Master 2 Internship

Title: Charged aqueous interfaces studied by Second Harmonic and Sum Frequency Generation

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Project:

Abstract

Interfaces of water and aqueous solutions play a prominent role in many technological and natural processes. The liquid/solid interface is the main driver for many electrochemical reactions. Water being present everywhere; the fields of applications are numerous. The adsorption and release of various gases by the oceans and rain droplets is one of them. The aim of this project is to study the interactions between water and charged interfaces. We will establish an advanced nonlinear optical spectroscopy setup and combine it with terahertz excitation, thus revealing the vibrational properties of the interface and controlling the surface charge via the terahertz electromagnetic field. We will first develop and validate the technique on water and will then proceed in applying the technique to study various aqueous interfaces such as fatty acid/water systems, lipid/water interface, mineral oxide/water interfaces.

Objectives and overview of the project

The main idea of this project is to develop a hybridized Second harmonic generation (SHG)/ sum frequency generation (SFG) spectroscopy to study vibrational modes for aqueous interfaces. One of our goal is to develop a method based on Terahertz field-induced surface charging and study its consequent interface dynamics through SFG/SHG spectroscopies. This technic will be applied to study the air/water interface by SHG/SHG.

By taking account definitions of both nonlinear properties and the electric double layer, one can express the effective surface nonlinear susceptibility $\chi^{(2)}_{S,eff}(\omega_0;\omega_1,\omega_2)$ where $\omega_0 = (\omega_1+\omega_2)$ is the sum-frequency for the two incident beams as[14]: $\chi^{(2)}_{S,eff} = \chi^{(2)}_{S} + \chi^{(2)}_{DL}$

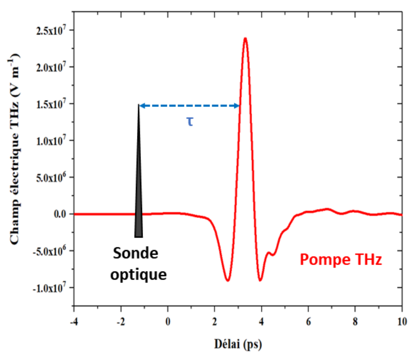
$$\chi^{(2)}_{DL} \equiv \int_0^\infty \chi^{(3)}_B.\hat{z}.E_0(z')e^{i\Delta k_z z'}dz' \equiv \chi^{(3)}_B.\hat{z}.\psi,$$

with

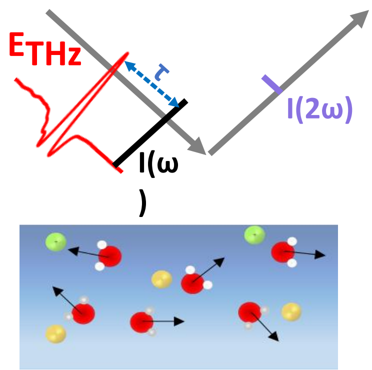
$$\psi \equiv \int_0^\infty E_0(z')e^{i\Delta k_z z'}dz'$$

, $\chi^{(3)}_B$ denoting the third-order bulk nonlinear susceptibility of water, $E_0(z')$ the surface electric field distribution, Δk_z describing the phase mismatch of reflected SFG, $\chi^{(2)}_S$ and $\chi^{(2)}_{DL}$ acting as surface nonlinear susceptibilities of the Stern layer and the diffuse layer, respectively. It is worth noticing that the reflected SF signal is then proportional to the effective surface nonlinear susceptibility. $\chi_S^{(2)}(\omega_{IR})$ spectrum gives the molecular vibrational strength and structural information about the network bonding in the Stern layer. $\chi_{DL}^{(2)}(\omega_{IR})$ offers quantitative information about the surface charge density σ, since it arises from the charge distribution in the diffuse Layer due to $E_0(z')$. To get the global understanding of the interfacial processes, both $\chi_S^{(2)}$ and $\chi_{DL}^{(2)}$ are needed.

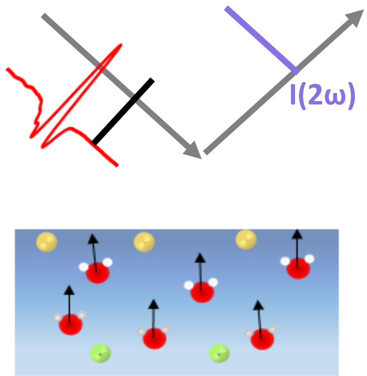
To prove the physical concept, we shall start this project by measuring, as mentioned previously, the surface nonlinear signal $\chi_{S,eff}^{(2)}$ for a charged interface and control the surface charge thanks to a intense THz field focus at the interface. We already built an SHG optical setup, and before the internship the THz beam will be implemented. During the internship, you will first study the water structure dynamics through SHG measurements. The second step will be the SFG setup implementation, i.e. adding an IR beam light. You will then be able to study the microscopic water structure, deduce the vibrational spectra of the Stern layer at the air/water interface as a function of electric field *for the first time* without adding any chemical, providing microscopic insight into the interfacial bonding structure at the air/water interface.



Pump THz – Probe SHG



Pump-Probe out of phase : Properties of the neat interface



Pump-Probe in phase : Properties of the bulk

References

1. Wen, Y.-C.; Zha, S.; Liu, X.; Yang, S.; Guo, P.; Shi, G.; Fang, H.; Shen, Y. R.; Tian, C., Unveiling Microscopic Structures of Charged Water Interfaces by Surface-Specific Vibrational Spectroscopy. *Physical Review Letters* 2016, *116*, 016101.
2. Dalstein, L.; Chiang, K.-Y.; Wen, Y.-C., Direct Quantification of Water Surface Charge by Phase-Sensitive Second Harmonic Spectroscopy. *The Journal of Physical Chemistry Letters* 2019, *10*,5200-5205.