Supporting Information for

Second Harmonic Scattering Reveals Ion-Specific Effects at the SiO$_2$ and TiO$_2$ Nanoparticle/Aqueous Interface

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1. AR-SHS model and theory

In the following we briefly summarize some of the essential aspects of the AR-SHS model and the nonlinear optics theory relevant to the fitting procedure. A more detailed description can be found elsewhere.\textsuperscript{1–5} In a non-resonant AR-SHS experiment, the fundamental frequency of a high-energy femtosecond laser pulse interacts with an aqueous solution that contains particles. The intense femtosecond laser pulses distort the electron clouds of all non-centrosymmetric molecules, which causes a displacement of charge with a frequency component of $2\omega$. These induced charge oscillations are, to leading order, the origin of second-order induced molecular dipole moments. The sum of all second-order induced molecular dipoles results in a macroscopic polarization $\mathbf{P}^{(2)}$. This polarization $\mathbf{P}^{(2)}$ is equal to:

$$
\mathbf{P}^{(2)}_{2\omega} = \varepsilon_0 \chi^{(2)} : \mathbf{E}(\omega) \mathbf{E}(\omega)
$$

where $\varepsilon_0$ is the vacuum permittivity, $\chi^{(2)}$ is the second-order susceptibility, which describes the local second harmonic response of the medium, and $\mathbf{E}(\omega)$ is the incoming electromagnetic field for SHS. The generated electromagnetic wave has double the frequency ($2\omega$) of the incoming light. In the electric dipole approximation, the emission of SH light is forbidden in the bulk of centrosymmetric media as they possess inversion symmetry. Considering a spherical particle with an isotropic amorphous interior and water as an isotropic liquid, the SH signal originates specifically from the non-centrosymmetric regions at the interface. Under non-resonant conditions, the second-order polarization $\mathbf{P}^{(2)}$ depends on the molecular electron density in the interfacial region. Therefore, every non-centrosymmetric molecule in the non-centrosymmetric region around the particle contributes equally to the SH polarization. Because the SH intensity scales quadratically with the number density of molecules, the majority of the SH signal intensity originates from water molecules at the interface, as the number of non-centrosymmetrically distributed surface groups of the particle is much smaller than the number of oriented water molecules at the interface. The SHS signal then arises from the net orientational order of water molecules along the surface normal. Besides the $\chi^{(2)}$ contribution to the SHS signal that describes the orientational order induced by all (chemical) interactions confined to the particle surface plane, the electrostatic field $\mathbf{E}_{DC}$ generated between
the counterions and the charged surface affects the SHS signal. The effective third-order susceptibility tensor $\chi^{(3)'}$ represents all processes that lead to the emission of SH light and require an interaction with $E_{DC}$. This includes the reorientation of water molecules in the interfacial region up to the maximum penetration depth of $E_{DC}$ into the solution (main $\chi^{(3)'}$ contributions) as well as a pure third-order interaction that arises from the isotropic third-order susceptibility of bulk water, which is in practice negligible. The resulting effective third-order polarization $P^{(3)'}$ is defined as:

$$P^{(3)'}_{2\omega} \propto \varepsilon_0 \chi^{(3)'}: E(\omega) E(\omega) \Phi_0$$

with $\Phi_0 = \int_{0}^{\infty} E_{DC}(z) dz$ being the surface potential. We then obtain for the total SHS intensity $I_{2\omega} = |P_{2\omega}^{(2)} + P_{2\omega}^{(3)'|}^2$. Thus, within the Rayleigh-Gans-Debye-(RGD) approximation, which assumes no reflection nor absorption by the scatterer, the SHS intensity can be given as:

$$I_{2\omega} \propto \left[ \Gamma^{(2)}(R, \chi^{(2)}, \theta) + \Gamma^{(3)'}(R, \chi^{(3)'}, \theta, \kappa^{-1}) \cdot \Phi_0 \right]^2$$

Where $R$ is the particle radius, $\theta$ the scattering angle, and $\kappa^{-1}$ the Debye length (directly correlated to the ionic strength of the solution). The general expression of the Debye length for electrolytes is

$$\kappa^{-1} = \sqrt{\left( \frac{\varepsilon_0 \varepsilon_r k_B T}{1000 e^2 N_A \sum_i z_i^2 c_i} \right)}$$

and takes into account the vacuum and relative permittivity $\varepsilon_0$ and $\varepsilon_r$ respectively, the Boltzmann constant $k_B$, the temperature $T$, the elementary charge $e$, the ion valency $z$, Avogadro’s number $N_A$, and the ionic concentration $c_i$. $\Gamma^{(2)}$ and $\Gamma^{(3)'}$ are respectively the effective second- and third-order susceptibilities that are connected to the two SH contributions $\chi^{(2)}$ and $\chi^{(3)'}$ through multiplication of geometrical form factors that are specific to the geometry of the scatterer and the geometry of the incoming and outgoing electromagnetic fields. In the experimental geometry that we use, we obtain nonzero normalized SHS signal in two independent polarization combinations of light: PPP and PSS (for spherical particles, PSS=SSP=SPS). Here the first letter refers to the polarization state of the SH beam and the second and third letter refer to that of the fundamental incoming beam. P polarized light is parallel and S polarized light is perpendicular to
the scattering plane. Within the aforementioned RGD approximation, the scattered intensity from a sphere or shell in the two independent polarization combinations normalized by the bulk water signal can analytically be expressed as:

\[
\frac{I_{ppp}(\omega)}{I_{sss}(\omega)} = \frac{\varepsilon_0^2 (E_p(\omega))^2 \left[ \cos\left(\frac{\theta}{2}\right) (\Gamma^{(2)} + \Gamma^{(3)}) (2\cos(\theta) + 1) \right]}{\mu^2 N_b / N_p}
\]

