The Journal of Physical Chemistry B

© Copyright 1998 by the American Chemical Society

VOLUME 102, NUMBER 11, MARCH 12, 1998

LETTERS

Interrogation of Nanoscale Silicon Dioxide/Water Interfaces via Hyper-Rayleigh Scattering

Fredrick W. Vance, Buford I. Lemon, Jessica A. Ekhoff, and Joseph T. Hupp*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208 Received: October 30, 1997; In Final Form: January 28, 1998

Hyper-Rayleigh scattering (HRS) experiments performed on nanometer-scale SiO₂/water interfaces (aqueous colloidal suspensions) display finite, measurable signals. HRS is not constrained by the orientational, size, and/or charge restrictions inherent to conventional interfacial second harmonic generation (SHG) or electric-field-induced SHG measurements. Thus, apparently for the first time, the second-order nonlinear optical (NLO) response of ultrasmall interfaces has been measured. pH- and electrolyte-dependent experiments show the response to be sensitive to changes in chemical composition at the silicon dioxide/solution interface. HRS provides detailed information about the surface of these technologically interesting and important particles in their native solution-phase environment.

Introduction

Metal oxide and semimetal oxide/solution interfaces are utilized in a variety of devices and device components including batteries,¹ electrochromic devices,² photoelectrochemical cells,³ chemical separations materials, condensed-phase catalysts (platforms as well as active sites),⁴ and hybrid biosensors (enzyme supports and encapsulation media).⁵ Nanoscale forms of these interfaces, both films and colloidal dispersions, have attracted particular attention in the context of photocatalytic waste remediation and dye-sensitized solar energy conversion.⁶ In many cases the stability, energetics, and/or efficacy of these interfaces depend crucially upon their precise chemical and physical structure (e.g., degree of crystallinity, degree of protonation, extent of adsorbate coverage, etc.). A detailed knowledge of structure, therefore, is often a prerequisite to understanding the molecular-level behavior of such interfaces.

Among the more powerful methodologies for interface characterization are those based on second harmonic generation (SHG).⁷ For otherwise centrosymmetric materials, interface formation breaks the centrosymmetry and provides for interface-localized signal generation. Indeed, SHG techniques have been widely applied to chemical and electrochemical interfaces where

they have proven useful for evaluating chemisorption,⁸ space charge properties,9 and surface symmetry and orientation problems.¹⁰ Because of the finite coherence length of the required incident radiation, however, a practical sample size limitation (lower limit) exists for conventional coherent SHG approaches.¹¹ We suspected that the size/coherence problem might be overcome by turning instead to incoherent second harmonic generation or hyper-Rayleigh scattering (HRS) spectroscopy.¹² HRS has emerged as a powerful new tool for resolving a related problem: the assessment of molecular first hyperpolarizabilities, β , for charged chromophores and nondipolar chromophores dissolved in isotropic media.¹³ Briefly, the HRS method relies upon random density fluctuations to create conditions compatible with net frequency doubling (i.e., minute reductions in overall solution symmetry). Recently, the technique has been advanced beyond molecular systems and applied to nanocrystalline metal colloid particles, where surface termination of the crystalline lattice apparently creates a condition of noncentrosymmetry observable by HRS.14 Here we report on the successful chemical interrogation of nanoscale silicon dioxide/water interfaces via the HRS technique.



Figure 1. Signal intensity versus wavelength, based on mode-locked excitation of a colloidal silica suspension at 820 nm. The width of the band is due to spectral broadening of the femtosecond laser excitation pulses used (dots indicate actual data, line is fit to Gaussian curve).

Experimental Section

SiO₂ colloids were purchased from Alfa-Aesar as 15% dispersions in H₂O. TEM experiments revealed the particles to be ca. 10 nm in diameter and completely amorphous. Samples were prepared by diluting the as-received sols with water (Millipore Milli-Q) 10-fold so that the final *molar* concentration of SiO₂ was 0.27 M. Within the pH's studied no flocculation or changes in the UV–vis spectrum were observed. Titrations were performed with 0.58 M HClO₄, 0.6 M HCl, 0.6 M NaClO₄, and 0.6 M NaCl as indicated below. In some experiments pH's were adjusted with NaOH prior to titration.

HRS measurements were performed by using a setup similar to one previously described.¹⁵ The incident radiation was generated by a mode-locked Ti:sapphire laser operating at 820 nm. Detection was accomplished via a cooled photomultiplier tube by utilizing a mechanical chopper and lock-in amplifier. Wavelength discrimination was accomplished by means of a 10 nm bandwidth interference filter centered at 410 nm or a double monochromator. To minimize uncertainties due to fluctuations in laser power or mode-locking quality, HRS signals were generally referenced against the simultaneously acquired output of a doubling crystal.

