



**Experiment title: X-Ray spectroscopic study of metal-oxide/light absorption perovskite heterojunctions for solid-state solar cell applications**

**Experiment number:**  
CH4414

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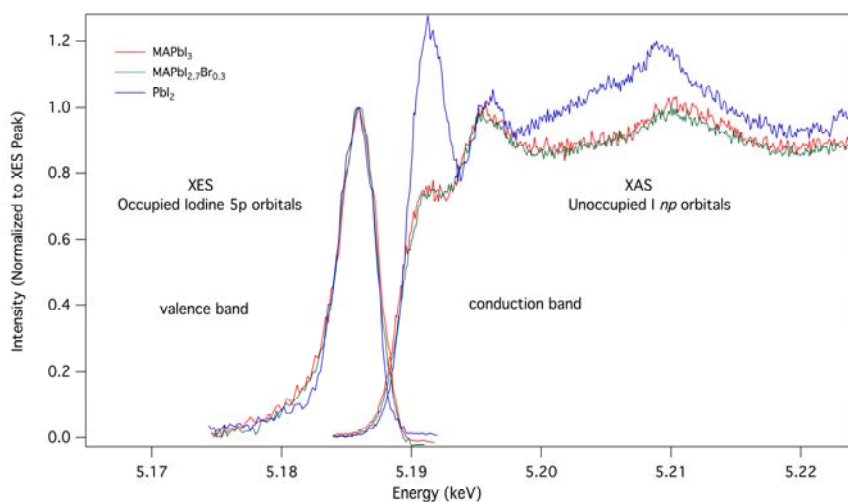
## Report:

X-Ray absorption (XAS), x-ray emission (XES), and resonant x-ray emission (RXES) spectroscopies are powerful tools to probe the electronic structure of new solar cell materials. Thus far, only calculations have probed the partial density of states for Iodine in the conduction and valence band regions. With the advent and proliferation of synchrotron sources with high brilliance, there are broader opportunities to use these tools for more sensitive samples. Due to the small spot size and flux orders of magnitude higher than conventional sources, one is effectively able to probe this promising solar material without damaging it.

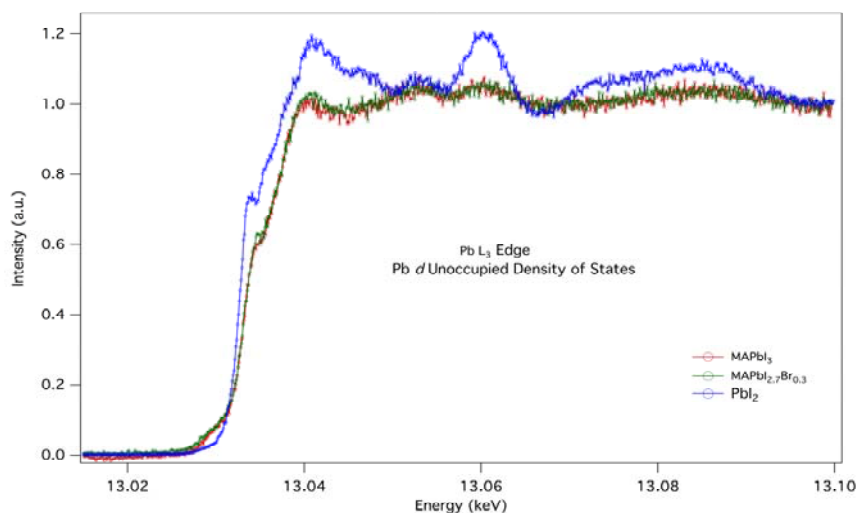
Here we report on the investigation of high-energy-resolution fluorescence-detected x-ray absorption near edge structure (HERFD-XANES) of inorganic-organic mixed halide perovskites, namely  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_{2.7}\text{Br}_{0.3}$ . HERFD-XANES, XES, and RIXS setup at ID26, equipped with a wavelength dispersive spectrometer using bent Bragg crystals, allows one to probe the unoccupied states of Iodine with significantly improved resolution not available in conventional XAS. The second portion of the experiment was valence-to-core XES on the Iodine partial densities of states. By tuning the incident energy to salient features of the absorption edges, the various valence states can be resonantly enhanced. This enables an accurate determination of the spectral weight corresponding to each

valence character, thus providing a precise picture of occupied states. The samples were cooled to 100 K and the Rowland circle was kept in a pressurized helium bag, and no preparation was necessary. A time scan of the samples was performed with no observed damage to desired signals.

HERFD-XANES at the Iodine  $L_1$  ( $2s-5p$  transitions) was probed using the ID26 x-ray spectrometer set to the maximum of Iodine  $L_{\gamma_{2,3}}$  ( $4p-2s$ ) emission line along with XES spectra is displayed together in Figure 1. The XANES spectra were measured at a fixed spectrometer energy set to 5.066 keV. The spectra measured show the unoccupied and occupied partial density of states for iodine in the doped and undoped material compared with the reference and precursor  $PbI_2$ . They have very similar spectral features (as well as at the Lead  $L_3$  edge shown in Figure 2 where the unoccupied Pb  $s,d$  states are probed), since the Bromine doping concentration was only 30%, which alters the band gap slightly. In the future, we expect to replace the Iodine entirely with Bromine, which is expected to have different spectral weights in the conduction band.



**Figure 1 (left):** HERFD-XANES at the Iodine  $L_1$  edge and valence-to-core XES spectra taken for  $CH_3NH_3PbI_3$ ,  $CH_3NH_3PbI_{2.7}Br_{0.3}$ , and our reference  $PbI_2$ . The onset of absorption for  $MAPbI_3$  is slightly before  $MAPbI_{2.7}Br_{0.3}$  due to a smaller band gap. The spectra are normalized for clarity.



**Figure 2 (left):** HERFD-XANES at the Lead  $L_3$  edge taken for  $CH_3NH_3PbI_3$ ,  $CH_3NH_3PbI_{2.7}Br_{0.3}$ , and our reference  $PbI_2$ . The spectra are normalized for clarity.

*Let us highlight that new proposal (standard) was recently submitted along with this report to study the Lead and Bromine partial density of states in the conduction and valence bands. This knowledge will allow us to tailor these materials with dopants that alter the electronic band gap states, and to better gaps the fundamental electronic structure of these solar cell materials.*