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Structure and conformational dynamics of molecules in the excited electronic states: theory and experiment

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Abstract. The structure of conformational non-rigid molecules in the excited electronic states are investigated by joint theoretical and experimental methods. The theoretical part of work consist of two stages. In first stage the *ab initio* quantum-chemical calculations are carried out using high level methods. In second stage the vibrational problems of the various dimensions are solved by variational method for vibrations of large amplitude. In experimental part of work the vibronic spectra are investigated: gas-phase absorption and also, fluorescence excitation spectra of jet-cooled molecules. Some examples are considered.

The strategy of the joint theoretical and dynamics of conformational non-rigid molecules in the excited electronic state is presented.

The theoretical part consist of the two stages. In the first stage the *ab initio* quantum chemical calculations are carried out, using high level multiconfigurational methods. The number and types of conformers, adiabatic energies of the excited electronic states, geometrical parameters, vibrational frequencies, values of conformer energy differences and potential barriers of conformational transitions are determined, and in addition — the sections of the potential energy surface (PES) of various dimensions on the coordinates of large amplitude vibrations (torsional, inversional, etc.), which control the conformational dynamics of molecules.

Using these PES sections, in the second stage of theoretical work, the corresponding vibrational problems are solved by variational method and the sets of the energy levels are found.

In experimental part of work the vibronic spectra investigated: gas-phase absorption using multipath optical cell with large length of optical path and also fluorescence excitation spectra of jet-cooled molecules. The energies of conformers in the excited electronic states and vibrational frequencies are determined. In some cases it is possible to estimate the molecular geometrical parameters from the analysis of rotation contours of vibronic bands.

The combination of consistent calculated and experimental data presents quite full picture of the structure and dynamics of conformational non-rigid molecules in the excited electronic states.

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The comparison of corresponding theoretical and experimental data demonstrates the potentialities and limits of using computational methods. Nowdays it is the topical and important problem for calculations of structure and properties of molecules in the excited electronic states.

The examples of investigations of propanal (CH_3CH_2CHO) [1-3] and cyclopropanecarboxaldehyde (c-C_3H_5CHO) [4] are considered.

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