Probing the Interface of Microscopic Clay Particles in Aqueous Solution by Second Harmonic Generation

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Second harmonic generation (SHG) is applied for the first time to study the surfaces of clay particles. An SHG signal was detected from an aqueous suspension of disk-shaped montmorillonite clay particles of 0.5 μm diameter and 0.01 μm thickness. The origin of the SHG signal is the polarization of water molecules by surface charges located in the edge region of the clay particles. On addition of the organic molecule 4-(2-pyridylazo)resorcinol (PR) to the clay aqueous suspension, a strong SHG signal originating from the PR molecules adsorbed onto the edge surfaces of the clay particles was obtained. The PR adsorbed on the basal planes do not contribute to the SHG signal because of cancellation effects. These experimental results demonstrate the applicability of the SHG method for studying molecular adsorption and the electrostatic properties of clay particles.
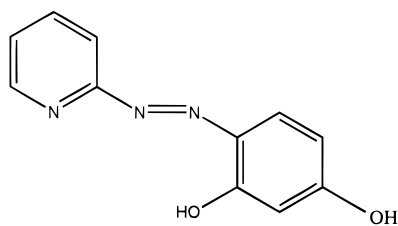
1. Introduction

The abundance in nature and the unique adsorptive and catalytic properties of clay particles make them a subject of fundamental and technological interest.[1−3] Clay particles have long been recognized as important catalysts in petroleum-forming reactions and in the chemical evolution of certain organic compounds related to the origin of life.[4,5] The large surface area make them excellent adsorbents and is the basis for their increasing use to remove organic and inorganic environmental pollutants. Industries also use them in a number of applications, e.g., decolorizing agents, carriers for insecticides, and detergent formulation. It is known that electrostatic characteristics of microscopic clay particles have a significant effect on a number of chemical and physical properties,[6,7] such as the populations and structural arrangements of neutral and ionic species in the surface region of the particles, the chemical reactions near the surface, the electrokinetic properties of the particles, and the stability of the suspensions in solutions. Knowledge of the electrostatic properties, e.g., surface potential and surface charge density, can yield a better understanding of the chemistry occurring at the surfaces of clay particles.

Second harmonic generation (SHG) has recently been shown to be a new method to study microparticle surfaces.[8−13] It has proven to be a useful surface-specific technique that can probe equilibrium and dynamic processes occurring at a variety of microparticle surfaces. Among these are the adsorption of organic molecules, e.g., malachite green, onto the surface of polystyrene microspheres in aqueous solution, and molecular adsorption onto the surface of oil droplets in an oil/water emulsion.[10] These studies yielded the adsorption free energy as well as the surface population of the organic molecules onto the surfaces of these microscopic structures. In another study the spectrum of a charge-transfer complex of catechol (OHC_6H_4-OH), adsorbed onto the surface of titanium dioxide microparticles in aqueous solution, and the free energy of the catechol adsorption were obtained.[11] The main advantage of using SHG to study the adsorption on micr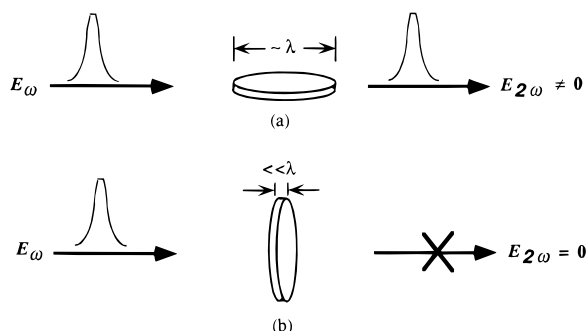oparticle surfaces over traditional techniques derives from the surface specificity of SHG. Other methods, e.g., centrifugation and filtration, require the separation of species adsorbed on the microparticles from the unadsorbed species present in the bulk suspension. Apart from its application in adsorption and interface spectral studies, SHG can also be used to probe the electrostatic properties of microparticle surfaces.[12] Surface potential and surface charge density of negatively charged polystyrene microspheres and those of oil droplets in oil/water emulsions have been measured by SHG. Unlike the conventional technique of electrophoresis, there is no perturbation of the systems during the SHG measurements and of particular interest is that the electric potential obtained is for the charge plane of the microparticles, not for the shear plane, which is the location where there is no solvent flow relative to the charged particle. The relation of the electrophoretic potential to the potential at the charge plane obtained from SHG has been determined in a recent study.[12] A further example of the utility of SHG in the study of microparticle surfaces is the real time measurement of the transport of organic molecules across a liposome bilayer.[13]

