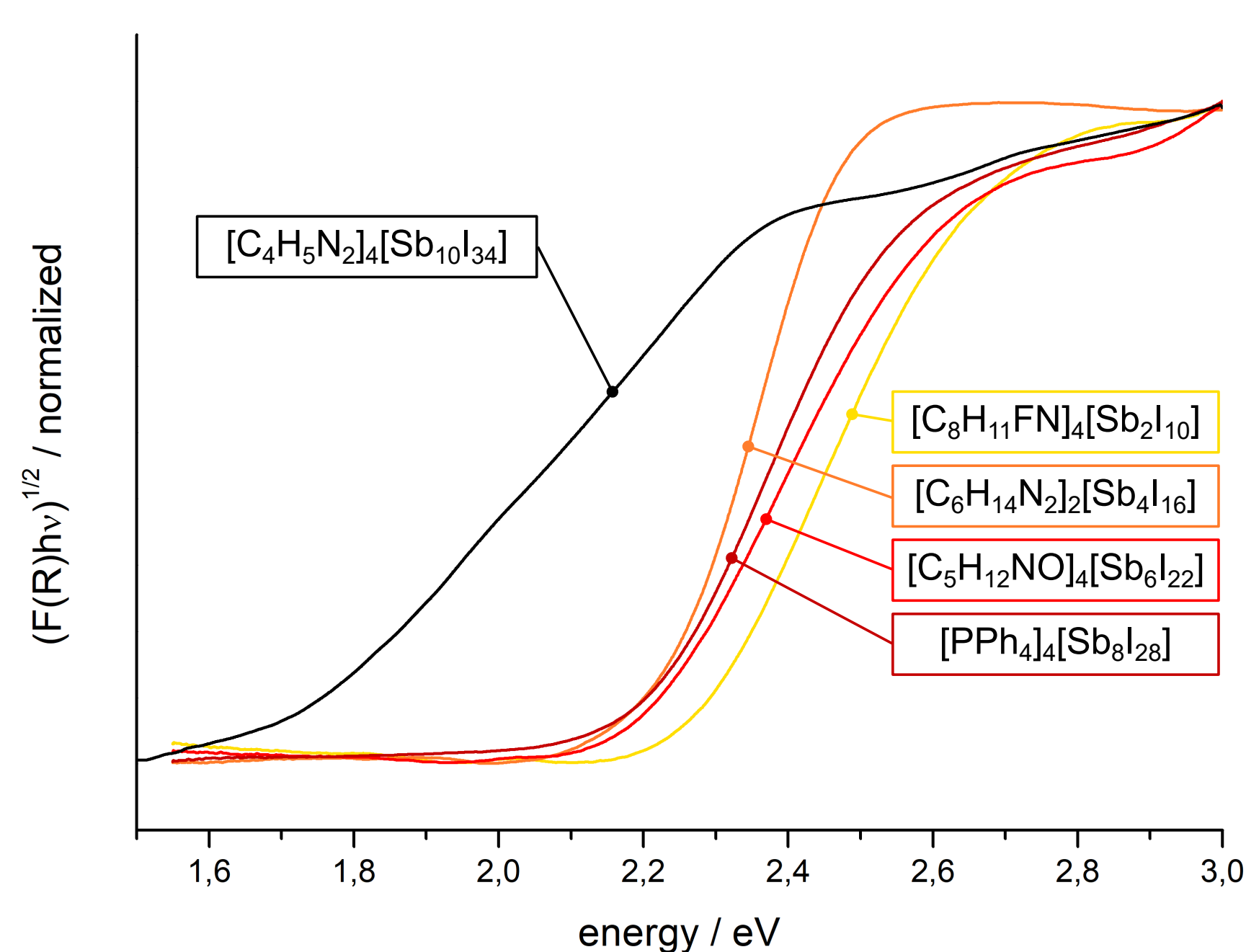


Introduction

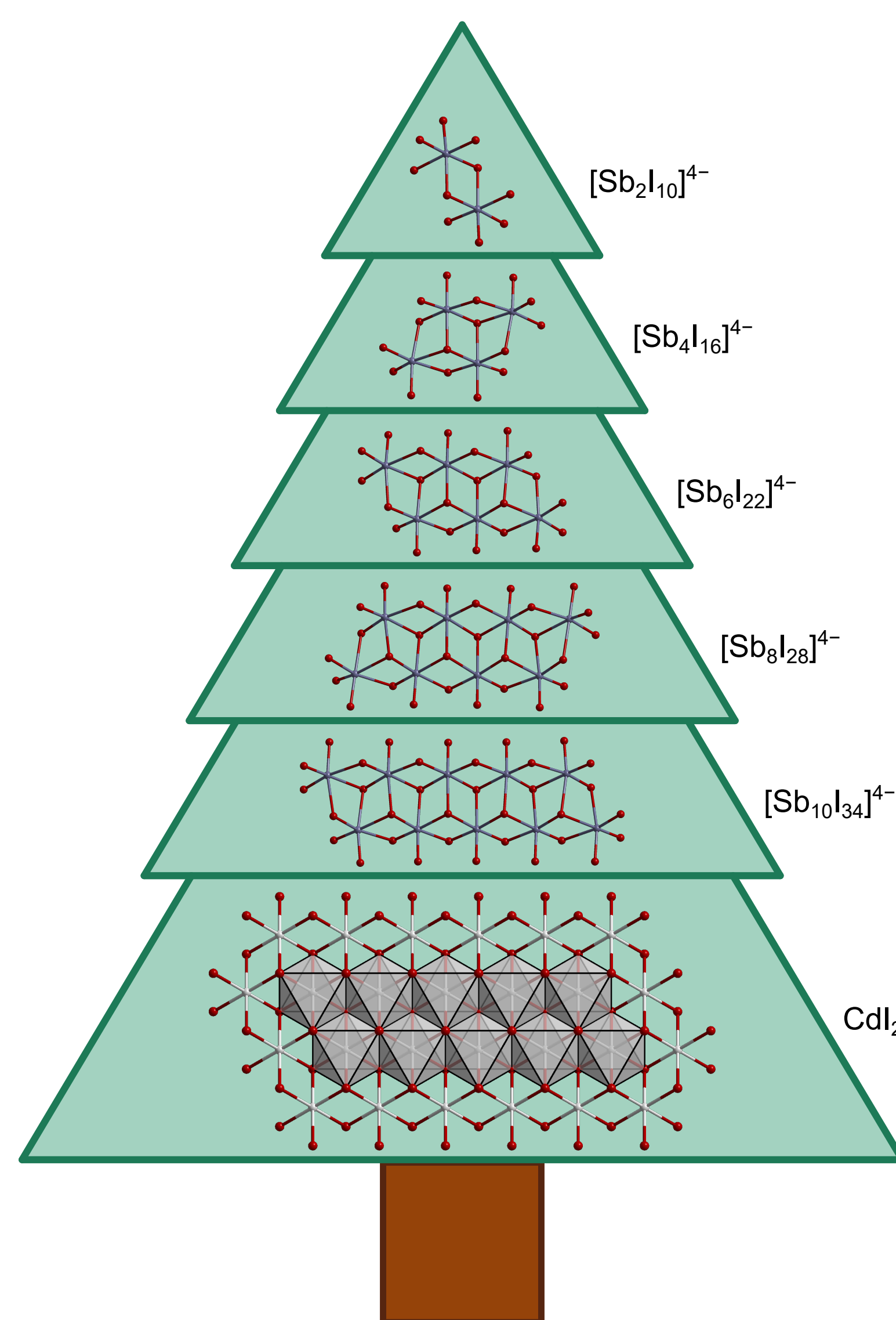
Halogenido complexes of heavy group 15 elements generally show semiconducting properties. This makes them interesting as substitutes for their excellently performing but also toxic lead counterparts like the famous methylammonium lead iodide.[1] However, especially the family of iodido antimonates is still scarcely investigated and the literature even states somewhat contradicting information with regard to the optical band gaps of these compounds. For example, the published band gaps for compounds featuring the one dimensional $[\text{SbI}_5]^{2-}$ -anion reach from 1.79 eV up to 2.41 eV [2-5], although data of closely related bismuth compounds suggests that this range should be much smaller.[6]

Recently we were able to synthesize $[\text{Hpyz}]_4[\text{Sb}_{10}\text{I}_{34}]$ (pyz = pyrazine, $\text{N}_2\text{C}_4\text{H}_4$), which features the largest discrete halogenido pentelate anion yet. Its structural motif can be understood as a cut-out from the CdI_2 -structure-type. This motif is common for iodido antimonates and ions of this type with the general formula $[\text{Sb}_{2n}\text{I}_{6n+4}]^{4-}$ are known for $n = 1 - 5$. [7-9] We decided to prepare all the compounds of this series and investigate their optical properties under closely monitored and equal conditions since the comparability of the published data is quite limited due to differing spectroscopic setups. This way we were able to analyze the influence of the anion size on the optical band gap. In addition we also carried out theoretical calculations to back up our experimental findings and shed some more light on the electronic structure of iodido antimonates close to the absorption edge.

