Insights on Interfacial Structure, Dynamics and Proton Transfer from Ultrafast Vibrational Sum Frequency Generation Spectroscopy of the Alumina(0001)/Water Interface

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Supporting Information

1. Fitting of IR pump – vSFG probe (time-resolved vSFG) data

The kinetics of recovery of the bleach is clearly double-exponential in nature (Figure 3 and 7) as seen previously by Bakker et al. in their bulk water dynamics data,[1] and other IR pump – vSFG probe experiments on the O-H stretch of water.[2-5] Hence, a four-level system (Figure S1-1) is used to fit the IR pump-vSFG probe data.[4-5]
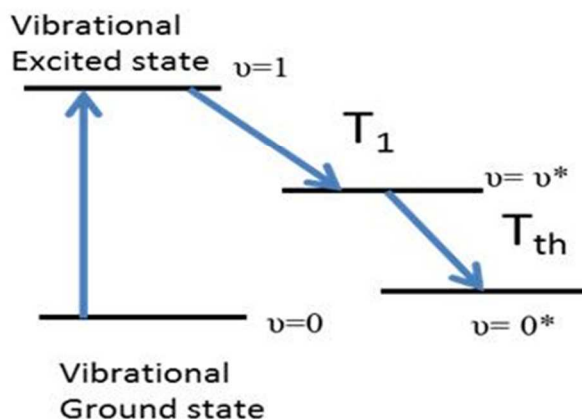
Figure S1-1. Four level model used to describe the vibrational relaxation of water in the bulk and at interfaces.[4-5]

The four coupled differential equations that describe the transfers of population in the four level model discussed above are:

$$\frac{dN_0}{dt} = -\sigma I_{pu}(t)(N_0 - N_1) \qquad (S1.1)$$

$$\frac{dN_1}{dt} = \sigma I_{pu}(t)(N_0 - N_1) - \frac{N_1}{T_1} \qquad (S1.2)$$

$$\frac{dN_2}{dt} = \frac{N_1}{T_1} - \frac{N_2}{T_{th}} \qquad (S1.3)$$

$$\frac{dN_3}{dt} = \frac{N_2}{T_{th}} \qquad (S1.4)$$

where N_0, N_1, N_2, and N_3 are the populations of the v=0, v=1, v^*, and v^*=0 states, respectively, σ is the IR cross section of the ground state (v=0), $I_{pu}(t)$ is the temporal profile of the pump pulse, and T_1 and T_{th} are the characteristic time constants of vibrational relaxation and thermalization processes, respectively.[4]

All four states (v=0, v=1, v=v^*, and v=0*) can absorb the incident probe IR photons, to varying degrees depending on the wavelength, and contribute to the vSFG response (Figure S1-2). The following is our understanding of the process. The dominant mechanism of vibrational relaxation is as follows: Intramolecular relaxation starts from the O-H stretch excited state (v =1) to the 1st overtone of the water bend (v=v^*). Molecules in the (v=v^*) state can still absorb incident IR probe photons via O-H stretch excitation (v=0 $\rightarrow$ v=1) and contribute to the vSFG probe signal. Hence, C_2N_2 is included in the equation for I_{SFG} (Equation S1.5) used to fit the data.

Subsequently, the energy in the water bend overtone can relax to the water bend fundamental of the same molecule or neighboring molecules through dipole-dipole coupling and the excess energy can be transferred into the librational modes and other low frequency modes (like H-bonds) which brings the system to a hot quasi-equilibrium state (v=0*). The (v=0*) state

