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BOOK of ABSTRACTS



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**CONFORMATIONALLY-DEPENDENT THEORETICAL
ANHARMONIC VIBRATIONAL SPECTROSCOPY OF
GUANOSINE AND ITS MONO- AND DIHYDRATED GAS-PHASE
COMPLEXES**

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Potential energy surfaces (PESs) of guanosine (the major component of most forms of RNA molecules) as well as its noncovalently bonded gas-phase complexes with one and two water molecules were explored employing second-order Möller-Plesset perturbation theory (MP2) with gradient optimization algorithms. The character of located stationary points on the MP2 PESs was tested employing technique of diagonalization of the mass-weighted Hessian matrices; absence of imaginary eigenvalues of these matrices served as an indication that the located stationary point is a real minimum on the explored PES. At the same time, the eigenvalues of the mass-weighted second derivative matrices correspond to molecular/complex harmonic vibrational frequencies. The located real minima were further characterized with an emphasis on the realistic description of the O-H stretching motions, which are notably anharmonic. To achieve such realistic description and to get a more in-depth physical insight into the available experimental spectroscopic data, the one-dimensional O-H stretching potentials of various intramolecular OH oscillators were computed in a pointwise manner, within the local oscillator approximation at MP2 level of theory. The computed 1D O-H vibrational potentials were subsequently fitted to a fifth-order polynomial in the stretching coordinate r (which was afterwards cut after fourth order terms), transformed into Simons-Parr-Finlan type coordinates, and the vibrational Schrödinger equation was solved variationally. For comparison purposes, the vibrational Schrödinger equation for each local OH oscillator was also solved in ordinary bond-stretching coordinates, employing the Numerov method. The obtained results appear to enlighten the experimental vibrational spectroscopic data in a sense of more exact clarifications of empirical band assignments.

Key words: guanosine, water complexes, OH stretching mode, Möller-Plesset perturbation theory, vibrational Schrödinger equation.

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ELECTRIC FIELD-CONTROLLED TAUTOMERISM IN 2-CARBAMIDO-1,3-INDANDIONE: UV-VIS, QUANTUM CHEMICAL AND MODEL HAMILTONIAN STUDY

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The influence of external electric field on the tautomeric equilibrium of 2-carbamido-1,3-indandione is investigated. This particular system is characterized with small energy difference between tautomers (in an absence of external field) and very low activation barrier to intramolecular proton transfer (IMPT). The geometries of the tautomers as well as the transition state are fully optimized at MP2 level of theory for a series of magnitudes and directions of the externally applied electrostatic field. Changes in electronic structures, as well as energetic of the two stable conformers as functions of the externally applied field strength and directions are followed and rationalized in terms of static and induced molecular multipole moments. Indirect conclusions concerning electric field influence on the dynamics of the IMPT are derived. Such conclusions, based on exact quantum chemical computations are further rationalized in terms of simulations based on model Hamiltonian containing a field-dependent term employing the effective local field approximation. As the different tautomeric forms are distinguishable by UV-VIS spectroscopy, electronic excitation energies are computed within the framework of time-dependent density functional theory approach (TD-DFT), at the minima located on MP2 potential energy surfaces. These are compared to the experimentally determined values in the present study. On the basis of model Hamiltonian and quantum chemical results, we propose a possibility to control the IMPT process in the title compound with an external electrostatic field. The outlined possibility for IMPT control is based on the fact that upon variation of the electric field strength and polarity, it is possible to stabilize different tautomeric forms of the molecule, and also to modify the overall reaction path corresponding to the IMPT process.

Key words: 2-carbamido-1,3-indandione, intramolecular proton transfer, electric field control, Möller-Plesset perturbation theory, model Hamiltonian calculations.