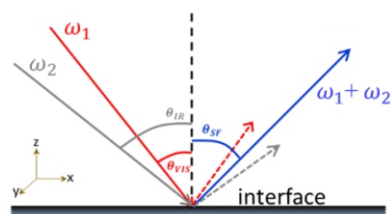


अंतरापृष्ठ पर स्पेक्ट्रमिकी

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पराद्भूत लेजर का उपयोग करके सॉफ्ट अंतरापृष्ठ पर अंतरापृष्ठ-चयनात्मक अरेख स्पेक्ट्रमिकी

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इंटरफेस पर सम फ्रीक्वेंसी पीढ़ी

ABSTRACT

अंतरापृष्ठ पर रसायन विज्ञान, जहां दो अमिश्रणीय स्थूल माध्यम मिलते हैं, विषमदेशिक वातावरण के कारण स्थूल चरणों से काफी भिन्न होते हैं। अंतरापृष्ठ-चयनात्मक स्पेक्ट्रमदर्शिकी, विशेष रूप से कंपन योग आवृत्ति जनन (वीएसएफजी), अंतरापृष्ठ पर आण्विक व्यवहार में अंतर्दृष्टि प्रदान करता है। वीएसएफजी, जैसे कि तरल सतह "नरम अंतरापृष्ठ" के लिए विशिष्ट रूप से अनुकूल है, कंपन संक्रमणों के माध्यम से अणुओं की अंतरापृष्ठ-चयनात्मक अन्वेषण को सक्षम बनाता है। चयनात्मकता की कमी या कठोर परिस्थितियों से बाधित पारंपरिक तरीकों के विपरीत, वीएसएफजी ऐसे नरम अंतरापृष्ठ की विशेषता बताने में उत्कृष्ट है। यहां, हम वीएसएफजी के सिद्धांत की रूपरेखा तैयार करेंगे, इसकी अंतरापृष्ठ-चयनात्मकता का पता लगाएंगे, और जलीय अंतरापृष्ठ पर पर्यावरण और जैविक अध्ययनों में इसके अनुप्रयोगों पर चर्चा करेंगे।

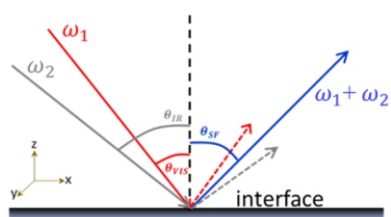
मुख्य शब्द : सतह और अंतरापृष्ठ, कंपन योग आवृत्ति उत्पादन (वीएसएफजी), स्थायी कार्बनिक प्रदूषक (पीओपी), फॉस्फोलिपिड।

Spectroscopy at Interface

7

Interface-Selective Nonlinear Spectroscopy at Soft Interfaces using Ultrafast Laser

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Sum frequency generation at interface

ABSTRACT

Chemistry at interfaces, where two immiscible bulk media meet, differs significantly from the bulk phases due to the anisotropic environment. Interface-selective spectroscopy, particularly vibrational sum frequency generation (VSFG), offers insights into molecular behaviors at interface. VSFG, uniquely suited for "soft interfaces" like liquid surfaces, enables interface-selective probing of molecules through vibrational transitions. Unlike traditional methods hindered by lack of selectivity or stringent conditions, VSFG excels at characterizing such soft interfaces. Here, we outline the theory of VSFG, explores its interface-selectivity, and discusses its applications in environmental and biological studies at aqueous interfaces.

KEYWORDS: Surface and Interface, Vibrational sum frequency generation (VSFG), Persistent organic pollutant (POP), Phospholipid

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Introduction

Interfacial chemistry is associated with intricate molecular interactions transpiring at the juncture between two immiscible media, where the symmetries of bulk materials are disrupted. With water pervading as Earth’s most abundant liquid, aqueous interfaces manifest ubiquitously across biotic and abiotic realms, from the ocean’s surface (air-water interface) to mineral surfaces (gas-solid or liquid-solid interface), and within cellular domains (lipid or protein-water interface). Water as well as other reactants exhibit preferential orientation and non-uniform distribution across interfaces, leading to the various interface-selective physicochemical phenomena. Achieving a molecular-level comprehension of these interfacial processes necessitates precise probing of interface with molecular specificity.