(4)

\[
\frac{I_{pss}(\omega)}{I_{sss}(\omega)} = \frac{\varepsilon_0^2 (E_s(\omega))^2 \left[ \cos\left(\frac{\theta}{2}\right) (\Gamma^{(2)} + \Gamma^{(3)}) \right]}{\mu^2 N_b / N_p}
\]

(5)

where \(\mu = \beta^{(2)} H_2O E(\omega)^2\) is the averaged induced second-order dipole moment with \(\beta^{(2)} H_2O\) being the averaged hyperpolarizability of water. \(N_p\) is the number of colloidal particles per volume and \(N_b\) is the density of bulk water \((3.34 \cdot 10^{28} \text{ molecules/m}^3)\), so that \(N_b / N_p\) is the number of bulk water molecules per particle. A summary of all the relevant constants and analytical expressions used can be found in Ref 6. Note that the effective third-order susceptibility \(\Gamma^{(3)}\) is directly related to the surface potential \(\Phi_0\) and the effective second-order susceptibility \(\Gamma^{(2)}\) is related to the orientation of water molecules at the interface given by \(\chi^{(2)}\) as described in Eq. 3. By fitting the measured and normalized AR-SHS patterns in two different polarization combinations according to Eqs. 4 and 5, absolute values for the surface potential and the orientation of water molecules at the surface can be extracted.

In order to obtain absolute values for the surface potential \(\Phi_0\) and of the tensor elements of \(\chi^{(2)}\) as a measure of surface molecular orientation of water molecules, the relative measured SHS signal needs to be related to absolute quantities. Here we use the fact that the second-order hyperpolarizability \(\beta^{(2)}\) and the third-order hyperpolarizability \(\beta^{(3)}\) of uncorrelated water are known, so that through normalization by \(I_{sss}\), the measured SHS response can directly be linked to an absolute value of the \(\beta^{(2)}\) component of the solution containing particles. The second-order hyperpolarizability \(\beta^{(2)}\) is connected to the second-order susceptibility \(\chi^{(2)}\), which then can be used to determine the orientation of water molecules at the interface. The particle interface of a spherical scatterer can be considered as isotropic in the
interfacial plane (tangential coordinates are degenerate). This reduces the 27 possible \( \chi^{(2)} \) tensor elements to only 4 non-zero \( \chi^{(2)} \) elements (\( \chi_{S,1}^{(2)}, \chi_{S,2}^{(2)}, \chi_{S,3}^{(2)}, \chi_{S,4}^{(2)} \)).

Considering a lossless medium (appropriate for non-resonant SHG) and Kleinman symmetry, 3 of the 4 remaining elements are degenerate (\( \chi_{S,2}^{(2)}, \chi_{S,3}^{(2)}, \chi_{S,4}^{(2)} \)). Assuming that the orientational distribution of water molecules at the interface is broad, \( \chi_{S,1}^{(2)} \) can be neglected.\(^{1,6}\) Knowing \( \chi_{S,2}^{(2)} \) is therefore sufficient to describe the molecular ordering at the surface.

The fitting procedure using the AR-SHS model that allows determining \( \Phi_0 \) and \( \chi_{S,2}^{(2)} \) is described in detail elsewhere.\(^{3,7,8}\) It uses the analytical Eqs. 4 and 5 and takes into consideration the particle radius \( R \), as it was measured by dynamic light scattering (DLS), the ionic strength, as determined from conductivity measurements, the refractive indices of water (1.33)\(^9\) and TiO\(_2\) (2.61)\(^{10}\) or SiO\(_2\) (1.46)\(^{11}\) , the SH wavelength \( \lambda = 516 \) nm, the temperature \( T \) and the number of particles/ml. We note that the error bars that we report for the surface potential \( \Phi_0 \) and the surface susceptibility \( \chi_{S,2}^{(2)} \) are based on the statistical errors of the measured AR-SHS patterns prior to normalization and are numerical errors on the fitting procedure. Other sources of error may contribute to the total error, such as the variations in the experimentally determined parameters (i.e. the particle radius, the number of particles or the ionic strength). An estimation of the influence of those uncertainties on the surface potential \( \Phi_0 \) and the surface susceptibility \( \chi_{S,2}^{(2)} \) is presented in the section 4 here below. From these results, it can be seen that in most of the cases only the magnitude of both \( \Phi_0 \) and \( \chi_{S,2}^{(2)} \) are affected by a large variation of the investigated parameter, but that the trends observed for the different ions and surfaces in this study are unaffected.
2. AR-SHS patterns of 100 nm diameter SiO$_2$ and TiO$_2$ particles in NaCl, RbCl and CaCl$_2$ solutions as a function of ionic strength

**Figure S1:** AR-SHS patterns of ~100 nm diameter SiO$_2$ particles (top) and ~100 nm diameter TiO$_2$ particles (bottom) in solution in PPP and PSS polarization combination as a function of ionic strength. The ionic strength was adjusted through the addition of NaCl (A), RbCl (B) and CaCl$_2$ (C). Plain data points of different colors represent different ionic strength of the aqueous environment. The particle density was kept constant for each sample and equal to 2.9 \cdot 10^{11} particles/ml for SiO$_2$ and 4.3 \cdot 10^{11} particles/ml for TiO$_2$. All measurements were performed at T=296.15 K. Solid lines represent the fits to the corresponding data points using the AR-SHS model. A summary of all parameters used for the fits can be found in tables S1 to S4.
3. Experimental parameters used for fitting the AR-SHS patterns and fitting results

Table S1 Parameters used to fit the normalized second harmonic scattering patterns with the AR-SHS model. These parameters are common to all sets of SiO$_2$ data presented and fitted.

