Polaron formation enables wavelength control of spin lifetimes in layered metal halide perovskites

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Layered metal halide perovskites (L-MHPs) are quantum well materials where photoexcitation results in the formation of very stable excitons.[1,2] Furthermore, L-MHPs typically exhibit a Rashba splitting of the electronic energy bands,[3] which allows the injection of spin-polarised excitons through photoexcitation with circularly polarised light, making them potential candidates for spintronics applications.[4] Recently, we have shown that it is possible to control the spin lifetime of photoexcited carriers in the L-MHP $(BA)_2FAPb_2I_7$ (where BA: Butylammonium; FA: Formamidinium) at 77 Kelvin by over two orders of magnitude by changing the excitation wavelength.[5] This was rationalized in terms of a polaron formation process that leads to a thermodynamic equilibrium between exciton and polaron states. Excitons are well-known to have spin relaxation dominated by a motional narrowing mechanism, which leads to faster relaxation at low temperatures. Polarons, however, are subject to different exchange interactions due to partial charge separation and are expected to present longer spin lifetimes at low temperatures. At low temperatures polaron formation is longer than the exciton-spin relaxation, unless excitation photons provide excess energy. However, if they do, the polaron relaxation will dominate the spin relaxation, enabling this wavelength-based control over two orders of magnitude.

In this work, we study the effect of the large cation of the perovskite structure on this process using femtosecond time-resolved Faraday rotation spectroscopy, systematically varying from the inorganic caesium $(Hexa)_2CsPb_2I_7$, to formamidinium $(Hexa)_2FAPb_2I_7$ and methylammonium $(Hexa)_2MAPb_2I_7$, where Hexa is hexylammonium. In all cases we observed the same trend of longer spin lifetime at low temperatures for excitation with excess photon energy. Moreover, all show a monoexponential spin lifetime of around 200 fs when no excess energy is provided. However, this monoexponential regime, which we attribute to pure exciton spin relaxation, is reached at different temperatures for each composition: ~64K for MA^+, ~77K for FA^+ and ~130K for Cs^+. This threshold signals the moment where exciton spin relaxation happens before any polarons can be formed, and thus offers a measure of the polaron formation barrier. These temperature thresholds follow the opposite trend of the dipole moment values of MA^+, FA^+ and Cs^+, suggesting that the larger the dipole moment of the cation, the lower the barrier of polaron formation is, indicating that the larger dipole moment helps stabilize the lattice distortion associated with polaron formation.

These results offer a general principle in terms of controlling and exploiting the wavelength dependent spin lifetime in L-MHPs for the realisation of opto-spintronic devices.

References

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