पराद्रुत बहुविमीय स्पेक्ट्रमिकी

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2D अवरक्तन स्पेक्ट्रमिकी: पराद्रुत टाइम स्केल में आण्विक गतिकी के अन्वेषण की एक नवाचार तकनीक

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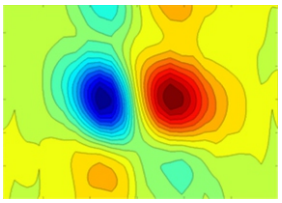

पानी का 2D स्पेक्ट्रा

सारांश

पराद्रुत 2D अवरक्त (2DIR) स्पेक्ट्रमिकी ने आण्विक गतिकी की हमारी समझ में क्रांतिकारी परिवर्तन किया है, जो जटिल वातावरण में अणुओं के संरचनात्मक और गतिशील गुणधर्मों के बारे में गहन जानकारी प्रदान करता है। यह लेख, विभिन्न सीमित माध्यमों में पानी के अणुओं की गतिशीलता को समझने के लिए 2DIR स्पेक्ट्रमिकी के स्वदेशी विकास और अनुप्रयोग पर प्रकाश डालता है।

मुख्य शब्द : पराद्रुत 2D अवरक्त स्पेक्ट्रमिकी आण्विक गतिकी ; हाइड्रोजन बंध ; सीमित जल प्रणालियां ; डीएमएसओ- जल मिश्रण।

Ultrafast Multidimensional Spectroscopy

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2D Infrared Spectroscopy: An Innovative Technique for Probing Molecular Dynamics in Ultrafast Time Scale

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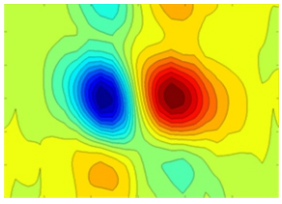

2D Spectra of Water

ABSTRACT

Ultrafast 2D infrared (2DIR) spectroscopy has revolutionized our understanding of molecular dynamics, offering deeper insight into the structural and dynamic properties of molecules within complex environments. This article highlights the indigenous development and application of 2DIR spectroscopy to understand the dynamics of water molecules in different confined media.

KEYWORDS: *Ultrafast 2D infrared spectroscopy, Molecular dynamics, Hydrogen bonding, Confined water systems, DMSO-water mixtures*

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Introduction

The exploration of molecular dynamics lies at the heart of deciphering the complex mechanisms driving chemical reactions, biological functions, and material properties. Traditional spectroscopic techniques often struggle with limitations when targeted for elucidating the intricate behavior of molecules on ultrafast timescales or within complex environments. Techniques such as nuclear magnetic resonance (NMR) and fluorescence spectroscopy, despite their invaluable contributions, offer a trade-off between temporal resolution and structural detail. This trade-off becomes particularly pronounced in scenarios involving rapid dynamic events in confined environments, such as electron transfer processes, protein folding, or solvent interactions, highlighting a critical gap in our experimental arsenal [1]. Ultrafast 2DIR spectroscopy emerges as a possible solution, bridging the experimental gap between time and structure resolution that has long constrained our ability to fully comprehend molecular dynamics [2]. Its unparalleled capacity for providing bond-specific structural resolution across a broad spectrum of timescales from femtoseconds to tens of picoseconds depending on the vibrational lifetime sets a new standard for spectroscopic inquiry [1]. The versatility of the technique extends to a wide array of samples, including dilute solutions, solid-state systems, and complex biological membranes, underscoring its universal applicability [3].

Ultrafast 2D infrared (2DIR) spectroscopy, pivotal since its inception in 1999, uniquely captures interactions between vibrational modes, manifested as infrared bands and cross-peaks, which serve as molecular fingerprints. This technique integrates experimental data with molecular dynamics simulations, offering profound insights into molecular structures and transient states with high temporal and spectral resolution. It is particularly transformative in studying the dynamic behaviors of water molecules in confined environments like reverse micelles(RMs) or biological systems, and in tracking solvent dynamics, electron transfer, and interactions at interfaces or within chemical reactions and protein folding processes. The extensive applications of 2DIR spectroscopy range from materials science to life sciences, interrogating protein, enzyme, and DNA dynamics in solutions, and advancing our understanding of complex chemical systems and disease mechanisms. This integration into interdisciplinary research continues to catalyze significant scientific breakthroughs, influencing fields from drug discovery to the design of novel biomaterials[4].

