

# **Molecular organization at charged solid-water interfaces: vSFG $\chi(2)(\omega)$ signal, $\chi(3)(\omega)$ contribution and how to use them for revealing interfacial structures**

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The understanding of the molecular organization at solid-water interfaces is a mandatory step in the process of rationalization of physical & chemical phenomena taking place at these interfaces and governing for example the transport of organic molecules and pollutants in soils, heterogeneous catalysis for e.g. photovoltaics, electrochemistry and batteries, drugs encapsulation, etc.

Vibrational Sum Frequency Generation (vSFG) spectroscopy is one of the most powerful and vastly used techniques to unravel the specific organization of interfacial molecules at the microscopic/atomic level. However, interpretation of SFG spectra is non trivial and requires associated theoretical simulations in order to make a direct link between structure at the interface and vSFG activities.

The rationalization of vSFG signals at charged interfaces is especially a complex task, needing further and new developments, both from experimental and theoretical sides. The knowledge of the structure at charged interfaces is crucial in relation for instance with electrochemistry, in order to reveal the molecular structure at electrode/electrolyte interfaces and its relevance for the efficiency of electrochemical reactions. From the point of view of vSFG spectroscopy, it is essential to disentangle second and third order contributions to vSFG spectra of charged interfaces, which represents the main issue in the current interpretation of experimental data.

To this aim we have developed in collaboration with the group of Prof Y.R. Shen at the University of Berkeley-USA a new universal methodology to deconvolve second and third order contributions to vSFG signals that arise from water layers at charged aqueous interfaces<sup>1,2</sup>. To that end DFT-based Molecular Dynamics simulations and vSFG spectroscopy are combined, the whole strategy is based on the analysis of the water structural properties only. See ref. 1 for full details. Thanks to this universal procedure, an unambiguous interpretation of vSFG spectra can be achieved in terms of the water layers organisation at the interface, and in terms of the thickness of the interfacial region effectively probed in the experiment.

Once this strategy is applied, specific molecular structures at solid-water interfaces can be revealed and this knowledge can be used in order to design solid/water interfaces with designed properties for instance of interest for electrochemical reactions.

[1] Pezzotti, S.; Galimberti, D. R.; Shen, Y. R., Gaijeot, M.-P. *Phys. Chem. Chem. Phys.*, DOI 10.1039/C7CP06110B (Jan 2018)

[2] Pezzotti, S.; Galimberti, D. R.; Shen, Y. R., Gaijeot, M.-P. *J. Phys. Chem. C.* (Submitted, Feb 2018)