二次元赤外分光法及び分子動力学計算による水溶液中における水素結合ダイナミクス

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(Degree)
博士（理学）

(Date of Degree)
2024-03-25

(Date of Publication)
2026-03-25

(Resource Type)
doctoral thesis

(Report Number)
甲第8853号

(URL)
https://hdl.handle.net/20.500.14094/0100490078

博士論文 (要約)

二次元赤外分光法及び分子動力学計算による水溶液中における水素結合ダイナミクス

令和6年1月
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Water is a ubiquitous solvent that can be a medium for various chemical reactions. One of the most important features is the intermolecular hydrogen-bond formation. It is well known that three-dimensional hydrogen-bond network reorganization caused by thermal fluctuation significantly affects the steady states and especially the dynamical states of solutes. Such dynamical fluctuation can be the onset of the expression of the functions of biomaterials exemplified by the large-amplitude rearrangement of the entire configurations. In this thesis, I mainly focus on the picosecond-fluctuations of the hydrogen bond dynamics that greatly perturbs the vibrational states. Frequency fluctuations originated from the fluctuations in the local hydration environments could clarify the details of solute-solvent interactions. The molecular-level fundamental knowledges and descriptions would be of great value to the entire field of chemistry.

Vibrational frequency fluctuation can be discussed by two-dimensional infrared (2D-IR) spectroscopy, which is one of the nonlinear infrared techniques. The advantage of this method lies in the frequency-resolved pump pulse excitation of the solutes unlike typical pump-probe experiments, which provides a detailed insight into the vibrational dynamics. 2D-IR spectra reflect vibrational spectral diffusions and analytically give frequency-frequency time correlation function (FFTCF). The decay behavior of the FFTCFs corresponds to the hydrogen-bond reorientations. Recently, FFTCFs of small ionic solutes in water have been extensively investigated, which are characterized by solute-independent 1-ps decay time. Furthermore, the solvent fluctuations can be examined by the computational method such as molecular dynamics (MD) simulation. All-atom MD simulation makes it possible to trace a specific atom evolution that significantly affects the hydrogen-bond dynamics. In addition, some physical observables that can only be defined in simulations possibly corroborates the experimental results. The complementary discussion with experiment and theoretical techniques provides a further insight into the fluctuation dynamics in aqueous solutions.

This doctoral dissertation is organized as follows. In Chapter 1, I briefly introduced the general background of this thesis related to the fluctuations of the hydrogen bonds in aqueous solutions. In Chapter 2, experimental and theoretical backgrounds for 2D-IR spectroscopy and MD simulation were summarized. From Chapters 3 to 7, I selected a wide range of solutes such as; small ionic solute, small neutral solute, and polymer in each Chapter and revealed a significant role of a specific solute-solvent interaction in aqueous solutions. Difference in the electrostatic charges of solutes and the molecular structure around the vibrational probe under investigation are highly responsible for the fluctuation behaviors of hydrogen bonds.

In Chapter 3, I compared vibrational dynamics of carbonyl stretching mode of 9-Fluorenone derivatives in D_2O; 9-Fluorenone-2-carboxylic acid (FL-2) and 9-Fluorenone-4-carboxylic acid (FL-4). The relative distance between the carbonyl and carboxyl groups is different in them, which is shorter for FL-2. The subtle molecular structure difference greatly influences the infrared lineshape in D_2O: FL-4 shows unimodal band, whereas FL-2 shows bimodal band of the carbonyl stretching mode. The origin of this observation is the number of intermolecular hydrogen bonds dependent vibrational chromophores at the carbonyl group. 2D-IR spectroscopic measurement revealed that the ultrafast chemical exchange of FL-2 system undergoing in sub-picosecond that is relevant for the intermolecular hydrogen-bond dynamics. In addition, MD simulation indicated that geometrical hydration structures in the vicinity of the carbonyl groups are remarkably different in these solutes. For FL-2, the continuous bridge-type hydrogen bonds across the carbonyl and carboxylate groups physically modulate the vibrational states. The fact eventually affects the number of hydrogen bonds and the infrared lineshapes. It is suggested that the local hydration environments affected by a specific interaction and a molecular structure have a substantial impact on the vibrational dynamics.

In Chapter 4, I investigated ruthenium metal complex ($[RuCl_5(NO)]^{2-}$, NR) in D_2O to explore a slower FFTCF decay time than 1 ps. Here, the nitrosyl stretching mode of NR was probed. Because a longer vibrational lifetime of the mode (ca. ~30 ps) even for a small ionic solute, the FFTCF until longer waiting time can be observed with a good signal to noise ratio, and therefore a slower spectral diffusion can be quantitatively discussed. The obtained FFTCFs are composed of about 1-ps and 10-ps exponential decays. Temperature-dependent measurements revealed that the former decay becomes faster due to the accelerated hydrogen-bond dynamics and the latter one did not depend on temperature. From MD simulation, it was found that the electrostatic charges are localized at chloride ligands rather than the nitrosyl group, which suggests that site-dependent interaction strengths with water. Spatially-resolved FFTCFs divided by the middle point of the nitrosyl group clearly demonstrated that the slow restricted water fluctuations nearby the negatively charged chloride ligands. The comparison with the results of thiocyanate ion emphasized that the importance of the site-dependent solute-solvent interaction based on the ligand properties.