In the present investigation, SHG is applied for the first time to probe the surfaces of clay particles. The clay particles used are the centrosymmetric disk-shaped Na−montmorillonite mineral with a diameter of 0.5 μm and a thickness of 0.01 μm. Since montmorillonite has a structure that is centrosymmetric,[1] SHG is not generated from the bulk of the montmorillonite. Because of the coherence properties of SHG, the SHG efficiency from microparticle surfaces greatly depends on the size of particles.[11] Since the diameter of the clay particle is on the length scale of the light, while the thickness is much smaller than the wavelength of the light, only the edge regions separated by roughly the diameter of the particle contribute to the SHG signal. This will be discussed in more detail in the next section. In this work we report (1) the adsorption of 4-(2-pyridylazo)resorcinol (PR; see Scheme 1) on the edge surfaces of the clay particles and (2) the electrostatic effects manifested by the SHG signal arising from the polarization of bulk water molecules by the charged surfaces of a neat suspension of the clay particles.

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SCHEME 1

SCHEME 2

Figure 1. Wavelength dependence of the output signal for the sample of (1) a mixture of 4-(2-pyridylazo)resorcinol (PR) at 10 μM and clay particles at 0.005 w/w %, (2) a clay suspension at 0.005 w/w %, and (3) a PR solution at 10 μM. The pH of the solutions are 3.2 $\pm$ 0.2. The output signal for the mixture of PR and clay particles peaks at the second harmonic frequency, which is well above the signal of the clay suspension or PR solution. The inset is the UV−vis spectrum of the aqueous solution of PR at 10 μM and pH 3.2.

2. SHG from the Edge Surfaces of the Clay Particles

SHG involves the conversion of incident light at a fundamental frequency ω to light at twice the frequency 2ω via a nonlinear interaction with the medium.[14−18] Under the dipole approximation, SHG is forbidden in centrosymmetric media, e.g., in bulk solution. Since surfaces are intrinsically noncentrosymmetric, SHG becomes dipole-allowed at an interface and is thus surface-specific. Two important sources of this noncentrosymmetry in the present studies are (1) the noncentrosymmetric alignment of molecules at the interfaces and (2) the polarization of bulk water molecules by surface charges, which breaks the centrosymmetry of the bulk water.

In general, if the size of the particle is comparable to the coherence length of the process, the second harmonic fields, $E_{2\omega}$, generated from the opposite sides of a centrosymmetric particle can add constructively to give an SHG signal. If the size of the centrosymmetric particle is much less than the size of the centrosymmetric particle is much less than the coherence length of the process, the SH field generated from the opposite sides of the particle cancel each other. In the present studies, the SHG observed from the clay particle is generated from the region near the edge surfaces of the disk-shaped clay particles of Na−montmorillonite, which has a diameter of 0.5 μm and a thickness of 0.01 μm (Scheme 2). Although the particle overall is centrosymmetric, the second harmonic fields, $E_{2\omega}$, generated at the locally noncentrosymmetric region near the edge surfaces can add constructively and give an SHG signal (Scheme 2a). On the other hand, the second harmonic fields, $E_{2\omega}$, generated at the opposing basal surfaces, are separated by the particle thickness, 0.01 μm, which is much smaller than the wavelength of the light, and thus cancel each other (Scheme 2b).

