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Impact of Atomic Structure on Absolute Energy Levels of Methylammonium Lead Iodide Perovskite

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There has been a staggeringly rapid increase in the photovoltaic performance of methylammonium lead iodide ($MAPbI_3$) perovskite - greater than 19 percent solar cell power conversion efficiency has been reported in less than five years since the first report in 2009. Despite the progress in device performance, structure-property relationships in $MAPbI_3$ are still poorly understood. I will present our recent findings on the impact of changing the Pb-I bond length and Pb-I-Pb bond angle on the electronic structure of $MAPbI_3$. By using the combination of temperature dependent X-ray scattering, ultraviolet photoelectron spectroscopy, absorbance and PL spectroscopy, we show that the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) shift in the same direction as $MAPbI_3$ goes through tetragonal-to-cubic structural phase transition wherein the rotational angle of PbI_6 octahedra is the order parameter of the transition. Our experimental results are corroborated by density functional theory calculations which show that the lattice expansion and bond angle distortion cause different degree of orbital overlap between the Pb and I atoms and the anti-bonding orbital nature of both HOMO and LUMO results in the same direction of their shift. Moreover, through pair distribution function analysis of X-ray scattering, we discovered that the majority of $MAPbI_3$ in thin film solar cell layer has highly disordered structure with a coherence range of only 1.4 nm. The nanostructuring correlates with a blueshift of the absorption onset and increases the photoluminescence. Our results underscore the importance of understanding the structure-property relationships in order to improve the device performance of metal-organic perovskites.