Probing the Intriguing Differences and Similarities in the Electronic Structure of 3D and 2D Halide Perovskites

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Two-dimensional (2D) halide perovskites have gained widespread interest due to their ability to enhance both the stability and efficiency of perovskite-based solar cells when used as interlayers. Investigating their electronic structure and comparing it with their 3D counterparts is crucial for improving our understanding and optimizing their application in devices. While changes in band gap and crystal structure are well established, the unique electronic structure and energy level positions of 2D perovskites remain less understood. Current literature reports disagree on whether both the valence and conduction bands are playing a role in increasing the band gap. If both energy levels are affected and move away from the center of the band gap, then this increase in ionization energy (IE) and decrease in electron affinity (EA) would result in a straddling junction (so-called type I) when combining a 2D with a 3D perovskite layer. While several studies come to this conclusion, a similar number of studies finds that the IE is barely affected or even decreases for the 2D perovskites, resulting in the prediction of a type II staggered junction between 2D and 3D layers.

In this talk, I will present a systematic study of lead-iodide-based Ruddlesden-Popper (RP) type 2D perovskites, focusing on systems with n = 1, where alkylammonium spacer cations of varying lengths were inserted. This allows tuning of the spacing between the inorganic PbI_x sheets from 12.62 Å (for propylammonium) to 21.38 Å (for decylammonium).

Using UV photoelectron spectroscopy (UPS), we compared the occupied density of states in RP films with different spacer lengths to that of the 3D perovskite $MAPbI_3$. Distinct differences were observed, which can be understood through density functional theory (DFT) calculations performed by Viren Tyagi and Shuxia Tao from TU Eindhoven. The comparison of DFT and UPS results suggests that all 2D surfaces are terminated by organic cations, which increasingly influence the spectral shape for longer chain lengths.

Surprisingly the ionization energy, i.e. valence band position, is barely affected by the change in dimensionality (3D → 2D) or when increasing the spacing of the inorganic sheets (propylammonium → decylammonium). Similar ionization energies in the range of 6 to 6.3 eV are found. The results therefore indicate that for the RP perovskite systems studied here, neither the reduction in dimensionality nor the increasing interlayer spacing significantly affect the position of the VB. This suggests that the increase in band gap, which is occurring upon 2D formation, must be due to an upward shift in conduction band. Unfortunately, inverse photoelectron spectroscopy measurements were not possible on these 2D systems, so we are unable to proof this CB change directly.

Throughout this study, a linear readout method was used to determine the valence band onset from the measured density of states. As sometimes also semi-logarithmic plots are evaluated in the literature I want to compare the findings of both readout procedures and encourage a discussion on the validity of either approach. Notably, even in the semi-logarithmic plot no significant variation in IE values between 3D and 2D perovskites was found. Using a dynamic range of three orders of magnitude for the main valence band feature, IE values consistently fall between 5.5 and 5.6 eV.

Finally, I will briefly discuss variations in optical properties for 2D films with different organic cations. Interestingly, no direct correlation with interlayer spacing is observed, instead an odd-even effect emerges. Films containing alkyl chains with an even number of carbon atoms exhibit the same optical gap, while some of the odd-numbered compounds show larger gaps. DFT calculations confirm this trend, linking it to variations in the Pb-I-Pb bond angle within the inorganic sheet, which arise from the less efficient packing of odd-numbered spacer molecules.