| Parameter                          | Value     |
|-----------------------------------|-----------|
| Second harmonic wavelength $\lambda$ [nm] | 515       |
| Refractive index $n_{\text{H}_2\text{O}}$ (@ 515 nm) | 1.33      |
| Refractive index $n_{\text{SiO}_2}$ (@ 515 nm) | 1.46      |
| Temperature $^\circ$C | 23        |
| Number of particles/ml | $2.91 \cdot 10^{11}$ |

Table S2 Parameters used to fit the normalized second harmonic scattering patterns with the AR-SHS model. These parameters are common to all the TiO$_2$ sets of data presented and fitted.

| Parameter                          | Value     |
|-----------------------------------|-----------|
| Second harmonic wavelength $\lambda$ [nm] | 515       |
| Refractive index $n_{\text{H}_2\text{O}}$ (@ 515 nm) | 1.33      |
| Refractive index $n_{\text{TiO}_2}$ (@ 515 nm) | 2.61      |
| Temperature $^\circ$C | 23        |
| Number of particles/ml | $4.26 \cdot 10^{11}$ |

Table S3 Parameters used to fit the normalized second harmonic scattering patterns of 100 nm SiO$_2$ particles in NaCl, RbCl, and CaCl$_2$ as a function of added ionic strength with the AR-SHS model. The effective ionic strength is determined via conductivity as described in Ref. 6 and includes the contribution from the added salt as well as the initial ionic strength of the solution of washed particles.

| Added ionic strength [µM] | 0  | 10 | 25 | 50  | 100 | 200 | 300 | 600 |
|---------------------------|----|----|----|-----|-----|-----|-----|-----|
| NaCl Radius [nm]          | 65 | 64 | 62 | 61  | 61  | 60  | 58  |     |
| Effective ionic strength [µM] | 13.0 | 23.0 | 57.5 | 96.6 | 268.0 | 561.0 |     |     |
| RbCl Radius [nm]          | 61 | 62 | 60 | 59  | 59  | 58  |     |     |
| Effective ionic strength [µM] | 14.1 | 16.6 | 59.2 | 112.6 | 198.8 | 323.3 |     |     |
| CaCl$_2$ Radius [nm]      | 65 | 60 | 59 | 58  | 59  | 58  |     |     |
| Effective ionic strength [µM] | 14.5 | 18.8 | 35.3 | 58.7 | 112.4 | 319.2 |     |     |

Table S4 Parameters used to fit the normalized second harmonic scattering patterns of 100 nm amorphous TiO$_2$ particles in NaCl, RbCl, and CaCl$_2$ as a function of added ionic strength with the AR-SHS model. The effective ionic strength, which includes the contribution from the added ionic strength as well as the initial ionic strength of the solution of washed particles, is determined via conductivity as described in Ref. 6.

| Added ionic strength [µM] | 0  | 10 | 25 | 50  | 100 | 200 | 300 |
|---------------------------|----|----|----|-----|-----|-----|-----|
| NaCl Radius [nm]          | 59 | 60 | 60 | 60  | 60  | 59  |     |
| Effective ionic strength [µM] | 40.4 | 46.5 | 91.2 | 134.7 | 311.0 |     |     |
| RbCl Radius [nm]          | 62 | 61 | 60 | 60  | 60  | 59  |     |
| Effective ionic strength [µM] | 37.9 | 45.6 | 87.3 | 102.4 |     |     |     |
| CaCl$_2$ Radius [nm]      | 63 | 65 | 63 | 62  | 62  | 59  | 59  |
| Effective ionic strength [µM] | 42.7 | 51.5 | 68.4 | 85.7 | 123.2 | 240.2 | 323.0 |
Table S5: Particle radius $R$, zeta potential $\zeta$, surface potential $\Phi_0$, and surface susceptibility $\chi_{S,2}^{(2)}$ of SiO$_2$ as a function of ionic strength, shown for three different salts (NaCl, RbCl, and CaCl$_2$). $\Phi_0$ and $\chi_{S,2}^{(2)}$ were obtained by fitting the corresponding AR-SHS patterns of ~100 nm diameter SiO$_2$ particles in solution in PPP and PSS polarization combination (see Figure S1). The particle radius $R$ was measured using dynamic light scattering and the zeta potential $\zeta$ was obtained from electrophoretic mobility measurements using Ohshima’s approximation as described in the Materials and Methods section. Error bars on $\Phi_0$ and $\chi_{S,2}^{(2)}$ are discussed in section 4.

| SiO$_2$ | added ionic strength [µM] | $R$ [nm] | $\zeta$ [mV] | $\Phi_0$ [mV] | $\chi_{S,2}^{(2)}$ [$10^{-23}$ m$^2$V$^{-1}$] |
|---------|--------------------------|---------|-------------|-----------|----------------|
| NaCl    | 0                        | 65      | -78         | -163      | -22.5          |
|         | 10                       | 64      | -66         | -130      | -27.6          |
|         | 50                       | 62      | -57         | -92       | -31.3          |
|         | 100                      | 61      | -54         | -54       | -33.9          |
|         | 300                      | 60      | -48         | -19       | 39.4           |
|         | 600                      | 58      | -50         | -428      | 90.8           |
| RbCl    | 0                        | 61      | -75         | -175      | -25.2          |
|         | 10                       | 62      | -71         | -141      | -47.9          |
|         | 50                       | 60      | -58         | -102      | -28.0          |
|         | 100                      | 59      | -57         | -60       | -32.2          |
|         | 200                      | 59      | -53         | -31       | 42.6           |
|         | 300                      | 58      | -49         | -160      | 58.3           |
| CaCl$_2$| 0                        | 65      | -76         | -161      | -21.1          |
|         | 10                       | 60      | -40         | -98       | -23.5          |
|         | 25                       | 59      | -33         | -48       | -31.0          |
|         | 50                       | 58      | -28         | -39       | -30.1          |
|         | 100                      | 59      | -25         | -78       | -19.6          |
|         | 300                      | 58      | -26         | -143      | 35.4           |

