

Title: Investigation of monomolecular organic layers and their interaction with atmospheric oxidants and pollutants

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**Abstract:** Using classical molecular dynamics simulations, we studied interactions between Langmuir monolayers of palmitic acid (PA) and haloalkanes as serious atmospheric pollutants, to model naturally occurring and atmospherically relevant complex surfaces of extended water bodies and aqueous aerosols. We investigated partitioning, orientation, solvation, as well as structure and morphology of the individual components and their mixture at water/vapor interfaces at different temperatures in order to validate our computational model and complement experimental data with molecular-level details. First, we have shown that halocarbon molecules adsorbed on amorphous ice nanoparticles at 100 K remain mostly isolated and do not form aggregates, in contrast to their clustering on cryogenic argon nanoparticles. Next, we report that chloro-, bromo-, and iodoalkanes with short alkyl chains (up to C5) exhibit high preference for the outermost region of the water/vapor interface. Their average residence times of several hundreds of ps to several ns at 300 K depend on the alkyl chain length and the nature of the halide atom. The calculated molecular orientation changes from a mostly dehydrated halide atom exposed to the vapor for halomethanes to a partially hydrated halide atom for halopentanes. In the next step, we show that multi-substituted chloro- and bromomethanes are readily adsorbed on water or crystalline ice surfaces. Based on free energy calculations we estimated that the concentration of multi-substituted chloro- and bromomethanes at the aqueous surface may be up to 4 orders higher relative to their concentration in the gas phase, depending on the particular species. Further, we investigated the PA monolayer at the water surface comparing calculated structural parameters as a function of film surface density with experimental data to validate our model. We have shown that the intact PA monolayer prevents mass transfer of chloromethanes across the water/vapor interfaces. Finally, we studied mixed PA monolayers with 1-bromoalkanes of different chain length (C5, C10, and C16). We observed that bromohexadecanes were incorporated into the PA monolayer, while bromoalkanes with shorter alkyl chains failed to form a stable mixed monolayer. Calculated structural properties as functions of composition and film surface density provided nanoscopic details about the organization and dynamics of mixed monolayers and supplemented experimental results from our collaborating group. Our results have important implications for (photo)chemical processes at the organic-coated aerosols in tropospheric and stratospheric regions.

**Keywords:** molecular dynamics, Langmuir monolayer, palmitic acid, haloalkanes, aqueous solvation, interfacial partitioning