3. Experimental Section

The setup for the second harmonic measurement is described in detail elsewhere.[10,12] Briefly, it consists of a Ti:sapphire oscillator, which provides 100 fs pulses at 844 nm at a repetition rate of 82 MHz. The fundamental light is focused into a sample cell, and the transmitted second harmonic photons at 422 nm are detected by a single photon counting system. Filters and a monochromator were used to separated the SHG output signal from any background signals.
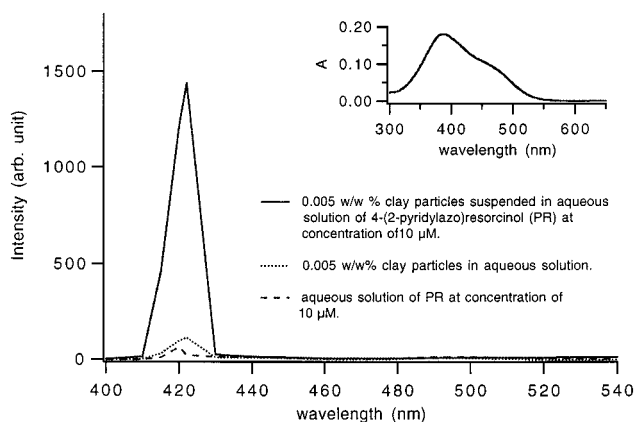
The clay sample of Na−montmorillonite was stored in 0.5 M NaCl solution until it was used. The suspension was centrifuged (15 000 rpm for 5 min), resuspended, and washed with doubly distilled deionized water until a negative chloride test was obtained with silver nitrate. The concentration of washed clay particles in aqueous solution was determined by a simple weighing method. It was then diluted to 0.005 w/w % in doubly distilled deionized water for the SHG measurement. In the adsorption experiments, the 4-(2-pyridylazo)resorcinol (PR) used for the adsorption experiment was from Aldrich. The pH values of the samples with PR were adjusted to 3 using HCl immediately before the SHG measurement. In the experiments having clay particles but not the organic adsorbate PR, the pH and electrolyte concentration of the aqueous suspensions of clay particles were adjusted by HCl, NaOH, and NaCl. All experiments were conducted at room temperature, 22 °C. The UV−vis measurements were performed with a Perkin-Elmer (Lambda 6) spectrophotometer.
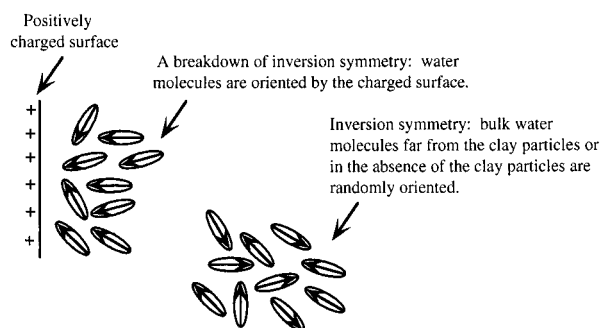
4. Results and Discussion

a. Adsorption of Organic Molecules on Clay Particles. Figure 1 shows the wavelength dependence of the output signal for (1) a system consisting of 10 μM PR and clay particles at a concentration of 0.005 w/w %, (2) an aqueous solution of 10 μM PR, and (3) a clay suspension at 0.005 w/w %. The output signal for the system consisting of PR and clay particles clearly peaks at the second harmonic frequency, which is well above the signal of the individual clay suspension and PR solutions. There is also a peak at the second harmonic wavelength observed in the clay suspension without PR. This second harmonic signal originates from the water molecules polarized by the electrostatic field due to the surface charges on the clay particles and will be discussed in the next section. Moreover, a small peak at 422 nm for the PR solution due to hyper-Rayleigh scattering is detected. The hyper-Rayleigh scattering, a second-order incoherent scattering, originates from the orientational and density fluctuations of the bulk molecules in the aqueous suspension.

The observed strong SHG signal from the mixture of PR solution and clay suspension is due to the molecular adsorption of PR on the edge surfaces of the clay particles. A 100-fold increase of SHG signal was observed from the clay particles

SCHEME 3

Positively charged surface

A breakdown of inversion symmetry: water molecules are oriented by the charged surface.

