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Second-harmonic generation and theoretical studies of protonation at the water/α-TiO_2 (1 1 0) interface

Jeffrey P. Fitts [a,1], Michael L. Machesky [b], David J. Wesolowski [c], Xiaoming Shang [a], James D. Kubicki [d], George W. Flynn [a], Tony F. Heinz [a], Kenneth B. Eisenthal [a,*]

[a] Departments of Chemistry and Physics, Environmental Molecular Science Institute, Columbia University, 3000 Broadway Ave, Mail Code 3107, New York, NY 10027, USA
[b] Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820-7495, USA
[c] Oak Ridge National Laboratory, Chemical Sciences Division, P.O. Box 2008, Oak Ridge, TN 37831-6110, USA
[d] Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, USA

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Abstract

The pH of zero net surface charge (pH_{pzc}) of the α-TiO_2 (1 1 0) surface was characterized using second-harmonic generation (SHG) spectroscopy. The SHG response was monitored during a series of pH titrations conducted at three $NaNO_3$ concentrations. The measured pH_{pzc} is compared with a pH_{pzc} value calculated using the revised MUltiSIte Complexation (MUSIC) model of surface oxygen protonation. MUSIC model input parameters were independently derived from ab initio calculations of relaxed surface bond lengths for a hydrated surface. Model (pH_{pzc} 4.76) and experiment (pH_{pzc} 4.8 ± 0.3) agreement establishes the incorporation of independently derived structural parameters into predictive models of oxide surface reactivity.

1. Introduction

Protonation reactions occurring at aqueous solution–oxide mineral interfaces serve as the foundation for theoretical models describing a wide range of physical phenomena, including sorption, dissolution, crystallization and charge development [1–3]. Models promising the most general application and predictive power relate protonation reactions to the molecular structure and bonding of surface oxygens [4–7]. The greater than 1000-fold difference observed between oxygen exchange rates of two distinct, but structurally similar, sites on the model oxide surrogate 'Al_{13}' polyoxocation highlights the strong correlation between oxide surface structure and reactivity [8]. No method, however, exists to unambiguously observe the protonation behavior of individual types of surface oxygens on mineral oxide particles suspended in liquid water, as commonly encountered in nature and in commercial applications of catalytic substrates and ceramic raw materials.

Planar single-crystal oxide substrates exposing a single crystallographic surface possess the structural constraints required to begin to investigate individual types of surface oxygens. The oxygen-terminated (1 1 0) surface of rutile (α-TiO_2) studied here, for example, possesses only three distinct types of surface oxygens. In addition, synchrotron X-ray scattering studies of these model single crystals [9–11] along with ab initio calculations [12–15] are beginning to provide a precise molecular picture of fully hydrated oxide surfaces.

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[*] Corresponding author. Fax: +1 212 932 1289.
E-mail address: eisenth@chem.columbia.edu (K.B. Eisenthal).

[1] Present address: Environmental Sciences Department, Brookhaven National Laboratory, Upton, New York, NY 11973-5000, USA.

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Validation of predictive models based on this molecular picture requires experimental measurements of single-crystal substrate reactivity. Titration methods commonly used to study the charging behavior of particle suspensions, however, are not readily applicable to single-crystal surfaces.

Four experimental techniques have been used to characterize the pH-dependent charging behavior of single-crystal surfaces, planar amorphous oxides and ultrathin films: second-harmonic generation (SHG) spectroscopy [16–18], sum-frequency generation spectroscopy [19,20], streaming potential [21], and surface force measurements [16,22–24]. The pH_{pzc} value, which corresponds to the pH where the net oxide surface charge is zero, is commonly predicted using a thermodynamic model of oxide surface protonation reactions. Several studies have demonstrated that SHG applied to a crystallographic plane exposed on the properly prepared single-crystal surface offers the high level of precision required for model validation [16–18].

In the current study, charge development at the aqueous-(1 1 0) rutile single-crystal interface was characterized by monitoring the second-harmonic intensity during consecutive titrations conducted at three different electrolyte concentrations. The measured pH_{pzc} is compared to a calculated value from a thermodynamic model that is constrained by Ti–O bond lengths independently derived from ab initio calculations of a hydrated surface structure.