Table S6: Particle radius $R$, zeta potential $\zeta$, surface potential $\Phi_0$, and surface susceptibility $\chi_{S,2}^{(2)}$ of TiO$_2$ as a function of ionic strength, shown for three different salts (NaCl, RbCl, and CaCl$_2$). $\Phi_0$ and $\chi_{S,2}^{(2)}$ were obtained by fitting the corresponding AR-SHS patterns of ~100 nm diameter TiO$_2$ particles in solution in PPP, and PSS polarization combination (see Figure S1). The particle radius $R$ was measured using dynamic light scattering and the zeta potential $\zeta$ was obtained from electrophoretic mobility measurements using Ohshima’s approximation as described in the Materials and Methods section. Error bars on $\Phi_0$ and $\chi_{S,2}^{(2)}$ are discussed in section 4.

| TiO$_2$ | added ionic strength [µM] | $R$ [nm] | $\zeta$ [mV] | $\Phi_0$ [mV] | $\chi_{S,2}^{(2)}$ [$10^{-23}$ m$^2$V$^{-1}$] |
|---------|--------------------------|---------|-------------|-----------|----------------|
| NaCl    | 0                        | 59      | -39         | -182      | -0.8           |
|         | 10                       | 60      | -43         | -57       | -4.0           |
|         | 50                       | 60      | -40         | -12       | 4.6            |
|         | 100                      | 60      | -40         | -57       | 4.5            |
|         | 300                      | 59      | -46         | -326      | 9.4            |
| RbCl    | 0                        | 62      | -43         | -124      | -2.0           |
|         | 10                       | 61      | -45         | -69       | -3.6           |
|         | 50                       | 62      | -38         | -7        | 4.8            |
|         | 100                      | 60      | -42         | -67       | 5.4            |
| CaCl$_2$| 0                        | 63      | -41         | -155      | -1.2           |
|         | 10                       | 65      | -33         | -79       | -2.9           |
|         | 25                       | 63      | -31         | -53       | -3.2           |
|         | 50                       | 62      | -31         | -21       | 3.3            |
|         | 100                      | 62      | -23         | -15       | 3.3            |
|         | 200                      | 59      | -21         | -135      | 0.3            |
|         | 300                      | 59      | -18         | -346      | 9.4            |
4. Variation of fitting parameters

The normalized second harmonic scattering patterns of 100 nm diameter particles (SiO$_2$ or amorphous TiO$_2$) in solution are fitted applying the AR-SHS model to determine the surface potential and surface susceptibility. As a mean to give an estimation of how much an error on the material-dependent and the experimentally derived parameters could influence the AR-SHS fits, in the following section we show how the surface potential $\Phi_0$ and surface susceptibility $\chi_{S,2}^{(2)}$ results change when modifying the fitting parameters, namely the size, the refractive index, the number of particles and the ionic strength. The influence of the fitting parameters on the surface potential and the surface susceptibility is discussed on the data collected for 100 nm diameter TiO$_2$ particles as a function of added NaCl (shown in the main text in Figure 2). Note that the results are plotted here as a function of NaCl concentration and are identical to the ones in the main text displayed as a function of ionic strength since NaCl is a monovalent salt. Only one fitting parameter is varied at a time while the other fitting parameters remain fixed, as stated in Table S2 and S4.

a) Variation of particle radius

Figure S2 shows the effect of smaller and larger particle radii on the surface potential and surface susceptibility. We use the normalized second harmonic scattering patterns measured for 100 nm diameter TiO$_2$ particles as a function of added NaCl and use the radius (R) measured by dynamic light scattering (DLS) for fitting. We then vary the radius fitting parameter by 10nm (R+10 nm and R-10 nm). Note that we use the same normalized SHS pattern for the fitting and only change the input fitting parameters.
Figure S2: Surface potential $\Phi_0$ (A) and surface susceptibility $\chi^{(2)}_{S,2}$ (B) of TiO$_2$ as a function of added NaCl concentration. $\Phi_0$ and $\chi^{(2)}_{S,2}$ were obtained by fitting the corresponding AR-SHS pattern of $\sim$100 nm diameter TiO$_2$ particles in solution in PPP and PSS polarization combination. The graph shows the effect of a variation of the particle size fitting parameter, where R is the radius of the particle as measured by dynamic light scattering (DLS).

Figure S2A shows that the surface potential trends remain the same when the particle radius R is varied by 10 nm in the fitting input parameters. The surface potentials at 0 $\mu$M and at 300 $\mu$M show the largest divergence when the size parameter increases or decreases by 10 nm. Although the surface potential values are not identical for different radius values, the same three regions (i, ii and iii) described in the main text can be identified. In Figure S2B a similar observation can be made regarding the trends of the surface susceptibility. While the surface susceptibility values change, the overall water orientation behavior remains the same, including the flipping point from negative surface susceptibility values to positive surface susceptibility values (change from average water orientation with oxygens pointing towards the surface to hydrogens pointing towards the surface).

b) Variation of the number of particles

Figure S3 shows the surface potential and surface susceptibility as a function of added NaCl concentration when varying the number of particles (NP) fitting input parameter (particles/ml). Similar to the previously shown variation of size in Figure S2, we see in Figure S3 that the overall trends of surface potential and surface susceptibility remain the same when fitting with a higher or lower number of particles by one order of magnitude. The same three regions as described in the main text (i, ii, iii) can be found (not visible on this y-scale for the largest amount of particles) and the flipping point of
the surface susceptibility remains between 10 \( \mu \text{M} \) and 50 \( \mu \text{M} \) added salt when the number of particles is changed in the fitting. Even though the values of the surface potential and surface susceptibility are changed when fitting with different numbers of particles, the overall surface potential and surface susceptibility trends are not impacted by one order of magnitude change in this parameter.

