

Low density of states at the valence band maximum of Metal Halide Perovskites: A Combined Experimental - Theoretical Study

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World-wide interest in hybrid metal halide perovskites has spurred numerous theoretical and experimental investigations of the electronic properties of these materials and their interfaces. Of specific interest for device engineering are electronic parameters such as ionization energy (IE), electron affinity (EA) or work function, which are key to understanding the energetics of interfaces formed between halide perovskites and organic or inorganic interlayers and carrier extraction/injection layers used in devices.

Direct and inverse photoemission spectroscopies are techniques of choice to investigate these materials and interface properties, and several studies have now been reported for halide perovskites and their interfaces. Emara *et al.*¹ used ultra-violet photoemission spectroscopy (UPS) to investigate methylammonium lead iodide (MAPbI₃) surfaces as a function of preparation method and film stoichiometry, and reported significant variations in IE. Miller *et al.*² reported X-ray photoemission spectroscopy (XPS) measurements of the valence band of MAPbI₃ films deposited on various substrates. Schulz *et al.* reported UPS and inverse photoemission spectroscopy (IPES) of MAPbI₃ and its bromide analogue, MAPbBr₃, and associated interfaces with hole and electron extraction layers.^{3,4} Endres *et al.*⁵ investigated the electronic structure of

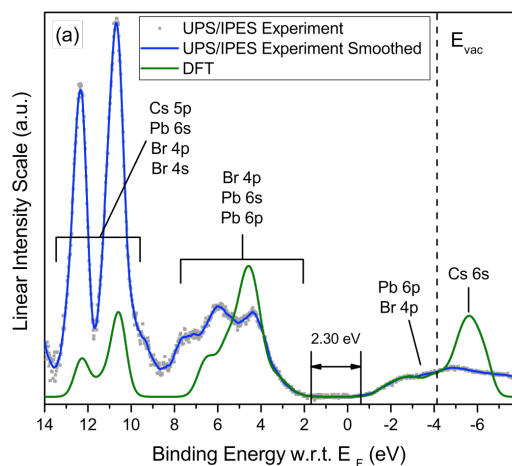


Figure 1: Comparison between UPS and IPES spectra measured from CbPbBr₃ and DFT-based theoretical simulations, plotted on a linear intensity scale. The energy scale is referenced to the Fermi level, E_F (0 eV). The position of the vacuum level E_{VAC} is indicated. Major atomic orbital contributions are indicated. (After⁶)

an interface between CsPbBr₃ and a hole-transport polymer as a function of the polymer p-doping. These investigations have pointed out several experimental issues such as the instability of some halide perovskite surfaces under vacuum irradiation, and the difficulties in pinpointing band edges and evaluating both IE and EA of these materials based on photoemission data.

In this talk, we describe a combined experimental – theoretical investigation⁶ of the valence and conduction band densities of states of three lead halide perovskites, MAPbI₃, MAPbBr₃ and CsPbBr₃. UPS and IPES spectra of the three compounds are collected on samples grown at two different institutions on different substrates. Theoretical densities of states (DOS) of the three compounds are calculated via hybrid density functional theory, including spin-orbit coupling. The very good agreement achieved between

experiment and theory, following standard corrections of the computation for band gap and energy scale, leads to the identification of all valence and conduction band spectral features, and allows a precise determination of the position of the band edges, and thus IE and EA of the materials (Fig. 1).

Most importantly, this comparison of experimental and theoretical spectra reveals an unusually low density of states at the valence band maximum (VBM) of these compounds. This had been anticipated in our initial UPS investigations of MAPbI₃ and MAPbBr₃, where data were recorded on a logarithmic scale in order to enhance signal at the VBM and obtain an energy gap consistent with optical absorption onsets. This peculiar aspect of the valence band DOS explains in part the fluctuations of reported values of IE on these compounds, generally based on standard extrapolation methods used in photoemission studies of semiconductor band edges. In that regard, it also relates to a recent investigation⁷ of quantum dots of a different Pb-containing compound, PbS, which similarly concluded that the DOS at the top of the valence band is too low for the determination of the VBM using standard linear extrapolation of UPS/XPS data. Finally, it is consistent with the recent theoretical predictions by Kawai *et al.*,⁸ who showed a large dispersion and a low DOS at the MAPbI₃ VBM, due to the strong coupling between I 5p and Pb 6s anti-bonding orbitals.

Finally, we conclude the talk by considering implications of such a low DOS at the band edges for device behavior, in particular halide perovskite solar cells, as recently proposed.

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