2. Experimental

The laser source for the SHG measurements was a modelocked Ti:sapphire laser (KMlab) which provided 35 fs pulses at wavelength of 800 nm (corresponding to the fundamental angular frequency ω) at a repetition rate of 80 MHz and an average power of 0.66 W. Additional details about the optics and experimental cell are described elsewhere [17]. Photo-chemical damage and thermal effects were detected by monitoring SH signal stability. The pulse repetition rate and, hence, average power were reduced by a factor of five using an optical chopper until signal drift was not observed over the course of an hour. Three replicate experiments, conducted on different days (i.e., different power levels) after freshly preparing the surface of the same crystal (preparation procedure described below) are consistent, and therefore, do not indicate photochemical damage or thermal effects. The second-harmonic photons at a wavelength of 400 nm (corresponding to the SH angular frequency of 2ω) were separated from fundamental and background light with an interference filter prior to collection by a single-photon counting system. Only the *p*-polarized component of the SH was detected. Each data point corresponds to the mean of three consecutive 100 s measurements.

Polished rutile single crystals (1 cm × 1 cm × 1 mm) were obtained from Princeton Scientific, with a miscut of 0.1–0.2° with respect to the (1 1 0) crystallographic plane. The surface preparation described in our previous work [10] produces a (1 1 0)-terminated surface with atomically flat terraces separated by single unit cell high steps.

Every effort was made to minimize aqueous species which might specifically adsorb onto the rutile surface. Specific adsorption could complicate both the SHG measurement as relatively slow adsorption may cause signal drift, and the data interpretation as the model describing surface charge does not consider surface species other than rutile surface groups. Carbonate was excluded during titrations by continuously purging the Teflon reaction cell as carbonate species are known to specifically adsorb on oxide surfaces and contribute to surface charge [25]. Only ultra high purity argon and nitrogen (99.999%) were used as purge gases. A.C.S. reagent grade nitric acid (Aldrich) and low-carbonate sodium hydroxide (J.T. Baker Dilut-it) were used as titrants. Low-carbonate sodium hydroxide solutions were prepared in an argon-purged glove bag and sealed with rubber septa prior to each experiment. Sodium hydroxide additions were made using a syringe. Nitric acid and electrolyte stock solutions were purged prior to use. The solution pH was continuously monitored during the titrations with a low-flow double junction glass electrode (Corning). Sodium nitrate (Aldrich-99.99%) was used as the electrolyte because X-ray scattering studies of ion adsorption on (1 1 0) rutile single-crystal surfaces indicate that specific nitrate adsorption is negligible above pH 3 and specific sodium adsorption is only observed above the pH_{pzc} as a minor species [10].

Reversibility of the pH-dependent processes responsible for the observed change in the SHG response was indicated by consecutive acid and base titrations that showed no significant hysteresis. Process reversibility, (i.e., reversibility of protonation and deprotonation of surface groups) indicates that a state of quasi-equilibrium was reached within five minutes following each acid/base addition. After completing 1, 10 and 100 mM $NaNO_3$ titrations, the cell solution was replaced with a fresh electrolyte solution and a titration at one of the electrolyte concentrations was repeated in order to check for both reproducibility and SH signal-level shifts caused by changes in alignment or laser power output.

3. Results and discussion

In the current study, charge development at the aqueous-(1 1 0) rutile single-crystal interface was characterized by monitoring the second-harmonic intensity during consecutive titrations (pH 3–7.5) conducted at three different electrolyte ($NaNO_3$) concentrations (Fig. 1). SHG, as a second-order non-linear optical process is electric dipole forbidden in centrosymmetric media [26]. SHG from the interface formed between water and any centrosymmetric oxide mineral is therefore sensitive to the structure and electronic properties of water molecules and oxide surface atoms in the narrow interfacial region where the inversion symmetry is broken. In particular, SHG is highly sensitive to the charge state of the surface through the non-linear response of water molecules that are partially aligned by the electric field [18,27]. The associated electric field will depend on the bulk electrolyte concentration through the ionic screening of charged surface groups [18]. The second-harmonic intensity will be independent of electrolyte concentration only at pH values where the surface has a net zero charge. In Fig. 1 the crossing point of the three titration curves at pH 4.8 ± 0.3 corresponds to the pH_{pzc} of the single-crystal surface. The non-zero second-harmonic intensity observed at the pH_{pzc} results from any partially aligned water dipoles and the surface oxygen and titanium atoms within the interfacial region where the inversion symmetry is broken.

