

Structure of Water at the Electrified Platinum–Water Interface: A Study by Surface-Enhanced Infrared Absorption Spectroscopy

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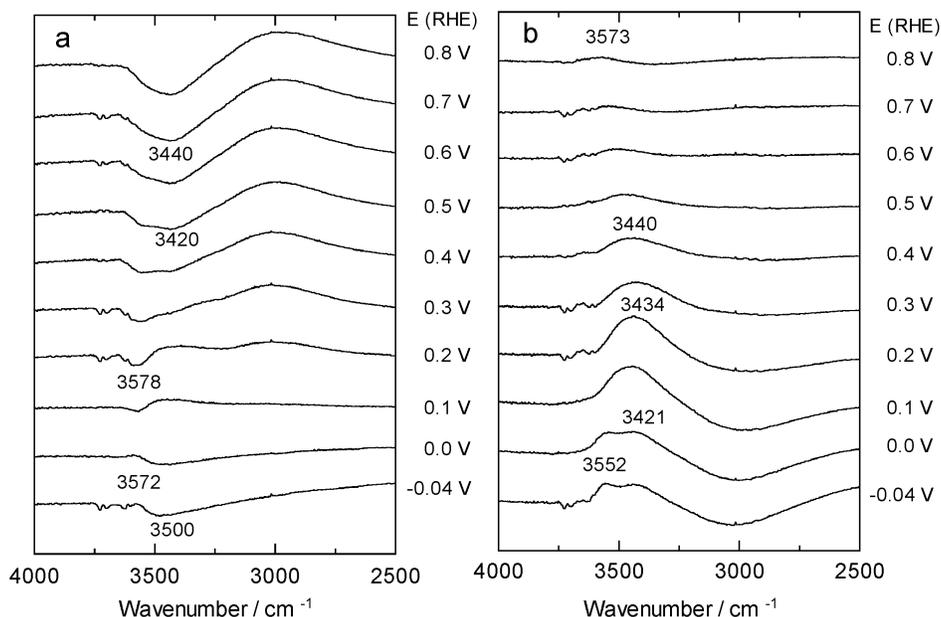


Figure S1. Potential difference SEIRA spectra of the interfacial water on a Pt electrode in 0.1 M H₂SO₄ recorded at various potentials shown in the figure and referenced to the single-beam spectrum collected at (a) 0.05 or (b) 0.9 V (RHE). The original spectral data used here were the same as used in Figure 4.

This figure suggests the presence of a strong band at ~ 3440 cm⁻¹. However, a careful inspection of Figure 3 reveals that this band corresponds to the valley in between the two bands at 3550–3570 and ~ 3000 cm⁻¹ and not the real absorption band (i.e., a ghost). In contrast, the band at 3550–3570 cm⁻¹ that is clearly observed in Figure 4 is obscured in the potential difference spectra. As is demonstrated here and in Figure 4, the potential difference spectra greatly depend on the reference potential, and hence, great care is required in interpreting the potential difference spectra.

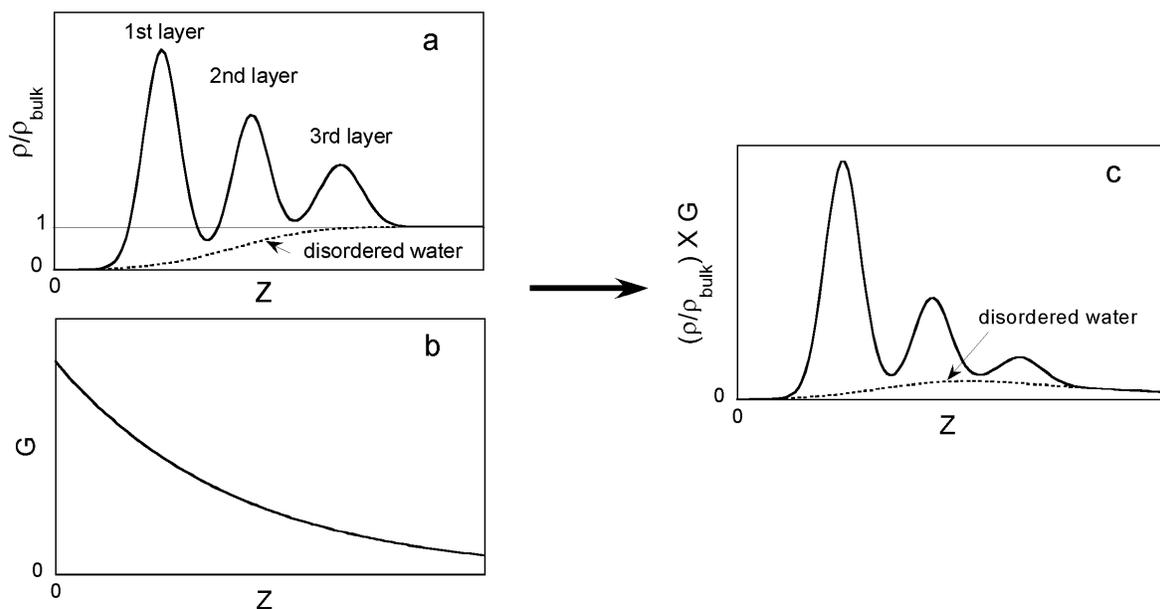


Figure S2. Schematic drawing for showing the selective observation of the first water layer in contact with the Pt surface by ATR-SEIRAS. Panel (a) shows the normalized oxygen atom density ρ/ρ_{bulk} based on the experimental result on Ag(111).¹ The ordering of the interfacial water molecules is lessened with increasing distance from the surface Z increases and completely disappears within three layers. Panel (b) is a rough sketch of the Z -dependence of the infrared absorption enhancement G . Infrared absorption of each water layer is proportional to $(\rho/\rho_{\text{bulk}}) \times G$. Accordingly, contributions of the second and higher overlayers to the total absorption are smaller than the first layer, as panel (c) shows. Since the bands characteristic of the disordered water (dotted curves) were not observed, G may decay more sharply. The signal from the bulk solution probed by the evanescent wave is cancelled out by background subtraction, and hence it was omitted from this figure.

References

- (1) Toney, M. F.; Howard, J. N.; Richer, J.; Borges, G. L.; Gordon, J. G.; Melroy, O. R.; Wiesler, D. G.; Yee, D.; Sorensen, L. B., *Nature* **1994**, 368, (6470), 444.