

**CURRENT PROGRESS IN VARIATIONAL CALCULATIONS OF  
POLYATOMIC HYDROCARBONS (C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>4</sub>, AND C<sub>2</sub>H<sub>6</sub>)**

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The prediction of the rovibrational energy levels of the acetylene molecule was studied using both the *ab initio*<sup>1</sup> 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 <sup>12</sup>C<sub>2</sub>H<sub>2</sub> isotopologue. The quality of the refined PES was analyzed by the variational calculations of the rovibrational energy levels of four isotopologues (<sup>13</sup>C<sub>2</sub>H<sub>2</sub>, <sup>12</sup>C<sub>2</sub>D<sub>2</sub>, <sup>13</sup>CH<sup>12</sup>CH, and H<sup>12</sup>C<sup>12</sup>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<sub>4</sub>, 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<sup>-1</sup> strongly depended on shape of the PES.

A novel methodology<sup>2</sup> for computing parameters of the effective both Hamiltonian and dipole moment was applied with respect to C<sub>2</sub>H<sub>4</sub>. The obtained for each polyad effective parameters will be used to improve the assignment of the C<sub>2</sub>H<sub>4</sub> absorption spectra, measured particularly, around 7000 cm<sup>-1</sup>.

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<sup>1</sup>[doi:10.1016/j.jqsrt.2022.108349](https://doi.org/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).

<sup>2</sup>[doi:10.1063/5.0089097](https://doi.org/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<sup>th</sup> 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<sup>3</sup>.

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