Fig. 2 is a schematic representation of the rutile (1 1 0) surface consistent with the revised MUSIC model [5]. This model assumes that metal ions exposed on the surfaces of metal oxides immersed in water will complete their bulk-crystal coordination geometry by chemisorbing water molecules on exposed metal atoms and by protonation of surface oxygens. The model provides a way of predicting the equilibrium constants (pK_a) for protonation of surface oxygens which may be bonded to one or more underlying metal ions. Inputs to the model include the number and formal charge of surface oxygens bound to a specific type and number of metal ions in the underlying crystal surface. Additional inputs include the number of donating or accepting hydrogen bonds associated with each type of surface oxygen, as well as the lengths of all metal–oxygen bonds in the surface region. Outputs from the model include both the partial charges of the surface sites and the pK_a values, from which it is then possible to calculate the pH_{pzc} of the surface. The MUSIC model in its calculation of pK_a values based on molecular level structures represents a significant advance beyond the traditional practice of assigning one or more generic surface protonation sites to explain experimental surface titration data (e.g., pH-dependent proton uptake and release, ion adsorption, streaming potential, electrophoretic mobility, colloidal dispersion/flocculation, etc.) [5].

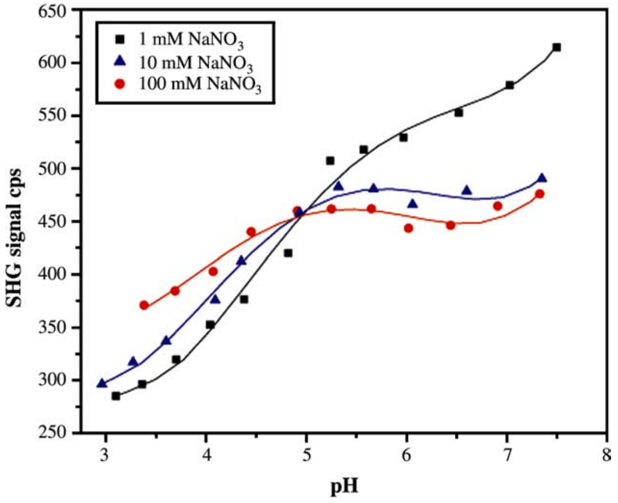

Fig. 1. SHG signal from the water–rutile (1 1 0) interface as the bulk solution pH was titrated from 3.0 to 7.5 at 1 (■), 10 (▲) and 100 (●) millimolar $NaNO_3$ concentrations. The pH_{pzc} of the (1 1 0) rutile surface (pH 4.8 ± 0.3) is identified by the crossing of the three 3rd-order polynomial fits. The uncertainty of the pH_{pzc} is based on the results of three replicate sets of titrations conducted on different days after freshly preparing the surface of the same crystal.

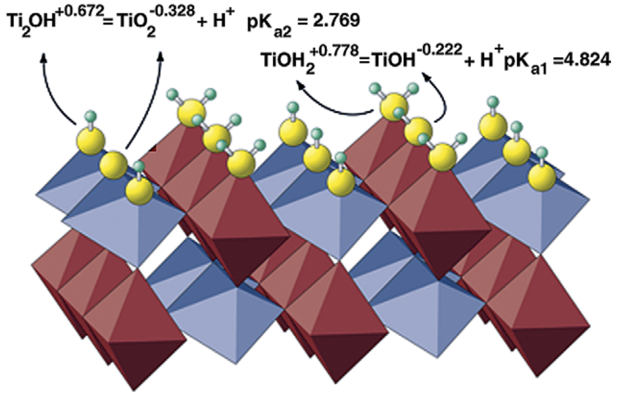

Fig. 2. Ab initio optimized MUSIC model-predicted protonation of hydrated (1 1 0) rutile surface. Protonation (green spheres) of surface oxygens (yellow spheres) reflect the four possible protonation states predicted by the revised MUSIC model: surface oxygens bridging two Ti octahedra (blue TiO_6 units) coordinate to one or zero protons, and surface oxygens at the apex of one Ti octahedral unit (red TiO_6 units) coordinate to one or two protons. The partial charges and equilibrium constants (pK_a) were calculated with the MUSIC model using surface oxygen–Ti bond lengths predicted by ab initio calculations.

