

Poster Sessions

It is concluded that the charge flipping is a good method to reconstruct the electron density distribution of illite polytype from which the rotation between adjacent M layers can be observed.

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Experimental Electron-Density Analysis without Multipoles

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The extraction of the electron density from the high-resolution X-ray diffraction experiment using the multipole model [1] is a mature technique, which has produced many interesting chemical applications.[2] However, there are known shortcomings in the multipole model regarding the limited flexibility of the employed set of functions to describe the aspherical electron density.[3] We present a new method to model the X-ray diffraction pattern and derive superior molecular geometries as well as electronic properties that go beyond the standard topological analysis of the electron density.

1) *Hirshfeld-atom refinement*. [4] The geometry is refined by using an Hirshfeld-type stockholder partitioning scheme based on ab-initio quantum-mechanical aspherical electron densities. With good data, precise anisotropic displacement parameters can be obtained even for hydrogen atoms.

2) *X-ray constrained wavefunction fitting*. [5] Using the final molecular geometry from 1), a wavefunction is fitted to the experimental data to reproduce the diffraction pattern and simultaneously minimize the molecular energy. In contrast to the multipole model, any basis set can be used.

3) *Electron-density analysis*. The electron density is derived from the constrained wavefunction. Visual inspection and analysis of the residual or static deformation densities serve as a test for the successful reproduction of the experimental crystal density. Subsequently a topological analyses using Bader's Quantum Theory of Atoms in Molecules can be carried out.

4) *Wavefunction analysis*. Several other molecular and electronic descriptors can be calculated from the constrained wavefunction which are not accessible through a multipole description and were thus not obtainable with respect to experimental data before. This includes *energies, electron-localization functions, bond orders and bond indices*. We will focus on information about electron-pair localization as derived from the Electron Localizability Indicator (ELI, [6]) and about bond orders as derived from the delocalization index [7] and the Roby bond index [8].

We will discuss the variety of chemical information that can be gleaned from the descriptors in 3) and 4) and contrast this with what is available from only the multipole model.

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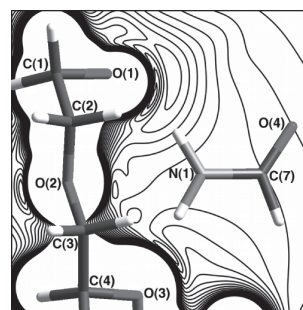
Electrostatics of host-guest interactions from charge density analysis of neutral complexes of 18-crown-6

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Electrostatic interactions play a central role in all host-guest interactions. The electrostatic potential (ESP) and, to a lesser extent, the electric field (EF), have been invoked in rationalizing biological processes for several decades. Host-guest chemistry of clathrates and crown ether complexes sits at the foundations of supramolecular chemistry, yet many of these simpler systems have been largely bypassed by today's researchers. The 18-crown-6 bis(guest) centrosymmetric trimer is a common motif formed with a wide variety of small guest molecules, and we have recently measured charge density-quality X-ray diffraction data for many of them. A focus of these studies is the polarization and dipole moment of guest molecules, as this property of the guest is an excellent probe of the electrostatic nature of the hosts.

As an example, charge density analysis for the formamide complex reveals that the magnitude of the EF in the vicinity of the formamide guest molecule is relatively constant (see figure below) and around 16 GV m⁻¹. The vector EF averaged over the formamide nuclei has been applied to an isolated molecule in an *ab initio* calculation to determine the extent of polarization resulting from a field of this magnitude. At the HF/cc-pVTZ level of theory, the molecular dipole moment is 4.50 D in the absence of a field, and 6.14 D with the field applied, an enhancement of 36%. This increase is in line with the estimate of 31% for the hydrogen-bonded crystal of formamide using dipole lattice sums [1]. The theoretical dipole moment in this applied field agrees well with the value of 6.9 ± 0.5 D computed directly from the multipole refinement.

