2D Ruddlesden-Popper Perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ as studied by Solid-State NMR Spectroscopy

Elena Maurina [a,b], Noemi Landi [a], Elisa Carignani [c], Silvia Borsacchi [c,d], Lucia Calucci [c,d], Daniela Marongiu [e], Michele Saba [e], Marco Geppi [a,c,d]

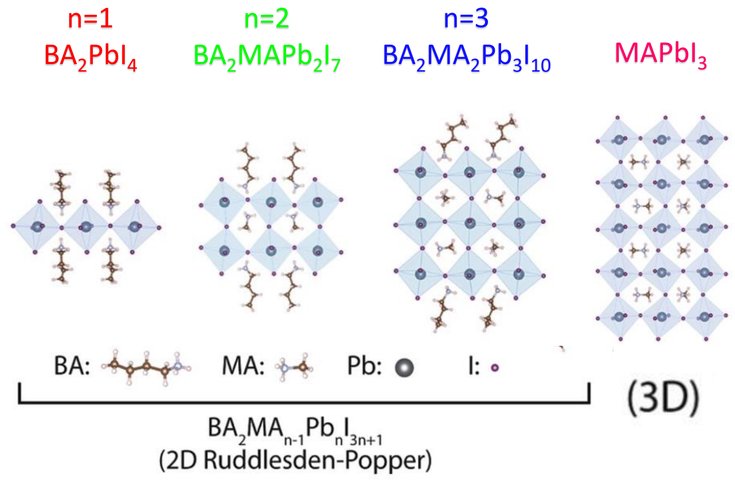
[a] *Department of Chemistry and Industrial Chemistry, University of Pisa, via G. Moruzzi 13, 56124 Pisa, Italy;* [b] *Scuola Normale Superiore, Piazza dei Cavalieri, 7, 56126 Pisa, Italy;* [c] *Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR/ICCOM, via G. Moruzzi 1, 56124 Pisa, Italy;* [d] *Center for Instrument Sharing, University of Pisa (CISUP), 56126 Pisa, Italy;* [e] *Department of Physics, University of Cagliari, S.P. Monserrato-Sestu Km. 0700, Monserrato, 09042 CA, Italy*

contacts: e.maurina@studenti.unipi.it

Introduction

2D Ruddlesden-Popper (RP) perovskites of general formula $BA_2MA_{n-1}Pb_nI_{3n+1}$ are layered materials made by n perovskite layers separated by butylammonium cations (BA). The perovskite layers consist of a network of corner-sharing PbI_6 octahedra, while the methylammonium cations (MA) fill the cavities between the octahedra. The number of perovskite layers, n, can be adjusted by tuning the stoichiometric ratio between precursors. According to XRD measurements, the polar heads of butylammonium cations are oriented towards the perovskite sheets [1].

In the present work, multinuclear Solid-State NMR was applied to investigate the structure and chemical interactions in 2D RP perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ for n=1, 2, 3 in comparison with the parent 3D compound $MAPbI_3$.



Materials and Methods

The samples were synthetized at the University of Cagliari following the recipe of Stoumpos et al. [1].

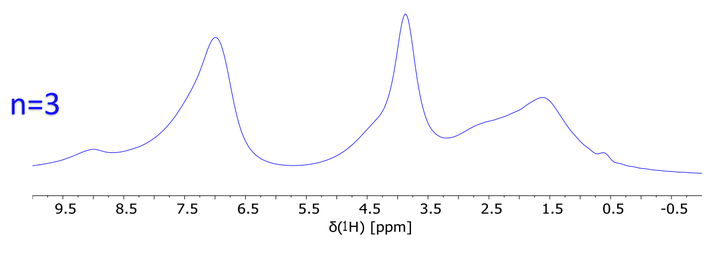
^{13}C and ^{1}H Solid-State NMR spectra were collected on a 11.7 T Bruker Avance Neo spectrometer equipped with a Bruker 2.5mm CP-MAS probe, with 90° pulse durations of 2.08 µs and 5.00 µs for ^{1}H and ^{13}C, respectively. ^{207}Pb NMR spectra were collected on a 9.4 T Varian Infinity Plus spectrometer equipped with a commercial double-resonance 3.2mm CP-MAS probe with a 90° pulse duration of 3.80 µs for ^{207}Pb.

