

The 2012 Colin Garfield Fink Summer Research Fellowship — Summary Report

Nonlinear Vibrational Spectroscopy
of High Frequency Bands of Interfacial Species

by Devika Sil

Obtaining molecular level information, with interface specificity, is challenging. If the species of interest are present in the bulk and at the interface, the bulk response typically overwhelms the response of the few layers of molecules present at the interface. Second order nonlinear optical techniques, such as Sum Frequency Generation (SFG) and Second Harmonic Generation (SHG), are exclusively allowed in media lacking inversion symmetry, interface between two isotropic environments being an example (Fig. 1). SFG and SHG are therefore inherently surface specific. These methods are also non invasive, and can probe surfaces *in situ*. SHG has been used to investigate the electronic spectroscopy of interfaces, whereas SFG has been extensively applied as an interfacial vibrational spectroscopic tool for detecting OH, CH, NH stretches of surface bound species.

The question arises as to why SHG has not been used to probe the vibrational transitions of surface species. The answer is that the fundamental vibrational modes are in the mid- IR (e.g., OH stretch at ~ 3000 nm) so that the second harmonic lies at wavelengths (i.e., ~ 1500 nm for vSHG of OH stretch) where single photon detection is challenging. SHG of the combination and overtone bands (transitions where change in vibrational quantum number is greater than ± 1) lies in regions of the near-IR (< 1100 nm) where efficient single photon detectors, e.g., Si based CCD, are available. Overtone transitions are orders of magnitude weaker than fundamental modes, making them difficult to detect. However, these high frequency transitions can reveal information not otherwise accessible, e.g., anharmonicity and bond dissociation energy reflecting the affinity of a particular hydroxyl group to proton exchange which provides access to the acidity/basicity of the hydroxyls.

We, for the first time, have used vSHG to detect the low cross section, overtones of interfacial OH ($6000\text{--}7700\text{ cm}^{-1}$ $1666\text{--}1333$ nm) at silica water interfaces, a system of interest to disciplines as diverse as geochemistry and semiconductor device processing. A broadband IR pulse generated from potassium-titanyl phosphate (KTiOPO_4 , KTP) based non-collinear Optical Parametric Amplifier (NOPA) was used to generate the second harmonic response at the interface. The broad spectral

