

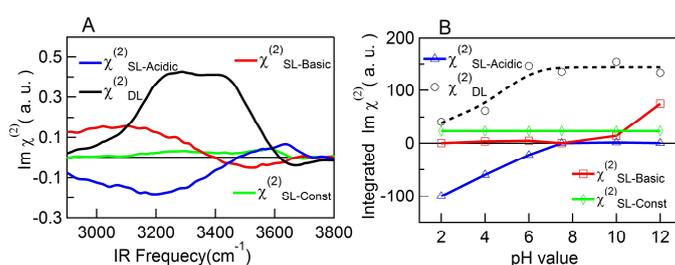
## Elucidation of $pK_a$ Value at Silica/Water Interface Using HD-VSFG Spectroscopy and Model-Independent Spectral Decomposition

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**Keywords:** silica/water interface, electrical double layer, HD-VSFG, charge density,  $pK_a$  value.

The silica/water buried interface is one of the most fundamental charged interfaces in nature.<sup>1</sup> In the present study, we applied heterodyne-detected vibrational sum-frequency generation (HD-VSFG) spectroscopy to obtain a molecular-level picture of silica surface,<sup>2</sup> by collecting the second-order nonlinear susceptibility ( $\chi^{(2)}$ ) spectra with different NaCl concentrations in a wide pH range. The obtained salt-dependent  $\chi^{(2)}$  spectra at each pH value were separated into the spectral components associated with water in the Stern layer (SL) and diffusely held Gouy-Chapman layer (DL) by model-independent SVD analysis. As shown in Figure A, the DL water spectrum (black line) show OH bands at  $3200\text{ cm}^{-1}$  and  $3450\text{ cm}^{-1}$ , which originate from the bulk-like water molecules in DL. The DL water contribution of the silica/water interface are positive at all pH studied, indicating that the silica surface is negatively charged in the pH range of 2.0 – 12.0. As shown in Figure B, the DL water contributions (black circles ○) show only one significant change between pH 2.0 – 6.0, which can be fitted with one  $pK_a$  value ( $3.7 \pm 0.4$ ) using the modified Gouy-Chapman model. On the other hand, the spectral component of SL water exhibits pH-dependent changes, which is explained by three spectral components (Figure A). It was found that the SL water at acidic pH (blue line) and basic pH conditions (red line) have the different conformations.



**Figure (A)** The spectral components of the water molecules at the silica/water interface: DL water ( $\chi_{DL}^{(2)}$ ) at 0.01 M and SL water ( $\chi_{SL-Acidic}^{(2)}$ ,  $\chi_{SL-Basic}^{(2)}$  and  $\chi_{SL-Const}^{(2)}$ ) at 5.0 M. **(B)** The pH dependent curves of integrated amplitude of each component of DL water and SL water.

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