

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 density¹.

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 table². 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 $\text{Yb}_3\text{Al}_5\text{O}_{12}$.

(1) Hohenburg, P. & Kohn, W. *Phys. Rev.* 1964, B136, 864-871

(2) Spackman, M. A. & Maslen, E. N. *J. Phys. Chem.* 1986, 90, 2020-2027

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)

G. te Velde, E.J.Baerends, *Phys. Rev* B44, 7888 (1991)

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.

[1] R. F. W. Bader, *Atoms in Molecules*, Clarendon Press, Oxford (1994)

[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.

The functions can be compared with experimental ones, obtained by refinements in small ranges of S , taking the positions from very high angle refinements as a reference. Calculated and experimental values are in excellent agreement.

Shifts observed can be rationalized in terms of competition of bonding and lone pair difference densities: the bonding densities dominating at low S , the lone pair densities at high S .

PS09.02.11 ON THE RELATION BETWEEN FREQUENCY SHIFTS AND ELECTRON DENSITY SHIFTS. Kersti Hermansson, Dept. of Chemistry, Uppsala University, Box 531, S-75121 Uppsala, Sweden

The frequency shift of the intramolecular stretching vibration of a diatomic molecule is a sensitive probe of the strength and nature of intermolecular bonding. For some diatomics, the intramolecular bond gets stronger, for others weaker, when the molecule is bound by intermolecular forces.

The poster explains how electron density maps of the vibrating free molecule will tell us if a frequency upshift or a downshift will occur when the molecule is bound in a crystal.

PS09.02.12 ELECTRON DENSITY DISTRIBUTION ON TWO IMINO COMPLEXES, $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2]^{2+}[\text{ClO}_4]_2^-$ AND $[\text{Cu}(\text{N}_2\text{O}_2\text{C}_{16}\text{H}_{14})]_2$. J. J. Lee, C. H. Hwang, G. H. Lee, Yu Wang*, Y. S. You, S. M. Peng, Department of Chemistry, National Taiwan University, Taipei, Taiwan

The crystal and molecular structures of $[\text{Co}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{H}_2\text{O})_2]^{2+}[\text{ClO}_4]_2^-$ and $[\text{Cu}(\text{N}_2\text{O}_2\text{C}_{16}\text{H}_{14})]_2$ have been determined by single-crystal X-ray diffraction method at 295 and 125 K. The former crystallizes in the space group of $Pbca$ at 125 K with cell parameters $a=11.655(2)$, $b=16.930(4)$, $c=10.508(2)\text{\AA}$, $M_w=556.27$, $V=2073.4(6)\text{\AA}^3$, $Z=4$. The molecular symmetry is C_1 with the Co atom at the 1 position; the latter one crystallizes in the space group $C2/c$ with cell parameters $a=26.609(2)$, $b=6.9143(4)$, $c=14.567(2)\text{\AA}$, $M_w=559.68$, $V=2073.4(6)\text{\AA}^3$, $Z=4$. The molecule is a dinuclear complex with molecular symmetry of C_1 .

In the Co complex, the Co atom is coordinated by four imino N at the macrocyclic plane and two water molecules at the axial position. The Co-N distances are $1.9026(7)\text{\AA}$ and $1.9153(7)\text{\AA}$. The CoN_4O_2 can be described as a tetragonal distorted octahedron due to Jahn - Teller distortion. The ligand is a partially π -delocalized α -diimine ligand, the C-N bond distance is $1.301(1)\text{\AA}$, indicating a double bond character, and the N-N bond is $1.373(1)$ and $1.382(1)\text{\AA}$, which is a single bond character. In the Cu complex, the Cu ion is five coordinated (N_2O_5) with one oxygen atom served as bridge between two Cu ions. The Cu-N distances are $1.9567(8)$ and $1.9596(8)\text{\AA}$. Electron density distribution based on multipole refinement confirms the prediction on the asphericity in electron density around the metals. The bonding between imino nitrogen and metal ions (Co and Cu) can be recognized as a σ -donor from N, the density depletion is found along the d_σ direction on both complexes. Electron density distribution on low spin d^7 Co(II) and d^9 Cu(II) will be displayed. Detail comparison between experimental and theoretical results will be presented for Co-complex. Strong covalent bond characters are found on ligand part in both complexes.