can also absorb incident IR probe photons via O-H stretch excitation ($v=0 \rightarrow v=1$) and contribute to the vSFG probe signal. Hence, C_3N_3 is included in the equation for I_{SFG} (Equation S1.5). Population of the bend overtone is not the only mechanism of vibrational relaxation, but has been proposed as the dominant one in many previous studies.[4-6]
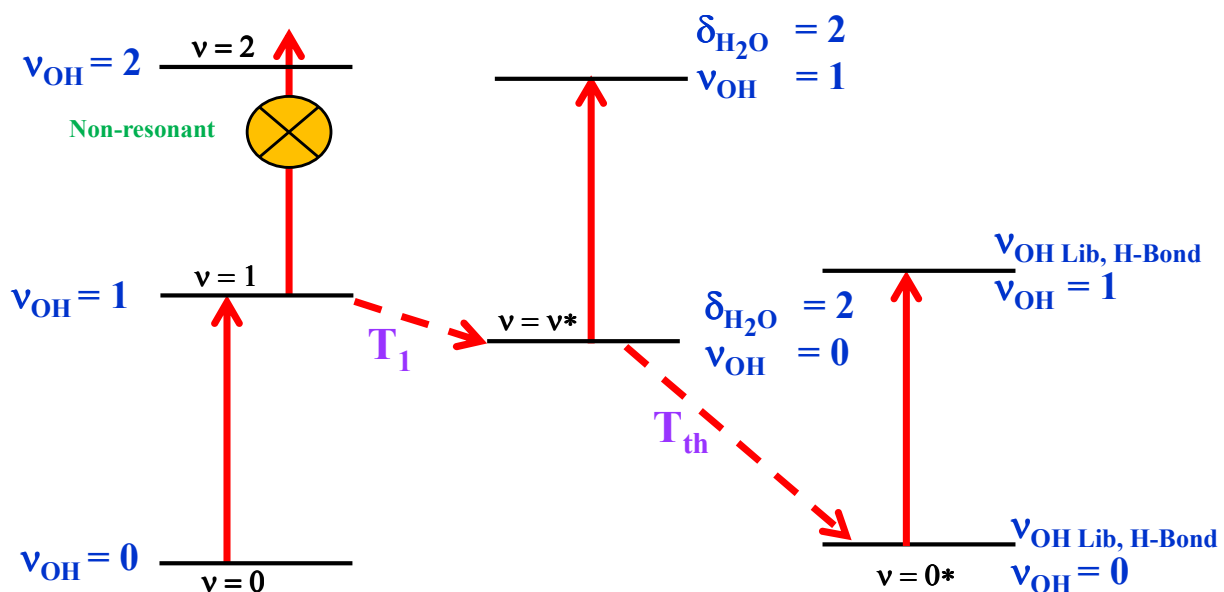

Figure S1-2. Allowed transitions and relaxation pathways in the IR pump-vSFG probe experiments.

The IR pump – vSFG probe data can be fit as a numerical solution to the system of coupled differential equations (Equation S1.1 - S1.4) describing the four-level system (Figure S1-1), convolved with a Gaussian instrument response function trace IRF(t), of the form:

$$I_{SFG} = \text{IRF(t)} * [N_0(t) - N_1(t) + C_2N_2(t) + C_3N_3(t)]^2 \qquad (S1.5)$$

where C_2 and C_3 are factors related to the nonlinear optical susceptibilities of the intermediate and final levels.[4] Here, we assume that the hot band signal ($v=1 \rightarrow v=2$) does not contribute to the SF signal due to anharmonicity. We expect the hot band to be red-shifted by 200-400 cm^{-1} from the fundamental O-H stretch region and therefore outside the window of the vSFG probe (Figure S1-2). Equation S1.5 successfully fits the IR pump-vSFG probe data suggesting the sequence of the energy transfer between different vibrational states is consistent with the 4 level model (Figure S1-3).
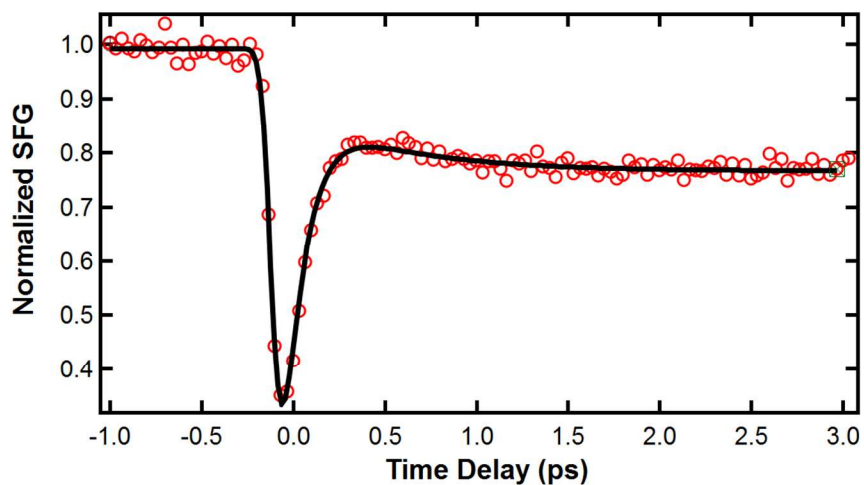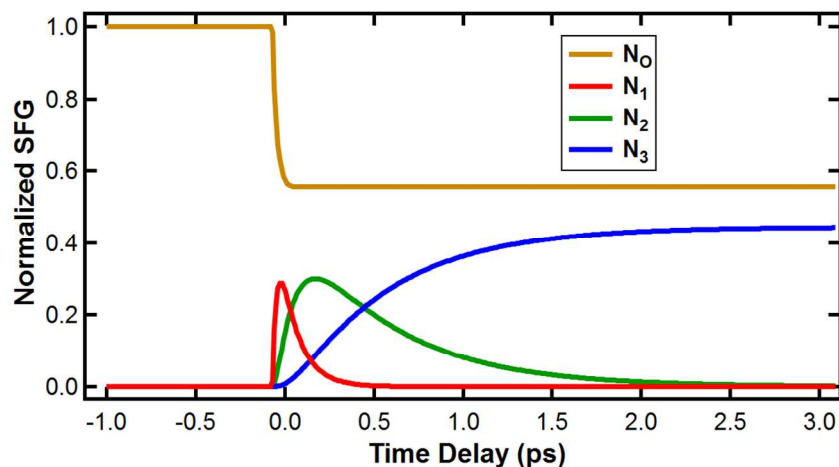
Figure S1-3. Top: IR pump-vSFG probe vibrational dynamics of the interfacial OH species at the α-Al$_2$O$_3$(0001)/H$_2$O interface for bulk pH 2. The black solid line is the best fit consistent with a four-level system (described above). Bottom: Population of the various energy level states described in the four-level model as a function of pump probe delay extracted from the fit result of the α-Al$_2$O$_3$(0001)/H$_2$O interface for bulk pH 2.

