Rotational Dynamics of Organic Cations in CH$_3$NH$_3$PbI$_3$ Perovskite

TIANRAN CHEN, BENJAMIN FOLEY, Univ of Virginia, BAHAR IPEK, Univ of Delaware, MADHUSUDAN TYAGI, JOHN COPLEY, CRAIG BROWN, NCNR, JOSHUA CHOI, SEUNG-HUN LEE, Univ of Virginia — Methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) based solar cells have shown impressive power conversion efficiencies of above 20%. However, the microscopic mechanism of the high photovoltaic performance is yet to be fully understood. Particularly, the dynamics of CH$_3$NH$_3^+$ cations and their impact on relevant processes are still poorly understood. Using elastic and quasi-elastic neutron scattering techniques and group theoretical analysis, we studied rotational modes of the CH$_3$NH$_3^+$ cation in CH$_3$NH$_3$PbI$_3$.[1]

Our results show that, in the cubic and tetragonal phases, the CH$_3$NH$_3^+$ ions exhibit four-fold rotational symmetry of the C-N axis (C$_4$) along with three-fold rotation around the C-N axis (C$_3$), while in orthorhombic phase only C$_3$ rotation is present. Around room temperature, the characteristic relaxation time for the C$_4$ rotation is found to be 5ps while for the C$_3$ rotation is 1ps. The T-dependent rotational relaxation times were fitted with Arrhenius equations to obtain activation energies. Our data show a close correlation between the C$_4$ rotational mode and the temperature dependent dielectric permittivity. Our findings on the rotational dynamics of CH$_3$NH$_3^+$ and the associated dipole have important implications on understanding the low exciton binding energy and slow charge recombination rate in CH$_3$NH$_3$PbI$_3$ which are directly relevant for the high solar cell performance. [1] T. Chen et al., Phys. Chem. Chem. Phys., 2015, DOI: 10.1039/C5CP05348J.

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