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 uantum-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.