

**MS09.02.03 BRAGG DIFFRACTION MEASUREMENTS ON CORUNDUM USING SYNCHROTRON RADIATION.** C.G van Beek\*, H.P Weber, P.Pattison and B.M. Craven\*. \*Department of Crystallography, University of Pittsburgh, PA 15260; Universite de Lausanne, CH-1015, Lausanne, Switzerland.

Data were collected at the Swiss Norwegian Beam Line at the ESRF. A spherical crystal of Corundum with diameter 0.20mm, as supplied by Sandoz Fils S.A., was used to collect Bragg diffraction intensities. Intensities were collected at wavelength of 0.5500 Angstrom using a Huber 6 circle diffractometer.

At room temperature, 5409 intensities were collected in an omega scan technique. The intensities covered a hemisphere in reciprocal space ranging from 0.70 up to 1.70 reciprocal Angstroms.

During the data reduction it was suspected that 222 reflections were affected by 'umweganregung'. Additional measurements on several of these affected reflections clearly shows the characteristics of 'umweganregung'. Rejecting these 222 reflections from the data gives 841 unique reflections with an internal agreement of  $R(I) = 0.030$ .

Additional data on the same crystal has been collected at room temperature at different wavelengths. A full sphere of reciprocal space was collected at a wavelength of 1.0000 Angstrom. The data at this wavelength consists of 2988 intensities going up to 0.95 reciprocal Angstroms. Additionally an hemisphere of reciprocal space was collected at a wavelength of 0.4000 Angstroms. The 1050 measured intensities at this wavelength cover reciprocal space up to 1.40 reciprocal Angstroms

Data will be analyzed by Mark Spackman, University of New England, Armidale, NSW 235, Australia.

**MS09.02.04 BOND CHARACTERIZATION OF CHROMIUM-FISCHER CARBENE COMPLEXES.** Yu Wang, C.C. Wang, H.J. Liu, K.J. Lin, L.K. Chou, K.S. Chan, Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Four pentacarbonyl chromium carbene complexes,  $(CO)_5CrC(X)R$ , have been studied via X-ray diffraction and molecular orbital calculations. One of the carbene complexes ( $X=OCH_3$ ,  $R=C\equiv CPh$ ) has been investigated extensively at 110K by X-ray diffraction using MoK $\alpha$  radiation. The electron density distribution of this compound as well as the asphericity in electron density around the Cr atom are clearly demonstrated. The comparison between experiment and theory is made in terms of deformation density, net atomic charge, and d-orbital populations of Cr. Further chemical bond characterization is based on quantum mechanical molecular orbital calculation. The resemblances and differences between amino- $(X=NR'R'')$  and oxy- $(X=OR')$  carbene complexes are of special interest. The results indicate that the competition between the  $\pi$ -characters of  $Cr-C_{carbene}$  and  $C_{carbene}-X$  bonds always exists, however the majority contribution comes from either Cr  $d_{xz}$ -orbital or the  $p_z$  orbital of X in carbene ligand. This makes the carbene carbon an electrophilic site at the  $p_\pi$  direction. Since the energy of  $\pi^*$  orbital of C-N is much higher than that of C-O, the amino-carbene is a poorer  $\pi$ -acceptor than the oxy-carbene. Furthermore, the energy of  $\pi^*_{C-N}$  is fairly close to that of  $\pi^*_{C=O}$ , the  $\pi$  bond character is even found on the  $M-C_{carbonyl}$  at the trans position. Therefore the axial carbonyl bond is a double bond i.e.  $N=C-M=C=O$ . This result is in accord with the differences found on bond lengths of axial carbonyl for many amino-carbene complexes. The bond dissociation energies of these carbene complexes are calculated at CASSCF level. The relative orbital energies are also checked upon with photoelectron spectroscopy(PES). The linear relationship exists between experiment and theory for all the MO calculations, however the result based on the density functional method (DFT) using the transition state approximation gives the best agreement with the experimental result.

**MS09.02.05 TOPOLOGY OF THE INTERATOMIC INTERACTIONS.** C. Lecomte<sup>1</sup> and E. Espinosa<sup>1,2</sup>, LCM3B, URA CNRS n° 809, Universite Henri Poincare Nancy 1, BP 1 239, 54506 Vandoeuvre-les-Nancy Cedex, France<sup>1</sup>, Instituto de Ciencia de Materiales de Barcelona (CSIC), Campus de la UAB, 08193 Bellaterra (Barcelona), Spain<sup>2</sup>.

