

Asymmetric Response of Interfacial Water to Applied Electric Fields and Field-Dependent Orientation of D₂O at an Electrode Surface

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In a recently published *Nature* paper, we demonstrated the first ensemble measurement of the Gibbs free energy profile of water at an electrode surface.¹ Here, we use sum frequency generation (SFG) spectroscopy, which uses the nonlinear optical mixing of visible and infrared laser pulses (i.e., Vis+IR), to measure the vibrational spectra (i.e., vSFG) of the topmost layer of water molecules. This is a surface-selective spectroscopy, which ignores the bulk water molecules and only “reports” the vibrational signature of the topmost layer at the aqueous-electrode interface. At large negative potentials (i.e., $V_{\text{potential}} < -1.6$ V vs. NHE), we see the emergence of the free OD peak, which is blue shifted with respect to the hydrogen-bonded peaks. Figure 1b shows the electric field dependence of the SFG spectra of the graphene/D₂O interface taken under various applied electrochemical potentials. The spectra of the OD stretch show a pronounced asymmetry for positive versus negative electrode charge. At negative charge below 5×10^{12} electrons per cm², a peak of the non-hydrogen-bonded OD groups pointing towards the graphene surface is observed at a frequency of 2,700 cm⁻¹. At neutral or positive electrode potentials, this ‘free-OD’ peak disappears abruptly, and the spectra display broad peaks of hydrogen-bonded OD species (at 2,300–2,650 cm⁻¹). Miller’s rule connects the vibrational sum-frequency generation response to the dielectric constant. The observed deviation from the linear response for electric fields of about $\pm 3 \times 10^8$ V/m calls into question the validity of treating interfacial water as a simple dielectric medium.

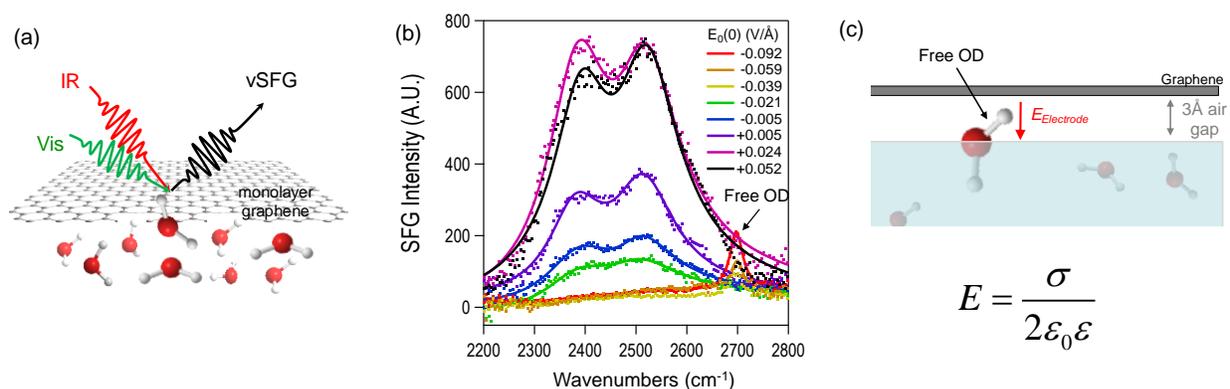


Figure 1. (a) SFG spectra of the graphene/hydrocarbon/D₂O interface under various applied electrode potentials.

This monolayer graphene/D₂O configuration also allows us to continuously tune the applied voltage from positive to negative through the potential of zero charge. The frequency shift of the G-band Raman mode of graphene was used as an internal calibration of the doping concentration as a function of applied potential, in addition to electrochemical measurements using a 3-terminal setup. The orientation of the D₂O molecules is extracted from the ratio of the amplitudes of SSP and PPP polarization signals. Several orientational distributions are considered for the D₂O molecules, and the average angle $\langle\theta\rangle$ is plotted as a linear function of the applied electrostatic field. We believe this general approach enables us to map out the free energy potential surface of this important molecule/electrode system.

1. Montenegro, A., C. Dutta, M. Mammetkuliev, H. Shi, B. Hou, D. Bhattacharyya, B. Zhao, S.B. Cronin and A.V. Benderskii, *Asymmetric Response of Interfacial Water to Applied Electric Fields*. *Nature*, DOI: 10.1038/s41586-021-03504-4 (2021).