Proton and ligand adsorption at silica- and alumina-water interfaces studied by optical second harmonic generation (SHG)

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Partitioning of aqueous solutes to mineral surfaces by adsorption is key to water-rock interaction (e.g. Stumm, 1992), and is important to many environmental and geochemical processes (from waste water treatment to global climate control). Most studies of adsorption, whether stoichiometric or spectroscopic, use mineral-powder suspensions to maximize surface area. Such methods are unable to discriminate between crystal faces, limiting our ability to form well-defined structure-reactivity relations for mineral surfaces. Here, we use second harmonic generation (SHG), an *in situ*, non-linear optical technique with inherent interface sensitivity, to examine 1) the surface charge of amorphous silica, 2) the adsorption of glyphosate, an herbicide molecule, to amorphous silica, and 3) the adsorption of a carboxylic acid-functionalized rhodamine dye to corundum, all within an analysis area of about 0.25 mm^2. The results show that surface charge, and adsorption of organic (and presumably other) species to mineral surfaces, can be studied using SHG with high spatial resolution. In addition, the polarization dependence and phase sensitivity of SHG can be used to assess molecular orientation at interfaces.

Experimental

In SHG, light of frequency ù interacts with a non-centrosymmetric medium to produce light with frequency 2ω. To a first approximation, centro-symmetric media cannot produce SHG, so SHG can come only from the interface between a centrosym-metric solid and a liquid (Shen, 1984). We used a fixed-frequency 1064 nm Nd:YAG laser (pulse energy ~600 µJ, pulse rate = 10 Hz; laser spot size = 0.25 mm^2). Light enters the fluid cell through an amorphous silica prism or corundum window; SHG is directed into a photomultiplier tube. Our corundum window was multicrystalline, and the other a [0001] oriented single crystal.

Results

Figure 1 shows SHG from a silica-solution interface as a function of pH in 0.5 M NaCl adjusted with NaOH and HCl. The data from pH 2 to pH 12 were fit to a two-pK model similar to that used by Ong *et al.* (1992). Best estimates for the pKs are 4.6 and 8.8, in close agreement with Ong *et al.* (1992), who suggested two different >SiOH sites that undergo the reaction >SiOH = >SiO$^-$ + H$^+$, one with pK = 4.5 and one with pK = 8.5.

Ong *et al.* (1992) suggest that above pH$_{PZC}$, SHG stems from a combination of an approximately electric field (E) independent contribution ($\chi^{(2)}$) from the silica surface, plus an E-dependent contribution ($\chi^{(3)} \cdot E_{dl}$) from polarization of water molecules within the double layer, where $\chi^{(2)}$ and $\chi^{(3)}$ are the second-order and third-order non-linear susceptibilities, respectively, and E_{dl} is the electric field in the double layer. Thus, at the pH$_{PZC}$, a minimum in the SH signal would be expected
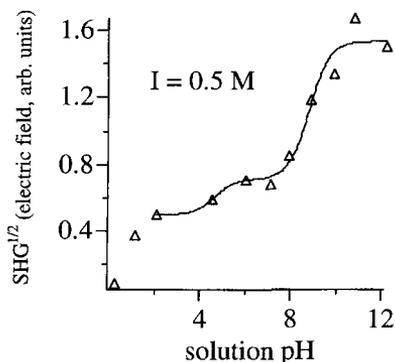

FIG. 1. pH-dependent SHG signal from the silica-solution interface as a function of pH. The two-pK model fit gives estimates of 4.6 and 8.8 for the two surface silanol pKs.
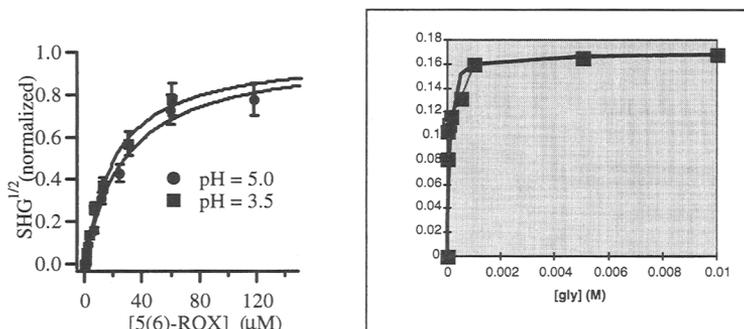
FIG. 2. (A) Langmuirian adsorption of 5,6-ROX (see text) to corundum at two pH values. Solid lines are Langmuir fits. (B) Langmuir adsorption of glyphosate to amorphous silica at pH 3.8; solid line is a Langmuir fit.

because the E_{dl} contribution to the SH signal should be approximately zero. Because the $\chi^{(2)}$ contribution predominates at pH_{PZC}, the further decrease in SH signal below pH 2 (and slightly above pH 2 for that matter) could be due to a significant dependence of $\chi^{(2)}$ on pH.

Figure 2a shows SHG results for the adsorption of 5,6-carboxy-X-rhodamine (5,6-ROX), an aromatic carboxylic acid attached to an aromatic 'sail' that provides resonant enhancement of the SHG signal (Shen, 1984), to crystalline corundum. Adsorption is Langmuirian, at least as far as our data can be fitted, at two different pH values. Figure 2b shows a SHG-obtained Langmuir adsorption isotherm for glyphosate, an herbicide molecule whose fate is of environmental interest, on amorphous silica at pH $\approx$ 3.8 in 0.01 M $NaNO_3$ adjusted with HNO_3.

Figure 3 shows SHG of 5,6-ROX adsorption to

corundum as a function of pH, as well as the results of a batch adsorption study. All results show a maximum in adsorption occurs at pH 3.5, in rough agreement with surface complexation models for other dicarboxylic acids adsorbing to alumina (Kummert and Stumm, 1980; Kallay and Matijevic, 1985). There is no significant difference between the (0001) surface and the multi-crystalline surface toward 5,6-ROX adsorption.

In future, SHG will allow crystal-face-specific measurement of the pH_{pzc} and of adsorption in order to develop well-defined structure-reactivity relations for mineral-water interfaces. Phase- and polarization dependent studies will allow characterization of molecular orientation at interfaces. SHG and a related vibrational technique, sum-frequency genera-tion (SFG) are likely to prove highly useful in the study of adsorption at mineral surfaces.
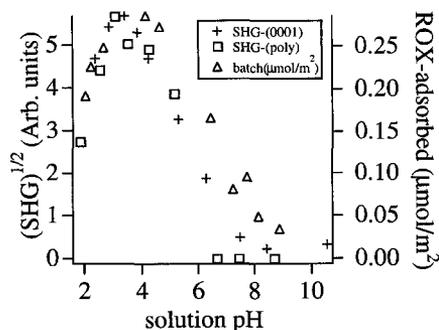
FIG. 3. SHG signal for 5,6-ROX adsorption as a function of pH, compared to stoichiometric experimental batch results. A maximum adsorption occurs at about pH 3.5, in rough agreement with surface complexation models for other dicarboxylic acids (Kummert and Stumm, 1980; Kallay and Matijevic, 1985).

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