

Cluster Distortions in Amorphous Organotin Sulfide Compounds by EXAFS Measurements

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Tailored light sources have greatly advanced technological and scientific progress by optimizing colour and brilliance, improving energy efficiencies or the quantum properties of light. So called supercontinuum generators are premier examples for media with nonlinear optical (NLO) effects – far superior in some respects to other sources such as phosphorescent white light-emitting diodes (LEDs). However, unlike LEDs, most of these advanced light sources are only used for scientific purposes, as they require extreme electric field strengths which are commonly realized by high-power pulsed lasers. In contrast, the materials of interest for this research project represent a new generation of supercontinuum emitters that are readily obtained from ubiquitous resources in a simple synthesis.

Our recent studies [1-4] investigated the local structure of 4 different amorphous organotin sulfide [(R-Sn)₄S₆] compounds by X-ray absorption spectroscopy and X-ray scattering measurements. These compounds exhibit a non-linear optical response upon irradiation with a continuous-wave near-infrared laser.[5-7] Their basic structural motif is a hetero-adamantane cluster with different organic substituents R. The nature of the NLO response depends strongly on the morphology of the material, which is influenced by the choice of the organic substituents, leading to either a second harmonic generation or the generation of a supercontinuum, potentially appearing as white light.

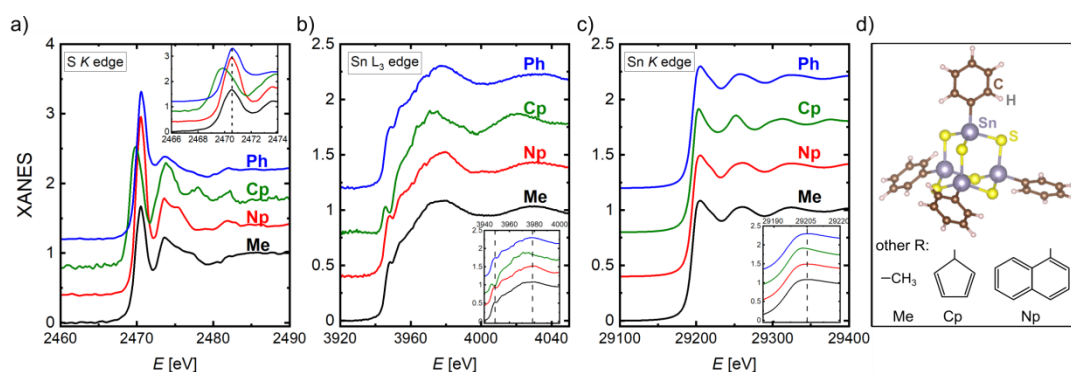


Fig. 1: XANES data for the 4 organotin sulfide samples (Me: black, Np: red, Cp: green, Ph: blue, shifted upwards for clarity) at the S K (a), the Sn L₃ (b) and the Sn K edge (c). The insets highlight the regions close the first maxima of the respective edges. A model of the Ph-Cluster from a DFT simulation[5] is illustrated in (d), along with schematic illustrations of the other organic substituents.

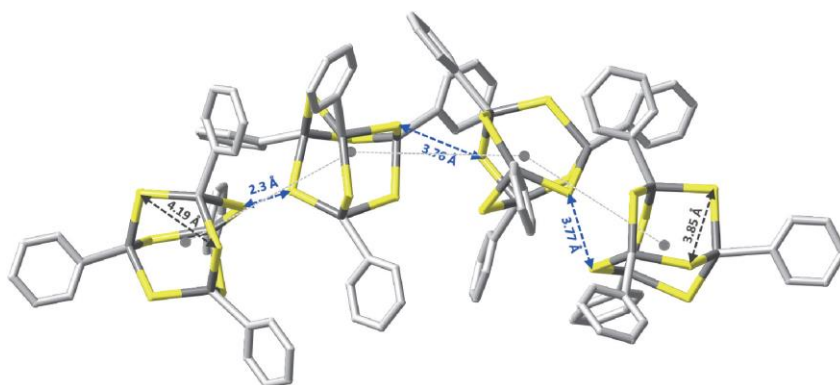


Fig. 2: Fourfold linear chain of $\{\text{Sn}_4\text{S}_6\}$ clusters from a dynamic molecular Reverse Monte Carlo simulation ensemble.[2] H-atoms have been omitted to retain clarity. Molecules in chains prefer a staggered mutual configuration with respect to the organic ligands. Also shown are some intramolecular and intermolecular distances, indicating similarity between intra- and intermolecular sulfur-sulfur spacings.

Due to the amorphous nature of the materials, their structural properties, and thereby the apparent origin of this effect, is difficult to determine [6]. Despite these difficulties, our results provide experimental evidence that the nature of the NLO properties is tied to distortions occurring at the cluster core, with almost ideal clusters in compounds that show second harmonic generation, and strongly distorted clusters in the case of compounds that generate a supercontinuum. These distortions may enable a closer proximity of the cluster cores, and thereby influence the NLO response by altering the intermolecular order.

As an example, Figure 1 illustrates the near-edge structure of the absorption spectrum (XANES) around the S K , Sn L_3 and Sn K edges (the latter was measured at P65 of the PETRA-III synchrotron). In all datasets, the edge of the cluster with R=Cyclopentadienyl (Cp) is shifted to lower energies (see insets in Fig. 1), indicating a change in the oxidation state of the cluster core. As we will show in the analysis of the XAFS data, this leads to a significant distortion of the cluster relative to the other compounds.

To conclude, the XAFS experiments at the S K edge performed at BL11 of HiSOR provide key information about the interaction of neighboring clusters, which determine the intermolecular order of the system and can be regarded as the origin of the differences of the non-linear optical properties.

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