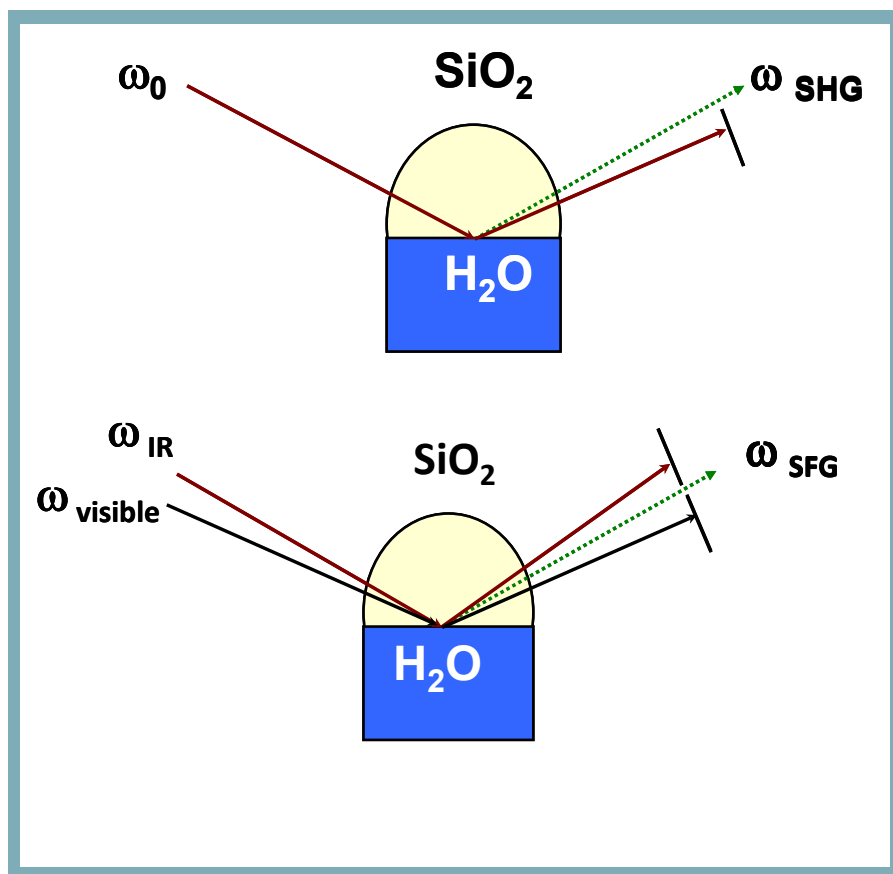


FIG. 1. Schematic of SHG and SFG at a mineral water interface.

output covered entire wavelength region of interest so that no tuning of the NOPA was required to capture SHG spectra of OH overtone region.

SiO_2 has surface bound silanols which can react with solution phase hydroxide ions to produce SiO^- at high pH. Consequently, as pH increases the interfaces become more negatively charged, inducing polar ordering of interfacial water thereby increasing the SHG intensity (Fig. 2). The first overtone of OH stretch may prove to be a more reliable probe of aqueous interfacial hydrogen bonding as it is not subject to the Fermi resonance that has plagued the interpretation of SFG of fundamental OH stretch at aqueous interfaces. It is evident that as pH is increased the peak red shifts, indicative of increased hydrogen bonding. In conclusion, these results illustrate the implementation

of a novel surface spectroscopy, vibrational second harmonic generation, and its use in the detection of high frequency low cross-section OH overtones. We anticipate that vSHG will develop as a useful and versatile tool for interfacial spectroscopic analysis.

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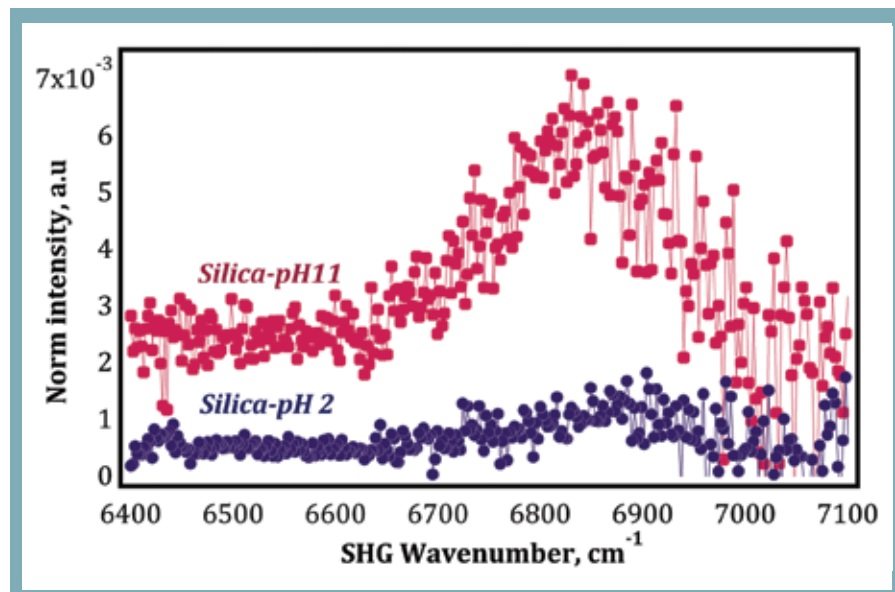


Fig 2. Normalized SHG generated at a silica-water interface at pH 2 and 11 in the spectral region of the first overtone of interfacial OH ($6000\text{--}7700\text{cm}^{-1}$, $1666\text{--}1333\text{ nm}$).

About the Author

DEVIKA SIL is a third year graduate student in the Department of Chemistry at Temple University. She works with Eric Borguet. Her research interests are in interfacial chemistry and material science. She is developing novel surface-sensitive vibrational spectroscopic techniques for detecting high frequency, vibrational overtone, and combination bands from mineral aqueous interfaces. In addition, she leads the sensor research team in the Borguet group, exploring thin films on surface acoustic wave (SAW) devices for the detection of chemical agents. Sil may be reached at devika.sil@temple.edu.

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