Optical Spectroscopy, Dielectric Properties and Structure Discrimination of Sn^{+}_{N} ($20 \leq N \leq 40$) Clusters

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Clusters
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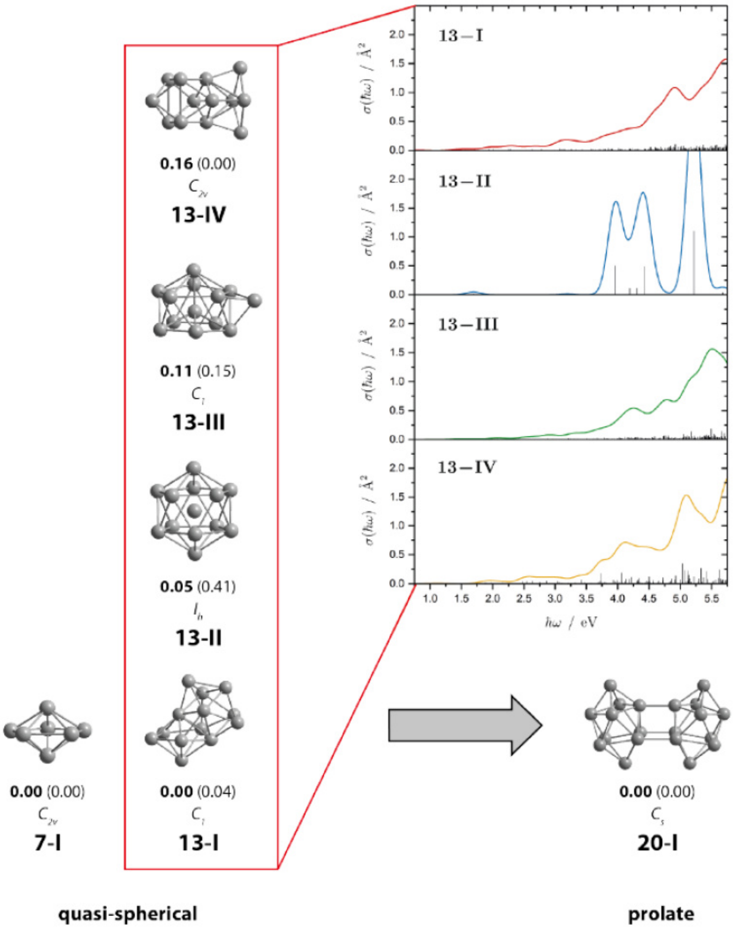

Figure 1: Selected Sn^{+}_{N} structural isomers stressing the quasi–spherical–to–prolate transition observed for this size regime. Relative energies in eV on the PBE0/cc-pVTZ-PP level of theory are given in bold letters, while LC-ωPBEh/def2-TZVPP results are shown in parantheses. The simulated optical spectra showing the absorption cross section σ as a function of the photon energy ħω are given for the Sn^{+}_{13} isomers, with isomer 13-II stating a stabilized icosahedral configuration with unusualy intense and discrete electronic transitions.

Introduction

Semiconductor materials are of great importance in the development of technological devices. In particular, the trend towards ever smaller and faster electronical and optical devices, as well as increasing digitalisation in society, science and industry, have led to a raise in interest in nanoscale and subnanoscale semiconductor materials. Especially the exploration of group 14 (tetrel) elements (Si, Ge, Sn) has drawn significant attention. While much is known about their bulk counterparts (and in the case of silicon also about larger, mostly colloidal nanoparticles), much less information is available about the smallest Sn species. These so-called clusters are agglomerates of few to thousands of atoms. Clusters propose an interesting research area, because their behavior differs strongly from the macroscopic solid state. Their size-dependent unexpected properties result from a high ratio of surface-to-bulk atoms in the cluster, which leads to a high number of uncoordinated and chemically unsaturated atoms. Their nanoscopic size further leads to discrete electronic states causing quantum size effects. Those effects are especially distinct for cluster sizes below hundred atoms and can result in intriguing catalytic, electric, magnetic or optical properties. For tuning several applications and therefore tailoring materials on an atomic scale, a fundamental knowledge of the size-dependent evolution of optical and electronic properties is necessary. Therefore, a combined experimental and quantum chemical description of such small tetrel nanoclusters is important. The quantum chemical description to support the experimental findings requires the employment of high-performance computers.

Methods

Energetically-favored geometries were generated using a Density Functional Theory (DFT) based Genetic Algorithm (GA) developed in our group. Frequency calculations verified the global minimum structures of the bare tin clusters employing the LC-ωPBEh/def2-TZVPP and PBE0/cc-pVTZ-PP functional/ basis set combination both for the ground state DFT and excited state time-dependent DFT. The absorption spectra are further analyzed by a natural orbital analysis making extensive use of symmetry considerations.

Results

By comparing the recently studied cationic Sn^{+}_{N} clusters with $6 \leq N \leq 20$ with their neutral counterparts, we aim to understand the impact of electronic effects on the geometric, dielectric and optical properties of this system. It was found that they share many of the structural motifs, although the charged clusters often appear to be more distorted. This observation is rooted in their electronic structure, i.e. neutral tin clusters were found to favor closed-shell configurations with a spin multiplicity of $2S+1 = 1$, whereas cationic tin clusters are always open-shell spin doublets with $2S+1 = 2$. This has far-reaching consequences regarding their optical properties. A lowering in symmetry on the one hand smooths the course of the absorption spectra and renders the electronic transitions less intense, while, on the other hand, an accompanied narrowing of the band gap shifts the onset of the absorption cross section to slightly lower energies. An exception to this is the Sn^+_{13} cluster, which has already been detected experimentally. [1] Here, the electronic ground state is non-degenerate and thus not subject to first-order Jahn-Teller distortions hence stabilizing the highly-symmetric I_h point group. The absorption spectrum interestingly shows strong discrete transitions rather than a monotonically increase in absorption cross section with little structure which is more common for semiconductor clusters of this size.

Discussion

Just as for the neutral tin clusters we found a structural transition between quasi-spherical molecular to prolate geometries from about 14 atoms onwards. Still under debate is if tin clusters form again spherical or compact structures and whether the smallest clusters rather represent the semiconducting α- or metallic β-allotrope of its bulk counterpart. [2] By applying the classical Mie theory for predicting the optical absorption of a homogeneous spheroid based on the bulk dielectric functions (see [3]), we recognized a resemblance with α-Sn for these small clusters. To show how the optical properties evolve towards the bulk, larger clusters – neutral and cationic – need to be investigated further shining light on the extent of the prolate structural regime as well as the formation of competetive β-Sn modifications.

Publications

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