Experimental Set-up

A Fourier transform spectroscopy-based two-dimensional infrared (2DIR) spectrometer (cf. Fig.1a) was developed indigenously for the first time in India around an amplified femtosecond laser system (800 nm, 1 mJ, 1 kHz)[5]. Two optical parametric amplifiers (OPA) in combination with difference frequency generator (DFG) were used to create mid-IR (3-10 μm) femtosecond pulses. A schematic diagram of the 2DIR setup developed in Chemistry Group, BARC is presented in Fig. 1b. The mid IR pulse from DFG was divided into pump (~ 96%) and probe (~ 4%) pulses using a CaF_2 wedge window. A simple Mach-Zehnder interferometer was used to create a collinear pump pair using two CaF_2 based 50:50 beam splitters ensuring uniform dispersion for both pump pulses. One of the pump pulses was traversed through a computer controlled retroreflector to control the time-delay between two collinear pump (τ). The interference between pump pulses was monitored through signal intensity fluctuations with τ using a PbSe photodiode. The probe pulse was directed through another retroreflector on a computer-regulated translational stage defining the pump-probe delay (T_w), also known as waiting time.

Both pump and probe pulses was focused onto the sample using a 2-inch off-axis parabolic (OAP) mirror and subsequently made parallel using a similar OAP mirror. The probe beam was detected using an Mercury Cadmium Telluride (MCT) dual array detector after passing through a scanning monochromator. The precise spatial overlapping of the pump and probe beams at the sample was ascertained using a pinhole (0.1 mm) on a XYZ translation stage, while their temporal alignment was monitored via the nonlinear signal produced in a 50 μm thick Germanium window. The sample, positioned between two CaF_2 windows with a 50 μM Teflon spacer, was subject to data collection by varying the time delay between pump pair pulses (τ) in 4 fs increments for a given T_w. The interferogram, generated as a function of the τ-axis upon Fourier transformation, generated the excitation frequency within the 2DIR spectrum.

Results and Discussion

Water is crucial in almost all chemical and biological processes happening on the earth, particularly at the solid-liquid interface, impacting heterogeneous catalysis and biomolecular activity in ion channels. At these interfaces, it shows significant changes in hydrogen bonding due to the disruption from the interface, leading to unique molecular

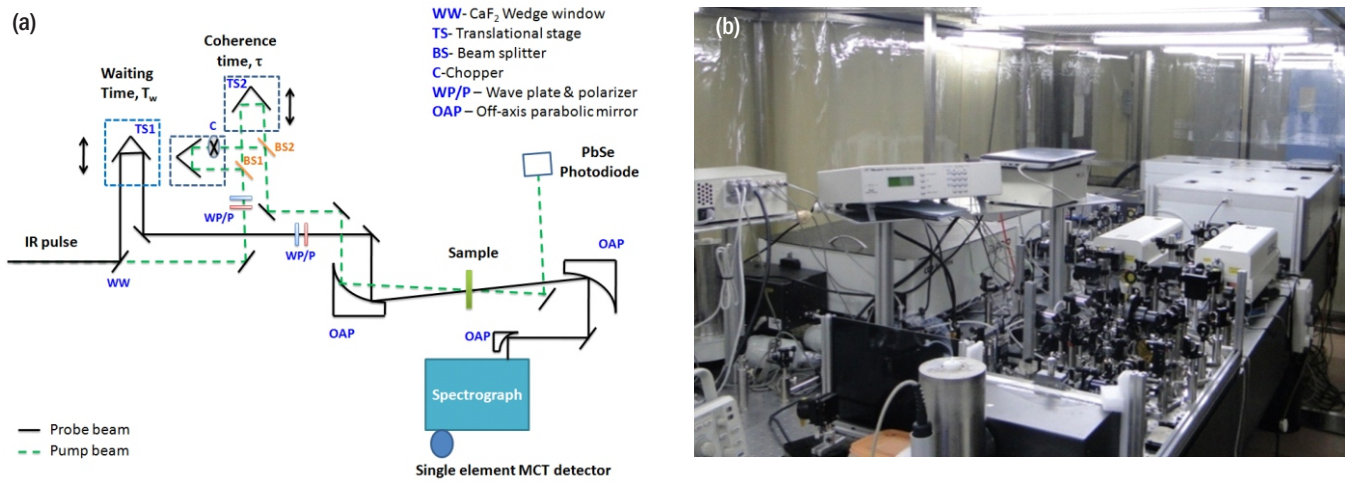

Fig.1: (a) Optical lay-out and (b) Photo of the 2DIR spectrometer developed in Chemistry Group, BARC.

behaviors [6]. Although extensively studied, many questions remain about the changes in the structure and dynamics of interfacial water, especially how these perturbations extend from the interface to resemble bulk combine these two paragraphs.

