

溶液中の核酸塩基の IR スペクトルの理解
Assignment of IR spectra of nucleobases in solution

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The first step of the project was to explain the steady state infrared spectra of the nucleobases uracil and thymine in aqueous solution. In aqueous solution the C=O stretch band has a more complex structure than in aprotic solvents. The assignment of peaks is additionally complicated by the fact that the experiment is performed in D₂O and that the nucleobases can exchange hydrogens with solvent. To clarify the origin of the multiple peaks in the C=O stretch region, force field molecular dynamics simulations were performed with N,N-deuterated nucleobases solvated in a large box of D₂O. Snapshots from the simulation showed that nucleobases occur in many different hydrogen-bonded environments. We optimized the snapshots locally and computed the harmonic vibrational frequencies with DFT using the QM/MM approach. Deuterated water molecules in the first solvation shell were included in the QM region. The IR bands for C=O and N-D groups shift depending on the number of attached hydrogen bonds. One hydrogen bond lowers the carbonyl peak by $\sim 50 \text{ cm}^{-1}$. The C=C stretch vibrations on the other hand are not affected by the presence of hydrogen bonds. Averaging the IR spectra over snapshots sampled from the thermal distribution, a broad band with multiple humps emerges that agrees qualitatively with the experimental spectrum. The peak intensity is determined by the relative stability of the hydrogen bonded complexes.

The next steps in the project consists of simulating the infrared spectra of meta-stable species in the excited state that are formed by the decay of the initially excited $\pi\pi^*$ state.