Even-order nonlinear spectroscopy, such as Vibrational Sum Frequency Generation (VSFG), emerges as a potent tool for interface-selective analysis of molecular interactions under ambient conditions. [1] Recent advancements, like phase-sensitive i.e., heterodyne detected-VSFG, enable precise recording of absorption spectra and absolute orientation of interfacial molecules. [2]

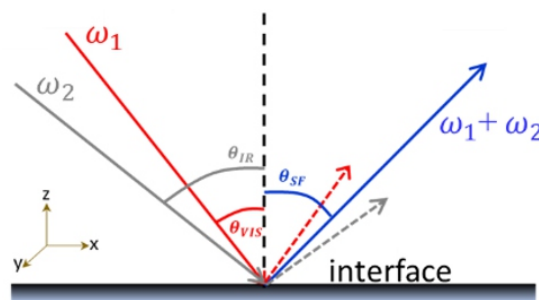
Theory of Vibrational Sum Frequency Generation (VSFG) and Interface-selective Spectroscopy

VSFG is one of the outcomes of nonlinear interaction of light with matter. The second-order polarization, P^2 generates the sum frequency signal from an anisotropic media where the constituting molecules have a preferred orientation.

$$P^{(2)} = \epsilon_0 \chi^{(2)} E_{\omega_1} E_{\omega_2} \tag{1}$$

where, ϵ_0 is the dielectric constant in vacuum; $\chi^{(2)}$ is the second-order electric susceptibility corresponding to the molecular hyper-polarizability, E_{ω_1} and E_{ω_2} are the electric fields of the interacting intense lights having angular frequencies ω_1 and ω_2 , respectively. The spectroscopy associated with $P^{(2)}$ or with the higher order polarizations (e.g., $P^{(3)}$, $P^{(4)}$ etc) are known as *nonlinear spectroscopy*. For an isotropic medium, $\chi^{(2)} = 0$ and hence, $P^{(2)} = 0$. Thus, in a centrosymmetric media, which is the case with isotropic bulk media, there is no VSFG signal, under electric-dipole (ED) approximation. However, at an interface, the inversion symmetry breaks down and $\chi^{(2)} \neq 0$ and hence $P^{(2)} \neq 0$. In other words, the sum frequency signal is generated only at the interface, making VSFG an inherently interface specific nonlinear spectroscopy technique (Scheme I). In reflection geometry, the sum frequency is generated at a

particular direction (θ_{SF}) which is different from the reflection angles of ω_1 and ω_2 . This has a technical advantage in selective detection of the SFG signal by spatial separation from the ω_1 and ω_2 .



Scheme I: Sum frequency generation (SFG) at interface in non-collinear reflection geometry.

Following equation (1), the intensity of the sum frequency light can be expressed as [3]

$$I_{SFG} \propto |P^{(2)}|^2 \propto |\chi^{(2)}|^2 I_{\omega_1} I_{\omega_2}$$

Or

$$\frac{I_{SFG}}{I_{\omega_1} I_{\omega_2}} \propto |\chi^{(2)}|^2 \tag{2}$$

Thus, a plot $\frac{I_{SFG}}{I_{\omega_1} I_{\omega_2}}$ against ω_2 (let ω_2 correlates to the vibrational transition of interfacial molecules and hence corresponds to IR light) provides the squared- $\chi^{(2)}$ spectrum of interfacial molecules. This is what is done in conventional VSFG measurement. The VSFG-intensity spectra at different polarization combinations (SSP, SPS, PSS and PPP) are used to deduce information about orientational distribution of interfacial molecules. [4] In the case of phase-sensitive VSFG, the sum frequency is detected by interferometric method, known as heterodyne-detection. The heterodyne-detection provides the real and imaginary components of $\chi^{(2)}$ independently.

