

Layered Organic Structure at the Carbon Tetrachloride–Water Interface

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The structure of organic–liquid interfaces continues to be of central interest to a wide variety of science and engineering disciplines on account of the applicability of this knowledge to chemical synthesis, purification, industrial cleaning, and nuclear waste remediation. The carbon tetrachloride–water interface in particular has been the subject of numerous experimental^{1,2} and computer simulation^{3–6} studies. This system has long served as a model for understanding aqueous–hydrophobic interactions, of central importance to surfactants, adsorbed biomolecules, salts, and ions at hydrophobic solid and liquid interfaces. In all of these investigations, the emphasis has been almost entirely on the interfacial water molecules. The only commonly reported CCl₄ statistic has been the density profile across the interface. No detailed studies of the carbon tetrachloride structure in the vicinity of an aqueous interface have been reported. This is due in part to the interest in water structure at hydrophobic surfaces and also due to the high symmetry of the CCl₄ molecule. Knowledge of bulk liquid CCl₄ molecules has come from numerous experimental,^{7–15} theoretical,¹⁶ and simulation^{7,8,13,17–19} studies over the last several decades. In bulk liquid, the primary issues surround the coordination of adjacent CCl₄ molecules. Until recently, the leading model formulated from neutron scattering data was one in which the corner of one tetrahedron was oriented toward the face of another, termed *Apollo*.¹⁵ More recent neutron diffraction experiments have challenged this picture, finding stronger evidence of corner-to-corner than corner-to-face contact.^{7,8,10} Our findings show that CCl₄ molecules form a fascinating structure at an aqueous interface, consisting of an alternating layered mixture of face and corner contacts of the CCl₄ tetrahedra. A study of the CCl₄–vapor interface has found no preferred orientations of the surface CCl₄ molecules,¹⁹ alluding to the role that water likely plays in supporting this layered structure.

We have used the Amber 7 package to perform equilibrium molecular dynamics simulations of the CCl₄–water interface with a 1 fs integration time and weak coupling to a heat bath at 300 K. Initially separate (40 Å)³ boxes containing 2135 POL3 water molecules and 400 CCl₄ molecules (using Dang's polarizable CCl₄ model and atomic charges¹⁹) were minimized, equilibrated for 200 ps, and then combined to create a 40 × 40 × 80 Å³ interfacial box. After the energy of this system was minimized and the system was allowed to equilibrate for 2 ns, atomic positions were recorded every 50 fs for an additional 10 ns. This provided 200 000 configurations of the system for our structural analysis.

In order to classify interfacial CCl₄ molecules as making either corner, edge, or face contact with the bulk water phase, the chlorine atom closest to the bulk water direction was identified, and the angle of this C–Cl bond with respect to the interface normal was determined. In such a scheme, θ may range from 0° (perfect corner alignment) to 70.5° (perfect face alignment); these cases are illustrated in Figure 1. This angle was then tabulated for every CCl₄

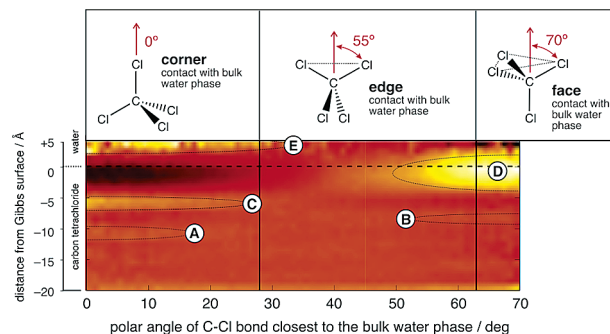


Figure 1. The orientation of carbon tetrachloride molecules is classified according to the polar angle, θ , of the C–Cl bond closest to the bulk water phase: $\theta < 28^\circ$ corner contact; $28^\circ < \theta < 63^\circ$ edge contact; $63^\circ < \theta < 70.5^\circ$ face contact. Thin dashed contours are drawn as a guide to the eye. Slices through regions A–E are shown in Figure 2.

molecule and a 2D histogram was constructed by binning the result according to angle and distance from the Gibbs surface. The location of the Gibbs surface was determined by fitting the density data to a hyperbolic arctangent and was set to $z = 0$. In this convention, negative values of z correspond to the organic side of the interface; positive values to the water side. The brightest areas (orange-yellow) of Figure 1 indicate the highest population of CCl₄ molecules. The stripes observed (labeled A–E) are therefore indicative of a layered structure. The histogram intensity values have been normalized so that an isotropic distribution (in the center of the organic box at $z = -20$ Å) appears as a vertical stripe with uniform intensity. One can see a dominant face-type orientation over a ~ 6 Å-wide region roughly centered at the Gibbs surface ($z = -4$ to $+2$ Å, region D). On either side of this region, there is a ~ 3 Å-wide corner-type region (C and E) with weaker orientation, as seen in the lower intensity of these bands. It is difficult to probe the orientation of CCl₄ molecules more than 5 Å into the bulk water phase since, even with this many configurations from long MD trajectories, there are simply too few organic molecules there. Probing deeper into the organic phase, however, one can notice a weak band with intensity corresponding to face alignment around $z = -9$ Å (region B). Finally, there is another weak band in the corner-type region at $z = -12$ Å (region A). It is easier to recognize these features by examining slices through specific values of the distance from the Gibbs surface; these are shown in Figure 2. The horizontal line is drawn as a guide to the eye to assist interpretation of the weak orientation deep in the organic phase. Although the orientation preference for layers furthest from the Gibbs surface is weak, it may be seen that the peaks of these distributions clearly lie toward the corner and face regions. One may also notice that the corner orientation of CCl₄ molecules 3 Å into the bulk water phase is quite strong, but noisy because of the poorer statistics here. The overall picture of carbon tetrachloride orientation at the CCl₄–water interface is shown in Figure 3.

