

**PS09.02.24 X-RAY SCATTERING FACTORS OF COMPRESSED ATOMS.** B. Craig Taverner & Jan C. A. Boeyens, Center for Molecular Design, Department of Chemistry, University of the Witwatersrand, Private Bag 3, WITS 2050, South Africa

In 1963 Herman and Skillman[1] produced the well known numerical atomic Hartree-Fock-Slater program to calculate the energies and densities of electron *nl* orbitals. The orbital energies for the entire periodic table were calculated and published. In 1994 this program was modified to allow for the simulation of the compression of the atoms by the multiplication of all wave functions by a step function at a particular radius, in each cycle of the self consistent field calculation. By squeezing the atoms in this way, the electron densities and orbital energies on compressed could be modeled. The increase in orbital energies can be used to model ionization and bonding phenomena. Compressed wave functions can be used to model electron densities in condensed phases, and therefore be useful in crystallographic studies of electron densities in crystals. Several crystals have been selected for electron density study using scattering factors calculated directly from the compressed atoms. These results are compared to those obtained using published scattering factors[3].

1.F. Herman and S. Skillman, Atomic Structure Calculations, Prentice-Hall, New Jersey, 1963.

2.J. C. A. Boeyens, Ionization Radii of Compressed Atoms, J. Chem. Soc. Faraday Trans., 90(0), 1994

3.International Tables for X-Ray Crystallography, Volume III, The Kynoch Press, Birmingham, 1968.

**PS09.02.25 VITAMIN C AT 120K: EXPERIMENTAL AND THEORETICAL STUDY OF THE CHARGE DENSITY.**

P. Ugliengo+ R. Bianchi\*B. Civalleri+ C. Roetti+ and D. Viterbo+Dip. di Chimica IFM, Torino, and \*CSR SRC, CNR, Milano, Italy.

The experimental charge density of Vitamin C, obtained from low temperature diffraction data, has been compared with that obtained from quantum-mechanical calculations performed both on isolated molecules and on crystals.

Vitamin C is an extremely interesting molecule, not only for its important biological properties, but also for its crystal structure in which the formation of several hydrogen bonds plays an important role. We have collected X-ray diffraction data at -153°C up to  $\sin\theta/\lambda \approx 1$ . The crystals do not undergo any phase transformation and the space group remains  $P2_1$  with two independent molecules in the asymmetric unit. In the final difference Fourier map bonding non-spherical electron density was clearly indicated. A study by means of a multipole expansion of the electron density has been performed and the experimental electrostatic potential obtained in this way has been compared with that computed by *ab-initio* calculations on the isolated molecule, in order to attain a better understanding of the effects of the crystal packing on the charge distribution. Other one-electron properties, such as the dipole moment, have also been evaluated and compared. A complete conformational analysis of the isolated molecule has also been carried and the most stable structure has a folded conformation with a strong intramolecular hydrogen bond. We have also computed the electrostatic potential by means of a crystal-orbital approach using the program CRYSTAL [R. Dovesi, M. Caus, R. Orlando, C. Roetti and V.R. Saunders, J. Chem. Phys. **92**, 7402 (1990)] with the MINI-1 basis set. The maps are in good agreement with the experimental ones. Because our system is relatively large, so far we have not been able to perform calculations with a more extended basis set, but we are presently checking our results with those obtained on smaller systems, such as urea and formamide.

**PS09.02.26 ELECTRON DENSITY DISTRIBUTION OF Fe(PHEN)<sub>2</sub>(NCS)<sub>2</sub> USING THE SYNCHRON RADIATION LIGHT SOURCE.** C. C. Wang<sup>1</sup>, H. S. Sheu<sup>1,2</sup>, C. R. Lee<sup>1</sup>, J. J. Lee<sup>1</sup>, Y. Wang<sup>1</sup>, A. Darovsky<sup>3</sup>, R. Bolotovskiy<sup>3</sup>, P. Coppens<sup>3</sup>, <sup>1</sup>Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC, <sup>2</sup>Synchrotron Radiation Research Center, Hsinchu, Taiwan, ROC, <sup>3</sup>X3, National Synchrotron Light Source, BNL, Upton, New York, USA

*Cis*-bis(thiocyanato)bis(1,10-phenanthroline)-iron(II), Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> has certainly been one of the most well studied iron(II) spin-transition complexes. It undergoes an abrupt HS $\leftrightarrow$ LS transition at 176K. However, the crystal structure does not undergo any phase transition at this temperature. The space group is *Pbcn*, cell parameters at 50K, *a*=13.242(2), *b*=9.884(1), *c*=17.123(6)Å, *V*=2241.17Å<sup>3</sup>. The structures of Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> were studied at three different temperatures (298, 140 and 50K), their structural parameters will be compared. Accurate diffraction data of this compound were collected on a 0.1x0.1x0.08 mm using the synchrotron radiation light source (NLS) with the wavelength 0.394Å at 50K, in order to investigate the electron density distribution of such complex at low spin state. Deformation density distribution according to the multipole model will be displayed. The strong covalent character of the ligand phen and NCS- are well illustrated. The d-orbital populations of Fe(II) at LS will be discussed. Parallel molecular orbital calculations on this molecule are also performed. A comparison between experimental and M.O. calculation will be given.

**PS09.02.27 PRESSURE-INDUCED CHANGE OF THE STEREOCHEMICAL ACTIVITY OF A LONE ELECTRON PAIR.**

Björn Winkler, Mineralogisch Petrographisches Institut der Christian Albrechts Universität, Olshausenstr. 40, D24098 Kiel, Germany; and V. Milman, BIOSYM/MSI 240/250 The Quorum, Barnwell Road, Cambridge CB5 8RE, UK.

Ab initio total energy calculations based on density functional theory and the generalized gradient approximation in conjunction with a constant pressure minimisation algorithm have been used to investigate the pressure induced phase transition in CsGeCl<sub>3</sub>. The results of the calculations are in good agreement with experimental data, in that the calculated zero pressure structure is rhombohedral, while the high pressure (5 GPa) structure is cubic. The calculations show that the transition from the rhombohedral to the cubic structure involves a fundamental change in the stereochemical activity of the 'lone electron' pair of Ge<sup>2+</sup> which has partially p-character in the low pressure phase and becomes an 'inert pair' with s-character in the high pressure phase.