In Chapter 5, I studied FFTCFs of solutes with a large hydrophobic group that show a more than 1-ps decay time even in aqueous solutions. The carbonyl stretching modes of the solutes were investigated by varying the size of hydrocarbon part from acetone to 9-fluorenone derivative. The obtained FFTCF decay times varies from about 1 to 3 ps with increasing the size of solutes, which is originated from the difference in the collectivity of hydrogen-bond reorientation. Besides, Arrhenius plot analysis for the FFTCF decay times revealed that the activation energy of water fluctuation also depends on the solute properties. In order to estimate the collectivity of the fluctuations, relative orientations between the carbonyl dipole and the surrounding water permanent dipoles were calculated. It was found that an effective interaction distance of water for the collective fluctuations is determined by the hydrocarbon group size. The larger amount of the activation energy can be understood from the successive hydrogen bonds breaking and the individually modulated rotational motion of water molecules on the hydrophobic groups.

In Chapter 6, I further investigated the influence of the hydrocarbon part on the slower FFTCF decays. From the results of Chapter 5, the configurational relationship between the transition dipole coordinates and the hydrocarbon group; that is, whether they are aligned or not is expected to play an important role. The solutes chosen in Chapter 5 are characterized by a structure of a hydrocarbon ring located next to the carbonyl axis, whereas the hydrocarbon group is not located along the carbonyl axis for solutes in this Chapter. The latter group shows the FFTCF decay time of ~1 ps irrespective of having a cyclopentane structure or a benzene ring. Almost twice faster decays were observed compared to the former group of solutes even with a similar hydrocarbon group. A high dielectric field around the carbonyl group is achieved because of the absence of the restrictedly rotating water molecules on the hydrocarbon ring and a complete orientational cancellation out of the surrounding water dipole moments, which is followed by the low-collective hydrogen bonds reorientations and hence the faster decay of the FFTCFs. The essential origin of the slower FFTCF decay of small neutral solutes is found to be the local configuration of solutes. This fundamental knowledge may be employed for understanding the vibrational probe inserted biomolecules to separately explore the original macromolecules fluctuations without any influence of insertion.

In Chapter 7, vibrational frequency fluctuations of thermoresponsive polymer and its repeating unit in water were investigated. The polymer solutions exhibit a phase-separation phenomenon at around room temperature, where the randomly extended polymer chain contracts into the globular state with increasing temperature and vice versa. Over the past few decades, the dynamics of the hydration water molecules has been examined by various spectroscopic measurements, but the great details on the ultrafast motions undergoing in sub-picosecond have not been fully revealed yet. Here, poly(*N*,*N*-diethylacrylamide) (PdEA) was used as a target molecule because its side chain only has a hydrogen bond donor part as a carbonyl group, which makes the simpler interpretation on the complicated vibrational dynamics. The FFTCFs of the carbonyl stretching mode of PdEA showed from 4 to 5 ps exponential decays at lower and higher temperatures, respectively. Based on the fact that the FFTCFs of monomer unit (ca. ~1 ps) was similarly described with the denoted interpretation in the other Chapters, the strongly restricted hydration water fluctuations are reflected in the slow FFTCF decays. It is possible that the confined water fluctuations by main or side chains and also rearrangement of the backbones themselves can induce the changes in the vibrational state. MD simulation results indicate that the correlation functions of local hydration water rotation and the dihedral angle motion of the carbon backbone exhibit both of a few tens of picosecond and a few hundreds of picosecond decays. It is also noteworthy that the local hydration environments are significantly affected by the backbone torsions. These facts suggest that not only the individual dynamics of hydration water and polymers but also the coupled dynamics affects the frequency fluctuations of the carbonyl stretching mode.

As a conclusion, I investigated frequency fluctuations of solutes from small ionic and neutral solutes to large polymer in water to gain a detailed molecular interpretation on the fluctuations by using a combination of 2D-IR spectroscopy and MD simulation. In Chapters 3 and 4, specific solute-solvent interactions originated from the configuration of solute itself or the distributed electrostatic charges were discussed. The atomic-level understanding could be employed for some relevant systems. In Chapters 5 and 6, a role of hydrophobic group nearby the vibrational probe (e.g., carbonyl group) was extensively discussed by changing the size of hydrocarbon ring and its relative configuration with respect to the carbonyl group. The influence of the modulated rotational motions of water molecules on the hydrophobic groups on the frequency fluctuations can become a critical clue for other systems such as amino acids, biomaterials, and small infrared-active probes inserted systems. In Chapter 7, a complicated vibrational dynamics of hydration water in the vicinity of thermoresponsive polymer was examined. It is suggested that the associative fluctuations of hydration water and the polymer itself could be a key for the comprehension of the vibrational dynamics of polymer solutions. Finally, I profoundly discussed vibrational frequency fluctuations of several solutes in water from the point of view of molecular dynamics. The proposed interpretations in this thesis provide new fundamental understandings for the frequency fluctuations.