Inversion symmetry: bulk water molecules far from the clay particles or in the absence of the clay particles are randomly oriented.

with adsorbed PR compared with the individual clay suspension and the individual solution of PR. It is known that when the adsorbed species has an electronic transition at the fundamental or second harmonic frequency, the SHG intensity is greatly enhanced because of the resonance. The UV−vis spectrum of PR at pH 3 indicates that PR has an absorption at the second harmonic frequency, 422 nm (Figure 1 inset). Preliminary results showed that the SHG intensity increases with the bulk concentration of PR, as expected in an adsorption isotherm, and will be reported in a future publication.

Adsorption of organic materials, especially organic cations[19,20] and aromatic compounds,[21−23] on montmorillonites has long been a subject of interest. Most of the previous studies investigated the adsorption on the basal surfaces and the interlayers of montmorillonites. The methods used generally involve the incubation of clay particles in the solution of organic materials followed by separation of the organic material adsorbed onto the clay particles from the unadsorbed organic molecules remaining in the solution. These separations are usually done by filtration or centrifugation. The amount of adsorption is then quantitatively analyzed by various techniques, such as UV−vis spectroscopy, gas chromatography, high-performance liquid chromatography, radiation decay of isotopically labeled materials. In our studies, there is no coherent SHG contribution from the very large population of unadsorbed organic molecules in the bulk solution. The edge surfaces of montmorillonites are of special interest because they have catalytic activity for specific reactions, e.g., reduction of hydrogen peroxide[24] and chromate.[25] In the present studies, we have shown that the molecular adsorption onto edge surfaces of clay particles, important in clay catalysis, can be selectively probed by SHG. Furthermore, the resonance enhancement of the SHG signal from the adsorbates provides an analytical capability for differentiating among adsorbed chemical species.
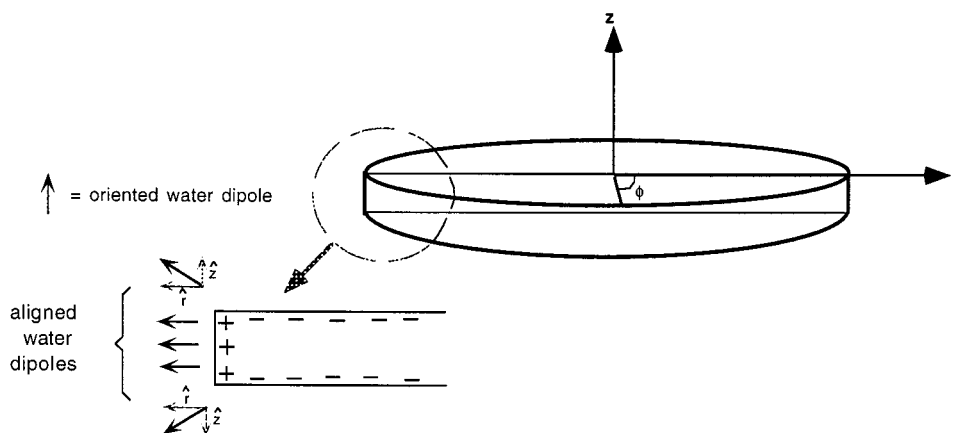
b. SHG Due to the Surface Charges on Clay Particles. An SHG signal was observed from the clay particles suspended in water in the absence of the organic molecule PR in the system. The SHG signal of the neat clay suspension in water is 5 times greater than the signal from neat water at pH 6. The observed SHG signal is due to the surface charges on the clay particles. It is known that an external electric field applied across a centrosymmetric bulk media can generate a field-induced second harmonic signal from the bulk media.[25−31] The external electric field polarizes the molecules in the bulk and thus breaks the centrosymmetry of the bulk material. In previous experiments, we have observed a similar effect from the intrinsic charges at the interfaces with no external field applied.[12,32−34] The electric field due to the surface charges polarizes the solvent molecules, i.e., water in the present studies, resulting in the breakdown of the centrosymmetry of the bulk solution (Scheme 3). When there are no surface charges, i.e., in the absence of a static field, the water molecules beyond the first few layers would be randomly oriented and consequently would not contribute to the SHG signal. The contribution of SHG from the surfaces charges is determined by the degree of the alignment of water molecules and the nonlinear electronic polarization induced by the static field of the surface charges.

