

Chromium(VI) Binding to Functionalized Silica/Water Interfaces Studied by Nonlinear Optical Spectroscopy

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Surfaces and interfaces control chemical binding and transformation reactions in many areas of chemistry, ranging from environmental science and catalysis to materials science and biology. In the context of environmental molecular science, significant emphasis has been placed on surfaces of mineral oxides that are ubiquitous in soils^{1,2} and the lower atmosphere^{3,4} such as silicates. Silicate surfaces often contain organic adlayers that stem from microbial and plant excretions or biodegradation^{3,5–8} and that contain functional groups such as carboxylic acids, esters, α -hydroxy carboxylic acids, and polyphenols.^{1,2,5,6,9–12} Understanding how such functionalized organic adlayers regulate the interactions of mineral oxides with solvated species in the aqueous phase allows for the improved modeling and manipulation of environmentally relevant species in geochemical, biological, and atmospheric environments.

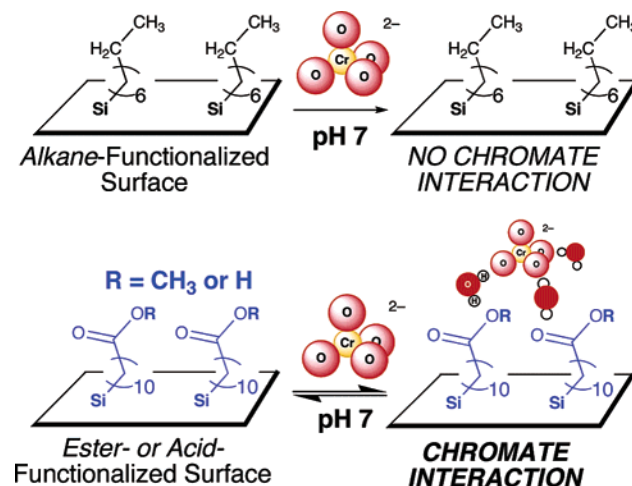
Herein, we report a laboratory study of how organic adlayers on silica can control the mobility of chromium(VI), a priority toxic metal ion in the soils.¹³ Resonantly enhanced surface second harmonic generation (SHG) measurements carried out in situ and in real time at pH 7 show, for the first time, that Cr(VI) ions bind to ester- and acid-functionalized surfaces but not to alkane-functionalized surfaces (Scheme 1). The implications with respect to organic adlayers at mineral oxide/water interfaces are that Cr(VI) mobility in soils can be lowered by ester and acid groups common in biopolymers but not by alkyl groups common in biosurfactants.

Ester- and alkyl-terminated silica surfaces were prepared by exposing a silica substrate to the corresponding trichlorosilanes (see Supporting Information). Hydrolysis of the ester-terminated surfaces in hot HCl (aq) yielded the acid-functionalized surface. The functionalized surfaces were characterized using isotopic labeling experiments and broadband sum frequency generation (BBSFG), following Richter and co-workers.¹⁴ The progress of the hydrolysis reaction can also be monitored via BBSFG (see Supporting Information).

Figure 1 shows the SHG vs time traces of three differently functionalized surfaces that were exposed, in succession, to water, aqueous Cr(VI), and again water. The ester- and the acid-functionalized surfaces bind Cr(VI) strongly, while the alkane-functionalized surface shows no discernible interaction. This latter observation suggests that there are relatively few Si–OH groups available for Cr(VI) binding, i.e., most of the surface siloxy groups are associated with the alkylsiloxane. Together with our earlier SHG studies, which demonstrate Cr(VI) surface coverage sensitivities down to 10% of a monolayer for silica/water interfaces,^{15,16} we conclude that the degree of surface functionalization by the siloxanes is high.

Unlike the acid-functionalized surface, the ester-functionalized surface has no hydrogen-bond donors. The interaction of Cr(VI) ions with the ester groups could be governed by ion–dipole interactions¹⁷ or mediated by water molecules in the presumably strongly bound Cr(VI) hydration sphere,¹⁸ which can form hydrogen

Scheme 1. Schematic Representation of Cr(VI) Affinity to Alkane-, Ester-, and Acid-Functionalized Surfaces



bonds to the carboxylate groups of the ester. The latter is consistent with increasing evidence that carboxylates interact with metal hydroxides primarily through hydrogen bonding.¹⁹ Interestingly, Cr(VI) desorption from the nonfunctionalized¹⁵ and acid-function-