**Figure S3:** Surface potential \( \Phi_0 \) (A) and surface susceptibility \( \chi_{S,2}^{(2)} \) (B) of TiO\(_2\) as a function of added NaCl concentration. \( \Phi_0 \) and \( \chi_{S,2}^{(2)} \) were obtained by fitting the corresponding AR-SHS pattern of \( \sim \)100 nm diameter TiO\(_2\) particles in solution in PPP and PSS polarization combination. The graph shows the effect of a variation of the number of particles (NP) fitting parameter (particles/ml).

**c) Variation of particle refractive index**

In Figure S4, the surface potential and surface susceptibility as a function of added NaCl concentration are shown with a variation of the refractive index. Previous reports in the literature have stated a value of 2.61\(^{10}\) for the refractive index of amorphous TiO\(_2\) films. We have therefore chosen this value to fit the normalized SHS patterns of the amorphous TiO\(_2\) particles used in this study to be comparable with our previous results.\(^6\) However, for amorphous particles, refractive index values as low as 1.9 have been reported.\(^{12}\) Additionally, a report on particles composed of an anatase core and an amorphous titania-shell structure has demonstrated tailoring of the shell refractive index from 1.5 to 2.3.\(^{13}\) Because of this wide range of refractive indices reported for amorphous TiO\(_2\), we here show the results of the fitting procedure using refractive indices of 1.8 as an intermediate value, and 1.46 as the lower limit (the latter one corresponding to the refractive index of silica). While the surface potential values differ by less than 100 mV, which is for most of the ionic strength points investigated a smaller deviation than the variation induced by the statistical error of our
measurements, the surface susceptibility values change by nearly one order of magnitude. Nevertheless, the surface susceptibility trends do not change as the flip in sign occurs between 10 µM and 50 µM added NaCl for all the three refractive indices used for the fitting. We can therefore conclude that the choice of the refractive index does mainly influence the values of the surface susceptibility, while the values of the surface potential are barely changed and only to the extent that is in most cases covered by the statistical error of the measurement. Despite these variations, the overall trends of surface potential and surface susceptibility as a function of salt concentration for all three refractive indices remain the same.

**Figure S4:** Surface potential \( \Phi_0 \) (A) and surface susceptibility \( \chi^{(2)}_{S,2} \) (B) of TiO\(_2\) as a function of added NaCl concentration. \( \Phi_0 \) and \( \chi^{(2)}_{S,2} \) were obtained by fitting the corresponding AR-SHS pattern of \(~100\) nm diameter TiO\(_2\) particles in solution in PPP and PSS polarization combination. The graph shows the effect of a variation of the refractive index (RI) fitting parameter.

**d) Variation in the ionic strength**

Figure S5 shows the influence of a decrease or increase of the ionic strength fitting parameter by one order of magnitude on the surface potential and surface susceptibility of \(~100\) nm diameter TiO\(_2\) particles as a function of added NaCl. In contrast to the change of size, number of particles or refractive index, the change of ionic strength strongly influences the values and trends of the surface potential and surface susceptibility. The surface potential values differ by up to one order of magnitude (from around 200 mV to 2 V) for a higher ionic strength. Regarding the surface susceptibility, the flipping point changes from between 10 µM and 50 µM to between 50 µM and 100 µM for an ionic strength that is one order of magnitude higher. Note that a lower ionic strength by one order of magnitude induces less changes in...
the surface potential values and does not change the surface susceptibility flipping point.

The hypothetical situation described in Figure S5 could only occur if there was an order of magnitude discrepancy between the ionic strength extracted from conductivity measurements, used to fit the data, and the real ionic strength in the solution. However, it is important to mention that it is implausible to introduce an error of one order of magnitude on the ionic strength parameter. In our experimental procedure, we measure the conductivity by two different means (conductivity meter and conductivity obtained through zeta potential measurements), which allows for a cross-check. We then convert the value obtained using a conductivity meter into ionic strength to perform our fitting (for more details see Ref 6). Nevertheless, compared to all the parameters shown above (radius, number of particles, refractive index) the ionic strength is the fitting parameter with the strongest influence on $\Phi_0$ and $\chi^{(2)}_{S,2}$ as it can change the general surface potential and surface susceptibility trends.

![Figure S5: Surface potential $\Phi_0$ (A) and surface susceptibility $\chi^{(2)}_{S,2}$ (B) of TiO$_2$ as a function of added NaCl concentration. $\Phi_0$ and $\chi^{(2)}_{S,2}$ were obtained by fitting the corresponding AR-SHS pattern of ~100 nm diameter TiO$_2$ particles in solution in PPP and PSS polarization combination. The graph shows the effect of a variation of the ionic strength fitting parameter.](image-url)
5. Comparison of different TiO$_2$ core-shell thicknesses

While the preparation of small-sized (< 20 nm) amorphous TiO$_2$ colloidal suspensions is well established,$^{14-19}$ the preparation of aqueous suspensions of uniform and monodispersed amorphous TiO$_2$ particles with a larger diameter (>100 nm diameter) remains challenging and is the subject of more recent work.$^{20,21}$ Commercially-available amorphous TiO$_2$ aqueous colloidal suspensions are therefore usually found as core-shell particles with a SiO$_2$ core. As the main contribution to the AR-SHS signal is given by water molecules oriented at the TiO$_2$ surface (see section 1), our experiment only requires the presence of a few atomic layers of TiO$_2$ in contact with the aqueous solution. To support this point, we show below that the AR-SHS data does not depend on the thickness of the TiO$_2$ shell. Therefore, this property allows us to use core-shell particles to study the colloidal amorphous TiO$_2$/aqueous interface, difficult to access otherwise.

