Supporting Information for

Interactions of Al(III), La(III), Gd(III), and Lu(III) with the fused silica/water interface studied by second harmonic generation

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Sensitivity Analysis. In order to test the robustness of this assumption, a sensitivity analysis was performed on the SHG triple layer expression. This analysis was carried out by taking the partial derivative of eqn 5 with respect to C_2. This derivative is plot as a function of C_2 in Figure S1 of the Supporting Information, and the value of 0.2 F/m^2 is indicated. Figure S1 illustrates that the value of C_2 can be varied by as much as ±50% of its assumed value of 0.2 F/m^2 while having little to no effect on the output of the model, indicating that the function is insensitive to variance in C_2 in this region.

Triple Layer Model. In this work, the triple layer model (TLM) was used to fit the adsorption isotherms. We found this model to most accurately describe the interactions under study in terms of reducing the errors in our fit parameters and experimental results. The TLM possesses a unique multi-layer structure and allows for the specific adsorption of electrolyte ions, resulting in several advantages over simpler models, such as the diffuse layer model (DLM) and the basic Stern model (BSM). For one, the chemical constants utilized within the TLM are applicable over a wide range of ionic strengths, allowing for greater versatility. Also, the potential at the diffuse layer plane can be used to estimate the electrokinetic potential of the system under investigation (*1*). It is known that the DLM does not accurately predict the surface charge density under high interfacial potential conditions (*2*). This is not an issue with the TLM, whose interfacial potential remains linearly proportional to the interfacial charge density, and thus we successfully employ this model when studying the adsorption of trivalent cations to mineral oxide interfaces.

Fitting Parameters. The parameters used to fit the experimental adsorption isotherms of each metal ion are listed in Table S1. The parameters A' and B consist of a collection of constants. A' incorporates the second-order nonlinear susceptibility, the incident electric field, the initial

surface charge density, and the capacitance of the inner layer (C_1). B represents the third-order nonlinear susceptibility and the incident electric field. Finally, s is the interfacial charge density due to the adsorbing metal ions, σ_m, and K represents the binding constant, K_{ads}.

Experimental Results. The complete experimental results of this work are summarized in Table S2. K_{ads} is the binding constant in 1/M, ΔG_{ads} is the adsorption free energy in kJ/mol, σ_m is the surface charge density of the silica surface when metal adsorbates are present in C/m^2, and N_{ads} is the adsorbate number density in ions/cm^2. The adsorbate number densities were calculated from the metal adsorbate surface charge densities assuming that each adsorbate carries a 3+ charge.

Figure S1 – Sensitivity analysis of the triple layer function with respect to the C_2 parameter. The dashed line indicates the commonly used constant of 0.2 F/m^2.

Table S1 – The fitting parameters used to fit each adsorption isotherm are listed for each metal ion. The errors associated with each parameter are also displayed.

Table S2 – The experimental results are summarized for each metal ion.

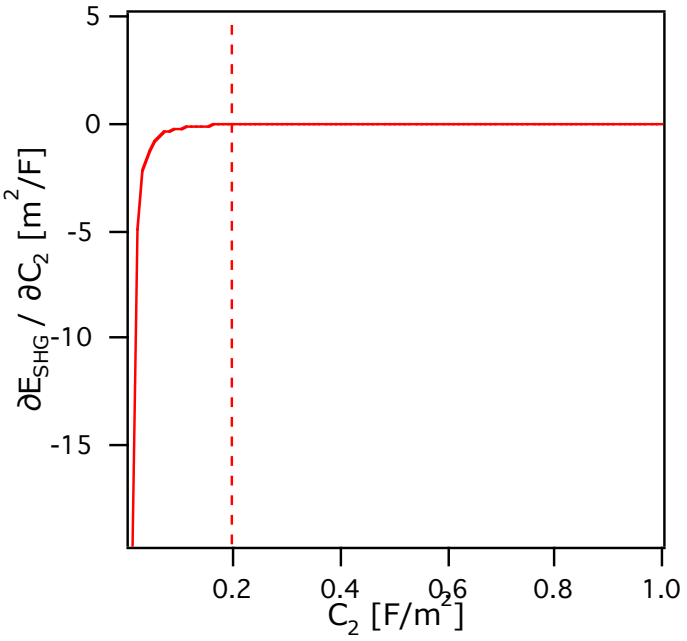

Figure S1

Metal	A'	B	s	K [mol^{-1}]
Al(III)	0.7 ± 0.2	0.6 ± 0.4	0.004 ± 0.002	60,000 ± 10,000
La(III)	0.89 ± 0.03	0.18 ± 0.07	0.009 ± 0.004	6,000 ± 3,000
Gd(III)	0.8 ± 0.2	0.5 ± 0.4	0.004 ± 0.003	3,100 ± 900
Lu(III)	0.95 ± 0.01	0.10 ± 0.02	0.009 ± 0.003	8,000 ± 2,000

Table S1

Metal	K_{ads} [1/M]	ΔG_{ads} [kJ/mol]	σ_m [C/m^2]	N_{ads} [ions/cm^2]
Al(III)	60,000 ± 10,000	–37.2 ± 0.4	0.004 ± 0.002	8(4) x 10^{11}
La(III)	6,000 ± 3,000	–31 ± 1	0.009 ± 0.004	1.9(8) x 10^{12}
Gd(III)	3,100 ± 900	–29.9 ± 0.9	0.004 ± 0.003	8(6) x 10^{11}
Lu(III)	8,000 ± 2,000	–32.2 ± 0.7	0.009 ± 0.003	1.9(6) x 10^{12}

Table S2

1. Westall, J.; Hohl, H., A comparison of electrostatic models for the oxide/solution interface. *Adv. Colloid Interface Sci.* **1980,** *12*, 265 - 294.
2. Malin, J. N.; Hayes, P. L.; Geiger, F. M., Interactions of ca, zn, and cd ions at buried solid/water interfaces studied by second harmonic generation. *J. Phys. Chem. C* **2009,** *113*, (6), 2041-2052.