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Decoupled Structural Responses upon Light and Thermal Functional Activation in $CsPbBr_3$ Perovskites

Oliviero Cannelli[1], Julia Wiktor[2], Nicola Colonna[3,4], Ludmila Leroy[5], Michele Puppin[1], Camila Bacellar[5], Ilia Sadykov[5], Franziska Krieg[6,7], Grigory Smolentsev[5], Maksym V. Kovalenko[6,7], Alfredo Pasquarello[8], Majed Chergui[1], Giulia F. Mancini[9]

[1] Laboratory of Ultrafast Spectroscopy (LSU) and Lausanne Centre for Ultrafast Science (LACUS), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.
[2] Department of Physics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden.
[3] Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute, CH-5232 Villigen-PSI, Switzerland.
[4] National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.
[5] Paul Scherrer Institute (PSI), CH-5232 Villigen, Switzerland.
[6] Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland.
[7] Laboratory for Thin Films and Photovoltaics, Empa-Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland.
[8] Chaire de Simulation à l'Echelle Atomique (CSEA), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.
[9] Laboratory for Ultrafast X-ray and Electron Microscopy (LUXEM), Department of Physics, University of Pavia, I-27100 Pavia, Italy.
Author e-mail address: oliviero.cannelli@epfl.ch

Abstract: We combine time-resolved and temperature-dependent X-ray absorption spectroscopy with state-of-the-art first principles simulations to quantify light- and thermally-induced structural distortions in $CsPbBr_3$ perovskite nanocrystals with atomic-level precision.

1. Introduction

The flexibility of lead-halide perovskites plays a crucial role in their functional response, but the exact structural distortions and their effects on physical properties are still unclear [1]. Here, we provide for the first time the description of the photoinduced and thermally-activated structural distortions in $CsPbBr_3$ perovskite nanocrystals with atomic-level precision. We combine time-resolved X-ray absorption spectroscopy (TR-XAS) and *ab initio* simulations to show that the photoexcitation of $CsPbBr_3$ nanocrystals (NCs) leads to well-defined polaronic lattice changes, rather than photoinduced structural phase transitions. Additionally, our analysis rules out thermal effects in the photoactivation of the system [2]. We also investigated the purely thermal response of $CsPbBr_3$ with temperature-dependent XAS and first principles molecular dynamics (MD) simulations across its phase diagram. We show that the thermally-activated lattice cannot be reduced to a cubic average structure, because of the presence of dynamically distorted local configurations and lattice anharmonicity [3].

2. Methods

TR-XAS measurements were performed at the 7ID-D beamline at the Advanced Photon Source (APS) of the Argonne National Laboratory, exciting the $CsPbBr_3$ perovskite NCs at 3.49 eV (8.8 mJ/cm^2, 10 ps pulse duration, 1.304 MHz) and probing it at the Br K-edge (13.45-13.53 keV) with 80 ps time resolution and at 6.52 MHz [2]. The NCs were dissolved in ethanol and flowed through a liquid jet. Temperature-dependent XAS experiments were conducted at the SuperXAS beamline at the Swiss Light Source (SLS) of the Paul Scherrer Institute on dry $CsPbBr_3$ NCs in a thermostated cell holder. Br K-edge XAS spectra (13.45-13.53 keV) were collected in the 25-140 °C temperature range, across the phase diagram of the NCs, which have phase transition temperatures at T=50-59 °C and T=108-117 °C [4]. A schematic layout and the steady-state Br K-edge XAS spectra are showed in the top panels of Figure 1a and 1b, respectively. *Ab initio* MD simulations were performed using the CP2K package in the isobaric (NpT) ensemble at 27 °C and 130 °C, initialized with orthorhombic and cubic supercells of 320 atoms, respectively. The XAS spectra were computed based on DFT calculations with the Quantum ESPRESSO distribution, explicitly accounting for core hole effects on supercells of 160 atoms (320 atoms for MD-based simulations) [2,3].

3. Results

Figure 1a (bottom panel) shows the Br K-edge experimental pump-probe spectrum at 100 ps time delay (blue), obtained as the difference of the excited minus the unexcited XAS spectra, and the DFT simulations of the XAS changes induced by a polaronic distortion of the lattice (green) and by an orthorhombic-cubic phase transition (gray dotted). The pre- and main-edge features of the pump-probe spectrum are related to transient electronic effects.