The data presented in the main text were obtained on ~100 nm diameter amorphous TiO$_2$ particles from Corpuscular Microspheres Nanospheres (2.5% w/v stock solution in water). Dynamic light scattering characterization data before and after growth of the TiO$_2$ amorphous shell were provided by Corpuscular Microspheres Nanospheres, indicating the growth of a 5-10 nm-thick layer of amorphous TiO$_2$ on a 90-100 nm silica core. In order to verify that the shell thickness of the investigated particles is sufficient to avoid any contributions of the SiO$_2$ core to our signal, we investigated identically-sized particles with a different shell thickness. Aqueous dispersions of 100 nm diameter particles with a 20-30 nm silica core and a 30-40 nm thick amorphous TiO$_2$ shell (custom amorphous TiO$_2$ dispersion, cat. number DNG-GT015) were purchased from Creative Diagnostics. The particles were prepared and washed in the same way as the Corpuscular Microspheres Nanospheres particles (described in the Materials and Methods section). In the following we show that the surface potential and interfacial water order as a function of NaCl concentration are independent of the thickness of the amorphous TiO$_2$ shell.

Figure S6A shows the surface potential of 100 nm diameter TiO$_2$ amorphous core-shell particles (Creative Diagnostics) with a shell thickness of 30-40 nm compared to identically sized TiO$_2$ amorphous core-shell particles from Corpuscular Microspheres Nanospheres with a shell thickness of 5-10 nm. It can be seen that the surface potential values are similar for the two different core-shell particles from different suppliers. The different core-shell thicknesses of the two particle types...
investigated do not notably influence the surface potential trends. Therefore, it can be concluded that our SHS surface potential is only influenced by a few atomic layers of TiO\textsubscript{2} in contact with the aqueous interface and independent of the nature of the core particle.

Figure S6B shows the surface susceptibility $\chi_{S,2}^{(2)}$ of 100 nm diameter particles with a 30-40 nm amorphous TiO\textsubscript{2} shell (Creative Diagnostics) compared to 100 nm diameter particles with a 5-10 nm amorphous TiO\textsubscript{2} shell (Corpuscular Microspheres Nanospheres). The values of the surface susceptibility of the two kinds of particles are slightly different (Creative Diagnostics shows about double the surface susceptibility value compared to the Corpuscular Microspheres Nanospheres particles) and the flip in sign of $\chi_{S,2}^{(2)}$ occurs in between 10 $\mu$M to 50 $\mu$M for the Corpuscular Microspheres Nanospheres particles whereas it occurs in between 50 $\mu$M to 100 $\mu$M added ionic strength for the particles from Creative Diagnostics. These differences can be explained by the Corpuscular Microspheres Nanospheres particles exhibiting a higher conductivity after the washing process, which translates into a higher intrinsic ionic strength of the particles when no salt is added to the solution. While the Corpuscular Microspheres Nanospheres particles have an ionic strength of $4.0\cdot10^{-5}$ M at 0 $\mu$M added salt, the Creative Diagnostics particles have an ionic strength of $2.4\cdot10^{-5}$ M at 0 $\mu$M added salt, assuming that the measured conductivity originates from residual NaOH that was used in the synthetic process. Adding the intrinsic ionic strength of the particles to the one due to NaCl incorporation (effective ionic strength), the flip in sign of the surface susceptibility $\chi_{S,2}^{(2)}$ of the Corpuscular Microspheres Nanospheres particles can be estimated in between $4.6\cdot10^{-5}$ M and $9.1\cdot10^{-5}$ M effective ionic strength, whereas the change in sign occurs in between $7.0\cdot10^{-5}$ M to $1.3\cdot10^{-4}$ M for the Creative Diagnostics particles. This comparison highlights that the flipping point of $\chi_{S,2}^{(2)}$ occurs in a similar ionic strength range for both shell thicknesses and confirms the results obtained above: as AR-SHS only probes a few monolayers at the surface, both surface potential and interfacial water orientation data are independent of the shell thickness. The slightly higher surface susceptibility values could be explained by minor variations in the surface structure of the colloids resulting from different synthetic procedures of the two suppliers. Additionally, the Creative Diagnostics particles display a higher amount of organic contaminants after two washing steps, as
determined by elemental analysis (4.36% C, 2.24% H, and 1.5% N for Creative diagnostics vs 1.04% C, 0.31% H, and 0% N for Corpuscular Microspheres Nanospheres). The presence of a higher organic residue after two washing steps, possibly due to stabilizing surfactants, could explain the slight differences in interfacial water order observed for the two different batches.

Figure S6: Surface potential $\Phi_0$ (A) and surface susceptibility $\chi^{(2)}_{5,2}$ (B) of ~100 nm diameter core-shell TiO$_2$ particles in solution as a function of added NaCl concentration. $\Phi_0$ and $\chi^{(2)}_{5,2}$ were obtained by fitting the corresponding AR-SHS pattern in PPP and PSS polarization combination. The graphs show identically-sized particles from two different suppliers (Corpuscular Microspheres Nanospheres vs. Creative Diagnostic) with different TiO$_2$ shell thicknesses: 5-10 nm (Corpuscular) vs. 30-40 nm (Creative Diagnostic).
6. Surface charge densities and deprotonation

For the SiO\textsubscript{2} and TiO\textsubscript{2} particles used in this study, the pH of the 0.05% solutions used for the AR-SHS measurements was \( \sim 7 \). Using surface charge density values found in the literature that were measured by potentiometric titration, we can estimate the percentage of deprotonation expected for both surfaces at pH 7. As the surface charge densities for both materials have been shown to be strongly size-dependent for particles < 25 nm\textsuperscript{22–24} all the references listed here have been selected to match the size range of our particles and excluded very small nanoparticles (< 25 nm). For both materials, the density of surface hydroxyl groups was taken from the literature. Zhuravlev\textsuperscript{25} showed for amorphous SiO\textsubscript{2} that the –OH surface density is a physicochemical constant for a fully hydroxylated surface and does not depend in a significant way on the type of silica.