PS09.02.13 COMPARING 90K DATA TO SOLID STATE AB-INITIO CALCULATIONS FROM CRYSTAL92 Anthony Martin, Dept of Chemistry, University of Toledo, Toledo, OH 43606, USA. A. Alan Pinkerton, Dept of Chemistry, University of Toledo, Toledo, OH 43606, USA, A. Barry Kunz, Dept of Electrical Engineering, Michigan Technological University, Houghton, MI 49931, USA.

Accurate X-ray diffraction measurements on Ammonium Dinitramide, Biguanidinium Dinitramide and bis-Biguanidinium Dinitramide have been made at 90K. The resulting multipole refinements are compared to the calculated charge densities at the 6-21G basis set level using CRYSTAL92 for each system. The solid state ab-initio calculations use the 90K unit cell and geometries. The N-H bonds are all fixed at idealised neutron positions. Thus, there is no geometry optimization in the ab-initio calculation. The ab-initio calculations are all at 0K and do not include any zero-point energy. Thermal motion has been taken into account by either setting the multipole thermal parameters to zero before calculating charge densities from the x-ray data or thermally smearing the ab-initio data with the experimental thermal parameters.

Preliminary work indicates that there are significant differences in the position of the bonds and lone pair peaks when the two methods are compared.

PS09.02.14 A DATABASE AND MOLECULAR ORBITAL STUDY OF INTRAMOLECULAR STRONG HYDROGEN BONDS IN METAL-DIGLYOXIME SYSTEMS. Kevin W. McConnell and Ronald F. See, Department of Chemistry, Saint Louis University, St. Louis, MO 63103

The nature of strong hydrogen bonds has long been of interest, both as a test to theories of chemical bonding and, more recently, as a key step in the hydrogen transfer mechanism of certain enzymatic catalysis. For O-H...O systems, strong hydrogen bonds may be defined as those with a distance of less than 2.8\AA between the oxygen atoms. Metal-diglyoxime complexes provide an excellent opportunity to compare strong hydrogen bonds, as changes in both steric and electronic effects are quantifiable. A search of the Cambridge Structure Database has resulted in approximately 150 known metal-diglyoxime structures, each containing two strong intramolecular hydrogen bonds, ranging from 2.40 to 2.80\AA between oxygen atoms. Results of this search suggest that electron-withdrawing substituents on the glyoxime backbone favor stronger intramolecular hydrogen bonds; a possible explanation for this trend will also be presented. In order to test theoretical predictions against experimental results, molecular orbital calculations (ZINDO) were performed on nickel diglyoxime model compounds containing the substituents $-\text{CH}_3$, $-\text{NH}_2$, $-\text{OH}$ and $-\text{F}$. The results of these calculations are not totally consistent with the empirical trends identified through the database search. These results will be analyzed in terms of Brown's bond-valence theory, as well as Gilli's resonance-assisted hydrogen bonding concepts.

PS09.02.15 DENSITY FUNCTIONAL STUDY OF AMMONIUM FLUORIDE: A COMPARISON BETWEEN THEORY AND EXPERIMENT Hans Overeem, Roelof Y. de Vries and Dick Feil, Chem. Phys. Lab. University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.

In the molecular ion of NH_4^+ a large part of the electrons is involved in bonding. The electron density distribution is strongly influenced by the electric field of the F⁻ ions.

The present study deals with quantum chemical density functional calculations on the crystal of NH_4F . In molecular crystals, cluster calculations have been successful (Krijn et al, 1988). For