

# Local potentials and dynamics at aqueous-oxide interfaces

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Interfacial water structure is key to diverse chemical and physical processes, including many of environmental and geochemical relevance. It can be probed by vibrational sum-frequency generation (vSFG) spectroscopy as well as ultrafast time-resolved vSFG.[1] However, a more complete microscopic understanding requires additional techniques such as molecular dynamics simulations.[2] Our experiments show that in the absence of surface charge (pH 2), water at silica surfaces exhibits significantly slower OH stretch vibrational relaxation (~600 fs) compared to bulk water. However, at charged silica surfaces (e.g., pH 6), bulk-like fast dynamics (~200 fs) are observed at low ionic strength. This decelerates to ~600 fs with the addition of NaCl. In parallel, vSFG results demonstrated that silica interfacial water structure is most sensitive to ions at pH=6-8, correlating with the known salt and pH dependence of silica surface reactivity. Consequently, it is unclear whether the observed slowing of the vibrational dynamics is due to the reduction in the Debye length, or because of changes in the local hydrogen bonding environment caused by the electrolyte and how this might depend on the identity of the ions or the solid surface. The combination of molecular dynamics simulations with spectroscopic and time-resolved vSFG experiments on aqueous Al<sub>2</sub>O<sub>3</sub> interfaces, along with the use of a molecular probe SCN<sup>-</sup>, that is sensitive to the local potential and the vibrational density of states,[3] sheds light on the ongoing debate on the role of ions in interfacial water structure and whether the observed behavior is specific to silica/water interfaces or can be generalized to other aqueous interfaces.

1. Vibrational Dynamics at Aqueous-Mineral Interfaces, Stefan M. Piontek and Eric Borguet, *The Journal of Physical Chemistry C* 126(5) 2307–2324 (2022) DOI: 1021/acs.jpcc.1c08563
2. Investigation of Water/Oxide Interfaces by Molecular Dynamics Simulations, Ruiyu Wang, Michael Klein, Vincenzo Carnevale, and Eric Borguet, *WIREs Computational Molecular Science*, 11(6) e1537 (2021) DOI: 1002/wcms.1537
3. Probing Heterogeneous Charge Distributions at the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001)/H<sub>2</sub>O Interface, Stefan M. Piontek, Mark DelloStritto, Bijoya Mandal, Tim Marshall, Michael Klein and Eric Borguet, *Journal of the American Chemical Society* 142, 28, 12096–12105 (2020) DOI: 1021/jacs.0c01366