

The Effect of Electric Fields on the Ultrafast Vibrational Relaxation of Water at a Charged Solid-Liquid Interface as Probed by Vibrational Sum Frequency Generation

Ali Eftekhari-Bafrooei and Eric Borguet

Department of Chemistry, Temple University, Philadelphia PA 19122

Corresponding author:

Eric Borguet

Tel: (215) 204 9696

Fax: (215) 204 9530

Email: eborguet@temple.edu

Supporting information

Comparison of dynamics of interfacial and bulk water in the presence of salt:

In the bulk vibrational dynamics of HDO, a single time constant for the vibrational dynamics was observed (700 fs for the HDO:D₂O and \sim >1400 fs for HDO:H₂O)¹⁻⁴. However, in the vibrational dynamics of HDO in aqueous salt solution fast and slow components were observed¹⁻⁴. While the time constant of the fast component is similar to the T₁ of the HDO in neat water, the time constant of the slow component was 3-4 times longer (compared to the neat water) in salt concentrations ranging from 0.5-10.0 M¹⁻³. The slow component, which accounts for approximately 10% of the total dynamics, was attributed to the perturbation (weakening) of the hydrogen bond network by the anions with negligible effect from cations¹⁻³.

The concentration of salt in the experiments explored here is considerably smaller (especially in the range C_{NaCl}<0.005 M) than those where effects on the bulk water vibrational dynamics were observed. Thus, the weakening of the hydrogen bond by

anions should have negligible contribution to the interfacial dynamics. Besides, rapid resonant vibrational energy transfer between the H₂O molecules in the current experiment (in contrast to the bulk dynamics where HDO:D₂O(or H₂O) was used ¹⁻⁴) should smear out any salt effect. However, due to the presence of surface charge, one may expect that there is an enhanced concentration of salt near the surface in the Debye layer volume. If the surface concentration of salt in the Debye volume is comparable to the molar concentration of water, one should be cautious in interpreting the vibrational dynamics based on the response of water and not water perturbed by the ions. This excess surface concentration can be calculated assuming that the ions accumulate within the region over which the surface potential drops, i.e., the Debye length which is calculated in the Gouy-Chapman model with the experimental values of surface charge density at different ionic strength and the value of bulk dielectric constant of water (~78). It should be noted that at relatively small surface charge density of silica at pH~6 (~0.01 C/m²), the dielectric constant of water near the surface is predicted to not be significantly different from the bulk value ⁵. The C_s (M) at each bulk concentration is calculated according the following formula:

$$C_s = \frac{\sigma_0}{d_{EDL}} \times \frac{10^6}{F} \quad (\text{S-1})$$

where σ₀ , d_{EDL} and F are the experimental surface charge (C/m²) , Debye length (nm) and Faraday number (96500 C).

The estimated excess concentration (C_s) of salt in the Debye layer volume suggests that there is not a significant difference between the bulk concentration and the concentration in the Debye volume (Table S1). Thus even at the maximum salt concentration explored here (~0.5 M), the majority of species in the Debye volume are

solvent (water) and not the salt. It is noted that this model does not include the specific adsorption of cations on the Helmholtz plane. However, the result of specific adsorption of cations is the faster screening of the surface potential and not an increase in the excess salt concentration in the Debye volume. In fact the specific adsorption might lead to a decrease in the excess salt as a smaller effective charge has to be neutralized. Thus, even with the inclusion of the specific adsorption of cations, the conclusion that the majority of the probe molecules in the Debye volume are the solvent molecules (and not the solvent molecules perturbed by the ions) remains valid.

I (M)	σ_0 (C/m²) (experimental ^{6,7})	ϕ_0 (mV)	d_{EDL} (nm)	E(V/m)	C_s (M)
0.001	0.006	65	9	4.5*10⁶	0.0069
0.01	0.009	36	3	7.7*10⁶	0.03
0.1	0.02	27	1	1.7*10⁷	0.2
0.5	0.03	18	0.4	2.8*10⁷	0.8
1	0.04	17	0.3	3.6*10⁷	1.4

Table S1. Estimated surface potential (ϕ_0) and excess salt concentration (C_s) in the electrical double layer (EDL) volume at a silica surface at pH~6 and different ionic strengths (I). The surface charge density (σ_0) at different ionic strength are taken from the experimental data^{8,9}. The values of ϕ_0 are calculated based on the Gouy-Chapman model. d_{EDL} is the Debye length. The values of E, the electric field in the Debye layer, are estimated as $\Delta\phi_0/d_{EDL}$ where $\Delta\phi_0$ is $\phi_0 - \phi_0/e$. The excess concentrations (C_s) are calculated assuming that the ions accumulate within the Debye length (see text).

