

small building blocks is dictated by stringent demands on the hydrogen bond formation by the peptide main chains and the aggregation of hydrophobic entities in the side chains. Some of these peptides have a marked propensity for cocrystallization, thus forming layered crystal structures as inclusion compounds with peptide hosts and various simple organic molecules as guests. A systematic survey of structures derived from single crystal X-ray diffraction studies has furthermore revealed the existence of two large classes of nanotubular microporous structures, differing in the dimensionality of the hydrogen bonding patterns in the crystals and the nature of the channels. The lecture gives an overview of the structural aspects of the hydrophobic dipeptides and discusses the potential applications of these remarkable organic materials.<sup>[1]</sup>

[1] Görbitz, C. H., *Chem. Eur. J.* 2007, 13, 1022-1031.

#### KN05

**Crystallography in Art and Archaeology** Eric Dooryhee, *Institut Neel, CNRS Grenoble, France*  
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**Keywords:** symmetry, applied crystallography, work of art

The regular, and sometimes particularly complex, inner arrangement of atoms and molecules in a crystal has always had a naturally artistic appearance. It is undeniable that subdivisions of the 2D or 3D space based on crystal-like shapes, repeated patterns, symmetry groups and crystallographic rules have been and still are a source of profound inspiration for many artists. Symmetry, or the lack of symmetry, has been a central concept in science since ancient times, and prevail in various fields of art: painting, sculpture, architecture, music, dance, poetry... In the first part of the talk, various examples and illustrations will show how the formal qualities of a work of art intersects the basics of crystallography.

Symmetry is often assimilated to the idea of harmony, based on a rational and clear principle of organization and order. The concepts of symmetry convey a charming impression and sometimes provide the artist with appropriate solutions. They produce a pleasant balance between our senses and our thought, enhance our perceptions of harmony and contribute into higher understanding and emotions in front of a master piece. Crystallography and crystal physics provide a cognitive basis for deriving the descriptive morphological and structural classifications of natural objects, and their real or imaginary analogues in art and archaeology.

The diffraction techniques reveal the regular arrangement of the atoms and molecules in an orderly solid. Crystallographic modelling shows the symmetry rules underlying this assembly. Many crystallographic representations (such as ball-and-stick models or measured electron density maps) can be considered themselves as artistic and symbolic views of the reality. Some of them closely resemble a scaffold, which gives us a feeling for the representation of infinity but which may also appear like a dead body without a soul. Only after putting back the fundamental motifs (the atoms, the molecules, or any man-made form) does the fascination for symmetry plainly appear again.

The last part of this talk discusses the recent implementation of crystallographic methods while

addressing some enigmas in the fields of archaeology and art: the identification and provenance of the materials, the trading routes, the elaboration procedures and the artists' know-how, the authentication, the transformation and preservation of the artefact with time. The history of these objects, as part of our cultural heritage, is often embedded in the structure and micro structure of the component materials, and needs to be deciphered every time ancient texts are silent or absent.

#### KN06

**Dynamic Electron density: a unique link between advanced X-Ray experiments and reactivity** <sup>a</sup>Pierre Becker, <sup>b</sup>Nour Eddine Ghermani, <sup>a</sup>Jean Michel Gillet, <sup>a</sup>Blandine Courcot, *a: Ecole Centrale Paris, Laboratoire SPMS, Grande Voie des Vignes, 92295 Chatenay Malabry Cedex, France – b: Faculty of Pharmacy, University Paris XI, 92295 Chatenay Malabry Cedex, France*  
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**Keywords:** electron density, high resolution scattering, time resolved scattering, microscopic time evolution of matter.

Charge, spin and momentum density studies lead to a challenging interplay between experimental and theoretical viewpoints concerning binding and cohesive effects in condensed matter. Recent achievements concerning pharmaceutical or biological systems allowed for a critical estimate of the level of transferability of charge density, with an important impact towards modelling physico-chemical mechanisms in those complex media.

Charge density indeed plays a crucial role, owing to its leading character in the description of the electronic ground state of any system. Though most studies have focused on one type of density, it is clear that the three density components are linked through the reduced one particle density matrix (1RDM). Through combined studies of momentum and charge density, we have been able, in our group, to show that the 1RDM in a solid can be developed as a sum of fragment contributions: each of them incorporates interactions with neighbouring fragments through finite clusters ("cluster partitioning method"). It is thus possible to overpass the strict periodicity condition and to consider systems that are disordered or undergoing structural changes. This method will be discussed, focussing towards modelling of a given fragment in variable environments. It has recently been possible to extend this approach to pharmaceutical molecules and to reach the key question of their activity within biological medium.