UV-vis spectra

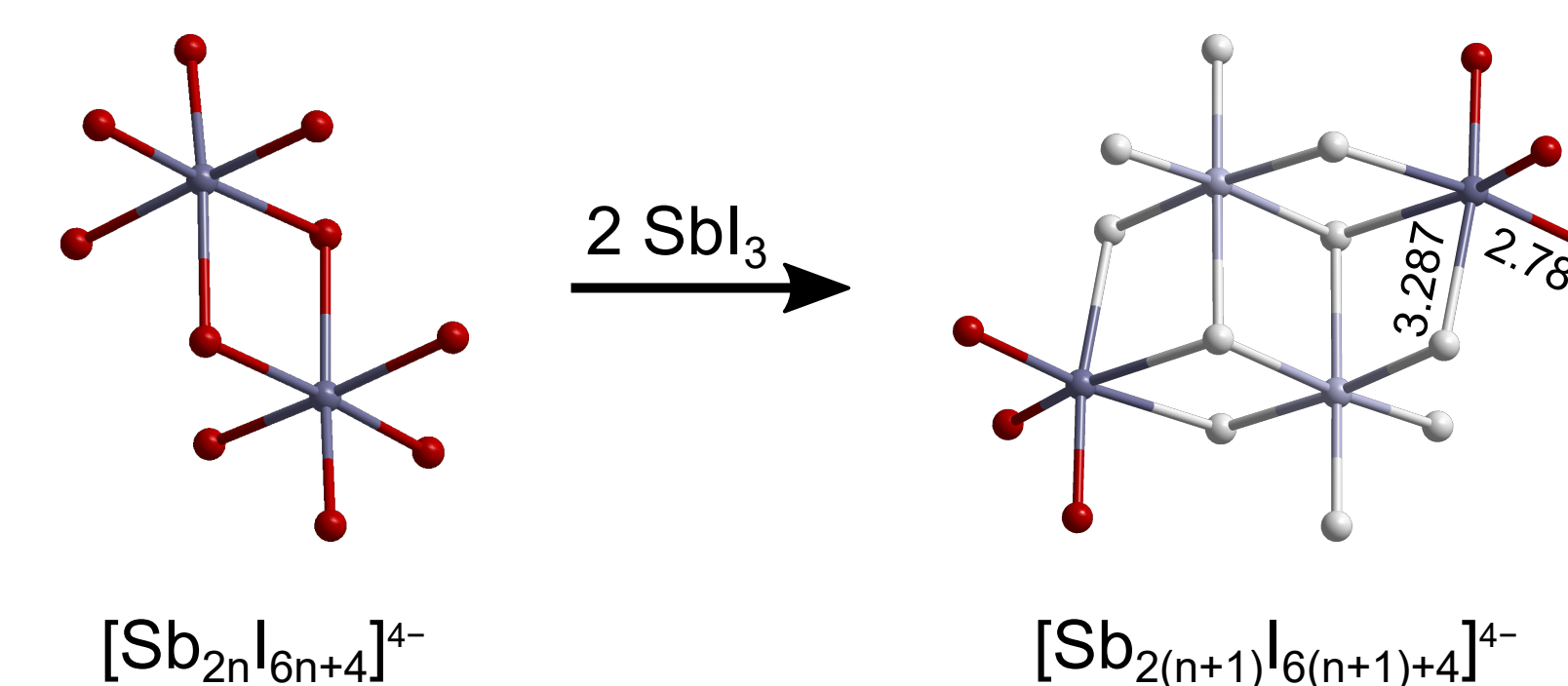


The Tauc-plots from diffuse reflectance uv-vis data (~10 % substance in BaSO_4) reveal that the band gaps of the compounds with the bi- to octa-nuclear anions lie quite close together, while that of the deca-nuclear anion is significantly smaller. Still a general trend of narrowing band gaps with increasing anion size can be observed. The only exception here is the $[\text{Sb}_8\text{I}_{28}]$ -compound, whose band gap lies slightly above that of the $[\text{Sb}_6\text{I}_{22}]$ -compound. It should be noted that due to its very steep absorption edge the band gap of the $[\text{Sb}_4\text{I}_{16}]$ -compound seems much smaller on first glance than it actually is. Linear interpolation of the background region and the edge region of the spectra place it neatly between the band gaps of the compounds with bi- and hexa-nuclear anions.



