

[2] are favorite tools of crystal engineering, since the orientation of molecules in the solid state can be predicted with a reasonable degree of accuracy. Two such interactions stand out: hydrogen bonding and halogen bonding. The marked directionality of the hydrogen bond (HB) is well established and is the basis for efficient and reliable topologies of intermolecular motifs. The strength of the hydrogen bond can be estimated from high resolution X-ray diffraction as proposed by our group [3], [4] and this method based on the topological analysis of the electron density ρ at the HB critical point is now widely used.

On the other hand, the *halogen bonding* interaction has been much less investigated. It occurs in the systems C–Hal...X (X = L, Hal) where an organic halogen atom approaches either a Lewis base (L) or a halogen atom (Hal). Halogen bonding can be as effective as hydrogen bonding for driving highly specific crystal packing motifs, as synthons. It finds its origin in the anisotropy of ρ around the halogen nucleus, leading to a smaller effective atomic radius along the extended C–Hal bond axis than in the direction perpendicular to this axis, a feature called polar flattening.

In a recent experimental charge density analysis of hexachlorobenzene (C₆Cl₆) [5] we have confirmed the anisotropy of the electron distribution around the chlorine nuclei, leading to the formation of electrophilic and nucleophilic sites in the valence-shell charge concentration of chlorines. In the crystal structure of C₆Cl₆, main halogen...halogen interactions are thus electrophilic-nucleophilic in nature, being established between oppositely polarized regions in front of each other within a Cl₃-synthon. The Atoms in Molecules theory [6] has been applied to crystalline C₆Cl₆, demonstrating those features and indicating that the electron density properties at Hal...Hal bond critical points correlate with the strength of the observed interactions.

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Keywords: electron density, halogen bonding, topological analysis

MS.41.3

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Joint densities and density matrices refinements: First attempts and first results

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Although analysis of joint experimental data as diverse as x-rays structure factors, polarized neutron flipping ratios, neutron structure factors, CBED measurements, x-ray Compton magnetic (and non magnetic) profiles, among others, is theoretically feasible and desirable, to this day only few attempts have been made

We will remind some of the important strategies that have been elaborated in the past and we will propose a new possible way of combining and exploiting the richness of the diversity of experimental methods.

We will show that as long as the data are issued from elastic coherent

scattering experiments only marginal changes have to be made to the usual pseudo-atoms model. This will be illustrated with recent results obtained on magnetic compounds.

We will finally address a critical discussion concerning the difficulties occurring in combining real and momentum space data.

Keywords: density matrices refinement

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Quantitative information on polarization of ED from multipolar model – possible?

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We performed systematic analysis of electrostatic properties of a molecule estimated from Hansen-Coppens multipolar model [1] of crystal density. We verified an accuracy of electrostatic properties estimated from the multipolar model, and whether it is enough to study changes of electrostatic properties caused by crystal field effect.

For the purpose of the study, perturbation of electron density of individual molecule was induced by cluster of atom charges, dipoles and quadrupoles surrounding molecule, as to simulate influence of crystal environment. Perturbed and unperturbed wave functions were calculated on the bases of the same crystal geometries of a few amino acids and dipeptides. In following step, electrostatic properties were derived directly from either perturbed or unperturbed wave functions. Moreover, multipolar models were fitted to the subsequent theoretical perturbed and unperturbed electron densities.

Comparison of the electrostatic properties obtained either directly from the perturbed theoretical densities, or from SAPT(DFT) [2] calculations, with the results derived directly from wavefunctions of isolated molecules, gave us possibility to study influence of crystal field on electrostatic properties. We characterized trends in changes of electrostatic properties due to polarization of electron density induced by crystal field.

Additional analysis of the electrostatic properties obtained from corresponding multipolar models fitted to the theoretical electron densities enabled us to check whether systematic information about the trends could be derived from multipolar models. Multipolar models fitted to the theoretical electron densities of a crystals, obtained in periodic calculations, were also studied.

