Dynamical motion and IR spectra of glycine in aqueous solution by means of direct ab initio QM/MM-MD

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[Introduction] IR spectrum is often calculated by means of ab initio MO method in the gas phase or in dielectric field. Solvation effect, however, cannot be elucidated by taking into account only a few solvent molecules or only a few configurations of these, even if high level of theory is used. It is necessary to treat many solvent molecules explicitly.

[Method] (case-1) IR spectrum of glycine in the gas phase

A glycine molecule was optimized in the gas phase at HF/6-31G* level of theory and vibrational analysis was performed to calculate IR spectrum of glycine.

(case-2) IR spectrum of glycine in water cluster using PCM method

The structure of glycine with 9 solvated water molecules was optimized at the theoretical level of HF/6-31G* with the PCM method using UAHF cavity to mimic a circumstance in aqueous solution. Vibrational analysis was performed to obtain IR spectra of glycine with solvated 9 water molecules.

(case-3) IR spectrum of glycine by Fourier transformation using QM/MM-MD trajectories

The method of direct dynamics was applied in which the trajectories are calculated by integrating Newton's equations of motion with the energies and forces obtained directly from ab initio QM/MM calculations at each time step. The theoretical level of HF/6-31G* was used for the energy and force calculations of the QM sub-system. We performed QM/MM-MD simulation in 101 MM water molecules (NVT constant, T=298 K) and obtained IR spectrum of glycine in aqueous solution by performing Fourier transformation of the MD trajectory.

[Results and Discussion] The structure of glycine in aqueous solution is different from that in the gas phase. The strong peak corresponding to the NH stretching (2688 cm^{-1}) of case-1, which is originated from the intramolecular hydrogen bond disappears in the spectra of case-2 and case-3. The calculated spectrum of case-2 resembles that of case-3, while the peaks of NH stretching of case-2 (~3530 cm^{-1}) are lower than those in case-3 (~3670 cm^{-1}). Thus, it is essential to consider solvent molecules explicitly, to calculate IR spectrum of glycine in aqueous solution by means of ab initio MO theory.

case-1
glycine in the gas phase

case-2
glycine and 9 water molecules
with PCM

case-3
glycine in 101 water molecules
using QM/MM-MD