Broadband Heterodyne-Detected VSFG Spectrometer Based on a Femtosecond Laser System

Fig.1 shows a picture of the broadband HD-VSFG setup at Radiation & Photochemistry Division, Chemistry Group, BARC. The spectrometer is based on a femtosecond Ti:sapphire amplified laser system with specifications: central wavelength 800 nm, pulse width ~50 femtosecond, energy

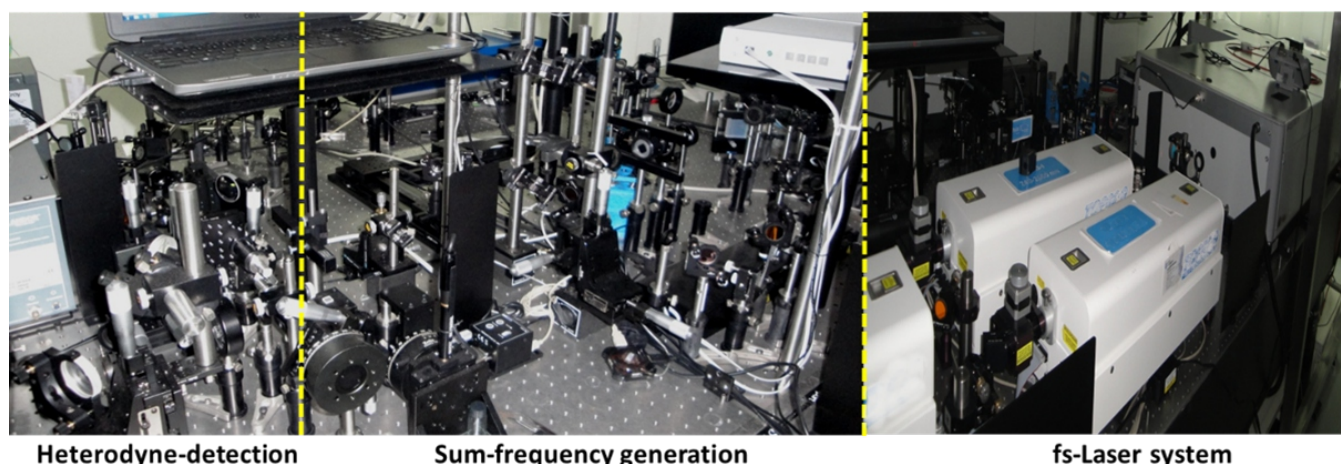


Fig.1: Indigenously developed broadband HD-VSFG setup at Radiation & Photochemistry Division, Chemistry Group, BARC. The spectrometer is based on a femtosecond Ti:Sapphire amplified laser system.

~3mJ/pulse, and pulse repetition rate 1.0 kHz. One part of the amplified output (~ 1 mJ/pulse) is passed through a narrow band pass filter (center wavelength 800 nm) that converts the broad band femtosecond pulse into a narrow band picosecond pulse (fwhm ~ 16 cm⁻¹, energy ~ 15 μJ/pulse), known as the visible pulse (ω_{vis} or ω₁). The second part of the amplifier output (~ 1 mJ/pulse) is frequency converted to a broad band IR pulse (ω_{IR} or ω₂ pulse; fwhm ~ 300 cm⁻¹ @ 3400 cm⁻¹) using an optical parametric amplifier (OPA) followed by a difference frequency generator (DFG). The spatio-temporal overlap of the ω₁ and ω₂ pulses on the sample surface generates the sum frequency signal. For the *heterodyne detection* of the generated sum frequency, it is mixed with a local oscillator (LO) signal which has a constant phase-difference from that of the former. The mixing generates an interference pattern. The interference pattern from the sample surface is compared with that from a reference surface (Z-cut quartz) to obtain the *Re* [X⁽²⁾] and *Im* [X⁽²⁾] spectra [5,6] The *Im* [X⁽²⁾] spectrum thus obtained provides the accurate absorption characteristics of interfacial molecules while the real component, *Re* [X⁽²⁾], shows a dispersive band shape. Thus, unlike in conventional VSFG spectroscopy, the sign of X⁽²⁾ is retained in the *Im* [X⁽²⁾] spectra, which reveals the absolute orientation of molecule at the interface. [7]

Interaction of Perfluorinated Persistent Organic Pollutant (f-POP) with Biological Lipid Monolayer/Water Interface