Adsorption energy of Na⁺:

As described in the main text, we hypothesize that the accumulation of cations near the silica surface prevents the penetration of the surface electric field into the bulk, leading to the observation of long vibrational lifetimes even though the classical Debye length is still several nm. Cations can also specifically adsorb onto the silica surface if they lose all or part of their solvation shell ¹⁰. By assuming that the variation of vibrational lifetime as a function of NaCl (Figure 2) is due to the adsorption of Na⁺, we can extract the adsorption energy. The reason why T₁ might scale with Na⁺ surface coverage is that the specific adsorption of Na⁺ would effectively neutralize the surface charge (SiO⁻), through formation of SiO⁻...Na⁺ complexes rather than covalent bond formation, providing a mechanism for screening of the electric field, essentially rendering the SFG sensitive to the first one or two layers of interfacial H₂O.

By assuming a simple Langmuir model for the adsorption of Na⁺, and relating the T₁ to the surface coverage (equation S2) the adsorption energy of Na⁺ at silica (ΔG_{ad}) at room temperature was found to be $\sim 22 \pm 4$ kJ/mol.

$$T_1(C) = T_1(C=0) + T_1(C_{max}) \frac{(K_{eq}C / 55.5)}{(1 + K_{eq}C / 55.5)} \quad (S2)$$

A Langmuir model is reasonable as the coverage of charged sites, at the pH and ionic strength used in this experiment, is low enough that they can be considered independent and non-interacting. Specifically speaking, the highest surface charge density that creates at the highest salt concentration explored here (0.5 M) is 0.03 C/m² (table S1), which corresponds to 0.2 e/nm². In equation S2, T₁(C=0) is the vibrational lifetime in the

absence of the NaCl, C is the bulk concentration of NaCl , and $T_1(C_{\max})$ is the vibrational lifetime at saturation coverage of Na^+ .

The adsorption energy has chemical and electrostatic contributions. The contribution of electrostatic term in the potential range of 18-65 mV is estimated to be ~2-6 kJ/mol, which indicates the main driving force for the adsorption of sodium is chemical rather than electrostatic. It should be noted that this conclusion is drawn for low surface charge density ($<0.03 \text{ C/m}^2$). The value of ΔG_{ad} of sodium estimated here (22 kJ/mol) under the low surface coverage ($<0.03 \text{ C/m}^2$) is smaller than the ΔG_{ad} of sodium estimated at high surface charge; 4 kJ/mol at $\sim0.8 \text{ C/m}^2$ where the electrostatic contribution appears to dominate¹¹. The value of ΔG_{ad} of sodium estimated here is, however, close to the ΔG_{ad} of adsorption of divalent cations to the silica surface at near neutral pH ($\sim30 \text{ kJ/mol}$)^{12, 13}.

Acceleration of the vibrational dynamics at high salt concentration (~0.5 M)

There are multiple effects that could contribute to the acceleration of the vibrational relaxation rate at high salt concentration. The strength of the surface electric field at different salt concentration, which is determined by the gradient of the surface potential in the Debye layer, increases with increase in the salt concentration (Table S1). The increase in the surface electric field strength at high salt concentration (~0.5 M) could possibly be the origin of the slightly faster vibrational lifetime observed at 0.5 M compared to 0.01 M.

Another explanation arises from the reported effect of cations to induce some polarization of the hydrogen bond³, making the hydrogen bond stronger. At higher

