

**MS89 STRUCTURAL CHARACTERIZATION OF CONTROLLED SOLID-LIQUID INTERFACES****Chairpersons:** José Martín-Gago, Giovanna Fragneto**MS89.30.1***Acta Cryst.* (2005). A61, C113**Neutron Reflection from Complex Layers Adsorbed at the Solid/Aqueous Interface****Robert K. Thomas**, *Physical and Theoretical Chemistry Laboratory, University of Oxford*. E-mail: robert.thomas@chemistry.oxford.ac.uk

Neutron reflection gives information about structure of a layer normal to an interface and also about composition. Adsorption at solid/aqueous interfaces often leads to bilayer and more complicated structures with thicknesses in the range 20-100 Å. This is the range of optimum sensitivity of the neutron technique. Given also that isotopic labelling may be used to discriminate the different components within a mixture or within a molecule, the technique is uniquely sensitive to complex structures at these interfaces. Examples of the application of neutron reflection to bilayers, bilayer mixtures and to the evolution of structure during enzyme attack of the bilayer will be given.

**Keywords:** neutron reflection, interfaces, applications of neutron reflection**MS89.30.2***Acta Cryst.* (2005). A61, C113**Self Assembled Thiols Monolayers on Au(111) Surfaces: Structure Defects and Dynamics****Roberto C. Salvarezza**, *Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA) Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina*. E-mail: robsalva@inifta.unlp.edu.ar

Alkanethiolate self-assembled monolayers (SAMs) on metals, particularly alkanethiolates on Au, Ag and Cu have attracted considerable scientific and technological attention because they provide a route to control corrosion, wetting and wear properties of metal surfaces, they serve to anchor different functional groups used as chemical and biochemical sensors, they are used as building blocks in nano-devices for electronics, and they are promising candidates as surface active agents in new nano/microfabrication methods. Two-dimensional alkanethiolate SAMs result from the self-assembly of molecules on a metal surface by simple adsorption from the vapor or liquid phases. The control of SAMs quality is a crucial point in many technological applications of SAMs. Here we discuss surface structures, adsorption sites, defects and dynamics of alkanethiolate and sulfur adlayers formed on Au(111) substrates. By using in situ and ex situ STM combined with AES, XPS, and SXRD a detailed picture at the molecular levels of these fascinating two-dimensional structures is presented.

**Keywords:** surfaces, defects, dynamics**MS89.30.3***Acta Cryst.* (2005). A61, C113**Fluctuations of a Single floating Lipid Bilayer: a Specular and Off-specular Reflectivity Study****Thierry Charitat**<sup>a</sup>, Jean Daillant<sup>b</sup>, Edith Bellet-Amalric<sup>c</sup>, Alan Braslau<sup>d</sup>, Giovanna Fragneto<sup>e</sup>, François Graner<sup>f</sup>, Serge Mora<sup>d</sup>, François Rieutord<sup>h</sup>, Barry Stidder<sup>c</sup>, <sup>a</sup>ICS-Université Louis Pasteur, Strasbourg, France. <sup>b</sup>LIONS-CEA, Saclay, France. <sup>c</sup>DRFMC-CEA, Grenoble, France. <sup>d</sup>SPEC-CEA, Saclay, France. <sup>e</sup>Institut Laue Langevin, Grenoble, France. E-mail: charitat@ics.u-strasbg.fr

We have recently succeeded in preparing samples consisting of a homogeneous lipid bilayer (di-acyl phosphocholines, with 16 to 20 carbons per chain), floating near an identical bilayer deposited on the surface of a silicon single crystal.

I will first present a neutron specular reflectivity study of the temperature effect on such a floating bilayer. We determine both average and r.m.s. positions of the floating bilayer and observe a large increase of the water layer spacing. I will present an interpretation of this effect in terms of competition between the interbilayer potential

and membrane fluctuations leading to an estimation of bending rigidity of the bilayer.

In the second part, I will present recent off-specular x-ray reflectivity results. We measure for the first time the fluctuation spectrum in submicrometric range on a single fluctuating bilayer leading to the determination of three main physical quantities which govern the bilayer height fluctuations: bending modulus, surface tension and wall attraction potential.

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**Keywords:** membrane structure, X-ray neutron reflectivity, X-ray diffuse scattering**MS89.30.4***Acta Cryst.* (2005). A61, C113**The New Distributions of Water Molecules at Ni(111)-2x2-O and Cu(111) Electrode Interfaces****Masatoki Ito**<sup>a</sup>, Masashi Nakamura<sup>b</sup>, <sup>a</sup>Department of Chemistry, Keio University, <sup>b</sup>Chiba University, Japan. E-mail: masatoki@chem.keio.ac.jp

[I] The structures of a monomeric water molecule adsorbed on  $p(2 \times 2)$ -Ni(111)-O surface were determined by difference Fourier calculations (unique reflection intensities observed are 120(140K) and 80(25K)). At temperatures of 25 K, water molecules chemisorb predominantly at  $2 \times 2$  oxygen atom sites, forming an OH---O<sub>ad</sub> ( $2 \times 2$ ) hydrogen bond. A  $2 \times 2$  oxygen atom (O<sub>ad</sub>) is surrounded by one to three monomeric water molecules, which take statistically disordered positions with threefold symmetry. At temperatures of 140 K, monomeric water molecules occupy a top site of Ni atoms via an oxygen lone pair and are stabilized as a singleton molecule on the surface with a distance of 0.2241(22) nm.

[II] Further, we report surface X-ray scattering measurements result of the water distribution perpendicular to a Cu(111) electrode in 0.05M H<sub>2</sub>SO<sub>4</sub> solution at -0.40V (vs, NHE). The new water phase on Cu(111) was found with a space group, P3m1, a=b=0.31 nm, c=0.63 nm, Z=3, ρ=1.62(g/cm<sup>3</sup>). The important features of the water distribution are (1) the network structure is a simple closest pack type and not a honeycomb or a diamond-like structure, (2) oxygen positions of water molecules show continuous disordering in time and space (fluctuating), (3) configuration around oxygen is not a tetrahedral but a three- (or six) coordination. Proton (electron) transfer across water double layer could be facilitated by flipping of water molecule toward the electrode surface.

**Keywords:** water adsorption, water double layers, new water structure**MS89.30.5***Acta Cryst.* (2005). A61, C113-C114**Structural Dynamics of the Competing Forces of Light and Matter****Jens Wenzel Andreasen**<sup>a</sup>, Dag Werner Breiby<sup>a</sup>, Sonja Rosenlund Hansen<sup>a</sup>, P.S. Ramanujam<sup>b</sup>, Martin Drews<sup>a</sup>, Martin Meedom Nielsen<sup>a</sup>. <sup>a</sup>Danish Polymer Centre, Risø National Laboratory. <sup>b</sup>Optics and Plasma Research Department, Risø National Laboratory, Denmark. E-mail: jens.wenzel.andreasen@risoe.dk

The microstructure of azobenzene-based and azobenzene dyed liquid crystals deposited on pre-aligned polymer surfaces has been studied by grazing incidence X-ray diffraction (GIXRD) at the HASYLAB synchrotron facility and by optical measurements. It is demonstrated that a high degree of in-plane (azimuthal) orientation is induced by the alignment layer.

Irradiating the sample with a laser induces trans-cis isomerisation of the azobenzene. This provides a torque when the polarisation direction of the laser light is at an angle to the alignment layer orientation, causing a re-orientation of the liquid crystal structure, directly observable by GIXRD. When the laser light is switched off, the structure re-aligns with the alignment layer during a relaxation period of several minutes. This has been observed with different kinds