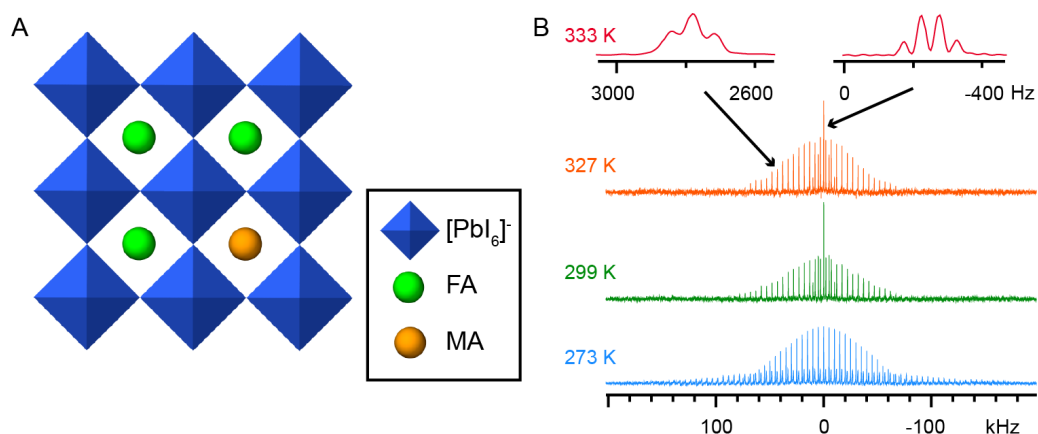


## Correlation Between Charge Carrier Lifetimes and Cation Dynamics in Mixed Double A-Cation Lead Halide Perovskites Revealed by Solid-state NMR

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Mixed cation organic lead halide perovskites emerged as an attractive alternative to silicon-based solar cells. Currently, one of the best performing materials contains 4 cations and provides power conversion efficiencies up to around 22 %.[1] Here, we report the first quantitative, cation-specific data on cation rotational dynamics in hybrid double-cation formamidinium (FA)/methylammonium (MA) lead iodide perovskites using <sup>14</sup>N and <sup>2</sup>H MAS NMR. Our findings suggest that the excellent photovoltaic properties of perovskite materials are directly correlated to cation reorientation dynamics, and corroborate the polaronic nature of charge carriers in these materials.



**Fig. 1.** A) A cartoon showing the structure of the double-cation three-dimensional perovskite phase of  $\text{FA}_{0.67}\text{MA}_{0.33}\text{PbI}_3$ , B) and the corresponding solid-state <sup>14</sup>N echo-detected variable-temperature 5 kHz MAS NMR spectra. The top insets (red) show a close-up of the isotropic peak at 333 K and 20 kHz MAS, conditions under which a characteristic splitting due to the  $J$ -coupling between the nitrogen and the proton is resolved, making the signal assignment straightforward. The arrows indicate the corresponding SSB manifolds.

[1] Saliba, M.; Matsui, T.; Domanski, K.; Seo, J. Y.; Ummadisingu, A.; Zakeeruddin, S. M.; Correa-Baena, J. P.; Tress, W. R.; Abate, A.; Hagfeldt, A.; Grätzel, M., *Science* 2016, **354**, 206.