Watching molecular motion at interfaces

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6. Appendix

6.1 Solvent effects: Effects of H$_2$O vs. D$_2$O

In chapters 3 and 4, the orientational dynamics of leucine as a monomer and as a side chain within a model peptide were measured. When performing experiments with LK peptides adsorbed on the surface of H$_2$O as opposed to D$_2$O, the pump-probe signal is observed to first recover in an ultrafast (sub 100 fs) way before later equilibrating with the vibrational relaxation time of the methyl stretching vibration. Presumably, this ultrafast response is due to interference from the underlying OH stretching band which subsequently interferes with the methyl resonances. Of note, however, there appears to also be an influence of reorientational dynamics because the s and p signals do not scale with one another. This experiment was performed for LK peptides in PBS buffer, water, and finally, the results displayed in Chapter 3 were performed in D$_2$O because, in this way, the L residue dynamics can be disentangled. Notably, though, experiments for L-Leucine and Sodium decanoate were also carried out, and in these instances, the response from the OH band appears to dominate the response in both cases. Lastly, IR-pump SFG experiments of dodecanol adsorbed to an H$_2$O surface showed negligible effects on the measured ps lifetimes because the methyl modes in question do not interfere with the underlying water band.

Figures 6.1-6.2 show the remarkable effect of H$_2$O versus D$_2$O on the measured dynamics of LK peptides and leucine monomers at the vapor/air interface. For the case of the LK peptide, the initial recovery of the signal is faster than the 150 fs instrumental response, and after this sharp rise, a slower modulation process appears to influence the population recovery. Notably, the s and p signals do not scale with one another. That is, molecular reorientation could influence the recovery of the signal. When the LK peptide is placed in D$_2$O, the solvent effects are decoupled from the underlying methyl dynamics, and the recovery of the signal is on a ps time scale which is in line with what is known from the literature.
In Figure 6.2, the same experiment is performed for an 8 M solution of leucine in H₂O with HCl at pH 0.1, that is: positively charged L-leucine above saturation coverage. The signals show a fast recovery which is appears to follow a single exponential. There appears to be only a contribution from the underlying water band (perhaps an underlying hot band\textsuperscript{161} which represents the 1 – 2 transition). No slower modulation of the
signal is observed, and the s and p pumped traces recover at similar timescales in contrast to what is seen in LKα14 where the s and p pumped traces appear to recover at different time scales presumably due to reorientation. In panel b of Figure 6.2, the solvent is changed to D₂O, and the lifetime measured is that of the symmetric CH₃ stretch. Panels 6.1 b and 6.2 b display similar effects, and this shows that by changing from H₂O to D₂O, the dynamics of the aliphatic groups may be measured without interference from either the underlying water band or the nonresonant background.

**Figure 6.2** a. TP-SFG of 0.1 pH solution of L-leucine in H₂O b. TP-SFG of positively charged L-leucine in D₂O.
Figure 6.3 a. TP-SFG of Decanoic acid at pH 11 measured in H$_2$O b. TP-SFG of Dodecanol measured at H$_2$O surface. All traces depicted in panels a and b were measured using ssp polarization.

In Figure 6.3 a, we look at a negatively charged surface of 102 mM decanoic acid with NaOH added to bring the solution to pH 11, in this example where the vibrational modes over the aliphatic range have been reported to be delocalized, the bleach is also observed to recover at a single exponential rate without a slower modulation due to the underlying methyl population dynamics. The s and p pumped signals also scale with
one another. The likely main contributor to the signal is again the underlying OH band. Figure 6.3 b shows the terminal methyl units in the neutral long chain alcohol surfactant dodecanol do not interact with the underlying water. In this instance, the recovery of the signal occurs on a ps time scale in line with what was reported previously for the same long chain alcohol measured in D₂O.³⁹

6.2 Additional considerations

a. Effective susceptibility and TIR enhancement

Recalling that the intensity of the detected SFG signal is

\[ I_{SFG} \propto |P^{(2)}(\omega_{SFG})|^2 = |\chi^{(2)}_{\text{eff}}(\omega_{SFG}) : E_{\text{vis}}E_{\text{IR}}|^2 \]

Considering that the signal emanates from the interfacial layer between two media of refractive index \(n_1\) and \(n_2\) with a vanishingly thin interfacial sheet of nonlinear polarization given refractive index \(n'\) as in figure 6.4 below. The total reflected SFG intensity which is detected is:

\[
I_{SFG} = \frac{8\pi^2 \text{sec}^2 \theta_{SFG}}{c^3 n_1(\omega_{SFG})n_1(\omega_{\text{vis}})n_1(\omega_{\text{IR}})} |\chi^{(2)}_{\text{eff}}|^2 I_{\text{VIS}} I_{\text{IR}}
\]

(A.1)
Figure 6.4. Schematic representation of SFG signal generation. The signal is emitted from a vanishingly thin sheet of nonlinear polarization with refractive index $n'$. Angles $\theta_i$ are the angles relative to the surface normal which is defined as the $z$ axis. The x-y plane corresponds to the surface plane.

