

values at the bond critical points for covalent interactions depends on the level of theory / basis set and the polarity of the bond, and can exceed 0.15 a.u. Because of the bias in the Laplacian introduced by the pseudoatom projection, the corresponding KED values can increase by a factor of five. Detailed analysis of model data suggests that errors introduced by approximate KED functionals and those that arise due to the pseudoatom projection, fortuitously cancel each other, especially for non-hydrogen atoms. We thus tend to conclude that the analysis has little physical relevance, even if, theoretical and experimental figures appear to be in good agreement.

Keywords: charge density, kinetic energy, topological analysis

MS.68.2

Acta Cryst. (2008). A64, C117

Exploring pathways of structural phase transitions via experimental charge density analysis

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It has been a challenge to decipher the nature of a chemical bond between two atoms in a molecule and more so to evaluate the nature of interactions between molecules/ions in a crystal. Charge density analysis has gained immense importance in recent years, particularly because such studies allow one to observe and quantify chemical bonding beyond the criteria of mere geometry[1]. The theory of "Atoms in Molecules" [2,3] has not only provided a new pathway to evaluate derived properties on the basis of charge density measurements but also allows for comparison with theoretical estimates of such densities. Recent work in our laboratory is devoted to the analysis of complex inorganic sulfates in terms of bond paths, coordination spheres, electrostatic potential surfaces and in particular to observe the changes in one electron properties and the corresponding changes in chemistry across phase transitions with temperature. A new outlook to the definition of phase transitions in terms of the nature of the chemical bond pathways is observed.

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Keywords: charge density Inorganic Materials, phase transitions, properties

MS.68.3

Acta Cryst. (2008). A64, C117

Intra and intermolecular electron density properties of fullerene derivatives: First C₇₀ examples

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Although recent technical and methodical advances made experimental electron density determinations also on larger molecules possible, fullerenes with 60 or more atoms are still a major challenge. Their investigation is complicated by the generally poor crystal quality and by the high mobility of these molecules in the crystal lattice. That is why only a few electron density studies are reported on highly substituted C₆₀ fullerenes, while no such investigation is known for a C₇₀ fullerene or its derivatives until now. Here we report on three further fullerene electron density investigations. They include for the first time (to our knowledge) two C₇₀ fullerene derivatives [C₇₀(C₂F₅)₁₀] [1] and C₇₀(CF₃)₁₄] which have been studied based on data sets collected at the synchrotron beam lines F1 and D3 of the Hasylab, DESY. For a C₆₀ fullerene, C₆₀(CF₃)₁₂, crystal quality was sufficient for a high resolution data collection under home laboratory conditions (MoKalpha, T= 20 K). The electron densities were topologically analyzed to yield quantitatively atomic and bond topological properties, which is of special interest in the C₇₀ case because even for free C₇₀ the number of chemically independent atoms (na=5) and bonds (nb=8) is substantially higher than for free C₆₀ (na=1, nb=2). In the case of C₆₀(CF₃)₁₂, additional information about intermolecular electronic interactions in the crystal lattice was obtained which could be related to unusual physical properties of this compound such as low solubility and volatility [2]. Funding from the DFG (SPP 1188) is greatfully acknowledged.

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Keywords: fullerenes, C₇₀, synchrotron radiation

MS.68.4

Acta Cryst. (2008). A64, C117-118

Effects of crystal packing on the electron density of metal carbonyl complexes

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Carbonyl is the most important and versatile ligand in organometallic chemistry. The reference complexes are neutral M(CO)_n, where carbonyl ligands are coordinated to a zero-valent transition metal atom. However, anionic and, more recently, cationic metal carbonyl complexes have been reported and their importance in organometallic chemistry is now well recognized. Structures and properties of ionic complexes may vary dramatically. For this reason, a quantum chemical investigation of the effects of electric field on the isolated CO molecule was undertaken, together with the analysis of chemical bonding. This allows studying the modifications of CO electron density due to coordination to the metal (separating the effects of the chemical bonding from those due to polarization). Periodic calculations were carried out on salts of ionic metal carbonyl complexes with several (hard and soft) counter-ions, with the purpose to analyze packing abilities of these species and the electron density polarization caused by the crystalline environment. For example, a species like [Co(CO)₄]⁻ was computed in known salts of Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, [NH(C₂H₅)₃]⁺ and the newly determined salt of [N(CH₃)₄]⁺. Similarly, [Fe(CO)₆]²⁺ was investigated as salt of [BF₄]⁻ and [Sb₂F₁₁]⁻.