

CHARGE DENSITY STUDIES OF [Cu(bite)](BF₄)J. Kozisek¹ M. Fronc¹ M. Breza¹ G. Wu² B. Rodrigues² P. Coppens² H. Fuess³ C. Paulmann⁴¹Slovak University of Technology Department of Physical Chemistry Radlinského 9 BRATISLAVA SK-812 37 SLOVAK REPUBLIC²Chemistry Department, SUNY/Bufalo, Buffalo, NY 14260-3000, U.S.A.³Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany ⁴Mineralogisch-Petrographisches Institut, Universität Hamburg, Grindelallee 48, D-20146 Hamburg, Germany

Charge density of [Cu(bite)](BF₄) [1] (bite = biphenyldiimino dithioether) have been studied to understand the redox process in 'blue-protein' model compounds (so called gated electron transfer) [2]. Our studies were based on data collected at 20K at the SUNY X3 beamline at NSLS ($\lambda = 0.6430 \text{ \AA}$) and at 100K at beamline F1 at HASYLAB/DESY ($\lambda = 0.5604 \text{ \AA}$). Two crystals of different size were used to avoid absorption and to obtain high-angle reflection intensities. 109 890 reflections (17619 unique) were collected with the smaller crystal at 20 K. Starting parameters for XD [3] refinement were taken from SHELXL97 results (R1 = 0.0241). The density maps indicate significant non-equivalence of the two Cu-S interactions. DFT quantum-chemical calculations [4] on the geometry optimization of the quasi-tetrahedral and quasi-square-planar [Cu(bite)]²⁺ complexes were done.

References

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Keywords: CHARGE DENSITY, BLUE PROTEIN, AB-INITIO CALCULATIONS**ATOMIC INTERACTIONS IN ENERGETIC MATERIALS: NTO, (BIGH)(DN) AND (BIGH₂)(DN)₂**E. A. Zhurova¹ V. G. Tsirelson² A. I. Stash³ M. V. Yakovlev² A. A. Pinkerton¹¹University of Toledo Chemistry 2801 W. Bancroft St. TOLEDO OH 43606²Quantum Chemistry Department, Mendeleev University of Chemical Technology, Moscow, Russia ³Karpov Institute of Physical Chemistry, Moscow, Russia

For a series of energetic materials (β -form of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one, NTO, biguanidinium dinitramide, (BIGH)(DN), and biguanidinium bis-dinitramide (BIGH₂(DN)₂) the molecular and crystal properties were calculated from the electron density (ED) and the atomic interactions analyzed and discussed. The experimental ED's for all the compounds were obtained from X-ray diffraction data at low temperatures. For the NTO crystal the theoretical calculation was performed with the CRYSTAL98 program with a 6-21G** basis set. The ED was approximated with the multipole model using the program package XD for all experimental and theoretical (NTO) data. The critical point (CP) search and the integration of atomic charges were performed with the program TOPXD. The kinetic $g(r)$ and potential $v(r)$ energy density maps were calculated from the experimental (model multipole) ED with the winxpro program. The Kirzhnits second-order gradient expansion of the one-particle Green function around the Thomas-Fermi term was used to approximate $g(r)$, while $v(r)$ was calculated supposing that the virial theorem is valid for the model ED. For the single NTO molecule, the non-empirical Hartree-Fock ED, CP's, $g(r)$ and $v(r)$ functions were also calculated directly from the 6-311G** wave functions with the modified program PROAIM. Good agreement with the potential and kinetic energy density maps determined from the experimental model ED was found.

The potential energy densities reveal explicitly that the NO₂-group is the most potential energy-rich area in the molecules under investigation. The deformation potential energy density maps show that the formation of the crystals from unbound atoms is accompanied by the most enhancement of (negative) local potential energy on the N-O, C=O bonds and oxygen lone pairs. The comparison of the properties in the CP's with those in atomic procrystals revealed the contraction of the ED towards the bond CP's for the shared interactions during the crystal formation. At the same time, for all the hydrogen bonds, the ED contraction towards atomic nuclei is observed, which stresses the closed-shell atomic interaction in these bonds. Atomic interactions between oxygen atoms have been analyzed for the (BIGH)(DN) and (BIGH₂(DN)₂) crystals. Bond critical points have been found on the O(1)...O(4) interatomic line in both the electron density and potential energy density gradient fields. The bond path and its associated virial path have been obtained. The interaction has been identified as a bonding closed-shell type interaction.

Keywords: ELECTRON DENSITY ATOMIC INTERACTIONS ENERGETIC MATERIALS**EXPERIMENTAL CHARGE DENSITY ANALYSIS ON MODIFIED COUMARINS: TOPOLOGICAL PROPERTIES**

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Coumarins have been used in several areas of synthetic, medicinal and photochemistry. These compounds depict state dependent variation in static dipole moment and many crystallize in noncentrosymmetric space groups, a characteristic requirement for second harmonic generation (SHG). Crystal and molecular structure of 2H-Chromene-2-thione has been determined to belong to the space group $P2_12_12_1$ and the structure of coumarin belongs to $Pca2_1$. High resolution X-ray diffraction data has been collected at 90K on a Bruker AXS SMART APEX system for 2H-Chromene-2-thione and Coumarin in order to elucidate the differences in crystal structures of these two compounds. The presence of sulphur in place of oxygen in the structure of 2H-Chromene-2-thione and the consequent changes in the charge density distributions have been analysed using space partitioning based on the topology of the total electron density. The follow-up of calculations of one-electron properties have been performed using both XD and MOLLY packages.

Keywords: COUMARIN, CHARGE DENSITY, SHG**THE WIENER-KHINCHINE THEOREM FOR X-RAY RADIATION**

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The electromagnetic field used in X-ray diffraction experiments should be described in probabilistic terms due to the random character of the emission of photon packets. The wave-packets emitted from an X-ray tube or by electrons in a synchrotron form the statistical ensemble which should be considered. Normally the results of a short measurement do not depend on the moment of time chosen for the measurement. Therefore, it is useful to describe the X-ray radiation as a stationary ensemble and consequently the functions describing these packets as incident waves do not decay with time and the usual Fourier transformation cannot be done. However, it can be performed using the Wiener-Khinchine (W-K) theorem [1]. In the present paper a proof of this important theorem will be sketched and it will be shown that it can be a basis for an analysis of partial coherence of X-ray beams. Besides, in the particular case when the considered statistical ensemble is ergodic, the W-K theorem may be presented in more detail.

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Keywords: X-RAY WAVE-PACKETS COHERENCE FOURIER TRANSFORM