CC/DFT Route toward Accurate Structures and Spectroscopic Features for Observed and Elusive Conformers of Flexible Molecules: Pyruvic Acid as a Case Study

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Streszczenie

The structures and relative stabilities as well as the rotational and vibrational spectra of the three low-energy conformers of pyruvic acid (PA) have been characterized using a state-of-the-art quantum-mechanical approach designed for flexible molecules. By making use of the available experimental rotational constants for several isotopologues of the most stable PA conformer, *Tc*-PA, the semiexperimental equilibrium structure has been derived. The latter provides a reference for the pure theoretical determination of the equilibrium geometries for all conformers, thus confirming for these structures an accuracy of 0.001 Å and 0.1 deg for bond lengths and angles, respectively. Highly accurate relative energies of all conformers (*Tc*- , *Tt*-, and *Ct*-PA) and of the transition states connecting them are provided along with the thermodynamic properties at low and high temperatures, thus leading to conformational enthalpies accurate to 1 kJ mol^{-1}. Concerning microwave spectroscopy, rotational constants accurate to about 20 MHz are provided for the *Tt*- and *Ct*-PA conformers, together with the computed centrifugal-distortion constants and dipole moments required to simulate their rotational spectra. For *Ct*-PA, vibrational frequencies in the mid-infrared region accurate to 10 cm^{-1} are reported along with theoretical estimates for the transitions in the near-infrared range, and the corresponding infrared spectrum including fundamental transitions, overtones, and combination bands has been simulated. In addition to the new data described above, theoretical results for the *Tc*- and *Tt*-PA conformers are compared with all available experimental data to further confirm the accuracy of the hybrid coupled-cluster/density functional theory (CC/DFT) protocol applied in the present study. Finally, we discuss in detail the accuracy of computational models fully based on double-hybrid DFT functionals (mainly at the B2PLYP/aug-cc-pVTZ level) that avoid the use of very expensive CC calculations.