The dynamics of water at various chemical and biological interfaces have been extensively investigated to understand the impact of the chemical nature of these interfaces on the structure and hydrogen bond dynamics of water [7-8]. Traditional spectroscopic methods such as time-dependent fluorescence Stokes' shift (TDFSS) have been widely used to explore these dynamics [9-10]. However, TDFSS is limited by the size of the fluorescent probe used which are unable to predict actual dynamics of water due to the use of large probe molecules which perturb the system largely from its equilibrium configuration [9]. Further, the involvement of excited state molecules also make the system far from equilibrium.

To address these limitations, time-resolved vibrational spectroscopy, particularly infrared (IR) spectroscopy, offers a more refined approach. Unlike electronic excitation in TDFSS, vibrational excitation in IR spectroscopy causes negligible perturbation to the molecular system, allowing studies under thermal equilibrium conditions [11]. While time-resolved IR spectroscopy has improved our understanding of the hydrogen bond structure and re-orientational dynamics of interfacial water, it often lacks sensitivity to subtle molecular motions. The advent of 2DIR spectroscopy has revolutionized this field. With its ability to disperse spectral information across two dimensions coupled with ultrafast time resolution, 2DIR spectroscopy excels in unraveling complex structural and dynamic information in intricate environments [1].

Dynamics of water in AOT reverse micelle

The power of 2DIR spectroscopy to unravel the complexities of confined water dynamics is exemplified in its application to study water in AOT RMs. These micelles serve as a model system for biological water, offering a controlled environment to investigate the influence of confinement on the structural and dynamic properties of water. The study involved a detailed investigation into the dynamic behavior of water confined within Aerosol-OT (AOT) RMs, utilizing ultrafast 2DIR spectroscopy. Through the use of azide ions as an ultrasmall infrared (IR) probe, the study reveals critical insights into how molecular dynamics of water are altered by confinement, thereby challenging the prevailing notion that water in smaller RMs behaves akin to bulk water [5].