Results

^{1}H MAS

ν_{MAS} =15 kHz

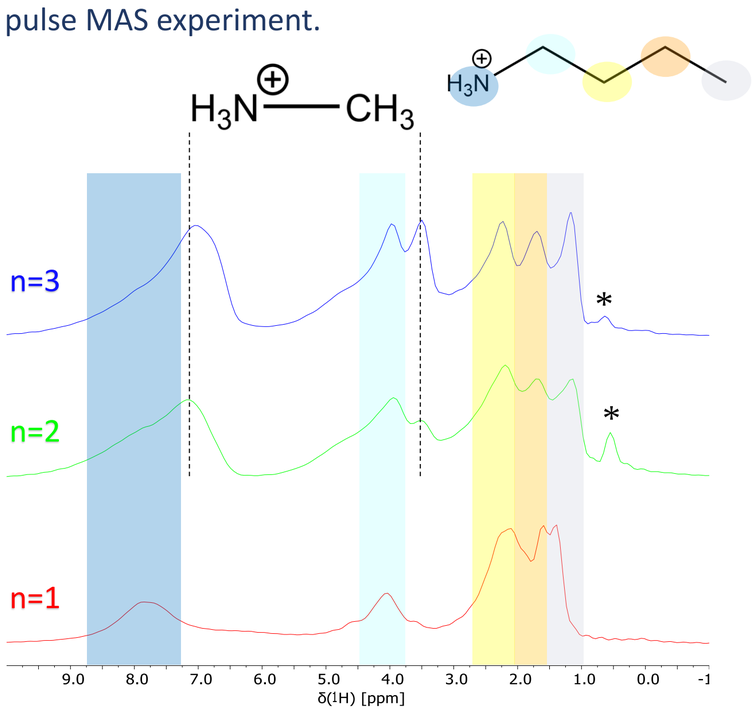
Example of achievable resolution by Magic Angle Spinning (MAS) alone.



^{1}H CRAMPS

ν_{MAS} =12 kHz

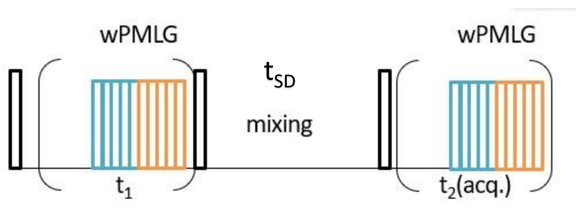
DUMBO pulse sequence was applied to increase spectral resolution with respect to the single 90° pulse MAS experiment.



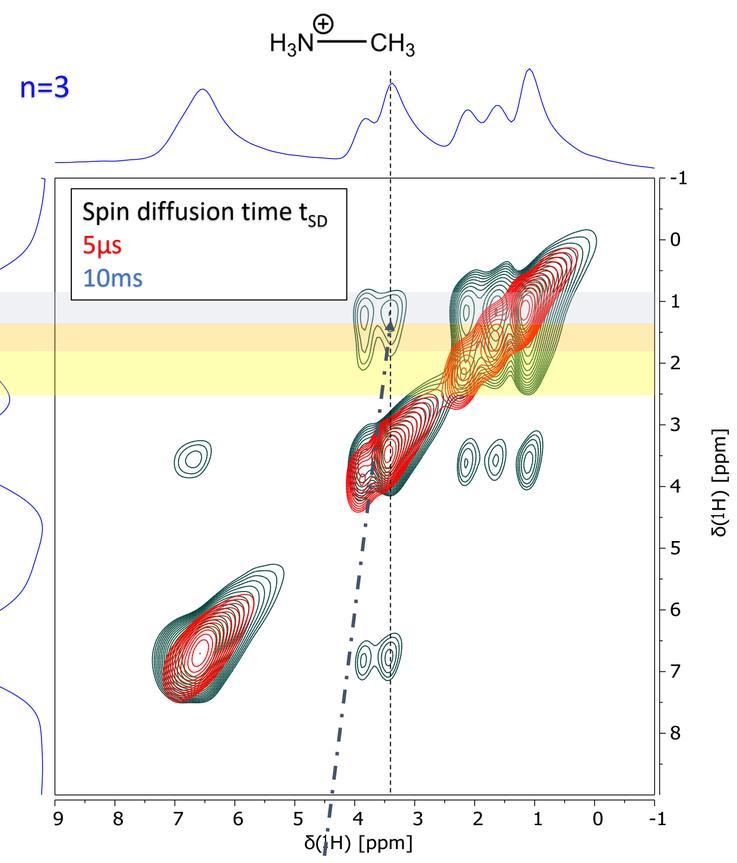
* artifacts arising from the DUMBO sequence

