

The abstract is in English but the presentation will be in French

Eppur si muove: Proton diffusion in Halide Perovskite Single Crystals

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ABSTRACT: Ion diffusion has been demonstrated to seriously affect the optoelectronic properties of Halide Perovskites (HaPs). Till now the fastest diffusion has been attributed to the movement of the halide anions, largely neglecting the contribution of mobile protons, on the basis of computed estimates of their density. Here we prove the process of proton diffusion inside HaPs following deuterium-hydrogen exchange and migration in MAPbI₃, MAPbBr₃ and FAPbBr₃ single crystals through D/H NMR quantification, Raman spectroscopy and Elastic Recoil Detection Analysis, challenging the original assumption of halide-dominated diffusion. Our results are confirmed by impedance spectroscopy, where MAPbBr₃-based solar cells respond at very different voltage frequencies compared to CsPbBr₃-based ones. We find that water plays a key role in allowing the migration of protons as we do not detect deuteration in its absence. The water contribution is modeled to explain and forecast its effect as a function of its concentration in the perovskite structure. These findings are of great importance as they evidence how unexpected, water-dependent proton diffusion can be at the basis of the ~7 orders of magnitude spread of diffusion (attributed to I⁻ and Br⁻) coefficient values, reported in the literature. The reported enhancement of the optoelectronic properties of HaP when exposed to small amounts of water, may be related to our finding.

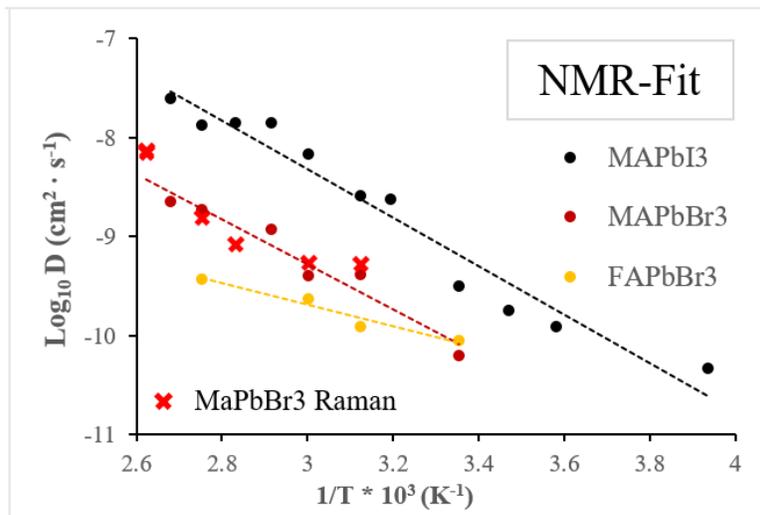


Figure : Arrhenius plot of the diffusion coefficients vs. temperature for the 3 materials investigated in this study. Circles correspond to NMR data while crosses correspond to Raman data.