



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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(別紙様式 3)

論 文 内 容 の 要 旨

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論文題目 (外国語の場合は, その和訳を併記すること。)

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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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.

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要 旨			
<p>水やアルコールなどの水素結合性液体では、分子間水素結合による特異的なネットワーク構造を形成する。このネットワーク構造は時々刻々変化しており、そのため系全体のポテンシャルエネルギーが動的に揺らいでいる。このような水素結合性の液体を溶媒として、溶質を導入すると、溶質の電子状態、振動状態もこの動的な揺らぎの影響を受ける。本研究では、水溶液中の溶質分子の振動状態に注目し、分子振動の振動数の揺らぎが、溶質—溶媒間のどのような相互作用により決まるのか、また溶媒のどのようなダイナミクスが溶質の振動数揺らぎに影響を与えているのかということ明らかにすることを目的とした。</p> <p>溶質の振動数の揺らぎを調べる手法として、二次元赤外 (2D-IR) 分光法によって振動数揺らぎの時間相関関数 (Frequency-frequency time correlation function; FFTCF) を得た。サブピコ秒の時間分解能を持つ中赤外パルスレーザーを用いた測定手法であり、励起された振動状態の時間発展を観測することができる。FFTCF は周囲の集団的な水素結合の再配向過程を反映して指数関数的に減衰することが知られている。先行研究により、小さなイオン性の溶質分子ではその種類によらず、約 1 ps の時定数で減衰することが知られている。当該論文では様々な溶質を対象とし、この減衰過程の変化から分子間相互作用を議論した。また、分子動力学 (MD) シミュレーション計算もあわせて行い、溶液中の分子運動に関する運動を分子レベルで得た。それにより実験結果の分子レベルでの詳細な検討を行い、振動状態に影響を及ぼす水素結合ダイナミクスの解析を行うことにより、振動数揺らぎに対する分子論的描像を得た。</p> <p>当該論文は7章で構成されており、第1章と第2章では導入と理論背景を紹介した。第3章から第7章までの各章では、それぞれ異なる溶質を対象としたときの研究成果をまとめている。</p> <p>第3章では、二つの9-フルオレノン誘導体のカルボニル (CO) 基の伸縮振動の吸収スペクトル線形について議論した。フルオレノン分子の2位又は4位にカルボキシラート (COO⁻) 基が存在する分子は、分子構造が似ているにもかかわらず、2位のものではスペクトルの分裂が見られる。この分子間水素結合に依存する CO 基の振動状態の時間発展を 2D-IR 分光法によって解析し、CO 基近傍の水和環境を計算によって明らかにすることで、分裂の起源がカルボニル基とカルボキシラート基間の特異な水素結合に由来することを明らかにした。</p> <p>第4章ではルテニウム金属錯体 ([RuCl₅(NO)]²⁻) を溶質とし、1 ps よりも遅い FFTCF の減衰に関する知見を得た。NO 伸縮振動が他の分子内振動と比べ振動数が非常に高いため、振動緩和時間が長い。そのため FFTCF についての長時間 (~20 ps) の解析が可能となり、希薄水溶液中におけるイオン性分子の系として初めて 10 ps 程度の減衰が存在することを明らかにした。MD 計算による実験の再現を行い、遅い減衰の起源として配位子の性質に由来する静電相互作用が重要であることを示唆した。</p> <p>第5章ではアセトンからフルオレノン誘導体まで分子内の炭化水素基の大きさを段階的に変化させた溶質を用意し、その CO 伸縮振動の FFTCF の変化について議論した。その減衰の時定数は約 1 ps から 3 ps まで分子サイズに依存して増加し、温度依存性もまた溶質に依存することを示した。MD 計算より溶質周囲の水分子の配向の変化に伴う誘電環境の変化の重要性が示唆された。分子サイズが大きくなるほど局所的な誘電率は減少するため振動数揺らぎへ影響を及ぼす水分子の集団性が増大し、同時にその再配向過程が長くなることが明らかにされた。</p>			

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第6章では、励起した振動部位(CO基)と近傍の炭化水素基との相対位置関係が振動数揺らぎへ及ぼす影響を検討した。第5章で用いた溶質は全て振動軸方向に炭化水素基が存在するが、のものは軸方向から離れた位置に存在する。同程度の大きさの炭化水素基を有するにも拘わらず、第6章で測定したものは約1 psでFFTCFが減衰した。振動数揺らぎが振動プローブ近傍の水和環境に大きく依存することを示し、振動軸方向のポテンシャルエネルギーの揺らぎが炭化水素基による影響を受けないことが重要であることを示唆した。

第7章では温度応答性高分子を溶質として用い、その水和水のダイナミクスについて検討した。側鎖のCO基の伸縮振動の揺らぎを観測し、また比較として単量体単位に相当する溶質の揺らぎもまた評価した。これまで調べた系とは異なり、周囲の水和水だけでなく、溶質分子自身をもつ自由度の揺らぎの影響もまたFFTCFの数psの減衰に現れたと考えられた。さらに、複雑な挙動を示す高分子の揺らぎをMD計算によって再現し、高分子水溶液における早い水和水のダイナミクスを明らかにした。

当該論文では小さいイオン性・中性分子から高分子までを対象とし、水溶液中における水素結合ダイナミクス並びに振動数揺らぎについて分子レベルでの知見を得た。これらは幅広い系における水溶液中の局所的な分子間相互作用を理解する上で有用になると考えられる。

以上、本研究は水素結合性液体中の溶質分子について、非線形赤外分光を用いて振動ダイナミクスの精密測定を行い、さらに分子動力学シミュレーションにより分子レベルでの解析を行ったものであり、水素結合性液体中における溶質分子の振動ダイナミクスについて重要な知見を得たものとして価値ある集積であると認める。よって、学位申請者の藤井悠生は、博士(理学)の学位を得る資格があると認める。