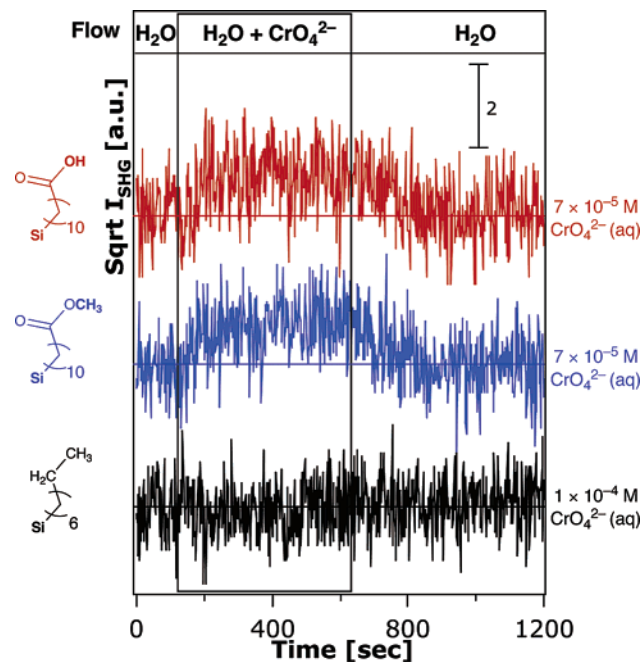


Figure 1. SHG vs time traces at $\lambda_{\text{SHG}} = 290$ nm and pH 7 for Cr(VI) binding to an acid-functionalized surface (top trace), an ester-functionalized surface (center trace), and an alkane-functionalized surface (bottom trace) that were exposed, in succession, to water, aqueous Cr(VI), and again water. The experiments were carried out as described previously.^{15,16}

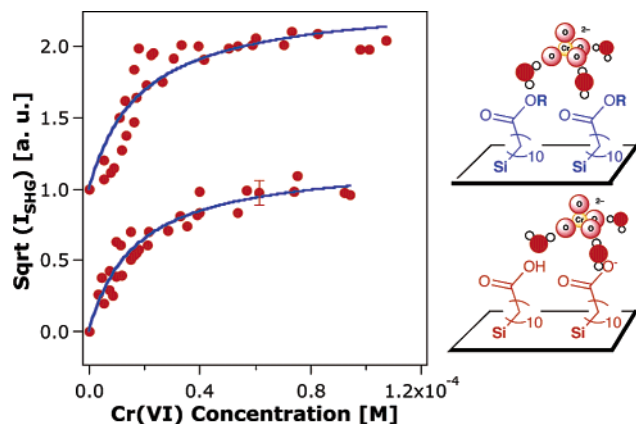


Figure 2. Cr(VI) adsorption isotherm measured at pH 7 on the acid- (bottom) and the ester-functionalized (top, offset for clarity) surfaces shown in Figure 1, indicating monolayer coverage in each case. For each interface, the data represent the composite of two runs on two freshly prepared samples. The experiments were carried out as described previously.^{15,16}

alized silica surfaces is slower than that from the ester-functionalized surfaces based on the shape of the desorption SHG time traces (Figure 1). This observation indicates that silica surfaces and those containing acid-functionalized organic adlayers can decrease Cr(VI) mobility to a larger extent than ester-functionalized organic adlayers.

The thermodynamics of Cr(VI) binding to the acid- and the ester-functionalized surfaces was investigated by recording the Cr(VI) adsorption isotherms at pH 7 on both surfaces (see Figure 2). At pH 7, the acid-functionalized surface contains both protonated and deprotonated carboxyl groups.²⁰ Cr(VI) binding is expected to occur predominantly at protonated carboxyl groups, while deprotonated carboxyl groups and CrO_4^{2-} should not interact due to Coulomb repulsion.²¹ By applying the Langmuir model¹⁷ to the isotherm data shown in Figure 2, we obtained free adsorption energies of 37.4 ± 0.5 and 37.1 ± 0.6 kJ/mol for the acid- and the ester-functionalized surface, respectively. The finding that the two different surface functionalities afford the same free adsorption energies is consistent with hydrogen bonding or ion–dipole interactions between Cr(VI) and the carboxyl groups on the surface.

The results presented in this work suggest that a high surface concentration of carboxyl groups on silicate surfaces can favor Cr(VI) adsorption and decrease the mobility of these metal ions in soil. This is consistent with the “surface chelate effect” recently reported by Major and Zhu,²² who used ex situ XPS to demonstrate that copper ions bind to acid-terminated thiols on gold but not to alkanethiols on gold. In addition, our results shed light on the initial phase of interaction between Cr(VI), a cytotoxin, and living cells: the high mobility of Cr(VI) across cell membranes²³ requires Cr(VI)–membrane interaction, which is expected to be facilitated by polar groups located at the membrane surface.

