

Title: CH₃NH₃⁺ Dynamics in CH₃NH₃PbBr₃ by Combining Solid-State NMR and Molecular Dynamics Calculations

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Content: The dynamical behavior of the organic cations in hybrid halide perovskites has triggered a wealth of experimental and theoretical investigations in the recent years. The intrinsic dynamical and electrical (dipolar) properties of the organic part were suggested to be responsible of some of the most noticeable features of these materials. Previous investigations [Phys. Chem. Chem. Phys. 2016, 18, 27133] have shown that static theoretical calculations of quadrupolar parameters (²H) in the orthorhombic phase of deuterated-MAPbBr₃ (MA = CH₃NH₃⁺), lead to an overestimation of the linewidth broadening. This was rationalized in terms of thermally activated internal rotational dynamics of the molecular cations. Impact of the dynamics is further inspected in the present paper by a joint experimental and theoretical effort with low temperature solid-state NMR measurements (< 25K). Starting from extensive Ab initio molecular dynamics trajectories performed on large (4x4x4) supercells for both the tetragonal and orthorhombic phases [J. Phys. Chem. C 2017, 121, 20729] we use a specifically designed procedure to account for the effect of the thermally activated cation dynamics in the calculated NMR parameters, which includes the quadrupolar lineshapes of the NMR spectra.

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