This section discusses the interfacial interaction of perfluorinated persistent organic pollutant (f-POP) with biological lipids and their surface prevalence using heterodyne detected VSFG spectroscopy. Unlike a degradable pollutant which has a short-term effect on the environment, persistent organic pollutants (POPs) have a long-term effect on aqueous interface and the associated biotic/abiotic systems. Cationic lipid, 1,2-dipalmitoyl-3-trimethylammonium-propane (DPTAP), monolayer/water interface shows an intense negative band in 3000 – 3560 cm⁻¹ region and a positive band above 3600 cm⁻¹ (Fig.2) which corresponds to the H-down oriented water (3000 – 3560 cm⁻¹) in the electric double layer (EDL) generated by cationic head group of DPTAP and the H-up oriented weakly interacting topmost water (> 3600 cm⁻¹) above the lipid head group region, respectively. [8,9] In presence of

perfluorohexanoic acid (PFHA), amplitude of the OH stretch signal is significantly reduced (red curve, Fig.2) due to neutralization of the surface charge by the anionic carboxyl group of PFHA, making the DPTAP/water interface nearly net neutral. The amplitude of the weakly interacting OH (above 3600 cm⁻¹) is also reduced in the presence of PFHA, which indicates that PFHA not only affects the water below the DPTAP head group (EDL associated water) but also the topmost water in the hydrophobic region of DPTAP monolayer. These perturbations are qualitatively similar to that of NaCl at the DPTAP interface (compare the purple and red curves, Fig.2).

The anionic lipid, 1,2-Dipalmitoyl-sn-glycero-3-phosphoglycerol (DPPG), monolayer/water interface (black curve, Fig.3) shows an intense positive band in 3000 – 3600 cm⁻¹ region and a negative band above 3600 cm⁻¹, pertaining to the H-up oriented water in the EDL and the H-down oriented weakly interacting water (>3600 cm⁻¹) in the hydrophobic region above the lipid head group. In the presence of PFHA, the water signal is decreased at the DPPG/water interface. From the perspective of electrostatics, this is unexpected as the head groups of both DPPG and PFHA are negatively charged. These observations suggest that PFHA exhibits different modes of interactions with DPPG than that with DPTAP at the aqueous interface.

We propose an acid-base reaction between DPPG and PFHA (dppg-PO₄⁻ + pfha-COOH ⇌ dppg-PO₄H⁺ + pfha-COO⁻) as the reason of such observation at the interface. The neutralization reaction makes the DPPG/water interface effectively uncharged. In addition, the oleophobic perfluorinated alkyl chain of PFHA⁻ experience repulsive interaction with the alkyl chains of the lipid. Hence, PFHA⁻ is expelled from the DPPG/water interface. [10]

Summary

Vibrational Sum Frequency Generation (VSFG) spectroscopy is an inherently interface-selective technique applicable at ambient condition to variety of surfaces and interfaces that are accessible to light. This technique provides a deeper understanding of the structure and orientation of molecules at surface and interface. Study of the f-POP-lipid/water interface as discussed here for example, demonstrates head group-specific interaction of f-POP with biological lipids at