The SFG electric field is also influenced by local interactions between the incident electric fields and the surrounding media. An effective second-order susceptibility which takes these effects into account is given by:

$$\chi_{eff}^{(2)} = [e_{SFG}L(\omega_{SFG})]\chi^{(2)}[e_{VIS}L(\omega_{VIS})][e_{IR}L(\omega_{IR})]$$

(A.2)

The $e_i$ are unit polarization vectors and $L(\omega_i)$ correspond to the Fresnel factors at the specified frequencies. Recall that for an azimuthally isotropic

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interface (i.e. non-chiral) there are four independent elements of the non-linear susceptibility i.e. \( \chi_{xx}^{(2)} = \chi_{yz}^{(2)}, \chi_{zz}^{(2)} = \chi_{zy}^{(2)}, \chi_{xx}^{(2)} = \chi_{yy}^{(2)}, \chi_{zz}^{(2)}. \) Due to the azimuthal symmetry, the x and y directions are interchangeable. The different components of the susceptibility tensor may be estimated by measuring four different polarization combinations where the indices are always listed in order of highest frequency to lowest frequency field i.e. SFG, VIS, IR. The allowed polarization combinations are ssp (s-polarized SF, s-polarized VIS, p-polarized IR), sps, pss, and ppp. The effective susceptibilities for these polarization combinations using equation A.2 are:

\[
\begin{align*}
\chi^{(2)}_{\text{eff, ssp}} &= L_{yy}(\omega_{\text{SFG}})L_{yy}(\omega_{\text{VIS}})L_{zz}(\omega_{\text{IR}})\sin \theta_{\text{IR}} \chi_{yyz}^{(2)} \\
\chi^{(2)}_{\text{eff, sps}} &= L_{yy}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{VIS}})L_{yy}(\omega_{\text{IR}})\sin \theta_{\text{VIS}} \chi_{zyy}^{(2)} \\
\chi^{(2)}_{\text{eff, pss}} &= L_{zz}(\omega_{\text{SFG}})L_{yy}(\omega_{\text{VIS}})L_{yy}(\omega_{\text{IR}})\sin \theta_{\text{SFG,r}} \chi_{zyy}^{(2)} \\
\chi^{(2)}_{\text{eff, ppp}} &= -L_{xx}(\omega_{\text{SFG}})L_{xx}(\omega_{\text{VIS}})L_{zz}(\omega_{\text{IR}}) \cos \theta_{\text{SFG,r}} \cos \theta_{\text{VIS}} \sin \theta_{\text{IR}} \chi_{xxz}^{(2)} \\
&- L_{xx}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{VIS}})L_{xx}(\omega_{\text{IR}}) \cos \theta_{\text{SFG,r}} \sin \theta_{\text{VIS}} \cos \theta_{\text{IR}} \chi_{xxz}^{(2)} \\
&+ L_{zz}(\omega_{\text{SFG}})L_{xx}(\omega_{\text{VIS}})L_{xx}(\omega_{\text{IR}}) \sin \theta_{\text{SFG,r}} \cos \theta_{\text{VIS}} \cos \theta_{\text{IR}} \chi_{xxz}^{(2)} \\
&+ L_{zz}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{VIS}})L_{zz}(\omega_{\text{IR}}) \sin \theta_{\text{SFG,r}} \sin \theta_{\text{VIS}} \sin \theta_{\text{IR}} \chi_{zzz}^{(2)}
\end{align*}
\]

(A.3)

The Fresnel factors \( L_{ii} \) are given by:

\[
\begin{align*}
L_{xx}(\omega_i) &= \frac{2n_1(\omega_i)\cos \theta_{\text{SFG,t}}}{n_1(\omega_i)\cos \theta_{\text{SFG,t}} + n_2(\omega_i)\cos \theta_{\text{SFG,r}}} \\
L_{yy}(\omega_i) &= \frac{2n_1(\omega_i)\cos \theta_{\text{SFG,r}}}{n_1(\omega_i)\cos \theta_{\text{SFG,r}} + n_2(\omega_i)\cos \theta_{\text{SFG,t}}}
\end{align*}
\]
The $r$ and $t$ subscripts represent reflected and transmitted beams respectively. Experiments for the silica-water interface are performed to enhance the non-HB region ($3600 - 3800 \text{ cm}^{-1}$) of the H$_2$O stretching region, and the angles of incidence were chosen largely to take advantage of the local field factors under total internal reflection conditions.

