

Electronic Structure of a Series of Two-dimensional Metal Halide Perovskites

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Air, moisture, and light vulnerabilities in the standard bulk metal halide perovskites (MHP) have led to considerable interest in the seemingly more stable homologous two-dimensional (2D) layered MHPs (2D-MHPs), of the type $A'_2A_{n-1}M_nX_{3n+1}$, where n is the number of inorganic repeat layers sandwiched between the organic ligands. These 2D-MHPs no longer exhibit the “perovskite” structure, and are more accurately described as Ruddlesden-Popper phases, still, they frequently bear the name “perovskites” in the literature due to their similarities to bulk MHPs in terms of constituents, properties, processing and applications. These 2D-MHPs, first synthesized in the 1990’s [1], have recently found applications as active layers for light-emitting diode and solar cell devices [2], as well as capping layers for bulk MHP cells, and also have the potential to serve in tandem solar cells. They have therefore recently been the object of considerable attention [3], and the importance of these materials warrants therefore in-depth investigations of their electronic properties.

Here we present recent electronic structure measurements of a series of solution-processed films of 2D butylammonium methylammonium lead iodide compounds, $BA_2MA_{n-1}Pb_nI_{3n+1}$, $n=1$ - 4. X-ray diffraction (XRD), atomic force microscopy (AFM), UV-vis absorption, and ultra-violet and inverse photoemission spectroscopies (UPS, IPES) and density functional theory calculations are used to investigate these compounds [4]. We measure valence and conduction band spectra, and determine ionization energy (IE), electron affinity (EA) and single particle gap as a function of n . We find that the single particle gap decreases from 2.77 eV for $n=1$ to 1.87 eV for $n=4$ (and 1.6 eV for the bulk MHP MAPbI₃), with IE decreasing and EA increasing in a nearly symmetric fashion, in contrast to previous results [3]. We use the single particle gap and the onset of optical absorption at the exciton peak to calculate the exciton binding energy E_B . In agreement with previous results, E_B is found to be large for $n=1$ and 2 (390 and 110 meV, respectively). However, we also find that the exciton binding energy decreases very rapidly thereafter, reaching below 50 meV by $n=3$.

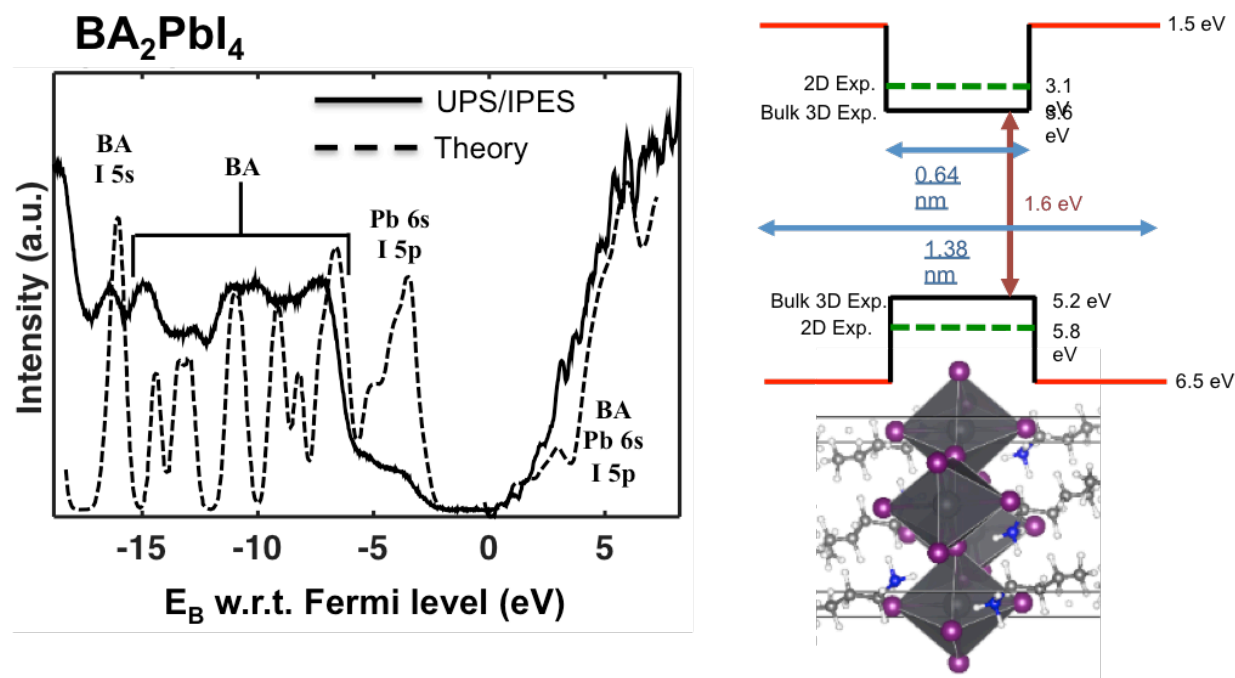


Figure: (left) DOS of BA_2PbI_4 as determined by UPS (He-II) and IPES experiments and DFT carried out at the HSE+SOC level as solid and dashed lines, respectively. (right) quantum well formed in BA_2PbI_4 . The ground state levels for the hole and electron are indicated by dashed lines.

The combination of experimental UPS/IPES measurements with the theoretical calculations performed on BA_2PbI_4 and BA_2PbBr_4 allows to precisely distinguish the contributions of the inorganic elements (Pb, I) from that of the organic elements (BA) in the valence and conduction band density of states (*Figure, left*). This leads to the determination of the depths of the valence and conduction quantum wells corresponding to the 2D layer, with the organic ligands constituting the confining potential barriers (*Figure, right*). This process opens an interesting avenue to design the organic ligand in order to modulate the depth of this quantum well. Finally, a simple model derived from the Kronig-Penney model adapted for superlattices is used to justify the electron and hole energy levels and the single particle gap in these quantum wells structures.

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