NON-STOICHIOMETRY AND ION TRANSPORT IN HALIDE PEROVSKITES: EQUILIBRIUM SITUATION AND LIGHT EFFECTS

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In recent years, hybrid halide perovskites have been attracting great attention due to their exceptional photoelectrochemical properties.[1-2] When used as light-harvesters in solar cells, device efficiencies exceeding 22% can be realized. We showed that a deeper understanding of (i) functionality, (ii) stability, as well as (iii) the possibility to improve the performance require a thorough insight into non-stoichiometry and ion transport.[3-5] In this contribution, we study the nature of the ionic conductivity in methylammonium lead iodide (MAPbI₃), the archetypal halide perovskite, by means of a great number of electrochemical and nuclear magnetic techniques.[4] To aid the experimental investigation, we include detailed defect chemical modelling describing the effects of iodine partial pressure (Fig. 1a), doping and interaction with oxygen.[5] We also discuss results that show the significance of ion redistribution phenomena for relevant interfaces. By extending this study to the situation under illumination, we observe a striking enhancement of ionic conductivity by more than 2 orders of magnitude in MAPbI₃, alongside the expected increase in electronic conductivity.[6] We provide a mechanistic explanation of this astonishing phenomenon and discuss its relevance for future light-triggered ionic devices ("opto-ionics", see Fig. 1b).



Figure 1- (a) Kröger-Vink diagram depicting defect concentrations in MAPbI₃ as a function of iodine partial pressure. (b) Potential opto-ionic device in which I_2 permeation through MAPbI₃ is triggered by illumination.

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