CURRENT PROGRESS IN VARIATIONAL CALCULATIONS OF POLYATOMIC HYDROCARBONS (C_2H_2, CH_4, C_2H_4, C_3H_4, AND C_2H_6)

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The prediction of the rovibrational energy levels of the acetylene molecule was studied using both the *ab initio*[1] and new empirically refined potential energy surfaces (PESs). The refinement of the PES was done by the fit of the available experimental data on the main $^{12}C_2H_2$ isotopologue. The quality of the refined PES was analyzed by the variational calculations of the rovibrational energy levels of four isotopologues ($^{13}C_2H_2$, $^{12}C_2D_2$, $^{13}CH^{12}CH$, and $H^{12}C^{12}CD$) including their isotopic shifts for some lower energy levels with $J \geq 5$. Although under the Born-Oppenheimer approximation the isotopic shift should be independent on the PES, we found that the refined PES gave more accurate results than those based on the *ab initio* one. The accuracy of the isotopic shift calculation was estimated as an order of magnitude better than the accuracy of the energy levels calculation. In the case of CH_4, the rovibrational energy levels in the region of the tetradecade polyad were computed with a high accuracy using the *ab initio* PES without any empirical corrections. It was found that the prediction of the vibrational energy levels up to 17000 cm^{-1} strongly depended on shape of the PES.

A novel methodology[2] for computing parameters of the effective both Hamiltonian and dipole moment was applied with respect to C_2H_4. The obtained for each polyad effective parameters will be used to improve the assignment of the C_2H_4 absorption spectra, measured particularly, around 7000 cm^{-1}.

[1] doi:10.1016/j.jqsrt.2022.108349, A. V. Nikitin, A. E. Protasevich, A. A. Rodina, M. Rey, A. Tajti, V. G. Tyuterev, *J. Quant. Spectrosc. Radiat. Transfer.*, **292**, 108349, (2022).

[2] doi:10.1063/5.0089097, M. Rey, *J. Chem. Phys*,**156**, 224103, (2022).

The full-dimensional *ab initio* PESs for two structural isomers of the hydrocarbon C_3H_4 (D_{2d}-propadiene and C_{3v}-propyne) were developed up to the 5^{th} order inclusively. The application of the rigid (D_{3d}) approximation for the variational calculations of the line list of C_2H_6 was discussed with respect to the new contraction approach implemented in the variational TENSOR code and presented previously *ab initio* PES and DMS[3].

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[3] O. Egorov, M. Rey, A. V. Nikitin, D. Viglaska, *27th Colloquium on High-Resolution Molecular Spectroscopy*, HRMS Cologne 2021 **A55**. https://hrms21.scg.ch.