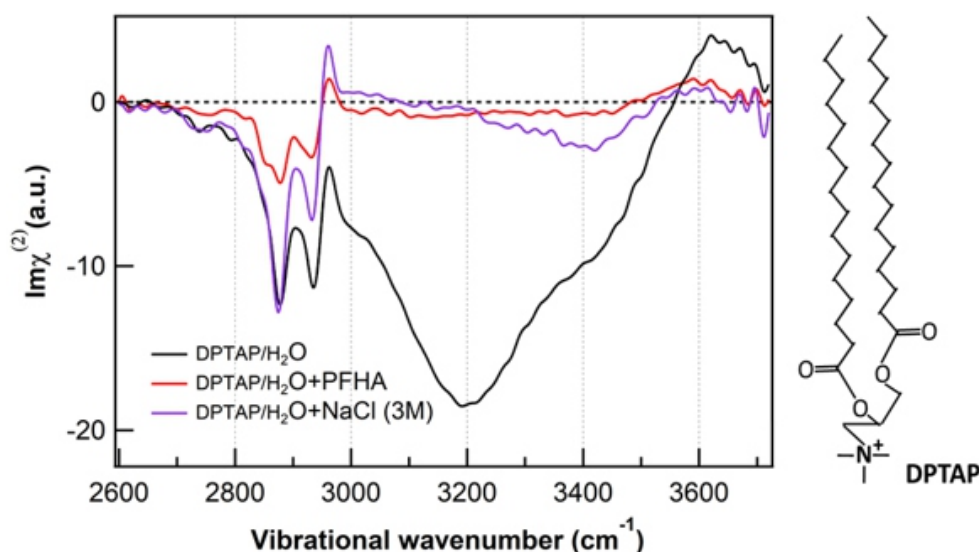


Fig.2: Effect of PFHA and NaCl (3.0 M) on the *Im*χ⁽²⁾ spectrum of the anionic DPPG monolayer/water interface (Surface pressure 30 ± 2 mN/m). Adapted with permission from ref 10.

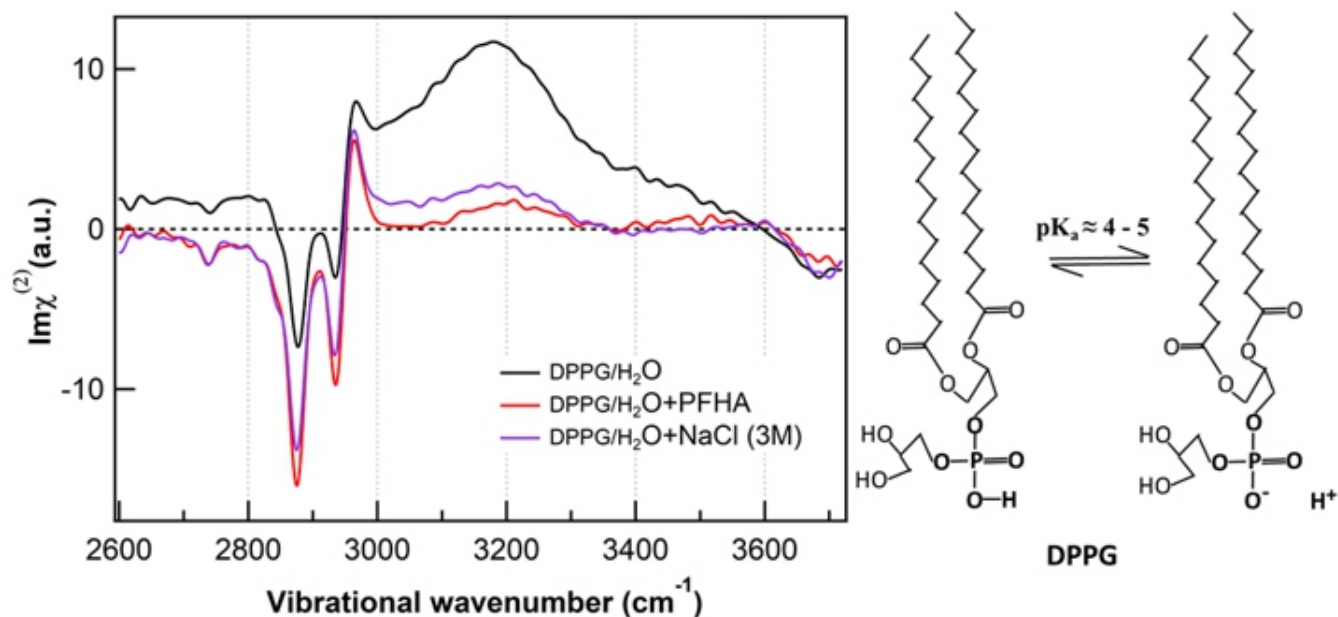


Fig.3: Effect of PFHA and NaCl (3.0 M) on the $Im\chi^{(2)}$ spectrum of the anionic DPPG monolayer/water interface (Surface pressure 30 ± 2 mN/m). Adapted with permission from ref 10.

aqueous interface. Specifically, the expulsion or penetration of PFHA into the phospholipid monolayer depends on the charge and chemical nature (e.g., pK_a) of the lipid head group, which has implications to the f-POP-induced perturbation of membrane fluidity and transmembrane electric potential.

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