For TiO\textsubscript{2}, we use an initial density of -OH groups of 4.8 OH/nm\textsuperscript{2} as determined for the hydroxylated surface of P25 TiO\textsubscript{2} particles (Degussa) taken from Ref.\textsuperscript{26} The radius of the particles is taken as 60 nm, based on our dynamic light scattering experiments for amorphous TiO\textsubscript{2} particles. We obtain a deprotonation value of 1% using the reported surface charge densities of -0.00763 C/m\textsuperscript{2} for P25 TiO\textsubscript{2} particles (Degussa) at pH 7.10 by Holmberg et al.,\textsuperscript{23} or -0.00833 C/m\textsuperscript{2} for rutile TiO\textsubscript{2} particles (CL/D 528 Tioxide International Limited) at pH 7.13 by Yates.\textsuperscript{27} Values up to -0.06417 C/m\textsuperscript{2} have been reported by Machesky et al.\textsuperscript{28} for rutile TiO\textsubscript{2} particles (Tioxide Specialties Ltd.) at pH 7.02, corresponding to deprotonation values of 8%. Similar values were reported by Akratopulu et al.\textsuperscript{29} for P25 TiO\textsubscript{2} particles (Degussa) at pH 6.93 who obtained a surface charge density of -0.05074 C/m\textsuperscript{2}, which corresponds to 7% deprotonation.

The percentage of deprotonation is estimated in the same way for SiO\textsubscript{2}. Here the initial density of -OH groups at the surface is taken as 4.9 OH/nm\textsuperscript{2}.\textsuperscript{25} The radius of the silica particles is set to 60 nm based on our dynamic light scattering measurements. Using the reported surface charge density value by Sonnefeld\textsuperscript{30} of -0.02153 C/m\textsuperscript{2} for hydrophilic fumed silica particles (Aerosil 300, Degussa) at pH 7, we calculate a deprotonation value of 3%. With the surface charge density reported by Bolt\textsuperscript{31} of -0.01 C/m\textsuperscript{2} for amorphous Silica (Ludox) at pH 7, we obtain 1% deprotonation.
Given the fact that the potentiometric measurements were performed at higher ionic strengths for TiO$_2$ (0.1 M NaNO$_3$ in Holmberg et al.,$^{23}$ 1 mM KNO$_3$ in Yates,$^{27}$ 0.03 M NaCl in Machesky et al.$^{28}$ and 0.1 M KNO$_3$ in Akratopulo et al.$^{29}$) as well as for SiO$_2$ (0.005 M KCl in Sonnefeld$^{30}$ and 10$^{-3}$ N NaCl in Bolt$^{31}$), the calculated deprotonation values can be regarded as an upper limit for the real deprotonation that we expect for our amorphous TiO$_2$ and SiO$_2$ particles at pH 7 and in the lower ionic strength region. For silica, a more realistic estimation of deprotonation in neutral pH for low ionic strength conditions can be obtained using effective surface charge densities reported by Yamamaka et al.$^{32}$ The authors performed conductivity measurements and conductometric titrations on silica particles (Seahoster KE-P10W, Nippon Shokubai Co.Ltd.) in salt-free conditions and calculated an effective surface charge density value of -0.0008 C/m$^2$, which corresponds to 0.1% deprotonation. This lower value is in good agreement with the surface charge density values calculated from surface potential measurements that we performed on silica particles (Bangs Laboratories Inc.) in our previous study,$^{7}$ where we reported surface deprotonation values of 0.04% (pH 5.7) to 0.06% (pH 10) in salt-free conditions. These results show that most silanol groups are expected to remain protonated in neutral pH and low ionic strength conditions. For TiO$_2$ particles, we are not aware of surface charge density values reported in salt-free conditions. However, the upper limit for surface deprotonation discussed above also indicates that most Ti-OH groups remain protonated in neutral pH and low ionic strength conditions.
7. AR-SHS patterns support evidence of inner-/outer-sphere adsorption

In general, the AR-SHS patterns are strongly dependent on the particle size and the ionic strength of the solution,\textsuperscript{2,4,33} which can also be seen from Eq. 3 in section 1. The SHS intensity is proportional to the effective particle susceptibilities $\Gamma^{(2)}$ and $\Gamma^{(3)^{\prime}}$ that contain form factors depending, amongst others, on the geometry of the particle.\textsuperscript{2,6}

One of the geometrical form factors contained in the $\Gamma^{(3)^{\prime}}$ contribution, $(F_3(qR, \kappa R))$, is a function of the inverse Debye length. Therefore, it is influenced by the ionic strength and by how far the electrostatic field generated between the particle surface and the ions reaches into the solution for a given ionic strength range. For spherical particles up to 100 nm, one can calculate that the $F_3(qR, \kappa R)$ factor has a significant influence on the scattering patterns up to 1 mM ionic strength, which include our investigated ionic strength range (0-600 $\mu$M). In this case, the AR-SHS intensity is mainly associated with the thickness of the shell of water molecules oriented by the electric field. A decrease in the AR-SHS signal can therefore be visualized as a scenario where the electrostatic field extends less deeply into the solution, which results in fewer water molecules that are oriented and probed by the AR-SHS scattering technique.

