

## **Second-harmonic generation studies of the noncentrosymmetric $\alpha$ - quartz/water interface**

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Second harmonic generation (SHG), a second-order nonlinear optical technique, is one of the few experimental techniques capable of providing molecular-level detail from geochemical interfaces but has been generally limited to probing the interface between two centrosymmetric media, where the technique is surface-specific. Here, we demonstrate that despite the bulk noncentrosymmetric nature of  $\alpha$ -quartz, we retain surface sensitivity under certain experimental geometries. This result opens up the ability to move beyond the commonly studied model system of fused silica and to directly study with nonlinear optics  $\alpha$ -quartz, the most common mineral form of silica. We use SHG to deduce interfacial chemical parameters such as silanol pKa values and interfacial potentials. The bulk noncentrosymmetric nature of  $\alpha$ -quartz also allows for internally-phase referenced measurements, which can be used to determine the phase of the interfacial signal, contributing to the fundamental understanding of nonlinear optical studies of charged solid/liquid interfaces as well as allowing for the experimental determination of the absolute orientation of molecules at the interface.