^{1}H-^{1}H 2D Spin diffusion correlation

(a) 2D wPMLG Spin diffusion pulse



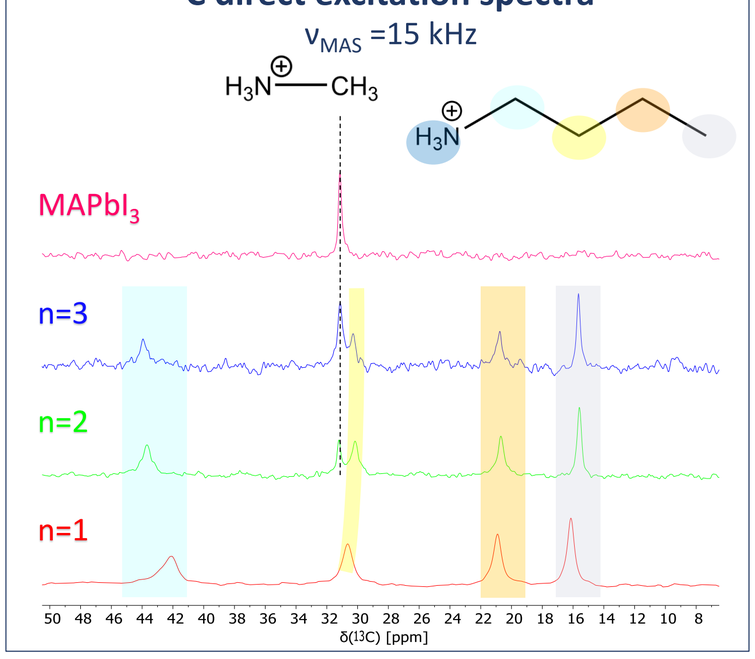
(b) ν_{MAS} =15 kHz



off diagonal peak that indicates a spin-diffusion exchange between the CH_3 protons of MA and the terminal alkyl chain of BA, proving their spatial proximity.

^{13}C direct excitation spectra

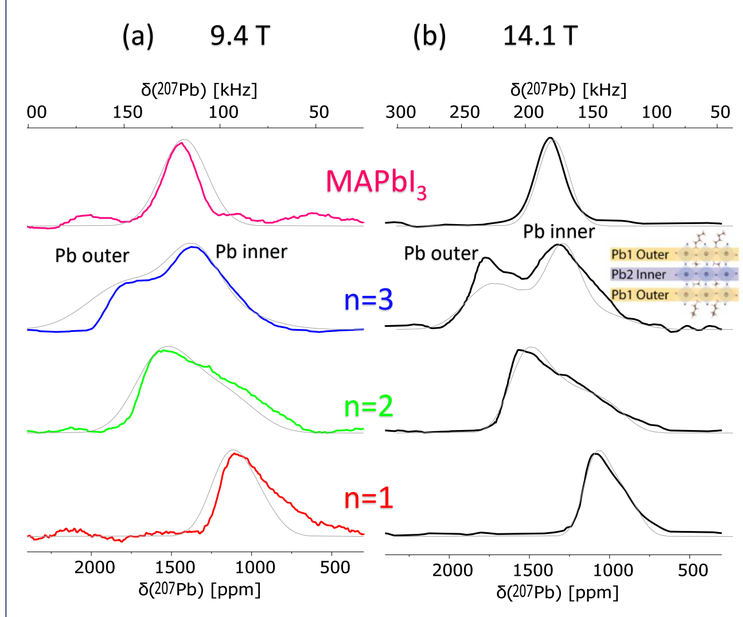
ν_{MAS} =15 kHz



^{207}Pb Hahn-echo static spectra

Comparison between our experimental result (a) acquired in a magnetic field of 9.4 T and that of Lee et al. [2] at 14.1 T (b), toghether with simulated spectra (grey) at the respective magnetic fields for the CSA tensor.

Different magnetic fields ⟷ Different line shapes



Variations in • peak positions, • line shapes and • line widths depending on n.

Discussion & Conclusions

- 2D PMLG ^{1}H-^{1}H spin diffusion experiments evidence the spatial proximity of BA and MA cations in the $BA_2MA_2Pb_3I_{10}$ perovskite.
- ^{207}Pb spectra allowed different chemical environments to be highlighted for Pb nuclei in 2D RP perovskites and in $MAPbI_3$.
- Our ^{207}Pb spectra acquired in a magnetic field of 9.4 T compared with the literature spectra [2] at 14.1 T highlight the influence of the magnetic field on the line shape.
- The good agreement between the experimental and simulated spectra at the two different magnetic fields suggest that the CSA tensor was quite well determined.

References

[1] C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, and M. G. Kanatzidis. *Chemistry of Materials,* **2016**.

[2] J. Lee, W. Lee, K. Kang, T. Lee, S. K. Lee. *Chemistry of Materials*, **2021.**

[3] A. J. Pell, R. J. Clément, C. P. Grey, L. Emsley, G. Pintacuda. *J. Chem. Phys*. 138, 114201, **2013**.

Acknowledgements

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