2.   Pump power and Polarization effect on the vibrational dynamics

The effect of pump IR power on the vibrational dynamics at the Al$_2$O$_3$(0001)/H$_2$O at bulk pH 10 was investigated (Figure S2-1). The IR pump power was attenuated by adding neutral density filters and the IR pump power was measured. Without any attenuation, the IR pump power was 4.7 μJ and the percent bleach observed in the experiment was ~50%. Upon adding a neutral density filter of 0.3 OD, the IR power decreased to 2.3 μJ and the percent bleach observed in the experiment was ~30%. And finally, when adding a neutral density filter of 0.5

OD, the IR power decreased to 1.8 μJ and the percent bleach observed in the experiment was ~25%. The IR pump power has little to no effect on the vibrational relaxation timescale; i.e., T_1 does not change significantly when the IR pump is attenuated. In contrast, the percent bleach is dependent on the IR pump power.

The linear dependence of percent bleach on the IR pump power can be shown as follows: For 4.7 μJ IR pump power, the bleach of 50% corresponds to excitation of 15% of the vibrational ground state ($v = 0$) population to the first vibrational excited state ($v = 1$).

$I_{SFG} \alpha (\Delta n)^2 = (n_o - n_1)^2 = (0.85 - 0.15)^2 = 0.5$

When 0.3 OD was added, IR pump power decreased to 2.3 μJ, which is decrease in pump power by 2 times. This means that the IR pump should excite 15% ÷ 2= 7.3% of the vibrational ground state ($v = 0$) population to the first vibrational excited state ($v = 1$).

$I_{SFG} \alpha (\Delta n)^2 = (n_o - n_1)^2 = (0.927 - 0.073)^2 = 0.73$

This corresponds to a bleach of 27%, consistent with the experiment.

Lastly, when 0.5 OD was added, the IR pump power decreased to 1.8 μJ, which is decrease in pump power by 2.6 times. This means the IR pump should excite 15% ÷ 2.6= 5.8% of the vibrational ground state ($v = 0$) population to the first vibrational excited state ($v = 1$).

