]. Thirdly, ethylene acts as a hormone in plants, and, for that reason, may be used to accelerate the ripening of fruits. In addition, ethylene molecule can be considered as a good model for solving problems of physical chemistry, such as the determination of potential hypersurfaces of many organic molecules or the study of the chemical reactions kinetics.

Ethylene molecule has been actively researched for many years. However, a complete study of this molecule, in particular, determination of its potential surface, is impossible without examination of all its isotopologues. This work is devoted to the consideration of one of the ethylene isotopologues, C_2HD_3, in the region of 1100-1400 cm^{-1}.

Experimental details. The Fourier transform infrared spectra of C_2HD_3 have been recorded in the wavenumber range from 1100 to 1400 cm^{-1} with a Brucker IFS 120 FTIR spectrometer (in the Braunschweig Infrared Laboratory, Braunschweig, Germany) in combination with a stainless steel White cell. Two spectra have been used for the present analysis. The first spectrum was recorded with the sample pressure of 1 mbar, the optical path length of 4 m, and scan numbers of 350 (Fig. 1). Experimental conditions for the second spectrum are as follows: 5 mbar, 24 m, and 300 scans. The experimental resolution was 0.0021 cm^{-1} for all spectra.

Assignment of transitions. Symmetry group of C_2HD_3 molecule is isomorphic to the C_s point symmetry group, which has only two irreducible representations (A' and A''). 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. Four bands are located in the investigated region: the ν_{12} (A') fundamental band and the $2\nu_{10}$ (A'), $\nu_7 + \nu_{10}$ (A''), and $\nu_4 + \nu_{10}$ (A'') combinational bands.

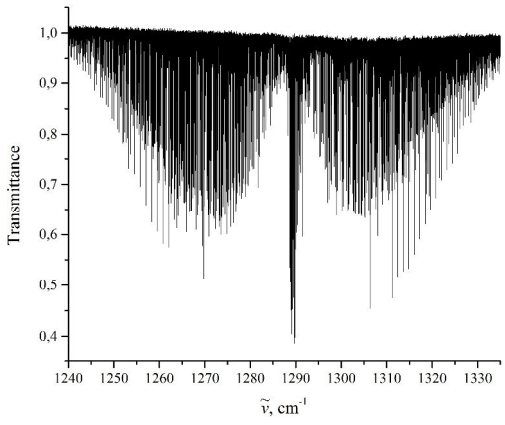

Fig. 1. Experimental spectrum of molecule C_2HD_3 in the region of the ν_{12} band. P = 1 mbar, l = 4 m

The fundamental band ν_{12} is the most intensive one as compared to other bands in the investigated region. Different bands cannot be assigned without strong local resonance interactions of Coriolis and/or Fermi types. This happens due to borrowing of intensities from adjacent bands. Consequently, analysis of strong intensive ν_{12} band will enable us to determine other combination bands in the target region.

Assignment of transitions was made on the basis of the Ground State Combination Differences (GSCD) method. The ground state rotational energies have been calculated with the parameters from [4]. It should be mentioned, that parameters from [4] have been obtained on the basis of only *c*-type from the ν_8 band. This means that parameters from [4] cannot be considered as good enough for other types of transitions. In our case, it was found out that the differences between the experimental GSCD and the ones calculated with the parameters from [4] were increased with the increasing of the value *J* for $J \geq 40$ (see Fig. 2, for illustration). This indicates that the set of parameters of ground state can be improved. A combination of differences obtained for the ν_{12} band (*a* and *b* – type transitions) and spectroscopic data of the ν_8 band (*c* - type) [4] were used for improving the ground vibrational state parameters. A new set of parameters enables one to make analysis of any type of transitions. As a result, about 1900 transitions with maximum values of upper quantum numbers $J^{max} = 52$ and $K_a^{max} = 13$ have been assigned to the ν_{12} band.

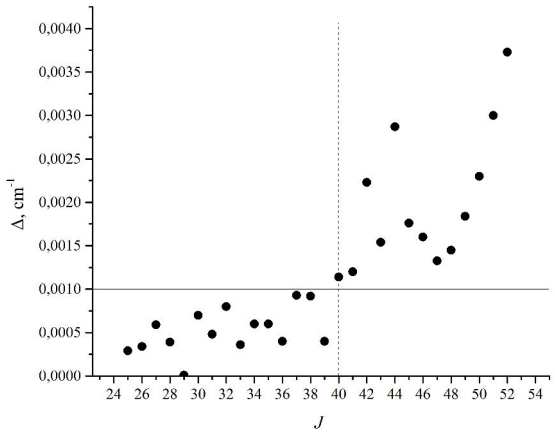

Fig. 2.Dependence of ground state combinational differences on quantum number J for $K_a = 0$

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