Results and Discussion

Hyper-Rayleigh scattering allows for the direct assessment of molecular hyperpolarizabilities, β , in multicomponent systems if β for one of the components has been previously established. If the intensity of the incident light is I_{ω} , then the frequencydoubled light observed at the detector ($I_{2\omega}$) for a two-component system is described by eq 1:

$$I_{2\omega} = G \langle N_s \beta_s^2 + N_a \beta_a^2 \rangle I_{\omega}^2$$
(1)

In eq 1, G is a parameter that encompasses collection efficiencies as well as local-field corrections, s and a denote solvent and analyte, N is the number density of each component, and the brackets indicate orientational averaging.

Figure 1 shows a wavelength scan centered at 410 nm. The nearly monochromatic nature implies that the observed signal is indeed HRS, a conclusion also supported by the observed quadratic dependence of signal intensities on incident power.¹⁶ Further evidence that the signal is HRS is found in Figure 2,



Figure 2. Dependence of HRS signal intensity on sample concentration, over the range from 0.011 F (6.6×10^{18} SiO₂ units/cm⁻³) to 0.27 F (1.6×10^{20} SiO₂ units/cm⁻³) at pH = 10.4.

where the dependence on concentration is shown. As predicted by eq 1, the signals scale linearly with the concentration of colloid present; residual SHG, on the other hand, would have yield a squared dependence on colloid concentration.

If the HRS signal arises from *molecular* scale discontinuities (surface and internal inhomogeneities comprised of only a few atoms) the most straightforward manner in which to quantitate β is in terms of the formula unit SiO₂. Using water as an internal standard ($\beta_{water} = 0.56 \times 10^{-30}$ esu),¹⁷ the value of β per SiO₂ unit was determined to be between 60×10^{-30} and 250×10^{-30} esu. For comparison, this is larger than the commonly studied organic chromophore *p*-nitroaniline by more than a factor of 2.¹⁸ Realizing that only a portion of the formula units present may actually contribute to the signal (those not strictly canceled by symmetry), the actual contribution from each "molecular" scatterer is probably higher.

The foregoing analysis assumes that scattering originates from localized, molecule-like sites imbedded within a nanoscale particle. If scattering instead originates from collective interactions, a more conventional interfacial analysis may be appropriate and a "per particle" β value may be more significant. In any case, the "per particle" value for β is estimated to fall between 6000×10^{-30} and $30\ 000 \times 10^{-30}$ esu.

The incident light used in the HRS experiment described here is vertically polarized; detection as a function of linear polarization can provide insight into the symmetry components of the β tensor. Figure 3 shows the result of such an experiment, where the vertical-to-horizontal ratio was found to be 22 ± 3 . This large degree of difference is remarkable when compared with molecular systems, where the ratio can be interpreted quantitatively by considering the symmetry point group under investigation. For example, one finds that for charge-transfer chromophores of $C_{2\nu}$ symmetry, the ratio is 5 when the component of β along the charge-transfer axis dominates.^{13b} For the colloids under study here, no such symmetry assumptions can be made, but it is apparent that if a "molecular" interpretation of the hyperpolarizability is appropriate, several of the 18 possible β components must contribute to the observed signal.

Surface perturbations can be easily accomplished by changing the pH of the bulk solution with addition of acid or base. The acid/base chemistry of macroscopic silicon dioxide/water interfaces is characterized by surface pK_a 's of ca. 5 and 9.¹⁹ Titration of diluted stock or base-adjusted colloidal suspensions allows the HRS response to be studied over a wide pH range



Polarizer Angle (degrees)

Figure 3. HRS signal for colloidal silicon dioxide/water sample excitation as a function of the polarizer angle, θ . Here 0° corresponds to vertical and 90° to horizontal polarization at the detector. (The excitation source is vertically polarized.) Fitting the data to $a \cos^2(\theta - c) + b$ yields the depolarization ratio, (a + b)/b, which was found to be 22 ± 3 .



Figure 4. Dependence of colloidal silica HRS signal intensity on solution pH (\bullet , \Box , and \bigtriangledown indicate three different dilution-corrected experiments that have been normalized in the mid-pH region).

(ca. 10 pH units). Figure 4 shows the results of pH-dependent HRS measurements. Accompanying passage through each pK_a (and concomitant with each pK_a on the resulting titration curve) is an attenuation of the HRS signal. Simultaneous evaluation of Rayleigh scattering, which should be strongly particle-size-dependent, shows that the effective particle size is not changing significantly during the HRS/pH titrations. Thus, alternative explanations for the HRS signal variations based on either particle aggregation or particle dissolution can be excluded.