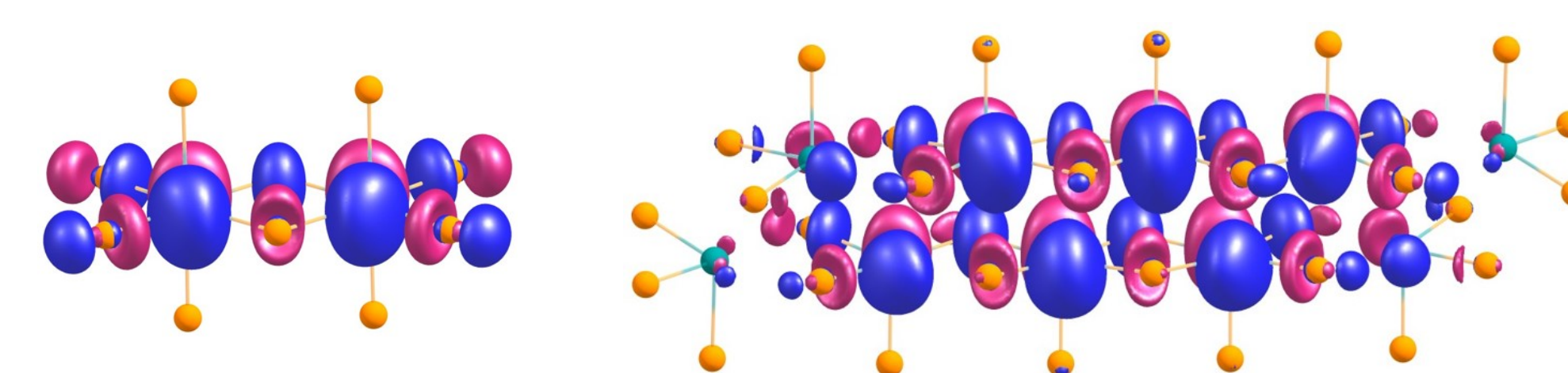
Crystal structures

The novel $[\text{Sb}_{10}\text{I}_{34}]^{4-}$ -anion is made up of a double row of edge sharing SbI_6 -octahedra. It is the largest known representative of the series of analogous ions shown in the center. Starting from the small di-nuclear ion the next layer one can always be constructed by adding neutral SbI_3 -molecules to opposing sides of the previous ion. This leads to a connectivity of the octahedra that is found in the same way in the layered CdI_2 -structure, so that the $[\text{Sb}_{2n}\text{I}_{6n+4}]^{4-}$ -ions can also be viewed as cut-outs of those layers. In each ion except for the bi-nuclear one the "latest" SbI_3 -units are still recognizable as the corresponding terminating Sb-I bonds are shortened while the bridging Sb-I bonds to these out-most antimony atoms are significantly elongated. Generally the SbI_6 -octahedra in the center of the double row are only slightly distorted with the distortion increasing towards the ends of the row.