This appears to be the first time that a molecular dipole moment determined from X-ray diffraction data has been rationalised quantitatively on the basis of the electric field it experiences in the crystal. Detailed results of this kind for several complexes of 18-crown-6 will be presented. As it is typically neglected in considerations of host-guest chemistry, the implications of this electrostatic description for a fuller and more detailed understanding of intermolecular interactions in supramolecular chemistry will also be discussed.



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Polymorphism studied with invariom-derived cluster dipole moments

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Polymorphism, the phenomenon that a compound occurs in more than one form in the solid state, is commonplace, but not well understood. While the research area of crystal structure prediction is most successful in predicting polymorphism for relatively small and rigid structures at high computational cost [1], to date no simple way of predicting polymorphism exists. Energetic considerations of packing energies as for example those obtained from the PIXEL approach [2] share computational requirements to some degree.

Our approach towards attempting an understanding of polymorphism is to exploit the benefits of invariom refinement [3]. First of all accurate molecular structures as obtained after invariom refinement [4] make subsequent energetic considerations from experimental coordinates generally more reliable. Furthermore, going beyond molecular properties in the gas-phase is required for understanding solid-state phenomena. We therefore look at dipole moments and electrostatics of clusters of molecules of a number of polymorphic structures. Cluster sizes are chosen as to grant successful optimization of a central molecule within a two-layer ONIOM approach [5]. We assume that such clusters are a suitable model for a molecular packing environment. Quantum chemical results for such clusters are compared to results from a superposition of isolated molecules, where the invariom approach is used to generate the non-spherical density of the isolated molecule. We look at trends that emerge from this comparison.

Polymorphic molecules investigated include glycine, dihydro-carbamazepine, the new case of hydroxylysine hydrochloride, and a number of other published cases, where intensities for invariom refinement were available from the IUCr webpage.

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Charge density analysis of the [RhCp*(N-Me-L-Pro)Cl] rhodium complex

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Organometallic chiral-at-metal rhodium or iridium complexes are commonly used in homogeneous catalysis as they lower the energy barrier and improve the selectivity in cycloaddition reactions [1]. Due to the presence of a second or third-row transition metal (with a large number of core electrons) the overwhelming majority of their structural studies have been carried on "in a classical way", using the independent atom model (IAM). However, a more accurate description of the metal bonding, as well as the most common ligands, becomes necessary as it may help in the understanding of their catalytic activity.

Here we present the analysis of the charge density of the rhodium complex [RhCp*(N-Me-L-Pro)Cl] obtained from high-resolution X-ray diffraction. Special features of the multipolar model refinement, as the choice of the electronic configuration and the radial function of the metal; the anharmonic nuclear motion, and the anisotropic thermal refinement of hydrogen atoms will be discussed. The electronic bonding distribution in the proline ligand will be compared to those in other proline derivatives. The deformation density has been interpreted according to the Quantum Theory of Atoms in Molecules [2]. Topological analysis allows for a description of the nature of the bonding involving the metal atom, in terms of charge density, laplacian and energy density at bond critical points.

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A qualitative and quantitative analysis of dynamic charge densities

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The dynamic electron densities of the amino acids α -Glycine and D, L-serine have been determined to understand the nature of the chemical bonds. Multi-temperature data sets of serine have been used to analyze the effect of thermal vibrations on the charge density distribution. Diffraction data of α -Glycine have been kindly supplied by Destro et al [1] and of D L-Serine by Dittrich et al [2]. Multipole refinements have been performed for both compounds, employing the computer program XD [3]. The dynamic densities have been obtained by an inverse fast Fourier transform (FFT) of the structure factors calculated from these models, employing the computer program PRIOR. Absence of series termination effects has been established for grid sizes smaller than 0.05 Å. The resulting densities are free of spurious critical points, and they exhibit maxima and bond critical points (BCPs) at expected positions. Topological analyses of these dynamic charge densities have been carried out according to Bader's quantum theory of atoms in molecules (QTAIM) [4], using the computer program EDMA [5]. The density and Laplacian at the bond critical point are obtained. The effects of thermal vibrations are clearly visible, especially in the values of the Laplacian at BCPs.

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