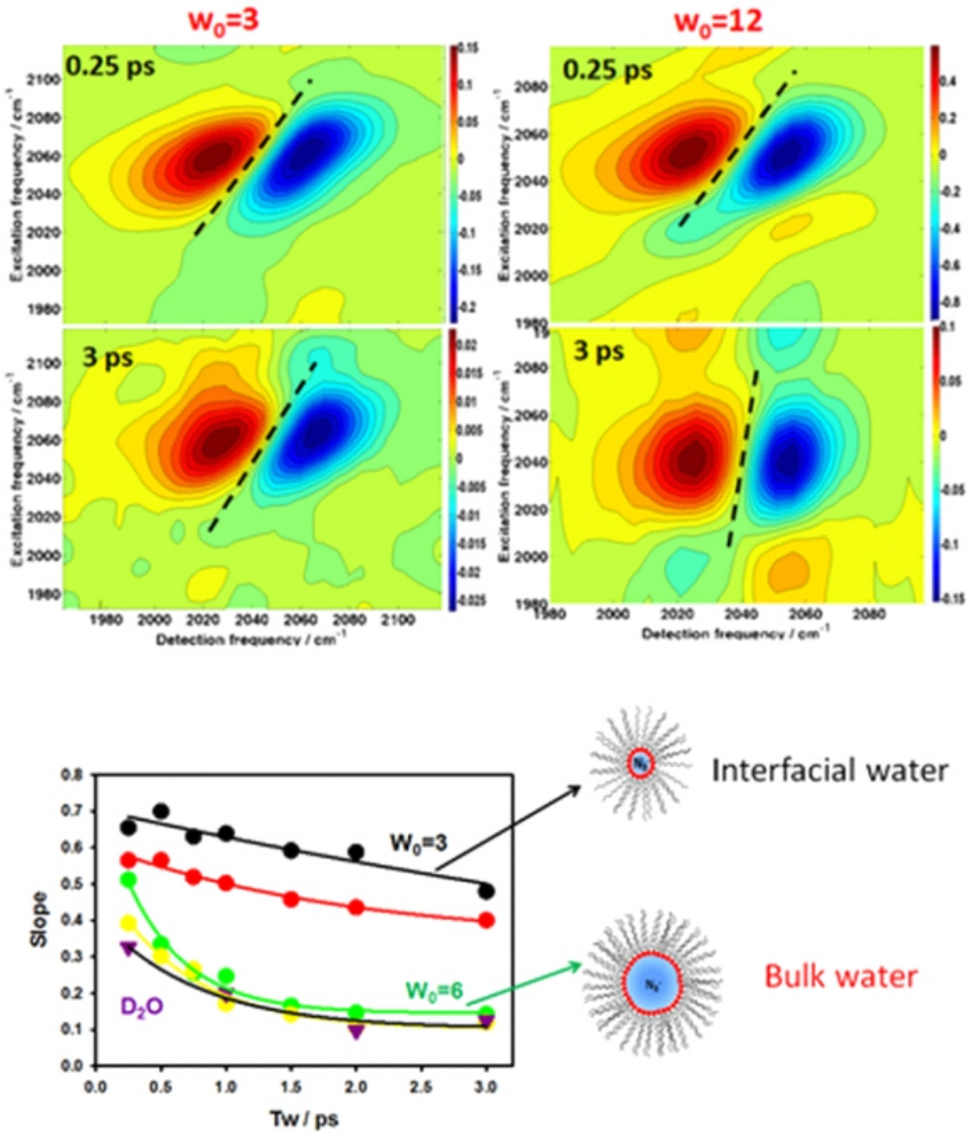

Fig.2: Upper panel: 2DIR spectra for antisymmetric stretch of azide in AOT RMs for w_0=3 (left) and w_0=12 (right) at waiting time of T_w= 0.25 ps (top) and 3 ps (bottom) the parameter w0 is defined as the ratio of water concentration to surfactant concentration, [H2O]/[AOT]. Lower panel: Variation in slope as a function of waiting time for w_0=3 (D_w = 2 nm), w_0=4.5 (D_w = 2.45 nm), w_0=6 (D_w = 2.9 nm), w_0=12 (D_w = 4.7 nm) and bulk D_2O.

Initial experiments on linear IR spectroscopy and vibrational lifetime measurements of azide ions in various sized AOT RMs revealed shifts in spectral features like peak position and width with changes in the water pool's radius, suggesting environmental variations for the azide ion. Despite these shifts, the vibrational lifetime of the azide ion remained consistent across different water pool sizes [5]. This suggested that azide ions were centrally located in the water pools, similar to bulk water, although this interpretation did not fully account for the complex dynamics of confined water molecules, especially hydrogen bond reorganization dynamics.

Notably, 2DIR spectroscopy revealed that for smaller water pools, the dynamics and structural characteristics of water molecules deviated substantially from those of bulk water. This observation starkly contrasted with previous interpretations based on vibrational lifetime measurements, underscoring the enhanced sensitivity of 2DIR spectroscopy to the complexities of confined water dynamics. 2DIR spectra analysis at various waiting times for different water pool sizes uncovered a pronounced sensitivity of the frequency-frequency correlation function (FFCF) to the size of the water pool. For smaller water pools (diameter, D_w = 2 nm), the FFCF measurements indicated a significant slowdown in the hydrogen bond reorganization dynamics compared to bulk water [5]. This slowdown was attributed to the confinement effects exerted by the interface of the Rms on the water molecules, a phenomenon that becomes progressively less pronounced as the size of the water pool increases [5]. The findings of this study through 2DIR spectroscopy illuminate the profound impact of confinement on molecular dynamics of water within RMs. Unlike vibrational lifetime measurements, which could not differentiate between the dynamics of water molecules in small and large water pools, 2DIR spectroscopy provided compelling evidence of the unique behavior of confined water. This behavior includes the extensive slowdown of hydrogen bond relaxation dynamics in smaller water pools, highlighting the superiority of the technique in capturing the subtle dynamics of confined water molecules. Moreover, the study advocates for the use of ultrasmall IR probes, like the azide ion, in investigating the dynamics of biologically relevant confined water molecules [5].

Investigation of H-bond Dynamics in DMSO-water mixture

In another study, we embarked on a comprehensive exploration of the structural dynamics within aqueous solutions of dimethyl sulfoxide (DMSO) and water, employing sodium nitroprusside (SNP) as a local vibrational probe [12]. Through a combination of infrared (IR) absorption spectroscopy, vibrational pump-probe spectroscopy, and 2DIR, the research illuminates the complex interplay of molecular interactions that define the behavior of DMSO-water mixtures, highlighting the presence of two distinct anomalous regions of hydrogen bond dynamics that were hitherto not fully elucidated by previous studies [12].

