

Solid state NMR structural characterization of halide perovskites: the potential contribution of atomistic DFT modeling

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Halide perovskites are a complex class of semiconductors whose structure features two apparently contradictory properties: long-range order associated to the regular crystalline structure,[1] and short-range dynamic disorder, related to the soft nature of the lattice and the libration motion of the organic cations.[2] While the former feature is routinely addressed via X-ray diffraction techniques, the latter requires more local “probes”, with solid state Nuclear Magnetic Resonance (NMR) being an ideal method-of-choice, in light of its sensitivity to local chemical composition and environment, as demonstrated in the recent literature [3-6]. However, the complex line-shapes of solid state NMR measurements, as due to the inherent anisotropic response of this technique, make their interpretation usually a delicate task, hence calling for additional supportive tools.

Here we show how periodic DFT simulations can ease the interpretation of the NMR spectroscopic features, providing a complementary perspective to experiments. Targeting nuclei with spin-quantum number $I=1/2$ for 3D methylammonium lead iodide, bromide and mixed halide systems, we demonstrate the reliability of DFT in reproducing experimental signatures of ^{13}C and ^1H light-atoms, with prospects in supporting the characterization of dimensionally confined or hollow perovskite architectures, where the organic component has more important structural/templating role. Quantitative prediction of ^{207}Pb nuclei is more challenging but the different response from pure phase iodide and bromide lead perovskites is well reproduced by DFT simulations. This motivated us to investigate on mixed halide compositions, confirming the sensitivity of NMR to the halide composition,[6-7] and

segregation, already at the scale of the individual PbX_6 octahedron.[8] Our results open the prospect for joint theoretical-experimental investigations of halide perovskite materials, that combine solid state NMR and periodic DFT simulations.

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