



Reliable vibrational wavenumbers for C=O and N–H stretchings of isolated and hydrogen-bonded nucleic acid bases

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The accurate prediction of vibrational wavenumbers for functional groups involved in hydrogen-bonded bridges remains an important challenge for computational spectroscopy. For the specific case of the C=O and N-H stretching modes of nucleobases and their oligomers, the paucity of experimental reference values needs to be compensated by reliable computational data, which require the use of approaches going beyond the standard harmonic oscillator model. Test computations performed for model systems (formamide, acetamide and their cyclic homodimers) in the framework of the second order vibrational perturbation theory (VPT2) confirmed that anharmonic corrections can be safely computed by global hybrid (GHF) or double hybrid (DHF) functionals, whereas the harmonic part is particularly challenging. As a matter of fact, GHFs perform quite poorly and even DHFs, while fully satisfactory for C=O stretchings, face unexpected difficulties when dealing with N-H stretchings. On these grounds, a linear regression for N-H stretchings has been obtained and validated for the heterodimers formed by 4-aminopyrimidine with 6-methyl-4-pyrimidinone (4APM-M4PMN) and by uracil with water. In view of the good performance of this computational model, we have built a training set of B2PLYP-D3/maug-cc-pVTZ harmonic wavenumbers (including linear regression scaling for N-H) for six-different uracil dimers and a validation set including 4APM-M4PMN, one of the most stable hydrogen-bonded adenine homodimers, as well as the adenine-uracil, adenine-thymine, guanine-cytosine and adenine-4-thiouracil heterodimers. Because of the unfavourable scaling of DHF harmonic wavenumbers with the dimensions of the investigated systems, we have optimized a linear regression of B3LYP-D3/N07D harmonic wavenumbers for the training set, which has been next checked against the validation set. This relatively cheap model, which shows very good agreement with experimental data (average errors of about 10 cm⁻¹), paves the route toward a reliable analysis of spectroscopic signatures for larger polynucleotides.

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