Interestingly, qualitatively similar pH behavior has been reported by Ong et al. based on coherent SHG studies of a planar, macroscopic silica/water interface.¹⁹ There the pH dependence was interpreted in terms of an interface charging effect associated with surface H⁺ loss. Charging yields a surface potential and field which, when combined with two optical fields, evidently generates a $\chi^{(3)}$ response from a preferentially oriented interfacial water layer. Support for the $\chi^{(3)}$ interpretation was provided by electrolyte concentration studies which showed that SHG signals substantially decrease with increasing concentration, as expected from a simple Guoy–Chapman description of the interfacial potential drop.

In contrast, the HRS signals observed here *increased* slightly with increasing solution ionic strength (see Supporting Information), implying that an alternative signal modulation mechanism is operative. We suggest that the alternative mechanism may involve changes in β itself with the extent of surface protonation. One way of describing "nonresonant" hyperpolarizabilities in the molecular limit is in terms of extreme *pre*resonance with one or more high-energy electronic transitions. To contribute to the tensor element, a transition must possess a finite oscillator strength and must involve a net redistribution of electronic charge leading to a change in dipole moment ($\Delta \mu$). Given these preconditions, the contribution of a particular electronic transition to $|\beta|$ will then scale roughly as $1/E_{op}^2$, where E_{op} is the transition's absorption energy maximum.²⁰

Given the pH dependence of β (HRS), obvious candidate transitions would include one or more surface or defect localized oxo-to-silicon charge-transfer transitions, such as that arising from a surface SiO⁻ functionality. Conversion of the oxo groups (formally 2–) to hydroxo functionalities (formally $1-)^{21}$ should substantially increase E_{op} and presumably diminish the contributions of the surface charge-transfer transition(s) to β . The presence of two types of Si-OH groups on the surface, isolated (Si-O)₃-Si-OH (Q³) and geminal (Si-O)₂-Si- $(OH)_2$ (diol, Q²), has been demonstrated by IR and CPMAS NMR studies on various silica solids, gels and sols.²² The number of Q^3 to Q^2 groups on the surface correlate with our observed signal attenuation observed with passage through each pK_a . This analysis is also supported by change in β per acid site calculations.²³ In contrast to the $\chi^{(3)}$ enhancement mechanism, however, the preresonant surface charge-transfer mechanism would yield little or no ionic strength sensitivity-again consistent with available experimental observations. Finally, we note that if the preresonance interpretation is correct, then significantly larger HRS signals and an enhanced sensitivity of HRS intensities to surface and interface chemical composition might be expected if HRS were attempted closer to resonance. We are currently exploring this possibility by utilizing nanoscale semiconductor/solution and metal/solution interfaces in place of the insulator/solution interface examined here.

Conclusions

HRS measurements of nanometer-sized SiO₂/water interfaces represent a new method for interrogating the surface chemistry and photophysical properties of these materials. The applicability of the HRS technique to ultrasmall interfaces, i.e., interfaces difficult to examine by conventional coherent SHG techniques, stems from the intentional detection of *incoherently* scattered light. Also, in contrast to the conventional "molecular" secondorder experiment, EFISHG, HRS sample preparation is quite facile. No electric field or sample orientation is required, allowing for the study of charged particles or materials and pHdependent experiments where charged species are necessarily present.

These results provide telling information concerning the nature of the silicon oxide/solution interface. Concentrationand wavelength-dependent measurements show that the effect seen is indeed hyper-Rayleigh scattering and that the observed β per SiO₂ formula unit is 60×10^{-30} to 250×10^{-30} esu. Experiments to elucidate the nature of the β response in SiO₂ show that the signal is strongly dependent on pH and weakly dependent on ionic strength. pH-dependent experiments show that the HRS signal tracks the titration curve, with a marked decrease in signal as each of the surface pK_a 's is passed. The results of variable ionic strength experiments support the speculation that the signals arise from a "molecular" (imbedded surface site) first hyperpolarizability effect rather than an interfacial double-layer-based $\chi^{(3)}$ effect. Acknowledgment. We thank the Office of Naval Research, the Army Research Office (MURI program), and the Materials Research Center at Northwestern University (NSF-DMR-9632472) for support of this work. J.A.E. thanks the NSF Summer Undergraduate Research Program in Solid State Chemistry for a fellowship (NSF-DMR-9300695). B.I.L. and F.W.V. additionally thank the VLCHC.

Supporting Information Available: A figure and text describing the dependence of interfacial hyper-Rayleigh scattering intensity on solution ionic strength (1 page). Ordering and accessing information is given on any current masthead page.

References and Notes

 Macklin, W. J.; Neat, R. J. Solid State Ionics 1992, 53–56, 694.
 Granqvist, C. G. Handbook of Inorganic Electrochromic Materials; Elsevier: Amsterdam, 1995.

(3) O'Regan, B.; Grätzel, M. Nature 1991, 353, 737.