Previous studies have shown that the alignment of water molecules in contact with a hydrophobic medium results in a net

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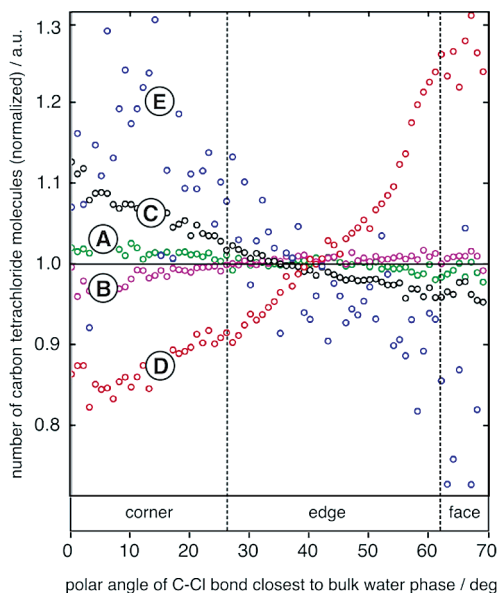


Figure 2. Some representative one-dimensional slices across the 2D orientation map in Figure 1, with normalized populations normalized relative to those of an isotropic CCl_4 bulk distribution. Molecules deep in the organic box (-12 Å, region A in Figure 1) are shown in green; -9 Å (region B) in magenta; -6 Å (region C) in black; at the Gibbs surface (region D) in red; $+3$ Å in the bulk water phase (region E) in blue.

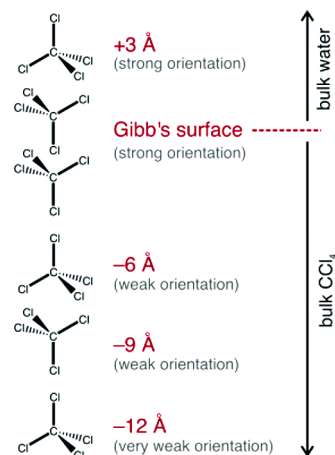


Figure 3. At an aqueous interface, carbon tetrachloride molecules form an alternating layer structure, consisting of corner and face contacts between tetrahedra. The width of most of the layers corresponds to that of a single CCl_4 molecule.

dipole moment perpendicular to the plane of the interface.²⁰ It has also been demonstrated that, in the presence of an intense laser field, gas-phase CCl_4 molecules are aligned such that a C–Cl bond is parallel to the polarization direction of the laser.²¹ Although dipole–dipole interactions in the plane of the interface have been shown to contribute to interfacial rigidity,²² there is no net macroscopic dipole moment in the plane of the interface as a result of the azimuthal isotropy of the liquid phase. It is therefore reasonable to suggest that the two dominant structures we observe—corners and faces pointing toward the bulk water direction—are aligned in response to the out-of-plane field of the water molecules.

The absence of oriented molecules at the CCl_4 –vapor interface¹⁹ further justifies this conclusion. The alternating nature of the layered structure is likely due to the same corner-to-corner and face-to-face packing preference that is currently believed to constitute the primary coordination in the bulk CCl_4 phase.^{7,8,10} The only deviation to this structure occurs closest to the Gibbs surface, where a 6 Å-wide region of face contact molecules would imply some *Apollo*-type corner-to-face coordination.

In summary, we have observed an alternating layered structure of ordered CCl_4 molecules at the CCl_4 –water interface. Given carbon tetrachloride's preference to align one of its C–Cl bonds along an external field, the observed corner and face CCl_4 orientations are likely due to the out-of-plane field created by the presence of polar oriented interfacial water molecules. These results contribute to our general understanding of neutral molecules at aqueous–hydrophobic interfaces, and to more complex systems based on these interfaces such as surfactants and ions. For example, the same field that we hold responsible for CCl_4 alignment as a result of ordered water molecules would be capable of orienting not only polar ions and surfactants but also polarizable neutral species. Future studies will probe these effects in more detail by varying the nature of the hydrophobic phase and strength of the interfacial dipole moment.

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