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Keywords: Pair Distribution Function, Total scattering, Nanomaterials

MS25-P06

Ab initio structure determination from unindexed powder patterns by a global optimization approach using pattern comparison based on cross-correlation functions

Stefan Habermehl[1], Carina Schlesinger[1], Martin U. Schmid[1]

1. Institute of Inorganic and Analytical Chemistry, Goethe-University Frankfurt/Main, Frankfurt/Main, Germany

email: **habermehl@chemie.uni-frankfurt.de**

A method for *ab initio* structure determinations from powder diffraction data (SDPD) of organic compounds, which does not require prior indexing of the experimental pattern, has been developed. The global optimization approach is based on the direct fit of random trial structures to the powder data using an algorithm called FIDEL ("FIt with DEviating Lattice parameters"). It uses a similarity measure based on cross-correlation functions, which allows the comparison of simulated and experimental powder data even if the lattice parameters do not match [1,2].

The structure determination process starts with the molecular geometry of the compound and a global search space setup in various crystal symmetries. The lattice parameters, molecular position and orientation, and selected intramolecular degrees of freedom are fitted simultaneously in an elaborated multi-step procedure. The hierarchical search strategy developed is based on similarity screening, structure fitting and iterative adaptation of parameter ranges. It combines various methodologies in order to realize an efficient and effective exploration of the global search space. The standard procedure includes an adaptive mechanism for the balancing of computing time spent on the generation of random structures, similarity screening, fitting and clustering of structural models. The structure determination proceeds stepwise from e.g. more than 20 million trial structures to a small number of promising structure candidates that are subjected to an automated Rietveld refinement with TOPAS [3]. Finally, a user-controlled Rietveld refinement with TOPAS is performed.

By exploiting the full potential and versatility of the pattern comparison approach based on cross-correlation functions and supported by the integration of 3rd party components, a complete SDPD framework evolved, that covers almost all scenarios of finding crystal structures corresponding to given experimental data.

The global optimization approach presented is suitable for a wide range of "problematic" powder patterns, including powders of low crystallinity, non-phase-pure samples or disordered structures. While pushing SDPD to its limits, applications of the method deliver valuable insights into ambiguities arising from low-quality experimental data, where the "one powder – one structure" paradigm of SDPD is beginning to collapse. Even if the results do not converge into a single solution qualifying as a publication grade structure determination, the method can provide a set of structural models that match the powder as much as possible, for further analysis.

Examples of (metal-)organic compounds are shown, including the previously unknown structures of nanocrystalline

phases of 2,9-dichloro- and 4,11-difluoro-quinacridone solved from powder patterns with 14-20 peaks only.

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Keywords: structure determination from powder data, global optimization, cross-correlation functions

MS25-P07

Associating X-ray structure and antioxidant activity through UV-vis spectroscopy, cyclic voltammetry and DFT methods in Emodin

Miriam Rossi[1], Stuart Belli[1], Kelly Wen[1], Francesco Caruso [1]

1. Department of Chemistry, Vassar College, Poughkeepsie, NY, United States of America

email: rossi@vassar.edu

Regulation of reactive oxygen species such as the superoxide ion is an important chemical process. Emodin (1,3,8-trihydroxy-6-methyl anthraquinone) is present in the root and rhizome of *Rheum palmatum*, and the goji berry (*Lycium barbarum* and *Lycium chinense*). Elucidating the manner in which emodin carries this out may provide insight into the chemical properties described in the literature.

The scavenging of the superoxide radical in this study was analyzed using a combination of several methods. We quantify the ability of emodin in scavenging the superoxide ion $O_2{}^{\cdot-}$ in an aprotic solvent, dimethyl sulfoxide (DMSO); since water interferes with superoxide, highly dehydrated DMSO was used. We describe the results of our antioxidant assay using the electrochemical method of cyclic voltammetry with a novel rotating ring disk electrode (RRDE) method. This powerful technique provides a quantitative measurement of a redox reaction and allows us to detect products, side-products or even short-lived intermediates of electrode reactions. Since this process was accompanied by a variation of color, the time evolution of this antioxidant process was followed using *in situ UV-Vis* spectroelectrochemistry. At the molecular level, the reactivity of this process was followed using DFT methods which could be applied after determination of the crystal structure using single crystal X-ray diffraction. The combination of these different methods allowed us to demonstrate the unusual manner in which emodin behaves when scavenging superoxide radical. Our results point to the importance of the electron transfer in this scavenging mechanism.

Keywords: antioxidant activity, cyclic voltammetry, emodin