Recent experimental developments have opened a revolutionary path combining X Rays and neutrons with laser pulses. Charge and spin density in photo-excited solids have led to crucial observation of electronic behaviour in non equilibrium states of condensed matter. The fast development of time resolved X Ray scattering allows for the observation and microscopic modelling of systems undergoing chemical reactions, phase transitions, response to applied actions. The key function associated to such mechanisms is the time dependent charge density  $\rho(\mathbf{r}, t)$  and its generalisation to time dependent 1RDM. We shall discuss the present status of time dependent scattering, together with some tentative modelling. For a system undergoing a chemical reaction, one must identify the reaction path, through the Fukui intrinsic reaction

coordinate, from which one can get the structural change and reaction speed as a function of time. Forces on atoms can be related to  $\rho(\mathbf{r}, t)$  via Hellmann-Feynman forces. Indeed it is also necessary to relate the behaviour of an isolated set of molecules to the real situation occurring in a chemical process. We feel essential to focus attention onto the key properties of  $\rho(\mathbf{r}, t)$ , that is the leading link between most aspects of a non stationary system, from microscopic or macroscopic experimental side, or from a theoretical viewpoint. The acquired experience concerning diversified systems in a steady state should help in finding original and simple models for time evolving systems, a fascinating challenge for the near future.

**KN07**

**Porous Nanomaterials**, João Rocha, *Department of Chemistry, CICECO, University of Aveiro, Portugal*  
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**Keywords:** Microporous, Silicates, MOF

Zeolites, the archetype of microporous materials, are well known as excellent molecular sieves, heterogeneous catalysts and ion exchangers. Although these 'conventional' areas of application will remain important in the nanotechnology era, microporous solids will find uses in new fields, such as optoelectronics and magnetism. In the early nineties of the last century, zeolite-type silicates built up of transition-metals (mostly Ti) heteropolyhedra, were developed [1]. By the turn of the century, the constituent elements of heteropolyhedral silicates were extended to lanthanides (Ln) and, thus, photoluminescence (PL) properties became available [1-3]. The work in the field of 'bright zeolites' culminated with the report of the intriguing chiral system  $\text{Na}_3[(\text{Y}, \text{Ln})\text{Si}_3\text{O}_9] \cdot 3\text{H}_2\text{O}$ : it was shown that  $\text{Eu}^{3+}$  PL spectroscopy with excitation by unpolarised light in the absence of an external magnetic field is able to identify enantiomeric domains in chiral frameworks [4].

With the turn of the century there was a surge of activity on inorganic-organic hybrid solids known as coordination polymers or metal-organic frameworks (MOFs). These materials are of considerable interest because the combination of inorganic and organic fragments produces a large number of new crystal architectures and allows the design of solids with specific functions [5]. Interesting properties which may lead to industrial applications include gas storage and separation, catalysis, guest-exchange and sensors based on optical and magnetic properties. So far, only 10% or so of MOFs are effectively microporous and exhibit zeolite-type behaviour and much work remains to be done. Outstanding examples include the MIL-88 family [6].

In this talk I wish to review the recent developments in the field of microporous heteropolyhedral silicates. I shall also show the kaleidoscopic opportunities provided by inorganic-organic hybrid systems to engineer new nanoporous materials [7]. Finally, I shall pay attention to an often overlooked feature of nanoporous materials: the assembling of water molecules into small clusters, chains, layers [7] and 3D structures, in the voids of silicates and MOFs.

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**KN08**

**Structural aspects of chiral-at-metal complexes: On the origin of stereoselectivity** Fernando J. Lahoz, Daniel Carmona, M. Pilar Lamata, Fernando Viguri, Joaquina Ferrer, Luis A. Oro *Departamento de Química Inorgánica, IUCH, ICMA, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain.*  
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**Keywords:** Asymmetric catalysis, metal complexes, inter- and intramolecular interactions

Asymmetric catalysis is an efficient method for synthesizing optically active organic compounds and the use of chiral metal complexes as homogeneous molecular catalysts is one of the most powerful strategies. Half-sandwich complexes of the three-legged piano-stool type have been extensively used as catalyst precursors in organic transformations often with a high degree of asymmetric induction and, in addition, their four-coordinate, pseudo-octahedral geometry facilitates the investigation of the stereochemistry of reactions at the metal centre.

Starting from some classical related contributions relating weak interactions and stereoselectivity, we will review the different half-sandwich chiral-at-metal complexes prepared and essayed in catalysis from our group. Complexes are of the general type  $[(\eta^5\text{-arene})\text{M}(\text{A-B}^*)\text{L}]^{\text{m}}$  with  $\text{M} = \text{Ru}, \text{Os}, \text{Ir},$  or  $\text{Rh}$ ,  $\text{A-B}^*$  being different bidentate ligands (diphosphines, amino-acidates, pyridylamines or imines, etc) containing, at least, one previously controlled chiral centre [1]. We will discuss the different strategies for the synthesis of these complexes, the characterization of diastereomers equilibria and their behaviour as catalyst precursors in different reactions (hydrogen transfer or diverse Diels-Alder processes).

We will focus on the structural characterization of the different species that have been suggested to be involved in the catalytic cycles, and especially in the description of feeble non-bonding interactions that seem to be at the origin of stereoselectivity [2].

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