Toward Feasible and Comprehensive Computational Protocol for Simulation of the Spectroscopic Properties of Large Molecular Systems: The Anharmonic Infrared Spectrum of Uracil in the Solid State by the Reduced Dimensionality/Hybrid VPT2 Approach

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Feasible and comprehensive computational proto- cols for simulating the spectroscopic properties of large and complex molecular systems are very sought after. Indeed, due to the great variety of intra- and intermolecular interactions that may take place, the interpretation of experimental data becomes more and more difficult as the system under study increases in size or is placed in a complex environment, such as condensed phases. In this framework, we are actively developing a comprehensive and robust computational protocol aimed at quantitative reproduction of the spectra of nucleic acid base complexes, with increasing complexity toward condensed phases and monolayers of biomolecules on solid supports. We have resorted to fully anharmonic quantum mechanical computations within the generalized second-order vibrational perturbation theory (GVPT2) approach, combined with the cost-effective B3LYP-D3 method, in conjunction with basis sets of double-ζ plus polarization quality. Such an approach has been validated in a previous work (Phys. Chem. Chem. Phys. 2014, 16, 10112−10128) for simulating the IR spectra of the monomers of nucleobases and some of their dimers. In the present contribution we have extended such computational protocol to simulate spectroscopic properties of a molecular solid, namely polycrystalline uracil. First we have selected a realistic molecular model for representing the spectroscopic properties of uracil in the solid state, the uracil heptamer, and then we have computed the relative anharmonic frequencies combining less demanding approaches such as the hybrid B3LYP-D3/DFTBA one, in which the harmonic frequencies are computed at a higher level of theory (B3LYP-D3/ N07D) whereas the anharmonic shifts are evaluated at a lower level of theory (DFTBA), and the reduced dimensionality VPT2 (RD-VPT2) approach, where only selected vibrational modes are computed anharmonically along with the couplings with other modes. The good agreement between the theoretical results and the experimental findings allowed us to extend the interpretation of experimental data. Our results indicate that hybrid and reduced dimensionality models pave a way for the definition of system-tailored computational protocols able to provide more and more accurate results for very large molecular systems, such as molecular solids and molecules adsorbed on solid supports.

Słowa kluczowe

Cluster chemistry, Monomers, Oligomers, Quantum mechanics, Uracil

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