

MS25 P01

Organic monolayers and lipid-protein nanostructures on solid and liquid surfaces studied by TR-XSW technique. S.I.Zheludeva, N.N.Novikova, N.D.Stepina, E.A.Yurieva, E.Yu.Tereschenko, O.V. Kononov*, *Shubnikov Institute of crystallography RAS, Moscow, Russia.* * *European Synchrotron radiation facility (ESRF), Grenoble, France.*

Keywords: X-ray standing wave, Liquid surfaces, Langmuir-Blodgett films

Model cell membranes can be obtained using the Langmuir-Blodgett method of layer-by-layer deposition of amphiphilic organic molecules on solid substrate. Langmuir molecular layers on the surface of a liquid subphase can be used as a basis for formation of lipid-protein membrane systems in native state under the conditions close to physiological. Investigation of barriers, transport and protective functions of membrane is connected with necessity of ion localization in such molecular systems.

In the present paper it is shown that X-ray standing wave technique at total reflection (TR-XSW) allows to reveal the position of atoms in organic macromolecules and nanostructures of nm range linear dimensions on solid or liquid substrate.

The technique was used to study:

- the molecular mechanisms of the protective effect of bisphosphonate drug xydiphon on biomembrane model on the base of Ca-ATPase damaged by heavy metals (station EKMC 2; BESSY II); [1]

- organic surfactants containing heavy ions and forming well-ordered Langmuir layers on liquid surface: metal-substituted phthalocyanines, polyorganosiloxanes and phospholipids. Quantitative structural information from an individual organic monolayer on a liquid surface was obtained. (station ID10B, ESRF); [2]

- lipid-protein system containing enzyme alkaline phosphatase, formed by Langmuir technique on water subphase. The analysis of angular dependent fluorescence intensities from metal ions that enter into the composition of a protein molecule; from phosphor ions of phospholipids and from trace bivalent metal ions (Ni) that have been incorporated into nanostructure, allowed to localize ions and to propose complicated layered model of molecular self-organization on water surface. (station ID10B, ESRF).

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MS25 P02

Biomolecular hydrogen bonds assessed by neutron inelastic scattering Ahmed Aamouche^a, Mahmoud Ghomi,^b ^a*Matter science department, Faculté Polydisciplinaire, CadiAyyad University, Safi, Morocco.* ^b*BioMoCeTi-CNRS UMR7033, Paris, France.* E-mail: a.aamouche@gmail.com

Keywords: Neutron inelastic scattering spectra, nucleic acid structures, hydrogen bonding.

Neutron inelastic scattering (NIS) is now a powerful tool to analyze molecular vibrations. Since hydrogen atoms have the highest NIS cross-section and are significantly the main constituent of the biological systems NIS spectroscopy is advantageous than other vibrational spectroscopies for hydrogen motions monitoring.

NIS spectra of nucleic acid bases are recorded from polycrystalline samples on time-focused crystal analyzer spectrometer (Rutherford Appleton Laboratory, UK). Harmonic wavenumbers and intensities are predicted via Density Functional Theory (DFT) calculation at B3LYP/6-31G* level. The predicted DFT atomic displacements have been used to simulate first-order NIS spectra. [1]

As X-ray diffraction patterns show an intermolecular H-bond network between NH and C=O groups, we have taken into account explicitly intermolecular effects in our DFT calculation to imitate condensed phase environment. The comparison of the resultant spectra with the experimental ones corrects considerably the assignment particularly for the normal modes involving hydrogen. [2] The determined structural properties are of primary importance as H-bonding play a functional role in molecular shape and dynamic throughout bases pairing and stacking.

[1] Aamouche A. and al. *J.Phys. Chem.*, 1996, 100, 5224.

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MS25 P03

Analogy of Polymorphism in Salicylideneaniline and its Ethoxy Derivative. Frédéric Arod^a, Philip Pattison,^{a,b} Kurt J. Schenk,^a and Gervais Chapuis,^a ^a*Laboratoire de Cristallographie, EPFL, Switzerland.* ^b*SNBL-ESRF, Grenoble, France.* E-mail: frederic.rod@epfl.ch

Keywords: photochromism, phase transitions crystal characterization, structure-property relationships in solids.

Organic compounds exhibiting photo- or thermochromicity are of considerable interest owing to their properties and possible applications. The photochromism of salicylideneaniline (SA) was discovered by Senier *et al.* at the beginning of last century, and in 1964, Cohen *et al.* [1] established its polymorphism. We have recently demonstrated its thermochromism in solids [2] by differential scanning calorimetry and also by *in situ* X-ray diffraction.

We report on three polymorphs of SA, two of its ethoxy derivative (ESA) and their inter-relation, in particular, an irreversible phase transition between the β and α_1 forms of SA leading to a less stable α_1 form. We discuss the different packings observed in these polymorphs, with the goal of understanding their structure-property relationships in solids.