TIR may be reached at angles above the critical angle of $\theta_c = \arcsin(n_2/n_1)$ where $n_2$ is the refractive index for the higher refractive index material. For the ppp polarization combination, the angle of incidence of the visible field largely influences the effective susceptibility and in works by Tyrode et al., enhancement factors of 4-5 times were found at angles above the critical angle.$^{129,146,154,163}$

b. **Brief overview of phase-resolved SFG**

In a conventional SFG experiment,

$$I_{SFG} \propto |P_{i, SFG}^{(2)}|^2 \propto |\chi_{i, j, k}^{(2)}|^2 \propto |E_{SFG, sample}|^2$$  \hspace{2cm} (A.5)

and the second-order susceptibility tensor, in general, is a complex quantity which contains information about the magnitude and phase of the signal. This information is lost in a typical measurement because the intensity squared spectrum is measured. This problem can be circumvented if one takes advantage of spectral interferometry with another electric field of known phase, a.k.a. the local oscillator (LO). This is the phase-resolved SFG experiment.$^{141,148,164}$ Consider an electric field oscillating at the same frequency as the SFG beam, which is temporally delayed by an amount $\Delta \tau$ with respect to the sample beam. These beams will spectrally interfere on a detector to produce a pattern of fringes of known spacing and phase. By
measuring a reference sample of known phase, the relative phase difference between the reference sample and the sample can be extracted.

\[ I_{\text{SFG}} \propto |E_{\text{SF},LO} + E_{\text{SF},\	ext{sample}}|^2 \]

\[ = \propto |E_{\text{SF},LO}|^2 + |E_{\text{SF},\	ext{sample}}|^2 + E_{\text{SF},LO}^* E_{\text{SF},\	ext{sample}} e^{i\omega \tau} + \text{c.c.} \]

(A.6)

Recalling that \( E_{\text{SFG}} \propto \chi^{(2)}_{\text{res},n} \propto \sum n \frac{A_n}{\omega_n - \omega_{IR} - i\Gamma_n} \)

The equation can be rearranged to

\[ \chi^{(2)}_{\text{res},n} \propto \frac{A_n(\omega_{IR} - \omega_n)}{(\omega_{IR} - \omega_n)^2 + \Gamma_n^2} + i \frac{A_n}{(\omega_{IR} - \omega_n)^2 + \Gamma_n^2} \]

(A.7)

\[ = \text{Re}(\chi^{(2)}_{\text{res},n}) + \text{Im}(\chi^{(2)}_{\text{res},n}) \]

The imaginary part of the response corresponds to the IR absorption spectrum, and in this case, the orientation of adsorbed molecular species at the interface can be better ascertained. The implementation of such an experiment is still quite difficult, and it is difficult to implement for buried interfaces such as those experiments performed in chapter 5.

c. Outlook

To carry out further experiments which take the effect of molecular reorientation into account, a setup should be designed carefully perhaps according to the theoretical work of Nienhuys\textsuperscript{38} but also taking more recent work of about dynamic measurements to determine the SFG magic angle and tilt angle distribution by Xiong\textsuperscript{165} into account. By applying a scheme in which the excitation pulse is normal to the surface and circularly polarized, the influence of vibrational dynamics and out of plane reorientation can be directly extracted from the experimental data. Using this knowledge, similar schemes using alternating linear polarization may be employed to attempt to
extract other information about reorientational dynamics. Furthermore, time, polarization, and phase-resolved experiments could hypothetically allow for the detection of additional tensor elements which are symmetry disallowed but upon breaking of azimuthal symmetry by the pump become symmetry allowed. A phase resolved experiment could enhance the weak transients. Additionally, the model could be refined to include orientational diffusion along the molecular twist angle $\psi$.

In terms of peptide dynamics at the surface, future research could look at the influence surface chemistry has on interfacial side chain dynamics. One experiment could look at the influence a hydrophilic substrate like silica has on the dynamical aspects of the hydrophobic side chain dynamics. These model amphiphilic peptides have been shown to be capable of nanoscale bioengineering of silica structures,\textsuperscript{108} and the dynamic understanding could help in designing peptides which can modify a surface in a targeted fashion. Other work could move to more complicated proteins by isotopically labeling side chains and subsequently follow the dynamics of binding events. Finally, relating the measured orientational dynamics to some sort of generalized order parameter to be able to consider how much conformational entropy is present in the side chains of larger proteins at a surface could help better compare to data of protein side chains in bulk solution.