The topological characterization of the electron density  $\rho(r)$  has been widely applied to isolated molecules and only a few theoretical studies has been devoted to hydrogen bonding (HB) in dimers. However, any experimental study of the HB topology involving both  $\rho(r)$  and the electrostatic potential  $V(r)$  functions has not been carried out. Comparison between crystal, procrystal (artificial crystal where the isolated molecules are placed at the crystallographic places) and IAM models lead to separate the effects involving chemical bonds and lone pairs (comparing procrystal and IAM models) from those of the molecular cohesion as HB. We will apply this method to the experimental electron density of L-arginine phosphate monohydrate (LAP) (monoclinic,  $P2_1$ ,  $Z=2$ ; X-ray and neutron, data:  $T=130K$ , 15513 and 4139 collected reflections, respectively, with  $R_{int}=0.013$  for X-ray measurements; X-(X+N) multipolar refinement: 6805 unique reflections,  $I>3\sigma(I)$ ,  $\sin\theta/\lambda < 1.20\text{\AA}^{-1}$ ,  $R_W(F) = 0.014$ ). *Ab initio* SCF theoretical models of  $\rho(r)$  and  $V(r)$  were calculated for the asymmetric unit of LAP with basis sets of triple- $\zeta$  quality for the valence shell, including both diffuse and polarization functions.

As hydrogen bonding is essentially an electrostatic interaction, it appears that  $V(r)$  is the observable really worth being considered and checked in regions where HB's occur. The first quantitative agreement between electrostatic potential calculations from experimental X-(X+N) and theoretical *Ab initio* SCF models in the hydrogen bonding region (within  $0.05\text{ e}\text{\AA}^{-1}$ ) of the unique HB existing in the asymmetric unit of LAP, allows us the study of HB effects from the comparison between crystal and procrystal models.

**PS09.02.06 A SIMPLE METHOD FOR PREDICTING ELECTRON DENSITIES IN COMPLEX AND FLEXIBLE MOLECULES. APPLICATIONS TO CONFORMATIONAL ANALYSIS.** Pierre J. Becker, Emmanuel Bec and Jean Michel Gillet, Laboratoire Structure Electronique et Modelisation Ecole Centrale Paris, Grande Voie des Vignes, 92295 Chatenay Malabry Cedex, France

A simple method is introduced to decompose the electronic density of a molecule into the sum of fragments. The method is based on the Hirshfeld's partitioning scheme, which is very general and independent on any basis set.

For flexible molecules, one can verify that the density of the fragments linked to a single bond is invariant (to an accuracy of the order of  $0.01\text{ e}\text{\AA}^{-3}$ ) through rotations around the single bond. The method has been carefully checked for alkanes, acetone, urea, water dimers, alanine and glycylglycine. The invariance of the density of fragments on each side of the peptide bond is well fulfilled.

Moreover, it turns out that some fragment densities can be transferred from one molecule to a bigger one within the same limit of accuracy. This allows for the possibility of predicting electron density of complex molecules that cannot be calculated by quantum mechanical methods.

The method is compared with the Mulliken's partitioning used in recent similar studies by Mezey. Within a given molecule, the two methods lead to similar conclusions for various conformations. However, transferability, which is the key for efficient use of such schemes, is significantly better with our present approach.

It is also possible to estimate the variations of energy with changes of conformational parameters, within a Density Functional

approach. This simulated energy surface is thus only dependent on the charge density. Preliminary calculations seem quite encouraging. This may be of interest for Molecular Dynamics, since such methods rely totally on the assumed energy surface. The method we propose is also quite adapted for critically reducing the number of leading conformational parameters in complex molecules.

We also considered polarisation effects in fragments. For example, for simple molecules, we study the evolution of fragments when changing interatomic distances. Simple and general trends appear, that can be empirically modelled and related to polarisabilities or vibrational parameters.

The method can be used either with theoretical or experimental densities.

**PS09.02.07 PROPERTIES OF THE PROMOLECULE.** B. Etschmann, E. N. Maslen. Crystallography Centre, The University of Western Australia, Nedlands, 6907, Australia

The power of the promolecule model, which consists of a (Hartree) product of the free atom wave functions, can be partly attributed to the number of chemical and physical properties that are unique functionals of the one-electron density<sup>1</sup>.

Evaluating atomic charges on overlapping neutral atoms in a promolecule may appear anomalous, but the close relationship between bonding and potential energies makes it physically reasonable to subdivide electron density in proportion to each atom's contribution to the electrostatic potential.

Atomic radii are determined in two stages. An invariant component of the radius associated with the atomic cores is first equated to the value at which the integral of the density equals the number of core electrons. The second most significant contribution is from the valence electrons, which must be treated as penetrable. The main requirement when evaluating atomic radii from atomic electron densities is to evaluate the penetrability of the valence subshells.