The basal surface of the disk-shaped montmorillonite is negatively charged because of the isomorphous substitution of higher valence metal ions by lower valence metal ions in the lattice.[1−3] This basal plane charge density is independent of solution pH. However, the sign and the density of surface charges on the edge surface is pH-dependent because of the protonation and deprotonation of the broken and hydrolyzed Al−O and Si−O bonds on the edge surface. Theoretical studies show that the electric field due to the negative charges on the basal surface can "spill" over onto the positively charged edge surface, contributing to a negative electric field in the edge regions.[35−37] This "spillover" effect has been used to explain the experimental results of boron adsorption on edge surfaces[38] and the electrophoretic mobility of clay particles.[39] The SHG signal observed in our experiments can arise not only from the electric field due to the positive charges on the edge plane but also the negative charges on the basal planes. It is the resultant of the electric fields originating from both basal and edge surface charges along the radial direction, $\hat{r}$, experienced by the water molecules near the edge surface that determines the observed SHG intensity. The edge fields on the opposite sides of the clay particle are separated by the diameter of the particle, 0.5 μm, which is on the length scale of the light used in these experiments (see Scheme 4). Because of this fact, the second
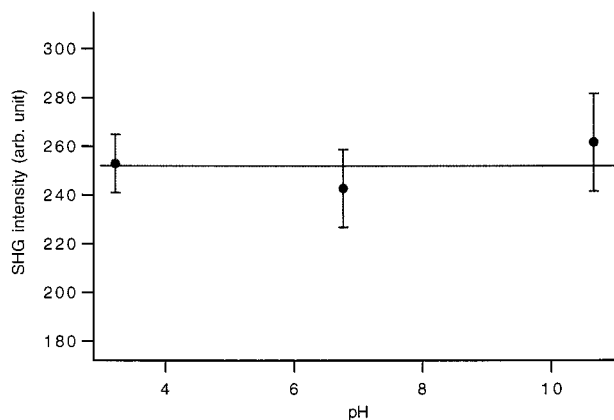
SCHEME 4

= oriented water dipole

aligned water dipoles

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Figure 2. pH dependence of SHG signal from the clay suspension at concentration of 0.005 w/w %. The electrolyte concentration is at 4.5 × 10^{-4} M. The pH is controlled by HCl and NaOH, and the electrolyte used is NaCl.

Figure 3. Electrolyte concentration dependence of SHG signal from the clay suspension, at concentration 0.005 w/w %. The solid line is the fit to the Gouy−Chapman model. The pH of the suspension is 6.1 ± 0.2, and the electrolyte used is NaCl.

harmonic fields generated from the polarized water molecules at the opposite edge surfaces of the clay particle do not cancel. Although the fields in the direction normal to the basal planes, $\hat{z}$, also polarize the water molecules, they do not contribute to the SHG signal because the opposing fields are separated by the thickness of the particles, 0.01 μm, which is much smaller than the wavelength of the light. The second-order polarizations induced in the solvent molecules have opposite phases and cancel; therefore, no SHG due to the electric fields normal to the basal plane is generated.

Figure 2 shows that the SHG signal does not depend on the pH of the aqueous solution in the pH range 3−11, at a constant electrolyte concentration of 4.5 × 10^{-4} M. Since the basal surface charges are independent of solution pH while edge surface charges are pH-dependent, this experimental result suggests that the observed SHG signal originates predominately from a spillover effect due to the permanent negative charges on the basal planes of the clay particle at this low electrolyte concentration. It is known that the isoelectric point of the edge surface of montmorillonite is ~9.5, and therefore, the edge surfaces are fully charged positively below pH 7. If the SHG signal originated chiefly from the water molecules polarized by the edge surfaces charges, the SHG signal would have changed as the pH of the aqueous suspension was varied from 3 to 11. It is to be noted that the basal surface area is much larger than the edge surface area, 50:1 for the particles used in this study. When the edge surface is positively charged to its maximum value, it comprises only 1% of the total surface charges of the montmorillonite particles. Our experimental results at an electrolyte concentration of 4.5 × 10^{-4} M reveal that a significant "spillover" effect occurs and that the electric field experienced by the water molecules near the edge surfaces is predominantly due to the basal surface charges.