We can use this property to examine the AR-SHS patterns presented in Figure S1. For Na\textsuperscript{+} and Rb\textsuperscript{+} on SiO\textsubscript{2}, the SHS intensity drops by a factor of 2 between 0 and 10 $\mu$M. For Ca\textsuperscript{2+} on SiO\textsubscript{2}, the SHS intensity drops by a factor 3 in the same interval. This result indicates that the probed shell of water molecules is smaller in the case of Ca\textsuperscript{2+} and that the electric field penetrates less deeply into the bulk solution. Such a situation would correspond to the presence of an outer-sphere layer around the particles, which starts to form at lower ionic strength for Ca\textsuperscript{2+} than for Na\textsuperscript{+} and Rb\textsuperscript{+} on SiO\textsubscript{2}. For Ca\textsuperscript{2+} on TiO\textsubscript{2}, the AR-SHS scattering patterns show a less drastic decrease in normalized SHS intensity at low ionic strength (0 to 10 $\mu$M) compared to SiO\textsubscript{2}. The decrease in SHS intensity is more similar to the case of Na\textsuperscript{+} and Rb\textsuperscript{+} on TiO\textsubscript{2} in the same ionic strength interval. This result suggests that the overall probed shell of the aqueous environment around the TiO\textsubscript{2} particles is not reduced in the same way as for Ca\textsuperscript{2+} on SiO\textsubscript{2}, supporting the idea of preferential inner-sphere adsorption of Ca\textsuperscript{2+} on TiO\textsubscript{2}.
8. Surface potential and surface susceptibility of 100 nm TiO$_2$ and SiO$_2$ as a function of ionic concentration

**Figure S7:** Surface potential $\Phi_0$ (A) and surface susceptibility $\chi_{S,2}^{(2)}$ (B) of SiO$_2$ as a function of added ionic concentration, shown for three different salts (NaCl, RbCl, and CaCl$_2$). $\Phi_0$ and $\chi_{S,2}^{(2)}$ were obtained by fitting the corresponding AR-SHS patterns of $\sim$100 nm diameter SiO$_2$ particles in solution in PPP and PSS polarization combination.

**Figure S8:** Surface potential $\Phi_0$ (A) and surface susceptibility $\chi_{S,2}^{(2)}$ (B) of TiO$_2$ as a function of added ionic concentration, shown for three different salts (NaCl, RbCl, and CaCl$_2$). $\Phi_0$ and $\chi_{S,2}^{(2)}$ were obtained by fitting the corresponding AR-SHS patterns of $\sim$100 nm diameter TiO$_2$ particles in solution in PPP and PSS polarization combination.
9. MD simulations at different concentrations

**Table S7** Ion adsorption partitioned as inner-sphere or outer-sphere complex or in diffuse layer at the quartz (101) surface by MD simulations for different concentrations and salts. The left column indicates the number of ion pairs introduced in the system and the corresponding bulk concentration in [M]. The rows in bold correspond to the values shown in Table 2 of the main text, where the number of NaCl, RbCl, or CaCl₂ ions added to the system was set to achieve a similar bulk ionic strength for all solutions (i.e., the ratio of bulk ionic concentrations of CaCl₂ and NaCl/RbCl was ~1:3). Error bars are shown in parenthesis.

| SiO₂ |#/bulk concentration [M] | inner-sphere [%] | outer-sphere [%] | diffuse layer [%] |
|------|--------------------------|------------------|------------------|-------------------|
| Na⁺  | 6/~0.09                  | 22 (<1)          | 20 (1)           | 58 (<1)          |
| Na⁺  | 9/~0.13                  | 23 (1)           | 19 (<1)          | 58 (1)           |
| Na⁺  | 18/~0.28                 | 20 (<1)          | 20 (<1)          | 60 (1)           |
| Rh⁺  | 6/~0.09                  | 26 (<1)          | 18 (<1)          | 56 (<1)          |
| Rh⁺  | 9/~0.15                  | 26 (1)           | 18 (<1)          | 56 (1)           |
| Rb⁺  | 18/~0.28                 | 25 (1)           | 18 (<1)          | 57 (1)           |
| Ca²⁺ | 6/~0.09                  | 4 (<1)           | 20 (<1)          | 76 (1)           |
| Ca²⁺ | 9/~0.14                  | 2 (1)            | 21 (<1)          | 77 (1)           |
| Ca²⁺ | 18/~0.29                 | 2 (1)            | 22 (<1)          | 76 (1)           |

**Table S8** Ion adsorption partitioned as inner-sphere or outer-sphere complex or in diffuse layer at the rutile (110) surface by MD simulations for different concentrations and salts. The left column indicates the number of ion pairs introduced in the system and the corresponding bulk concentration in [M]. The rows in bold correspond to the values shown in Table 4 of the main text, where the number of NaCl, RbCl, or CaCl₂ ions added to the system was set to achieve a similar bulk ionic strength for all solutions (i.e., the ratio of bulk ionic concentrations of CaCl₂ and NaCl/RbCl was ~1:3). Error bars are shown in parenthesis.

| TiO₂ |#/bulk concentration [M] | inner-sphere [%] | outer-sphere [%] | diffuse layer [%] |
|------|--------------------------|------------------|------------------|-------------------|
| Na⁺  | 6/~0.10                  | 83 (3)           | 6 (<1)           | 11 (1)            |
| Na⁺  | 9/~0.16                  | 82 (<1)          | 7 (<1)           | 11 (1)            |
| Na⁺  | 18/~0.33                 | 76 (1)           | 7 (<1)           | 17 (1)            |
| Rh⁺  | 6/~0.11                  | 75 (2)           | 7 (1)            | 18 (1)            |
| Rh⁺  | 9/~0.19                  | 73 (5)           | 7 (<1)           | 20 (2)            |
| Rb⁺  | 18/~0.36                 | 71 (<1)          | 7 (<1)           | 22 (<1)           |
| Ca²⁺ | 6/~0.08                  | 99 (7)           | 1 (<1)           | 0 (2)             |
| Ca²⁺ | 13/~0.12                 | 97 (1)           | 0 (<1)           | 3 (<1)            |
| Ca²⁺ | 18/~0.31                 | 93 (2)           | 0 (<1)           | 7 (<1)            |
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