The promolecule also gives a good first order prediction of bonding energies for atoms extending across the whole periodic table<sup>2</sup>. Energies predicted for diatomic molecules containing a monovalent anion or a cation at the equilibrium spacing approximate bonding energies more accurately than integral point charges at those locations.

Values for these properties predicted by the promolecule model will be compared with experimentally measured equivalents for the garnet  $\text{Yb}_3\text{Al}_5\text{O}_{12}$ .

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**PS09.02.08 QUANTUM CHEMICAL AND EXPERIMENTAL STUDY OF UREA.** Dirk Feil and Roelof de Vries, Chem. Phys. Lab, University of Twente P.B 217, 7500 AE Enschede, Netherlands; Vladimir Tsirelson, D. Mendeleev University of Chemical Technology, Moscow, Russia

#### Introduction

In urea crystals one finds a considerable interaction density due to the network of strong hydrogen bonds distorting the molecular electron density distribution. The infinite size of the network requires, strictly speaking, band structure calculations to determine this effect.

Crystal Hartree-Fock-calculations (HF) have been carried out by Dovesi et al while DFT-calculations on clusters and on the crystal were carried out with ADF and the Amsterdam BAND program, respectively, as part of the present study. The outcome of the calculations are compared with the experimental results of Swaminathan et al and of Zavodnik et al.

#### Results

- The difference between the HF and the DFT exceeds experimental uncertainty.
- The description of the atoms is an important part of the discrepancy between HF and experiment.
- The interaction densities, resulting from HF and DFT calculations, do not differ significantly.
- Band structure calculations are not essential for the determination of the interaction density; with well-chosen parts of many-molecule clusters one can construct molecules that hardly differ from molecules in the crystal. Cluster calculations allow the use of larger basis sets.

#### References

R. Dovesi et al. *J.Chem. Phys.* 92, 7402 (1990)

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S. Swaminathan et al. *Acta Cryst.* B40, 398 (1984)

Zavodnik, *Poster contribution to the present conference*

**PS09.02.09 THE CHARGE DENSITY OF DL-ASPARTIC ACID.** R. Flaig, T. Koritsánszky, P. Luger, D. Zobel, Institute for Crystallography, Freie Universität Berlin, Germany

A full topological analysis [1] of the electron density of DL-aspartic acid extracted from low temperature (20 K) X-ray data collected with solid state detector and  $\text{AgK}\alpha$  radiation has been completed and the results compared with those obtained from Hartree-Fock wavefunctions.

The multipole refinement of the diffraction data was performed with the XD program package [2]. The static electron density, its Laplacian and various one-electron properties were derived. All critical points of the electron density and the Laplacian were located to characterize the covalent bonds and intermolecular interactions.

Experimental topological parameters for C-O bonds were found to be sensitive to the refinement model applied in the multipole treatment of the X-ray data. The ab initio calculations [3] at the Hartree-Fock level show considerable basis set dependence of the bond topological parameters. To mimic the intermolecular forces in the crystal calculations on molecular clusters were also carried out. The effect of the inclusion of the neighbouring molecules on the topology of the charge density especially in the C-O bond has been analyzed.

A comparative study based on diffraction data collected with solid state detector and  $\text{MoK}\alpha$  radiation is in progress.

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[2] T. Koritsánszky et. al.: XD, A Computer Program Package for Multipole Refinement and Analysis of Charge Densities from X-ray Diffraction Data

[3] Gaussian 92/DFT, Rev. G. 1, M. J. Frisch et. al., Gaussian Inc., Pittsburgh PA, 1993

**PS09.02.10 ASPHERICITY SHIFTS FROM AB-INITIO DENSITIES COMPARED WITH EXPERIMENTAL RESULTS.** S. Harkema, B.J.M. Fransen, J.A. Romein and D. Feil, Chemical Physics Laboratory, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

It is well known that positional and thermal parameters derived from X-ray and neutron diffraction experiments differ. These differences are caused by deviations from local spherical symmetry in the electronic charge density due to chemical bond formation. These asphericity shifts are most pronounced for H-atoms, but have also been detected for other atoms (F.H. Allen, *Acta Cryst.* (1986), B42, 515). In order to study these effects in a quantitative way structure factors were calculated from ab-initio electron densities for urea-phosphoric acid, for which compound a very extensive X-ray data set is available. The calculated structure factors were used as input for a spherical atomic refinement and theoretical asphericity shifts were determined. The shifts observed are a function of S.