



# INSTITUTE SEMINAR

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## SPEAKER

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## TITLE

**Halogen in Materials Design: Revealing the Nature of Halogen-Centered Non-Covalent Interactions in the Polymorphic Transformations of Methylammonium Lead Trihalide Perovskites**

## ABSTRACT

The use of methylammonium lead halide perovskites as photovoltaic materials has recently attracted a great deal of interest (see, for examples, *Sci. Adv.* **2017**, *3*, e1602165; *Nature* **2017**, *545*, 208–212). Factors that are important in their application in optoelectronic devices include their fractional contribution of the composition of the materials as well as their microscopic arrangement that is responsible for the formation of well-defined macroscopic structures.  $\text{CH}_3\text{NH}_3\text{PbX}_3$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) assumes different polymorphs (orthorhombic, tetragonal and cubic) depending on the evolution temperature of the material. An understanding of the structure of these compounds will assist in rationalizing how halogen-centered non-covalent interactions play an important role in the rational design of these materials. Periodic and non-periodic Density Functional Theory (DFT) calculations have been performed on polymorphs of  $\text{CH}_3\text{NH}_3\text{PbX}_3$  ( $\text{X} = \text{Br}, \text{Cl}$ ) to demonstrate that the H atoms on C of the methyl group in  $\text{CH}_3\text{NH}_3^+$  entrapped within a  $\text{PbX}_6^{4-}$  perovskite cage are not electronically innocent, as is often contended (e.g., *Chem. Mater.* **2017**, *29*, 5974–5981). In this presentation, I will show using the results of the current state-of-the-art computational methods that they are involved in attractive interactions with the surrounding halides of corner-sharing  $\text{PbX}_6^{4-}$  octahedra of the  $\text{CH}_3\text{NH}_3\text{PbX}_3$  cage to form the  $\text{X}\cdots\text{H}(-\text{C})$  hydrogen bonding interactions. This is analogous to the way the H atoms on N of the  $-\text{NH}_3^+$  group in  $\text{CH}_3\text{NH}_3^+$  form  $\text{X}\cdots\text{H}(-\text{N})$  hydrogen bonding interactions to stabilize the structure of  $\text{CH}_3\text{NH}_3\text{PbX}_3$ . Both these hydrogen bonding interactions are shown to be persistent regardless of the nature of the polymorphic forms of  $\text{CH}_3\text{NH}_3\text{PbX}_3$ . These, together with the  $\text{X}\cdots\text{C}(-\text{N})$  carbon bonding, the  $\text{X}\cdots\text{N}(-\text{C})$  pnictogen bonding, and the  $\text{X}\cdots\text{X}$  lump-hole type intermolecular non-covalent interactions, are shown to be collectively responsible for the eventual birth of the orthorhombic geometry of the  $\text{CH}_3\text{NH}_3\text{PbX}_3$  system. While octahedral tilting has shown to be an important attribute controlling the photovoltaic properties, it is found in this study that this is not a solid state phenomenon since it can readily be produced even in the gas phase calculations without periodic boundary condition. All these conclusions are arrived at as a result of DFT and Quantum Theory of Atoms in Molecules calculations carried out on the various polymorphs of  $\text{CH}_3\text{NH}_3\text{PbX}_3$ .