

**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