KN-12

Analysis and Prediction of Physical and Chemical Properties by Charge Density Studies. Wolfgang Scherer, *University of Augsburg, Germany*
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Since the theoretical prediction [1] and experimental verification of Charge Concentrations (CCs) in the valence shell of transition metals several attempts have been undertaken to understand their origin and relevance in chemistry and physics [2]. In pioneering studies we could demonstrate that these CCs not only influence the *geometr*y of coordination compounds [3] and solids but also serve as controlling parameters for important *chemical reactions* like the activation of chemical bonds in catalytic reactions [4]. Furthermore, in covalent solids such as transition metal oxides and carbides they appear to signal *electron localization phenomena* which are reflected by metal-to-insulator transitions or the suppression of superconductivity [5]. The complex interplay of valence shell charge concentrations with the physical and chemical properties of molecules and solids will be the central topic of this contribution.

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Keywords: charge density, catalysis, superconductivity

KN-13

New phase transitions. Bertrand Toudic, *Institut de Physique de Rennes, UMR 6251 au CNRS, Université de Rennes 1, France*
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Much work has been dedicated to phase transitions characterizing broken symmetries and their associated critical fluctuations. In this talk, we will present two up to date research axes in the fields of phase transitions in crystals. The first one will concern ultra-fast phase transitions induced by femto-second pulsed lasers [1, 2]. These transformations use a new degree of freedom, the ultra-short time, coupling coherence, cooperativity and out of equilibrium. The second axis will concern symmetry breakings which take place in crystallographic superspaces. There, the new degrees of freedom come from the aperiodicity of the materials allowing very original structural instabilities [3].

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Keywords: Phase transitions, aperiodic crystallography, time-resolved structural studies

KN-14

Understanding Chemistry from Combined X-ray and Quantum Mechanical Studies. Carlo Mealli, *ICCOM-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.*
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X-ray diffraction has developed structural chemistry, hence the understanding of the matter and its behavior. 3D molecular pictures and their accurate geometries provide fundamental information about bonding between atoms and the associated chemical properties. Besides being beautiful, molecules raise thought-provoking questions about functionality. For this, it is important to establish proper structure-property relationships in terms of the electronic distribution and, in this respect, quantum mechanical theories have been useful even at some lower level of approximation. Today reciprocal validation of crystallographic results and electronic structures are possible by standard DFT approaches, which afford very good structural simulations. Not necessarily, the latter obtained with the introduction of most accurate physical-mathematical treatments (*reductionism*) mean also good understanding. This is the key to gain proper capabilities of controlling the matter, such as for example the improvement of a known chemical process or devising new potential ones. Fortunately, crystallography with the myriad of catalogued structures (data banks) allows *horizontal* comparisons of the chemistries and even a small difference can be enlightening. For instance, the geometric perturbation introduced by a different substituent can affect the electron density and this helps redirecting the chemical evolution of the species in a desired direction.
In the long run, our research has been devoted to evaluate minor structural differences and their consequences for properties and reactivity. Our approach is to combine crystallographic analyses and electron distributions through wavefunctions. Not only we could reach some good understanding of the 3D structures but also suggest interpretations or even make chemical predictions.
The lecture will present various cases in which a critical analysis of the crystallographic data (ours or from the literature) allowed significant conclusions. For instance, some published X-ray structure was demonstrated to be erroneous [1] or a rare and questioned crystallographic situation could be justified in chemical terms. Classes of related slightly different molecules suggested important trends for the chemical bonding and the control of chemical reactivity. This is the case of the early metal activation of the alkanes C-H bonds ("agostic" interaction), whose features we catalogued [2]. As another topic, the systematic study of series of structures allowed revising the parameters for the redox coupling/uncoupling between sulphido anions, namely the dichotomies $2S_2^{4-}/S_4^{2-}$ or $2S^{2-}/S_2^{2-}$ over one or more metal centers [3] The lecture will also illustrate how some key structures can be used as milestones along complicate patterns of reactivity also in processes of bio-catalytic relevance, such as the modeling of hydrogenases [4].

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Keywords: Structural Analysis, Quantum Mechanical Calculations, Structure/Properties relationships

KN-15

Phasing by SAD and Molecular Replacement in Phaser.

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Phaser is the program we are developing to apply maximum likelihood to phasing macromolecular crystal structures [1]. The current version can solve structures using molecular replacement, single-wavelength anomalous diffraction (SAD), or a combination of the two.
Molecular replacement can place one or more copies of one or more components. Each component can be specified by a single structure or by a superimposed ensemble, which is used as a statistically-weighted average structure. Searches are carried out to maximize rotation and translation likelihood targets, which can take account of the information from previously-placed molecules.
SAD phasing is carried out by maximizing a SAD likelihood target, which accounts for the effect of correlated errors in the plus and minus hands of the Friedel pair [2]. Phasing is initiated from an anomalous substructure, which need not be complete. Log-likelihood-gradient maps provide a sensitive indication of additional sites or the presence of anisotropy.
The substructure for SAD phasing can actually be a set of normal scatterers, such as a protein model obtained by molecular replacement. Even a poor molecular replacement model can be sufficient for log-likelihood-gradient maps to find the anomalous scatterers from weak anomalous differences. Alternatively, the log-likelihood-gradient maps can be used to identify anomalous scatterers at the end of refinement, even if the anomalous signal is too weak to contribute significantly to phasing.

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Keywords: maximum likelihood, molecular replacement, SAD

KN-16

Relevance of X-ray Structure Data to Kinetic Studies.

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Detailed knowledge of the different reaction steps by which many a 'small molecule' chemical process proceed, is of prime importance for understanding the complete reaction system. This knowledge allows subsequent manipulation of the process to ensure better yields, less by-products, and by implication, a smaller carbon footprint.
This presentation deals with a number of model systems in industrial process and metal based drugs chemistry and will discuss the importance of known structures, coupled with the kinetic behaviour, on the reaction mechanisms thereof. The solution behaviour of some homogeneous catalytic processes and model pharmaceuticals will be described, illustrating the importance of the detailed ground state structures as obtained primarily from X-ray diffraction, but integrated with spectroscopic and other techniques [1-7]. Moreover, different activated states, and the utilization of reaction kinetics, coupled with computational techniques, to produce overarching and more holistic perspectives on the complete reaction mechanisms, will be discussed.

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Keywords: reaction mechanisms, kinetics, spectroscopy

KN-17

Crystallographic studies of P-type ATPase cation pumps .

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P-type ATPase cation pumps energise the biomembranes by establishing and maintaining steep electrochemical gradients. The electrochemical gradients formed are of fundamental importance in physiology as they control ionic conditions in the cell, energise secondary transport and signalling through ion channels. The P-type pumps are essential to all eukaryotes and include for example Na^+,K^+-ATPase, H^+,K^+-ATPase, Ca^{2+}-ATPase and Cu^+-ATPase
From studies of the sarcoplasmic reticulum Ca^{2+}-ATPase we have gained a deep insight on the catalytic mechanisms in formation and breakdown of the phosphoenzyme intermediate and on conformational changes providing the basis of vectorial ion transport. We also gained a signficant insight on the structures of Na+,K+-ATPase and other pumps, and of the regulatory effects of inhibitors, cellular factors and modulatory effects of ATP as probed by biochemistry and electrophysiology.
The crystallographic studies providing our background for analysis of structure-function relationships have challenged us in all aspects of membrane protein crystallography such as in heavy-atom derived phasing from poorly diffracting crystals and model building from low-resolution electorn density maps, although in other cases higher resolution studies revealing putative proton-transport pathways have allowed us to establish new models of function.