Spectroscopic and computational study of acetic acid and its cyclic dimer in the near-infrared region.

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Streszczenie

Anharmonic vibrational analysis of near-infrared (NIR) spectra of acetic acid was carried out by anharmonic quantum chemical calculation in a wide concentration range of its CCl_4 solution. By predicting vibrational spectra of acetic acid for the first time over a wide NIR region, it was possible to elucidate the influence of the formation of acetic acid cyclic dimer on its NIR spectrum. Quantum chemical simulations were based on coupled cluster and density functional theory quantum methods. Additionally, Møller–Plesset perturbation theory was employed for the additional calculation of hydrogen bonding stabilization energies. An anharmonic vibrational analysis was performed with the use of generalized second-order vibrational perturbation theory (GVPT2). A hybrid approach was assumed, in which monomeric species was treated by CCSD(T)/aug-cc-pVDZ (harmonic approximation) and B3LYP/SNSD (anharmonic approximation) methods. For the cyclic dimer, B3LYP and B2PLYP single and double hybrid functionals, paired with an SNSD basis set, were employed. DFT calculations were augmented with additional empirical dispersion correction. It was found that quantum chemically calculated vibrational modes in the NIR region are in a good agreement with experimental data. The results of anharmonic vibrational analysis were supported by a harmonic shift analysis, for elucidating the very strong anharmonic coupling observed between stretching modes of hydrogen bonded bridge in the cyclic dimer. However, the calculated wavenumbers for combination modes of double hydrogen bonded bridge in the cyclic dimer, which are very sensitive to the formation of hydrogen bonding, were found to be underestimated by quantum chemical methods. Therefore, by band fitting, the wavenumbers and shape parameters for these bands were found, and the modeled spectra were adjusted accordingly. A high accuracy of simulated spectra was achieved, and a detailed analysis of the experimental NIR spectra of acetic acid was possible, with successful identification of numerous experimental bands, including those which originate from concentration effects. It was also found that the main spectral features observed in the NIR spectra of carboxylic acid upon the formation of hydrogen bond should be accounted for combination modes of the stretching and bending vibrations of double hydrogen-bonded bridge in the cyclic dimers of acetic acid.

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