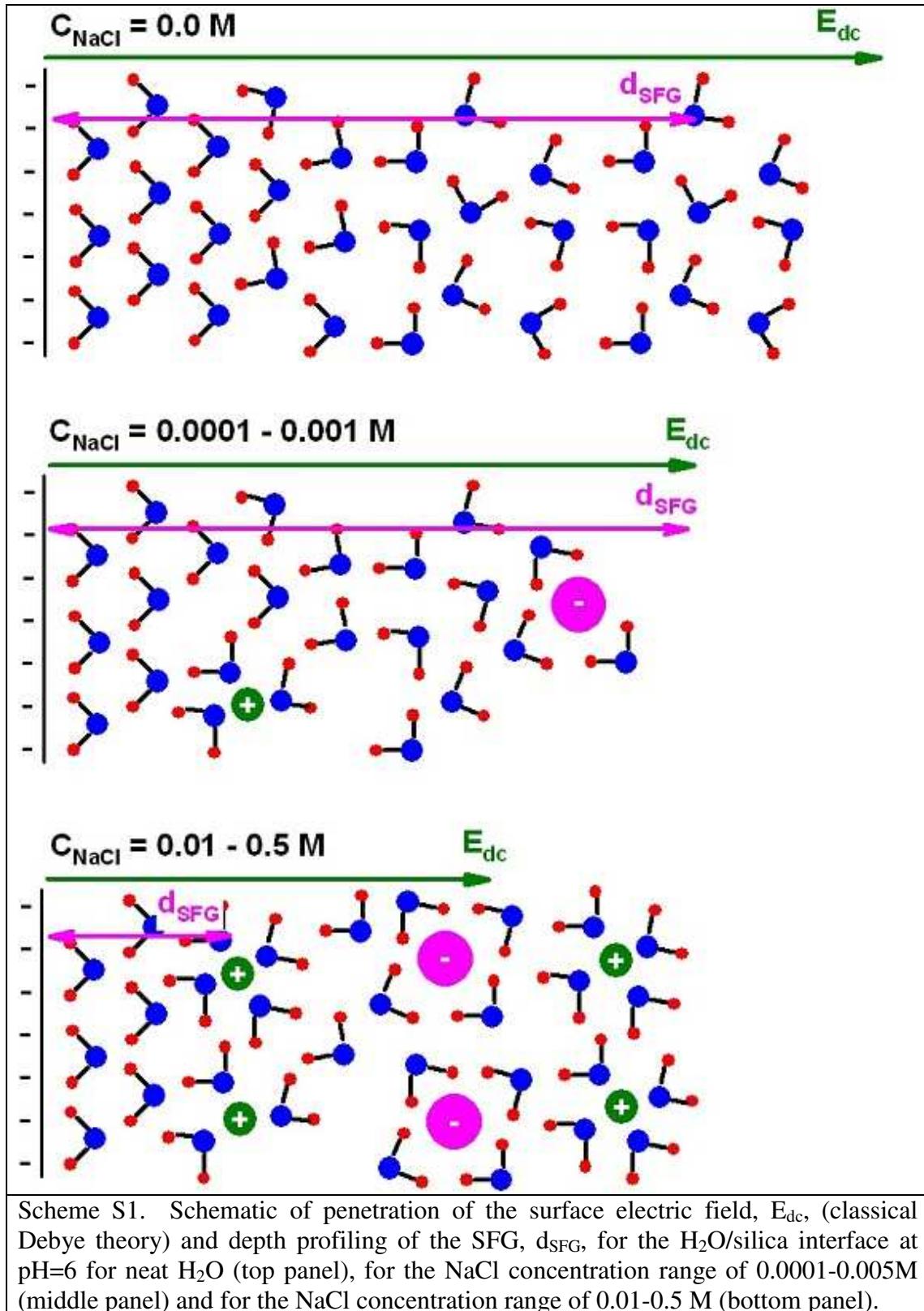
concentration ($C_{\text{NaCl}} > 0.01 \text{ M}$), because of the limited depth profiling of the SFG, the majority of the dynamics probed by SFG should reflect water contributions perturbed by solvated cations (rather than anions) accumulated at the negative silica surface. A slight decrease in the T_1 at concentration greater than 0.01 M can be due to the effect of strengthening of the hydrogen bond by the cations. In other words, moving from 0.01 to 0.5 M, the ratio of hydrated cations to un-perturbed water increases which in turn leads to the faster T_1 . This contribution is, however, not significant since at 0.5 M, where the fraction of water that hydrate cations is only 0.05³ (95% of the OH are still free bounded to other OH of water and not ions)

Alternatively, the faster vibrational lifetime at ~0.5 M salt concentration can also be explained by the fact that, at high salt concentration the dielectric constant of water molecules near surface is smaller than the bulk which leads to the stronger local electric field sensed by the water molecules in that region. The reduced dielectric constant may affect the Forster type transfer via increase in dipole coupling and increase energy transfer rates.

In addition, the increased local electric field can induce increased ordering of the water molecules, which have faster vibrational dynamics than disordered water^{14, 15}. The ratio of the induced dipole due to the electric field to the total dipole moment can be estimated from the Langevin-Debye theory of molecular polarization as $L(\mu E/kT)$, where $L(x)$ is the Langevin function ($L(x)=\coth(x)-1/x$)¹⁶. It should be noted, however, that the contribution of ordered (aligned) water to the total third order susceptibility (equation 2, text) is small because according to the Langevin-Debye theory in the presence of electric field on the order of 10^7 V/m , the fraction of aligned water is only 0.2%¹⁶. In summary,

there are multiple possible reasons for shorter vibrational lifetime at high salt concentration. These include the increase in strength of the electric field, the decrease in the dielectric constant of water and the polarization of hydrogen bond by the cations.

Schematic of the penetration of the surface electric field and depth profiling of the SFG at the silica/water interface in the presence of salt



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