The study meticulously identified two anomalous concentration regions within the DMSO-water mixtures, characterized by distinctive hydrogen bond dynamics. The first region, occurring at a DMSO mole fraction (X_{DMSO}) of approximately 0.2, and the second region, around X_{DMSO} of 0.4, signify the existence of varied hydrogen-bonded structures influenced by the concentration of DMSO. 2DIR spectroscopy furnished a detailed perspective on the time scales of hydrogen bond reorganization dynamics across different compositions of the DMSO-water mixture. The study notably highlighted the slower dynamics in intermediate DMSO concentrations and elucidated the structural dynamics in both anomalous regions, which had remained elusive in prior

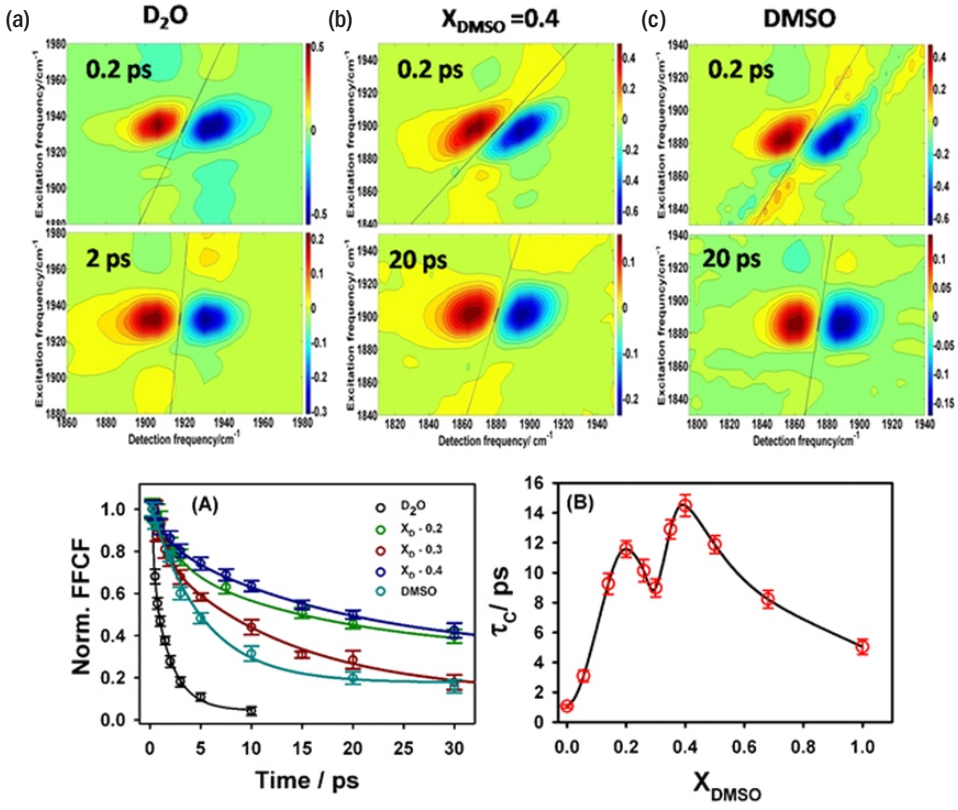

Fig.3: 2D-IR spectra of nitrosyl band of SNP in (a) D_2O at waiting times of 0.2 and 2 ps (b) In DMSO-water with X_{DMSO}~0.4 at waiting times 0.2 and 20 ps. (c) in DMSO at waiting times 0.2 ps (upper panel) and 20 ps (lower panel). (A) The FFCF decays of SNP in DMSO-D_2O solvents at various compositions. Circles represent the data points and solid lines represent their multi-exponential fits. (B) Variation in the correlation time with X_{DMSO}. The error bars represent the standard deviation of the measurements (n=3).

investigations. The analysis of FFCF decay times provided a nuanced understanding of the hydrogen bonding dynamics and the structural heterogeneity within the mixtures [12].

In summary, this research presents a pioneering examination of the structural dynamics and hydrogen bond interactions within DMSO-water mixtures, leveraging the sensitivity of SNP as a vibrational probe. The discovery of two anomalous regions of hydrogen bond dynamics enriches our understanding of the molecular mechanisms underpinning the unique properties of these mixtures [12].

Conclusion and Future Perspectives

Our studies have shown significant deviations in the behavior of water molecules confined within AOT reverse micelles, notably a slowdown in hydrogen bond reorganization dynamics compared to bulk water. This demonstrates the profound impact of confinement on molecular dynamics and highlights the capability of 2DIR spectroscopy to detect subtle molecular phenomena. Additionally, our research into DMSO-water mixtures has identified regions with unique hydrogen bond dynamics, offering new insights into molecular interactions in these mixtures. The use of 2DIR spectroscopy has proven invaluable in deciphering molecular dynamics, enhancing our understanding of chemical and biological systems. Looking forward, one potential direction is to extend 2DIR spectroscopy to other confined systems like biological membranes or nanostructured materials, potentially impacting drug delivery and materials science. This technique could also investigate electrolyte behaviors in supercapacitors or charge dynamics in photovoltaic materials, aiding in the development of efficient energy systems.

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