Spectra-structure correlations in NIR region : spectroscopic and anharmonic DFT study of *n*-hexanol, cyclohexanol and phenol.

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Streszczenie

We investigated near-infrared (7500-4000cm^{-1}) spectra of n-hexanol, cyclohexanol and phenol in CCl_4 (0.2M) by using anharmonic quantum calculations. These molecules represent three major kinds of alcohols; linear and cyclic aliphatic, and aromatic ones. Vibrational second-order perturbation theory (VPT2) was employed to calculate the first overtones and binary combination modes and to reproduce the experimental NIR spectra. The level of conformational flexibility of these three alcohols varies from one stable conformer of phenol through four conformers of cyclohexanol to few hundreds conformers in the case of n-hexanol. To take into account the most relevant conformational population of n-hexanol, a systematic conformational search was performed. Accurate reproduction of the experimental NIR spectra was achieved and detailed spectra-structure correlations were obtained for these three alcohols. VPT2 approach provides less reliable description of highly anharmonic modes, i.e. OH stretching. In the present work this limitation was manifested in erroneous results yielded by VPT2 for 2νOH mode of cyclohexanol. To study the anharmonicity of this mode we solved the corresponding time-independent Schrödinger equation based on a dense-grid probing of the relevant vibrational potential. These results allowed for significant improvement of the agreement between the calculated and experimental 2νOH band of cyclohexanol. Various important biomolecules include similar structural units to the systems investigated here. A detailed knowledge on spectral properties of these three types of alcohols is therefore essential for advancing our understanding of NIR spectroscopy of biomolecules.

Słowa kluczowe

Near-infrared spectroscopy, Alcohols, Phenols, Quantum chemical calculation, Overtones, Combination modes, Time-independent vibrational Schrodinger, equation, spectra-structure correlations, Anharmonic spectra

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