The thermal behaviour of the ESA polymorphs is similar to that of the SA phases. The non-planar α -phase undergoes the fusion transition at 88°C, but re-solidifies, in a two-step process, 30°C lower to a likely different form, which however has a similar melting point. The planar β -form transforms into the α -phase at 85°C, then becomes isotropic at 89°C, but does not seem to return to the same form during the solidification at 54°C. One might therefore conjecture that the liquid phase of ESA is not so

isotropic after all.

In conclusion, the thermal behaviours of SA and ESA are quite similar indeed, despite some minor differences in their packings, which appears to confirm our previous hypothesis, given in [2], regarding the geometrical reasons for the β to α transition.

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MS25 P04

Cobalt cations distribution in fully dehydrated CoX zeolite studied by XRD and XAS Elena Borissenko^a, Florence Porcher^a, Mohamed Souhassou^a, I-Jui Hsu^b, Yu Wang^b, Claude Lecomte^a, ^a*Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, LCM3B UMR 7036, CNRS - Université Henri Poincaré, BP 239, 54506 Vandœuvre-lès-Nancy, France.* ^b*Department of Chemistry, National Taiwan University, Taipei, Taiwan.*

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Keywords: zeolite X, XRD, EXAFS

The numerous applications of natural/synthetic zeolites as catalysts, ion exchangers and for gas separation rely on their porous crystal structure (sieving effect) together with their electrostatic properties (distribution of cations/acid sites). The zeolites hosting transition-metal cations have interesting catalytic activity and are already used, for example, in oxidation reactions of organic compounds. Stable complexes formed by insertion of pyridine-based molecules in transitional-metal zeolites (like (bpy)₃@zeolite CoX) have been evoked to exhibit remarkable magnetic properties [1]. In both cases, the macroscopic properties rely on the interactions of the guest molecules with the zeolite framework and cations and the precise knowledge of the crystal structures of these compounds is, therefore, of prime interest. However, most of these structures are not well known because of the difficulty to grow single crystals for XRD measurements, and of the disorder caused by partial cation exchange and hydration.

In this context, the crystal structure of fully dehydrated but partially exchanged Na₁₃Co₃₂X zeolite has been determined from single crystal and powder XRD. All the charge compensating cations were located in the structure (Sites I, I', II, III). The interpretation of a weak electron density peak close to Site I' found in XRD Fourier maps, but hardly assignable to Co²⁺ cation on the basis of XRD data was ascertained by X-ray Absorption Spectroscopy (XAS) (NSRRC, Taiwan). The combination of EXAFS and XRD analyses also indicates that the Co cations sitting in site I are involved in a distorted hexagonal antiprism (result also supported by Monte Carlo calculations [2]).

The migration of cations and the drastic structural modifications endured by the framework over dehydration were also studied from 3 partially hydrated crystals. The comparison of CoX dehydrated structure to the native NaX and other ion-exchanged dehydrated Mⁿ⁺ zeolite X structures evidences a relationship between these structural modifications and the nature of the charge compensating cation and its shielding by water molecules.

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MS25 P05

Synthesis and structural characterization of new organic-inorganic hybrids based on polyoxometalates. Mongi Debbabi^a, Hafedh Driss,^{a,b} and René Thouvenot,^b

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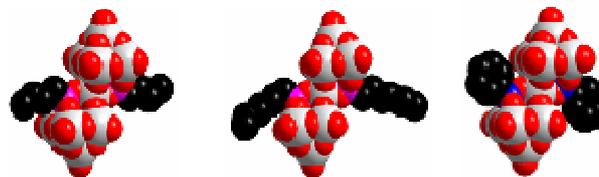
Keywords: Hybrid anion, polyoxometalate, Lindqvist structure.

Polyoxometalates (POMs) constitute an unprecedented class of compounds in terms of number and structural diversity. They exhibit remarkable chemical and physical properties and are of great interest in different fields such as medicine, biology, catalysis, material sciences, chemical analysis. Derivatization with organic groups attached covalently to the metal centers [1], [2] or electrostatically [3] to the periphery constituted by the oxo groups of the POM can alter the properties of POMs towards increased or decreased activity, efficacy and specificity in catalysis. The focus of this work is a new type of undeca-transition metaloxo anion cluster (polyoxometalate) derivatized with organophosphonyl groups NbW₁₀O₃₈(RP)₂³⁻. These compounds are resulting from reaction of organophosphonic dichloride RPOCl₂ (R = Et, Pr, Bu, Hexyl, Heptyl, Cyclohexyl, Ph) with monosubstituted isopolyanion NbW₅O₁₉³⁻. These new polyoxometalates have been characterized by infrared and Raman spectroscopy, multinuclear ³¹P and ¹⁸³W NMR, and X-ray crystallography. The anion is built-up from an {Nb(RPO)₂} group linking two W₅O₁₈ subunits which can be viewed as lacunary derivatives of the NbW₅O₁₉ structure. Infrared spectrums of all hybrid anions are very similar, except in the organic groups part.

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Space-filling representation of anion NbW₁₀O₃₈(RP)₂³⁻ respectively R=Bu, Heptyl, =Ph
C: black, O: red, W,Nb: light grey, P: bleu