Application of a recent modification [6] of the revised MUSIC model [5] to the vacuum-terminated rutile (1 1 0) surface predicts the formation and protonation of three unique types of surface oxygens upon surface hydration: (1) oxygen atoms in the Ti surface plane bonded to three Ti atoms that do not protonate in the accessible pH range (ca. 0–14); (2) bridging oxygens protruding above the Ti surface plane and bound to two surface Ti atoms that undergo a single protonation step in this pH range; (3) bare Ti atoms exposed at the surface that chemisorb a single water molecule, which may dissociate to form a hydroxyl group at sufficiently high pH. Bridging (Ti_2O and Ti_2OH) and terminal ($TiOH$ and $TiOH_2$) protolytic surface oxygens are highlighted in Fig. 2. This configuration is consistent with the 'associative' and 'dissociative' water adsorption models derived from spectroscopic and ab initio studies of rutile (1 1 0). These studies indicate that water adsorbs on this surface either as discrete water molecules directly atop the bare surface Ti atoms or, or alternatively, adsorbs dissociatively with a hydroxyl group bonding to the surface Ti and the released proton binding to an adjacent bridging oxygen [14,15,28,29]. X-ray scattering results, ab initio calculations and MD simulations indicate that the rutile 1 1 0 surface does not reconstruct in aqueous environments [10]. This behavior is in contrast to high-vacuum environments where surface reconstruction is a common phenomenon [30].

The revised MUSIC model has typically been applied with bond lengths of the surface species assumed to be the same as in the undistorted bulk crystal structure, 1.984 and 1.946 Å, respectively, for the Ti–O and Ti–O–Ti bonds on a rutile (1 1 0) surface [5]. This assumption, however, gives a calculated pH_{pzc} of 8.68 or 6.51 at 25 °C, depending on whether the bridging surface oxygen is assumed to form 1 or 2 accepting H-bonds with associated water molecules [5,6]. The values are significantly higher than the highly reproducible value of 5.4 ± 0.2 obtained from pH titrations in NaCl solutions over a range of ionic strengths using rutile powders which predominantly exhibit the (1 1 0) crystal face [31,32]. While the bulk titration results of particle suspensions are different from the SHG results to within the reported errors, the two results are similar, and therefore, consistent with the assumption that the charging behavior of the rutile particles is dominated by regular surface groups on the (1 1 0) crystallographic surfaces. The bulk-crystal bond lengths, however, had to be arbitrarily relaxed in order to closely match (to within 0.2 pH unit) experimental pH_{pzc} values from 25 to 250 °C with the revised MUSIC Model [6].

Our recent ab initio DFT calculations of hydrated 5-layer rutile slabs [12,13] provide an independent method for estimating the bond lengths of the relaxed rutile (1 1 0) surface, giving values of 1.90 and 1.87 Å for the Ti–O bond lengths of the Ti–OH and Ti–O–Ti surface oxygens. Using the calculated bond lengths and the crystallographically dictated 1:1 distribution of Ti–OH and Ti–O–Ti sites [33] (with the latter site accepting one H-bond from an associated water molecule), we find that the recently revised version of the MUSIC model [6] gives the fractional charges and pK_a values for protonation of these sites shown in Fig. 2. This results in a calculated pH_{pzc} of 4.76 at 25 °C, in quantitative agreement with the SHG experimental result of 4.8 ± 0.3 reported above. It should be noted that the calculations were not adjusted to yield agreement with the SHG results. The MUSIC model calculation of both the partial charges and pK_a values are sensitive to the bond lengths of the relaxed structures. It is therefore necessary that additional theoretical and experimental comparisons of other single-crystal oxide surfaces be carried out to further test the ability of the revised MUSIC model [5,6] and similar bond-valence [4,34] and molecular modeling approaches [35,36] to predict surface acidity based on independent ab initio and molecular dynamics calculations together with experimental determinations of surface structure.

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