

Analysis of near-infrared spectra of short-, medium-, and long-chain fatty acids supported by anharmonic quantum mechanical calculations

○Justyna Grabska¹, Krzysztof B. Beć¹, Mika Ishigaki¹, Marek J. Wójcik², Yukihiro Ozaki¹

¹ *School of Science and Technology, Kwansai Gakuin University, Japan*

² *Faculty of Chemistry, Jagiellonian University, Poland*

[Abstract]

We reproduce near-infrared spectra of several fatty acids by generalized vibrational second-order perturbation theory (GVPT2) on DFT level of electronic theory. The objects of study included simple carboxylic acids (butyric acid, crotonic acid, hexanoic acid, sorbic acid, etc.) as well as bio-significant fatty acids (arachidic acid, oleic acid, palmitic acid, etc.). The calculated data was used directly for explaining the experimental NIR spectra of these systems. Special attention has been paid to spectral features distinctive to saturated vs. unsaturated fatty acids. Theoretical methods allowed for assigning NIR bands observed experimentally in the spectra of saturated and unsaturated fatty acids and draw conclusions about structure-spectra correlations. An example of practical application of the results of theoretical study for biochemical studies is provided – NIR imaging of medaka fish embryo and support for the analysis of distribution of fatty acids in oil droplets of fish egg.

[Introduction]

Anharmonic calculations are much less straightforward than harmonic computations, with vastly increased resource demands. However, they offer a possibility of theoretical reproduction of experimental NIR spectra, which in return offers wide possibilities for applied NIR studies. Recent advances in theoretical methods allowed for very accurate calculation of NIR spectra of simple molecules. Recent reports on simple carboxylic acids demonstrate the capabilities of quantum chemical calculations in basic NIR studies. Here we report our progress in advancing these basic studies into the field of more complex fatty acids.

[Methods]

NIR spectra of the carboxylic acids were measured in CCl₄ solutions in a wide range of concentrations (5×10⁻⁴–0.05 M) in rectangular quartz cells of 10 mm and 100 mm optical paths. All spectra were acquired at the controlled temperature of 298 K.

NIR modes have been calculated with the use of generalized second-order perturbation theory (GVPT2) on DFT with B3LYP/SNST level of electronic theory for monomers and B3LYP/SNSD or B3LYP/N07D for dimers (medium chain/long chain fatty acids). Hybrid approach (harmonic part calculated on higher level, anharmonic part on lower level) was applied as the most efficient approach. Theoretical spectra were obtained with convolution model (4-parameter Lorentz-Gauss product function) of Boltzmann weighted spectra of conformational isomers.

[Results and Discussion]

NIR spectra of carboxylic acids carry rich information about the molecular structure, including the differences between saturated and unsaturated alkyl chains. The respective spectra can be divided into three major spectral subregions (7000-5500 cm⁻¹, 5000-4600 cm⁻¹, 4600-4000 cm⁻¹), into which different types of bands contribute the most.

The NIR spectra feature substantial intrinsic complexity, due to a large number of

contributing modes and the resulting band overlapping (Fig.1). The theoretical modeling of NIR line shapes is of crucial importance in advancing our understanding of NIR spectroscopy of complex molecules. The calculated spectra corresponded accurately to the experimental line shapes measured over a wide region of concentrations, indicating that dimerization of fatty acids occurs even in a very low concentration in a nonpolar solvent. Only in the NIR spectra of fatty acids in a high dilution ($5 \cdot 10^{-4}$ M) the dominance of monomers could be evidenced. With an increased concentration the NIR spectra are primarily influenced by the cyclic dimers, and the bands due to the monomeric species diminish gradually (Fig.2). Upon the formation of cyclic dimers, a prominent feature in the form of spectral baseline elevation could be noticed in the region of $6500\text{--}4000\text{ cm}^{-1}$ and presumably extending further into the IR region. The analysis of the calculated data indicated that this increase is mainly due to the combination bands, arising from the vibrations of the hydrogen-bonded OH groups in the cyclic dimers. Taking this effect into account allowed for a very accurate reproduction of the experimental NIR spectra of the studied fatty acids.

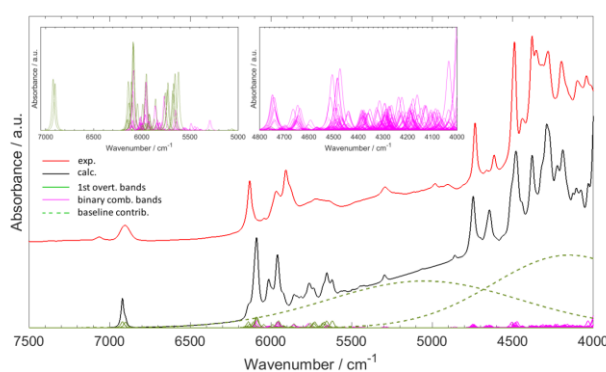


Fig.1. Contributions to the calculated NIR spectrum on the example of vinylacetic acid.

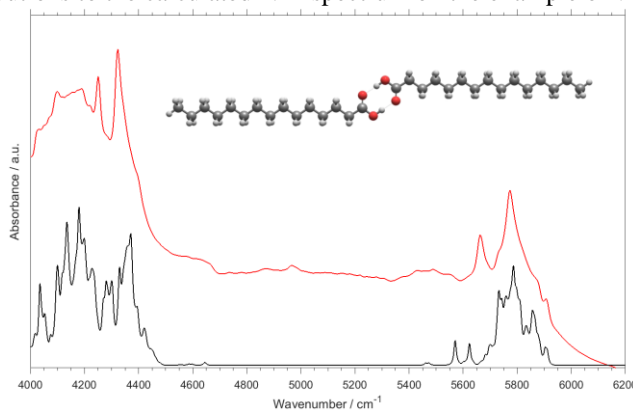


Fig.2. Experimental and calculated NIR spectrum of long-chain fatty acid of arachidic acid.

Based on the obtained theoretical NIR spectra, a detailed band assignment was provided, and the correlations between the spectra and structures were established. Numerous bands arising from vibrations of structural elements specific to either saturated or unsaturated alkyl chains were identified. Therefore, several NIR subregions were established, carrying highly specific structural information on the saturation level of the alkyl chain in fatty acids. The results presented here should provide better understanding of NIR spectra of various kinds of biological samples, i.e. NIR imaging data of biological structures.

[References]

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