$I_{SFG} \alpha (\Delta n)^2 = (n_o - n_1)^2 = (0.942 - 0.058)^2 = 0.78$
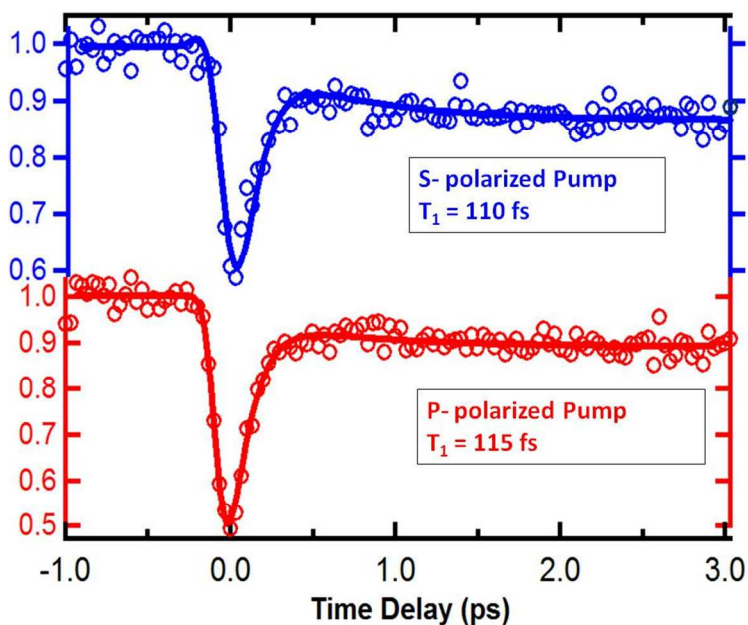
This corresponds to a bleach of 22%, consistent with the experiment.
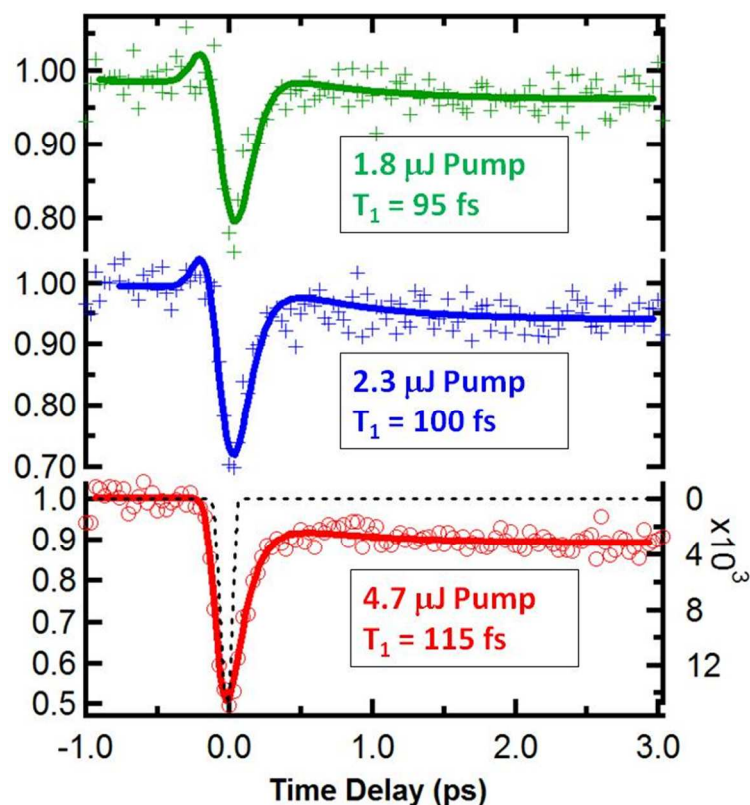
Figure S2-1. IR pump-vSFG probe vibrational dynamics of the interfacial OH species at the α-Al_2O_3(0001)/H_2O (pH 10) interface for 4.7 μJ IR pump (red open circle), 2.3 μJ IR pump (blue open circle), and 1.8 μJ IR pump (green open circle). The solid lines are the best fits consistent with a four-level system (described above). The third-order cross-correlation between IR pump, IR probe, and visible is shown by the black dashed line and has a FWHM of ~85 fs, suggesting IR pulse durations of ~60 fs. P-polarized IR pump and PPP-polarized vSFG probe was used.

Next, the effect of the polarization of the pump IR power on the vibrational dynamics at the Al_2O_3(0001)/H_2O at bulk pH 10 was investigated (Figure S2-2). The pump IR polarization (p- or s- polarized) had little to no effect on the timescale of vibrational relaxation.

Figure S2-2. IR pump-vSFG probe vibrational dynamics of the interfacial OH species at the α-Al$_2$O$_3$(0001)/H$_2$O (pH 10) interface for P-polarized IR pump (red open circle), and S-polarized IR pump (blue open circle). The solid lines are the best fits consistent with a four-level system (described above).

3. REFERENCES

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