

# Interfacial Depth Profiling of the Orientation and Bonding of Water Molecules across Liquid–Liquid Interfaces

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Molecular interactions that create the interfacial properties present at a junction between water and several hydrophobic liquids are the focus of this paper. This study employs molecular dynamics simulations to generate vibrational sum frequency (VSF) spectral profiles of water across the interfacial depth of three systems: the carbon tetrachloride–water, chloroform–water, and dichloromethane–water interfaces. These spectral profiles are calculated as functions of both frequency and interfacial depth, providing a visual description of interfacial water structure that can be difficult to elucidate from density profiles and sum frequency spectral intensities, or spectra that vary only as functions of frequency. VSF spectral intensities calculated for the OH stretch region that are integrated over the entire interfacial region are shown to compare well with the experimental VSF data for these systems. VSF spectral depth profiles show how the widths of the interfaces vary with the density and polarity of the organic phase and where different types of water species reside in the interfacial region. Furthermore they highlight the major molecular level differences found in these three interfacial regions and, in particular, identify oriented water monomers deeply immersed within the dichloromethane phase far removed from the Gibbs dividing surface. The penetration of water has important implications for how we view transport across water–hydrophobic liquid interfaces.

## Introduction

The interface between water and a hydrophobic liquid is the site for many important processes that are utilized for biological, environmental, and industrial applications. The carbon tetrachloride–water (CCl<sub>4</sub>–H<sub>2</sub>O), chloroform–water (CHCl<sub>3</sub>–H<sub>2</sub>O), and dichloromethane–water (CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O) interfaces serve as a series of model systems that are studied on a frequent basis due to their fundamental and simple nature, both experimentally and computationally. The organic molecules themselves comprise the simplest type of halocarbon, yet each molecule possesses unique physical properties that enable clear distinction between them. Their spectroscopic response within the vibrational OH stretch region of water is nearly transparent, making them ideal candidates for spectroscopic studies of water–hydrophobic surfaces. As a result, there is considerable interest in understanding the structural properties of water within these buried systems, especially by means of vibrational spectroscopy.<sup>1–10</sup>

Whereas both linear and nonlinear vibrational spectroscopic techniques have been shown to be powerful methods for studying the surface of water on a molecular level, understanding the nature of the water surface on the basis of its spectral response poses many challenges. The surface is comprised of a multitude of hydrogen-bonded water species of different bond lengths, strengths, and angles, making it nearly impossible to assign distinct frequencies and bandwidths to particular types of hydrogen-bonded water molecules as has been possible for gas-phase water and its simple clusters. Furthermore, current analytical approaches toward understanding the vibrational spectroscopic response of liquid surfaces cannot provide direct

information pertaining to the location of different contributing species within the interfacial region. Experimentally, techniques such as X-ray scattering,<sup>11–13</sup> neutron scattering,<sup>14,15</sup> and second harmonic studies<sup>16,17</sup> assist in our understanding of interfacial structure as a function of depth, but they cannot capture the molecular bonding nature of these interfacial water species that VSF studies can provide.

On a computational level, density profiles are common tools that are used to assess interfacial thickness, by correlating the interfacial region to changes in the molecular population of a given liquid.<sup>1,8,18–22</sup> In this work, molecular dynamics simulations are used to create spectral profiles of water at the CCl<sub>4</sub>–H<sub>2</sub>O interface, the CHCl<sub>3</sub>–H<sub>2</sub>O interface, and the CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O interface. These spectral profiles combine the methodologies behind vibrational sum frequency spectroscopy and density profiles to create spectral responses of water that vary as functions of both frequency and interfacial depth. By the combination of these two methods, properties such as interfacial depth and penetration of water into the adjacent medium are assessed by observing the molecular orientation of extant water molecules, as opposed to changes in molecular population. To emphasize these changes within the different interfacial systems, several species of water that interact directly with the organic phases are identified, and the spectral profiles from each species are evaluated. These results are compared with measurements obtained from density profiles and sum frequency spectral intensities to show how spectral profiles identify properties of water within the interfacial region that can be particularly difficult to deduce from these other standard treatments. These studies show how differently the interfacial water molecules behave when present at the surface of organic liquids of varying density and polarity.

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