The study revealed that electrostatic properties obtained from the multipolar models fitted to the electron densities are significantly different than ones obtained directly from the densities. Electrostatic properties of isolated molecule are reproduced better by multipolar models than electrostatic properties of molecules in crystal. Perturbation of electron density due to crystal field is hardly described by the multipolar models. The main difference in description of valence electron density between purely theoretical models and Hansen-Coppens multipolar models of the same theoretical densities occurred in the very positions of nuclei, where density is not exactly defined in multipolar refinement due to Fourier truncation error.

It seems that electrostatic properties obtained from multipolar models fitted either to theoretical, or experimental electron density of a crystal, have similar accuracy to those estimated with the use of the aspherical pseudoatom databases [3]. Nevertheless, qualitative analyses only could be performed with the electrostatic properties obtained with the use of both method.

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Keywords: electrostatic properties, induction energy, charge density

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Chemical bonds in aluminium

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Recent advances in quantitative convergent beam electron diffraction (QCBED) [1], [2], [3] have led to the solution of an 82 year old problem – determination of the bonding electron density in aluminium. Until the present determination [4], [5], there was considerable disparity between a large number of experimental and theoretical determinations. These disagreements culminated in two recent theoretical studies where one asserted that bonding in aluminium is octahedrally coordinated [6] and the other that it is tetrahedrally coordinated [7].

In addition to the present QCBED determination, a density functional theory (DFT) first-principles calculation of the ground state electron distribution was performed. The QCBED and DFT determinations are in close agreement and show that the bonding electron density is concentrated exclusively in the tetrahedral interstices.

The detailed understanding of bonding in aluminium resulting from the present work has led to a new understanding of the influence of interatomic bonding on the mechanical anisotropy of aluminium. Correlations between bonding and the morphologies of precipitates that form in aluminium alloys have also been identified.

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Keywords: chemical bonds, quantitative CBED, DFT, mechanical properties, alloys.

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Polarized XAS of photosystem II and relevant Mn model complexes

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The Mn₄Ca catalytic cluster of the oxygen-evolving complex (OEC) in Photosystem II (PS II) cycles through five oxidation states (S_i-states, i=0-4) coupling the one electron photochemistry of the reaction center with the 4 electron redox chemistry of water oxidation. The structure of the Mn₄Ca cluster has been extensively studied by X-ray [1] and other spectroscopic methods and by X-ray

crystallography between 3.8-2.9 Å resolution [2-5]. The most recent X-ray crystallography structure is at 1.9 Å resolution [6]. Radiation damage to the Mn₄Ca cluster, although much reduced in the most recent structure at the highest resolution, still remains a limiting factor [7].

We have previously reported detailed X-ray absorption spectroscopy studies from solution and single crystal XANES and EXAFS data from the native S₁ (dark) state and proposed structural models of the Mn₄Ca cluster of PS II within the context of the protein environment [1, 8]. This study used PS II dimer crystals obtained from *T. elongatus*, in which the crystal unit cell contains four PS II dimers. The structural parameters derived from X-ray spectroscopy in relation to the X-ray crystallography structure at 1.9 Å will be discussed. We have also collected polarized spectra of monomer PS II single crystals, which have been recently crystallized [9]. Monomer crystals have a favorable orientation for deriving a unique structure for the Mn₄Ca cluster.

We have extended the study to the higher S-states by illuminating the S₁ state solution and single crystals either by continuous illumination or by laser flashes to create intermediate S-states (S₂ and S₃). The solution state spectra show changes in the structure of the catalytic cluster as it advances through the intermediate states. Polarized XANES and EXAFS spectra from these crystals show unique orientation dependence and provide additional information about the structural changes taking place in these intermediate states. The relevance of the geometric and electronic structural changes derived from the XAS studies to the mechanism of water oxidation will be discussed.

The polarized XAS data from crystals of many multinuclear oxo-bridged Mn complexes have been collected. The polarized spectra have been used to understand the electronic structure of the Mn complexes, and these studies provide information that will be useful for understanding the structure and the mechanism of the Mn₄Ca cluster present in PS II.

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The synergism of XAS and crystallography

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In recent years, research on metalloproteins has benefited from synergism between bioinformatics, sample characterization, spectroscopy, and structural methods. The combination of these methods results in a pipeline that helps to establish an excellent basis for understanding necessities and variability of metal binding.

Bioinformatics is the established method to identify conserved