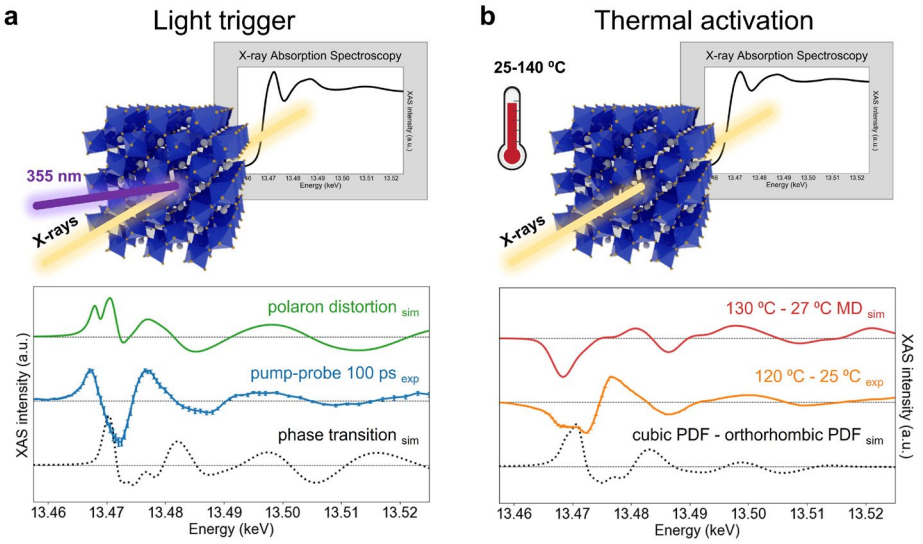

Figure 1: Br K-edge XAS spectra of $CsPbBr_3$: **(a)** pump-probe at 100 ps time delay (blue) and *ab initio* simulation for a polaronic distortion (green) and for a phase transition (gray dotted); **(b)** 120 ºC minus 25 ºC experimental XAS difference (orange), 130 ºC minus 27 ºC XAS difference from *ab initio* MD simulations (red) and cubic minus orthorhombic PDF structures (gray dotted).

Instead, the positive and negative modulations of the experiment at higher energies, which cannot be ascribed to an orthorhombic-cubic symmetry change based on the discrepancies with the phase transition simulation, are due to structural modifications of the orthorhombic lattice. The excellent agreement between experiment (blue) and simulation (green) was obtained introducing a lattice deformation along one specific longitudinal-optical (LO) phonon mode at 18.2 meV [2], for which the electron-phonon coupling is the strongest [5].

In Figure 1b (bottom panel) we report the difference XAS spectra across the Br K-edge between: (i) the 120 °C and the 25 °C in our experiment (orange); (ii) 130 °C and 27 °C from MD simulations (red), (iii) the thermal structural changes from averaged structures at 160 °C and 22 °C obtained from pair-distribution function (PDF) refinements (gray dotted) [4]. The agreement of the experiment and MD spectra shows that the T-induced XAS changes are due to an increase of dynamical disorder in the lattice [3], rather than to an increase of unit-cell symmetry. Moreover, we show that the experiment cannot be reproduced by the average structure determined through conventional PDF refinement methods (gray dotted). The observed behavior is due to the phonon anharmonicity of the lead halide sublattice, which causes the excess free energy surface to change as a function of temperature. As a result, phase transitions therein can be rationalized *via* the soft-mode model, which also describes displacive thermal phase transitions in oxide perovskites.

4. Conclusions

In this work, we demonstrate that the structural changes of $CsPbBr_3$ NCs induced by light and thermal functional triggers have fundamentally different physical origins. Even though both effects are related to the flexibility of the perovskite lattice, the photoexcitation is selectively driven by electron-phonon coupling, while the thermal activation drives lattice phonon anharmonicity, which leads to significant distortions from the $CsPbBr_3$ space- and time-average lattice symmetry, well rationalized by the soft-mode model as displacive thermal phase transitions.

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5. References

[1] T. Abraha Berhe *et al.*, 'Organometal halide perovskite solar cells: degradation and stability', *Energy Environ. Sci.*, vol. 9, no. 2, pp. 323–356, 2016, doi: 10.1039/C5EE02733K.
[2] O. Cannelli *et al.*, 'Quantifying Photoinduced Polaronic Distortions in Inorganic Lead Halide Perovskite Nanocrystals', *J. Am. Chem. Soc.*, vol. 143, no. 24, pp. 9048–9059, Jun. 2021, doi: 10.1021/jacs.1c02403.
[3] O. Cannelli *et al.*, 'Atomic-Level Description of Thermal Fluctuations in Inorganic Lead Halide Perovskites', *in prep.*, 2022.
[4] P. Cottingham and R. L. Brutchey, 'Depressed Phase Transitions and Thermally Persistent Local Distortions in $CsPbBr_3$ Quantum Dots', *Chem. Mater.*, vol. 30, no. 19, pp. 6711–6716, Oct. 2018, doi: 10.1021/acs.chemmater.8b02295.
[5] M. Puppin *et al.*, 'Evidence of Large Polarons in Photoemission Band Mapping of the Perovskite Semiconductor $CsPbBr_3$', *Phys. Rev. Lett.*, vol. 124, no. 20, p. 206402, May 2020, doi: 10.1103/PhysRevLett.124.206402.