Theoretical investigations

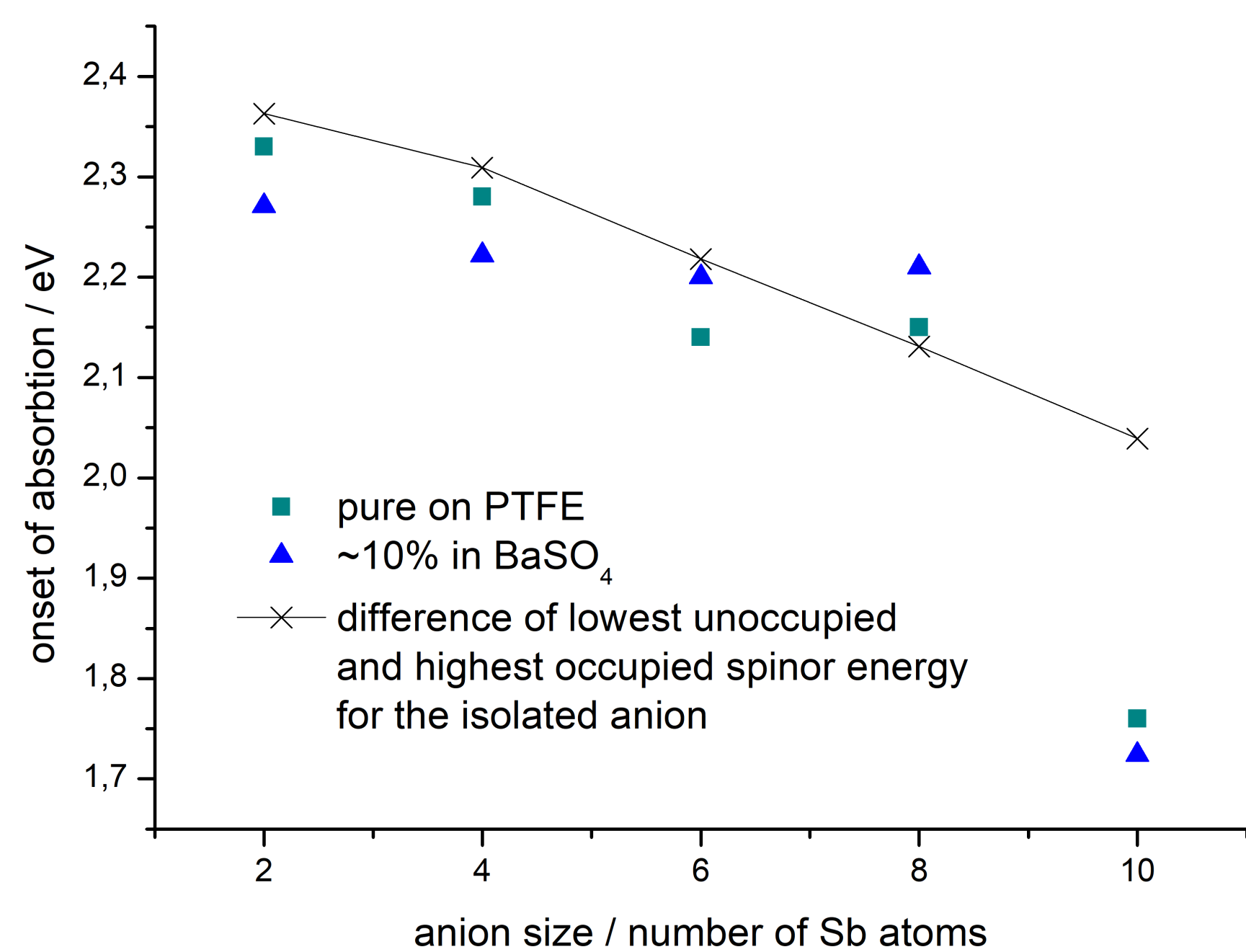
We carried out DFT calculations [10] on the isolated anions (PBE-functional, exact two-component decoupling [11] with x2c-TZVPall-2c bases; charge compensation with the conductor-like screening model). Lowest electronic excitations happen from the highest occupied to the lowest unoccupied spinor, their energies are very close (<0.1 eV) to the corresponding spinor energy gaps. Neglecting spin-orbit coupling yields excitation and gap energies larger by ca. 0.4 eV, but facilitates the more intuitive discussion based orbitals: Non-bonding I-lone pairs form the set of highest occupied, strongly Sb-I-antibonding that of lowest unoccupied orbitals. Both sets are energetically well separated from the other orbitals. The energy difference between the centers of the two sets stays the same throughout the series, while the anti-bonding set "fans out" towards lower energies for increasing anion size. This narrows the HOMO-LUMO gap and makes the LUMO less antibonding, as visible in the LUMO of $[\text{Sb}_{10}\text{I}_{34}]^{4-}$, where also some weak bonding interactions can be spotted. The very low measured band gap of $[\text{Hpyz}]_4[\text{Sb}_{10}\text{I}_{34}]$ is reproduced when the cations are included in the calculations: it comes from a strong charge-transfer excitation into the π -orbitals of the cation, which are the LUMOs of the composed system.



LUMO of $[\text{Sb}_2\text{I}_{10}]^{4-}$

LUMO of $[\text{Sb}_{10}\text{I}_{34}]^{4-}$

Measured optical band gaps and calculated energy gaps



Conclusion

Our measurements and calculations show that there is in fact a clear dependence of the optical band gap of iodido antimonates and the size of the anion, even if the widely scattered numbers reported throughout literature suggest otherwise. Although this finding is not surprising, as the far better investigated bismuthates show similar trends, the proof of this concept is important information when designing new semiconductors and tailoring synthesis routes towards promising new materials.

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