

## Hybrid perovskite photovoltaic materials under the atomistic microscope

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The field of photovoltaics is witnessing a revolution. The efficiency of *perovskite solar cells* has multiplied over six times since its emergence in 2009 [1]. Despite the large solar conversion efficiency, the mechanism for the remarkable light absorbing properties remains largely unknown.

The solar-to-electrical conversion of a solar cell proceeds via elementary quantum mechanical processes which convert light into electron-hole pairs. To further understand these processes, we choose an atomistic quantum mechanical description. At the atomic scale, hybrid perovskites consist of an inorganic perovskite scaffold (e.g. lead iodide ( $\text{PbI}_3$ ), whose holes are filled with organic molecules (e.g. methyl ammonium (MA:  $\text{CH}_3\text{NH}_3$ )) [2]. The atomic structure of the record breaking methyl ammonium lead iodide (MA)PbI<sub>3</sub> perovskite is shown in Figure 1.

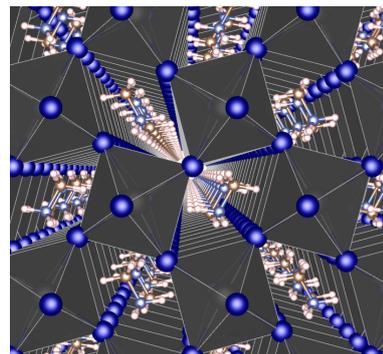


Figure 1: Atomic structure of  $(\text{CH}_3\text{NH}_3)\text{PbI}_3$

However, the structure of hybrid perovskites is not as static as Figure 1 suggests. Alternatively, according to recent literature reports [3], the structure may fluctuate considerably at temperatures above room temperature

Our *ab initio* molecular dynamic calculations and observations agree with recent studies [3] in that, above room temperature, the tilting motion of the octahedra is so large that perturbation theories (and eventually quasi-harmonic approximations) are no longer valid for this system under solar cell operating conditions. Simultaneously, our first principle calculations reveal that fundamental material properties, including carrier effective masses and optical absorption spectra, depend significantly on the octahedral tilting angle. In consequence, the temperature plays a substantial role for the efficiency of hybrid perovskites. To be able to numerically investigate the change in the optical absorption of (MA)PbI<sub>3</sub> upon structural fluctuations associated to the tilting of the inorganic network, i.e. upon temperature, we have to use first principle techniques that go beyond the ground state. To this aim, we propose a method based on Fourier decomposition of the atomic displacements that facilitates the computation of the associated absorption spectrum of any non-ground state atomic arrangement while employing a limited number of computationally intensive time-dependent density functional theory calculations. This method allows us to generate the temperature dependence of the optical absorption spectrum at low computational cost.

[1] L. Sun, *Nature Chemistry* (2015).

[2] T. Baikie *et al.*, *Journal of Materials Chemistry A*, 18, 5628 (2013).

[3] C. Quarti *et al.*, *Energy & Environmental Science*, 1, 155 (2016).