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Watching Molecular Motion at Interfaces

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Summary

Molecular reorientation is important for a variety of processes ranging from chemical reactions at the molecular level to cellular function. Until fairly recently, much attention has been paid to the structure function paradigm. However, it has become clear lately that molecular dynamics also play an important role in molecular function. In bulk, it has been shown that the orientational dynamics associated with protein side chain motions reflect the conformational entropy of the side chains. For example, protein side chains are shown to become less dynamic during binding events which means there are fewer total possible conformations that the side chain can assume. This directly impacts the function of the protein.

This thesis presents measurements of molecular orientational dynamics from systems ranging from the dangling OH of water in contact with a buried silica interface to the side chain orientational dynamics of hydrophobic leucine residues which point into the air. Experimental and computational methodology for the investigation of interfacial chemistry on molecular orientational dynamics is presented which involves vibrationally labeling molecules via an infrared pump pulse. The orientational dynamics of the labelled molecules at the interface may be followed in real time with sub-ps resolution through an IR-Vis SFG probe pulse. The experiments are complemented with numerical modelling through the help of molecular dynamics simulations.

Chapter 3 shows the real time observation of hydrophobic leucine monomers reorienting at the interface. Through experiments, an orientational relaxation time of approximately 20 ps is observed for the leucine monomers. Molecular dynamics simulations allow us to visualize the molecular fluctuations which are responsible for the estimated relaxation time. It is shown that the leucine monomers reorient at comparable rates parallel and perpendicular to the induced dipole. Furthermore, the measured and calculated rates of molecular reorientation were found to be on a similar scale to internal motions of hydrophobic leucines found within the hydrophobic core of proteins.

Chapter 4 continues the work from Chapter 3 by extending the measurement of interfacial orientational dynamics to the hydrophobic side chains found in model amphiphilic LK peptides. These peptides are known to form well defined secondary structures at the air/water interface. It is shown through experiments and simulation that the orientational dynamics of the hydrophobic leucine side chains are independent of the secondary structure present in the LK peptide. This might be indicative of a general mechanism of protein side chain coupling to surfaces.

In the chapter 5, the focus of the work turns to the buried silica water interface. First, the study of this buried interface provides a platform to further expand the studies of interfacial side chain dynamics by establishing a methodology to measure a surface which is impacted by a different surface chemistry. Next, the silica/water surface is interesting in its own right. We observe a seldom discussed high frequency resonance in the O-H stretching region of the SFG spectrum. Phase-resolved SFG measurements indicate that the molecular species detected is oriented toward

the silica surface which is indicative of weakly hydrogen bonded water. In addition, we measure the orientational dynamics of this high frequency water species, and it is found that the measured lifetimes are in line with previously measured values of the dangling OH at both the water/air and extended hydrophobic interface. This is surprising in light of the fact that the silica/water surface is generally considered to be very hydrophilic. A small population of non-hydrogen bonded water molecules which generally are associated with hydrophobic surfaces is shown to exist.

The study of interfacial motional dynamics could provide a new platform to determine conformational entropy at interfaces. Further insights into side chain function may also arise if this work is extended to study the side chains present in larger proteins. Much is left to be discovered about protein side chain dynamics at interfaces. For instance, through the use of vibrational labels which possess vibrational lifetimes on the order of those measured in NMR, slower side chain motions may be followed. In addition, the understanding of side chain motions can lead to a better understanding of protein-surface interactions.