We also observed that the SHG signal from the clay particles changed with electrolyte concentration (Figure 3), which indicates an electrostatic source of the SHG signal. The dependence of the SHG signal on electrolyte concentration is fitted to the Gouy−Chapman model, which describes the electric double layer of the charged surfaces. When a charged interface makes contact with an electrolyte solution, the ions in the solution redistribute themselves with respect to their distance from the charged interface.[6−7] The counterions in the solution screen the static electric field experienced by the water molecules in the solution. The number of water molecules that are polarized by the field as well as the magnitude of the polarization decreases as the electrolyte concentration increases.
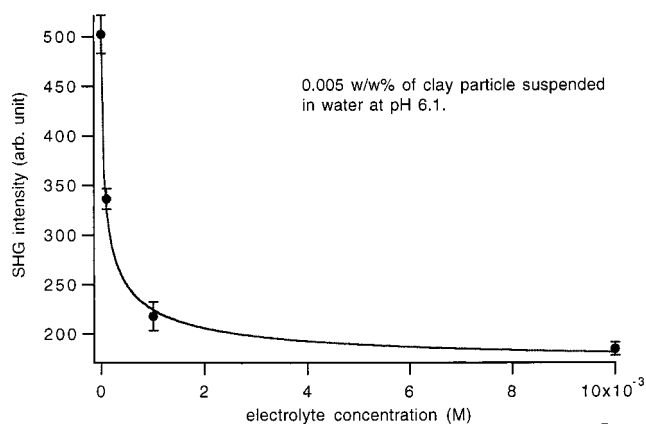
This leads to a change of the second harmonic field, $E_{2\omega}$. It has been shown that the surface potential and surface charge density of microscopic polystyrene particles and oil droplets in an oil/water emulsion can be obtained by measuring the SHG intensity at different electrolyte concentrations.[12] The observation of a SHG signal from clay particles due to the polarization of solvent molecules thus provides a method for investigating the electrostatic properties in the edge regions of clay particles.

The electrostatic properties of edge surfaces of clay particles are important to the stability of clay suspensions.[1] It is believed that flocculation of clay suspension can be induced by the "edge-to-face" interaction. At high electrolyte concentration (>10^{-2} M) the spillover effect is reduced and the electrostatic attraction between the positively charged edge surfaces and the negatively charged basal surfaces leads to aggregation of clay particles.[1,35,37] There are some theoretical studies of the electrostatic properties of clay particles in the region of the edge surfaces, which however cannot be examined because of a lack of in situ experimental techniques capable of selectively probing the local region near the edge surfaces of the clay particles. Our preliminary results indicate that applying SHG to the studies of clay particles provides a new method for investigating the local electrostatic properties of the edge surfaces.

c. Fluctuation of SHG Signal from the Anisotropic Clay Particles. It is worth mentioning that a fluctuation of SHG signals was observed from the clay particles both in the presence and in the absence of the adsorbate. These fluctuations have not been observed for isotropic microparticles, e.g., polymer particles, emulsions, and liposomes, in previous SHG studies.[8−13] We attribute the fluctuation to the rotational motions of the anisotropic disk-shaped clay particles. We will present these results and the inferred rotational relaxation time of the clay particles in aqueous solutions in a future publication.

5. Conclusions

The SHG method is applied for the first time to investigate the surfaces of microscopic clay particles. We observed the SHG signal originating from the edge regions of the centrosymmetric disk-shaped clay particles of Na−montmorillonite, which has a diameter of 0.5 μm and a thickness of 0.01 μm. A strong SHG signal was detected from an aqueous suspension of clay particles when the organic molecule 4-(2-pyridylazo)resorcinol (PR) was added to the aqueous clay suspension. The SHG signal results from PR adsorbed onto the edge surfaces of the particles, whereas adsorption onto the basal planes does not contribute

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to the SHG signal. Experiments on a neat clay suspension in water, i.e., no added organic species, yielded an SHG signal due to the polarization of water molecules in the edge regions of the clay particles. These observations demonstrate the applicability of the SHG method for studying molecular adsorption as well as electrostatic properties of clay particles.

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