# Ordering in the Subphase of a Langmuir Monolayer: Diffraction and Anomalous Scattering Studies

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## Introduction

Langmuir monolayers are often used as models of organic-inorganic interfaces at the air-water interface.[1] Several grazing incidence synchrotron x-ray diffraction studies[2,3] have reported that ions form commensurate superstructures under the organic film, an interpretation based on an observation of superlattice peaks in the diffraction pattern. We sought to learn more about this initial stage of bulk inorganic nucleation by studying fatty acid Langmuir films with $Pb^{2+}$ ions in the subphase. Lead is a heavy atom that scatters x-rays strongly and has an experimentally accessible (L3) absorption edge; this latter fact allowed us to perform anomalous x-ray scattering studies that directly test for the presence of lead in the superlattice.

## Methods and Materials

A dilute aqueous solution containing $10^{-5}$ M lead chloride was used as the subphase whose pH was not adjusted and measured to be ~5.5. A monolayer of heneicosanoic acid was spread and compressed to slightly above zero dynes/cm pressure and held at temperature of 10ºC.

## Results

In-plane diffraction scans reveal a total of 41 distinct peaks These correspond precisely to a superstructure commensurate in an unusual way with the organic monolayer lattice: the real-space basis vectors of the inorganic supercell ($\mathbf{a}'$, $\mathbf{b}'$) are related to those of the organic unit cell ($\mathbf{a}$, $\mathbf{b}$) by $\mathbf{a}' = 4\mathbf{a} + 2\mathbf{b}$ and $\mathbf{b}' = -3\mathbf{a} + 2\mathbf{b}$. The area of the superlattice unit cell is therefore fourteen times the organic unit cell area. It is very unlikely that such a large unit cell can be formed by lead ions alone.

If the superlattice peaks were solely due to lead ions, the contribution to the intensity of each weak peak should be proportional to the square of the lead form factor. Tuning the x-ray energy from 12.885 keV (below the L3 absorption edge of the lead atom) to 13.100 keV (slightly above the edge) reduces the lead form factor from $f = 70.21 + 4.187\, i$ to $f = 62.18 + 10.13\, i$, and so the absolute intensity of a diffraction peak due to scattering from lead atoms should decrease by ~20%. We have measured the intensities of 13 weak peaks with $K_{xy}$ between 0.6 $Å^{-1}$ and 1.4 $Å^{-1}$ at these two energies (data for some representative superlattice peaks, and also some organic lattice peaks are shown in Fig. 1). Within an experimental error of ~5%, we observed no change for any of these peaks.

## Discussion

Our results indicate that the interfacial superlattice is not simply an array of lead ions but consists primarily of other atoms. Since metal ions undergo hydrolysis and hydration in the aqueous solution, a wide range of complex polynuclear oxo(hydroxo)-bridged structures can, be formed. Thus, we expect that hydrolysis products and ions along with water molecules, arrange themselves under the Langmuir monolayer, interacting with the carboxyl head groups in such a way as to form the commensurate superlattice. The size of the superlattice unit cell is then much more plausible. We expect that the same thing happens in the presence of many other ions, such as cadmium[2] or silver,[3] as well. In this picture, the ratio of lead atoms to other atoms (hydroxyl ions, water) can be small enough that their presence is undetectable in our anomalous scattering studies.

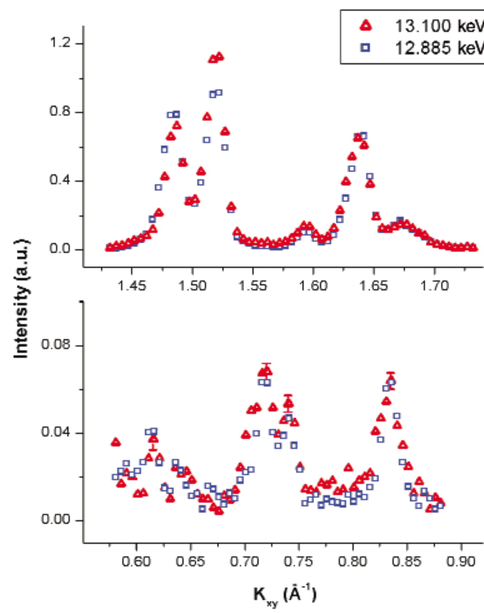


*FIG. 1. In-plane diffraction scan with x-ray energy below and slightly above the L3 absorption edge of lead. (a) Three peaks from the organic monolayer plus weak superlattice peaks. (b) Four representative superlattice peaks. We also looked at 12 other superlattice peaks not shown here, with the same results. If the inorganic structure consisted of lead atoms only, a 20% change in the intensity of the superlattice peaks would be expected. Within the experimental error (small red bars) of less than 5%, no change in the intensity was observed for any of the peaks studied.*

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