Correlations between structure and near-infrared spectra of saturated and unsaturated carboxylic acids : insight from anharmonic density functional theory calculations.

Autorzy

Justyna Grabska

Mika Ishigaki

Krzysztof B. Beć

Marek Janusz Wójcik

Yukihiro Ozaki

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Streszczenie

By near-infrared (NIR) spectroscopy and anharmonic density functional theory (DFT) calculations, we investigate five kinds of saturated and unsaturated carboxylic acids belonging to the group of short-chain fatty acids: propionic acid, butyric acid, acrylic acid, crotonic acid, and vinylacetic acid. The experimental NIR spectra of these five kinds of carboxylic acids are reproduced by quantum chemical calculations in a broad spectral region of 7500-4000 cm^{-1} and for a wide range of concentrations. By employing anharmonic GVPT2 calculations on DFT level, a detailed interpretation of experimental spectra is achieved, elucidating structure-spectra correlations of these molecules in the NIR region. We emphasize the spectral features due to saturated and unsaturated alkyl chains, the location of a C═C bond within the alkyl chain, and the dimerization of carboxylic acids. In particular, the existence of a terminal C═C bond leads to the appearance of highly specific NIR bands. These pronounced bands are located at wavenumbers where no overlapping with other structure-specific bands occurs, thus making them good structural markers. Most of the spectral differences between these two groups of molecules remain subtle, and would be difficult to reliably ascribe without quantum chemically calculated NIR spectra. Moreover, anharmonic DFT calculations provide insights on the manifestation of hydrogen bonding through distinctive spectral features corresponding to cyclic dimers. The resulting spectral baseline elevation is common for all five investigated carboxylic acids, and remains consistent with previous results on acetic acid.