(4) (a) Schmelling, D. C.; Gray, K. A.; Kamat, P. V. *Environ. Sci. Technol.* **1996**, *30*, 2547. (b) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1988**, *22*, 798.

(5) Dave, B. C.; Dunn, B.; Valentine, J. S.; Zink, J. I. Anal. Chem. 1994, 66, 1120A.

(6) (a) Hagfelt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (b) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69

(7) Corn, R. M.; Higgins, D. A. Chem. Rev. 1994, 94, 107.

(8) (a) Campbell, D. J.; Lynch, M. L.; Corn, R. M. *Langmuir* **1990**, *6*, 1656. (b) Lynch, M. L.; Barner, B. J.; Corn, R. M. J. Electroanal. Chem. **1991**, *300*, 447.

(9) Lantz, J. M.; Baba, R.; Corn, R. M. J. Phys. Chem. 1993, 97, 7392.
(10) (a) Lynch, M. L.; Corn, R. M. J. Phys. Chem., 1990, 94, 4382. (b)
Shen, Y. R. Nature 1989, 337, 519. (c) Peterson, E. S.; Harris, C. B. J. Chem. Phys. 1989, 91, 2683.

(11) For a quantitative discussion of effective sample size limitations in conventional (coherent) SHG experiments, see: Wang, H.; Yan, E. C. Y.; Borguet, E.; Eisenthal, K. B. *Chem. Phys. Lett.* **1996**, *259*, 15.

Importantly, these authors show that the limiting material's length can beat least an order of magnitude *less* than the wavelength of incident light.

(12) Clays, K.; Persoons, A. Phys. Rev. Lett. 1991, 66, 2980.

(13) (a) Verbeist, T.; Clays, K.; Samyn, C.; Wolff, J.; Reinhoudt, D.;
Persoons, A. J. Am. Chem. Soc. 1994, 116, 9320. (b) Kaatz, P.; Shelton, D.
P. J. Chem. Phys. 1996, 105, 3918. (c) Coe, B. J.; Chamberlain, M. C.;
Essex-Lopresti, J. P.; Gaines, S.; Jeffery, J. C.; Houbrechts, S.; Persoons,
A. Inorg. Chem. 1997, 36, 3284.

(14) Clays, K.; Hendrickx, E.; Triest, M.; Persoons, A. J. Mol. Liq. 1995, 67, 133.

(15) Clays, K.; Persoons, A. Rev. Sci. Instrum. 1994, 65, 2190.

(16) At high concentrations and high power, the power dependence of the observed signal is less than quadratic but greater than linear. The subquadratic dependence appears to arise from a thermal gradient effect and will be further explored in future work.

(17) Boutton, C.; Clays, K. Private communication.

(18) (a) Oudar, J. L.; Chemla, D. S. J. Chem. Phys. 1977, 66, 2664. (b)
Morrison, I. D.; Denning, R. G.; Laidlaw, W. M.; Stammers, M. A. Rev. Sci. Instrum. 1996, 67, 1445. (c) Pauley, M. A.; Guan, H.-W.; Wang, C. H.; Jen, A. K.-Y. J. Chem. Phys. 1996, 104, 7821. (d) Woodford, J. N.; Pauley, M. A.; Wang, C. H. J. Phys. Chem. A 1997, 101, 1989.

(19) Ong, S.; Zhao, X.; Eisenthal, K. B. Chem. Phys. Lett. 1992, 191, 327.

(20) The more general two-level expression is^{18a}

$$\beta = \frac{3\mu_{12}^2 \Delta \mu_{12} E_{op}^2}{2(E_{op}^2 - E_{ipc}^2)(E_{op}^2 - 4E_{ipc}^2)}$$

where μ_{12} is the transition moment, $\Delta \mu_{12}$ is the change in dipole moment, and E_{inc} is the energy of the incident light used.

(21) Recall that while the formal charge on the ligand is either 2- (oxo) or 1- (hydroxo) the resulting contribution to the total charge of the colloid is either 1- or 0 for the respective ligands because the oxo- and hydroxo-terminated colloid necessarily contains a slight excess of oxygen. Thus, the overall particle reaches a point of zero charge when all of the surface groups have been protonated.

(22) Bergna, H. E. *The Colloid Chemistry of Silica*, Bergna, H. E., Ed.; Advances in Chemistry Series 234; American Chemical Society: Washington, DC, 1994; pp 1–47 and references therein.

(23) A localized oxo- or hydroxo-to-silicon charge-transfer interpretation invites evaluation on a "per active site" basis. From the experimentally determined buffer capacities of the silica colloid solutions, the protonation-induced *changes* in β per active site are ca. 130×10^{-30} esu in the high-pH region (Q³) and 170×10^{-30} esu in the low-pH region (Q²).