In conclusion, our work demonstrates, for the first time, how the interaction of metal ions with organic adlayers at solid/liquid interfaces can be studied in real time using nonlinear optical spectroscopy. Our direct, surface-specific measurements show that Cr(VI) can bind to ester- and acid-functionalized surfaces and indicate that organic adlayers rich in carboxyl groups can decrease Cr(VI) mobility in soils, whereas alkyl groups, commonly present

in biosurfactants, will not. Future work will focus on exploring the pH and the temperature dependence of Cr(VI) binding to the functionalized surfaces. Furthermore, we plan to use functionalized siloxanes as scaffolds for ligating a wide range of bio- and geochemically relevant species such as metalloregulatory proteins,²⁴ as well as polyphenols and α -hydroxy carboxylic acids,⁵ and to study their chemical binding and transport properties in the presence of metal ions.

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Supporting Information Available: Silane synthesis and characterization and SFG spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Brown, G. E. *Science* **2001**, 294, 67–69.
- (2) Brown, G. E., Jr.; Henrich, V. E.; Casey, W. H.; Clark, D. L.; Eggleston, C.; Felmy, A.; Goodman, D. W.; Graetzel, M.; Maciel, G.; McCarthy, M. I.; Nealon, K. H.; Sverjensky, D. A.; Toney, M. F.; Zachara, J. M. *Chem. Rev.* **1999**, 99, 77–174.
- (3) Usher, C. R.; Michel, A. E.; Grassian, V. H. *Chem. Rev.* **2003**, 103, 4883–4940.
- (4) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: New York, 2000.
- (5) Schwarzenbach, R.; Geschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993.
- (6) Langmuir, D. *Aqueous Environmental Geochemistry*; Prentice-Hall: New Jersey, 1997.
- (7) Torrens, J. L.; Herman, D. C.; Miller-Maier, R. M. *Environ. Sci. Technol.* **1998**, 32, 776–781.
- (8) Newman, D. K.; Bandfield, J. F. *Science* **2002**, 296, 1071–1077.
- (9) Morel, F. M. M.; Hering, J. G. *Principles and Applications of Aquatic Chemistry*; Wiley-Interscience: New York, 1993.
- (10) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1996.
- (11) Al-Abadleh, H. A.; Grassian, V. H. *Surf. Sci. Rep.* **2003**, 52, 63–162.
- (12) Gustafsson, J. P.; Pechova, P. *Environ. Sci. Technol.* **2003**, 37, 2767–2774.
- (13) Katz, S. A.; Salem, H. *The Biological and Environmental Chemistry of Chromium*; VCH: New York, 1994.
- (14) Richter, L. J.; Petralli-Mallow, T. P.; Stephenson, J. C. *Opt. Lett.* **1998**, 23, 1594–1596.
- (15) Mifflin, A. L.; Gerth, K. A.; Geiger, F. M. *J. Phys. Chem. A* **2003**, 107, 9620–9627.
- (16) Mifflin, A. L.; Gerth, K. A.; Weiss, B. M.; Geiger, F. M. *J. Phys. Chem. A* **2003**, 107, 6212–6217.
- (17) Atkins, P. W. *Physical Chemistry*, 6th ed.; Oxford University Press: 1998. Applications of more complex isotherm models will be presented in forthcoming work.
- (18) Chlístunoff, J. B.; Johnston, K. P. *J. Phys. Chem. B* **1998**, 102, 3993–4003.
- (19) Boily, J.-F.; Nilsson, N.; Persson, P.; Sjöberg, S. *Langmuir* **2000**, 16, 5719–5729.
- (20) Gershevit, O.; Sukenik, C. N. *J. Am. Chem. Soc.* **2004**, 126, 482–483.
- (21) Preliminary experiments have indicated that at pH 10, Cr(VI) binding does not occur on the acid-functionalized surface. This is consistent with previous studies of the silica/water interface where no binding of Cr(VI) is observed above pH 10 (ref 15 and 16).
- (22) Major, R. C.; Zhu, X.-Y. *J. Am. Chem. Soc.* **2003**, 125, 8454–8455.
- (23) Nieboer, E.; Jusys, A. A. In *Chromium in the Natural and Human Environment*; Nieboer, E., Ed.; John Wiley & Sons: New York, 1988.
- (24) O'Halloran, T. V. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1989; Vol. 25, pp 105–146.

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