A photon ratchet route to high-efficiency hybrid halide perovskite intermediate band solar cells

Jarvist M. Frost, 1 Pooya Azarhoosh, 2 Scott McKechnie, 2 Mark van Schilfgaarde, 2 and Aron Walsh 1, 3
1) Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK 3
2) Department of Physics, Kings College London, London WC2R 2LS, UK
3) Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

The spin-split indirect bandgap in hybrid-halide perovskites provides a momentum-space realisation of a photon-ratchet intermediate band. Excited electrons thermalise to recombination-protected Rashba pockets at the same k in momentum space. A quasi-equilibrium distribution of electrons give rise to a low joint density-of-states for vertical transitions. We invoked a similar mechanism for conduction to valence band transitions in order to explain and quantify the long charge-generated carrier recombination times in lead halide perovskites with standard device architectures.

In this Letter, we propose that the spin-split indirect-gap 1 in methylammonium lead halide perovskite (CH3NH3PbI3) forms an intermediate band. A photon-ratchet effect is provided by carriers excited into this band, relaxing in momentum space to the Rashba pocket (see Figure 1). This mechanism is intrinsically present in the bulk material.

Electron-hole recombination to the valence band (VB) from both the intermediate band (IB) and conduction band (CB) is reduced by the slightly indirect gap originating from the mutually-orthogonal Rashba extremal points. Both the middle bands and the conduction bands are split due to spin-orbit coupling, but along different axes; thus none of the bands have extremal points at the same k in momentum space. A quasi-equilibrium distribution of electrons give rise to a low joint density-of-states for vertical transitions. We invoked a similar mechanism for conduction to valence band transitions in order to explain and quantify the long charge-generated carrier recombination times in lead halide perovskites with standard device architectures.

The excitation from the VB to IB is at 1.6 eV, while the direct VB to CB excitation at 3.1 eV. 5 These states are optically bright. The photon ratchet from the IB to the CB would operate at 1.6 eV. These energies are not well matched to subdivide the solar spectrum, but they are accessible in the laboratory. To exceed the SQ limit, a smaller bandgap material is required. However, we propose lead halide perovskites as a well understood test system in which the physics can be studied, to leverage expertise in making high-quality materials and devices. A working IBSC should also be an upconverter when operating at open circuit (or equivalently, with no contacts). This will require a pure material where non-radiative recombination pathways to be sufficiently suppressed to observe light output.

The higher lying conduction band provides a high dispersion (low effective mass) band from which to extract the charge carriers. The only change in device architecture required is a low work-function electron-accepting contact (such as Ba, Ca, LiF, or fulleroid adduct), to selectively collect from the higher energy CB. With suitable contacts, the material should thus be able to gener-

Keywords: photovoltaics, perovskites, recombination

1) Electronic mail: jarvist.frost@imperial.ac.uk
FIG. 1: A schematic of the proposed hybrid halide perovskite spin-split indirect-gap photon-ratchet. 3.1 eV excitation directly pumps to the higher lying conduction band. 1.6 eV excitation pumps to the spin-split indirect-gap intermediate band, where fast thermalisation relocates carriers slightly off the high symmetry location. Low hole density of states in the valence band means that direct recombination is severely reduced. Charges in this state can be excited to the second conduction band by a 1.5 eV excitation. Therefore, the direct 3.1 eV excitation and the two-step photon-ratchet proceed simultaneously, and energy can be extracted from the higher lying conduction band.

ate an anomalous photovoltage, above circa. 3 eV) when pumped with incident light of 1.6 eV.

Qualitative model: There are two necessary conditions for a working IBSC: (i) the CB and IB should develop independent quasi-Fermi levels; (ii) the CB must be electrically contacted independent of the IB. We can assess whether these conditions are achievable by inspecting the electronic band structure.

Band structures are usually presented as cross-sections of the Brillouin zone, with the path chosen to follow an irreducible representation of the underlying crystal symmetry. From the Bloch theorem, these high symmetry lines form the extrema and turning points in the electronic structure, and so fully characterise the band functions. In hybrid halide perovskites, the presence of a molecule (and large dynamical flexing of the octahedral cage) breaks the local $O_h$ symmetry of the underlying pseudo-cubic lattice. Practically, the spin-orbit coupling (due to atoms with large nuclear charges) interacting with local crystal fields moves band extrema to off-symmetry locations. Amongst other effects, this results in the splitting of the lower conduction band to give a spin-split indirect-gap. To guarantee that we are exploring all possible routes for recombination and thermalisation, we must integrate over the Brillouin Zone. By considering the reciprocal-space resolved difference in energy eigenstates, we can demonstrate whether the two conditions for an IBSC are met.

We use the QSGW electronic structure method as implemented in the Questaal codes$^6$, improving on our prior work$^7$ by using a larger and more converged basis on the same pseudo-cubic structure. It has been established$^{8,9}$ that QSGW yields very good Dresselhaus splitting in semiconductors, in contrast to the LDA. For convenience, the spin-orbit coupling was added only as a post-processing step: if it is included in the self energy the gap is reduced about 0.1 eV$^7$). These codes allow for the calculation of a self-consistent self-energy on a regular $k$-point mesh, which can then be used for calculation at an arbitrary $k$ point. This allows for sufficient finesse to locate and characterise the slightly off-symmetry extrema. Thus we consider this method to be of the highest quality available for broken-symmetry relativistic-ion semiconductors such as CH$_3$NH$_3$PbI$_3$.

We find no connection between bands in an energy window around the photo excited charge carriers, but at very high energies above the Fermi level, the bands do come together. This suggests that distinct quasi-Fermi levels are experimentally realisable. A consideration of the joint densities of state indicate that both the VB to IB and VB to CB photoexcitation channels will be simultaneously operational (Figure 2).

The band-edge electronic structure for hybrid perovskites is unique: there is a dispersive upper valence band (formed of I $p$ orbitals), an intermediate band (mainly hybridised Pb $p$ orbital), and the upper conduc-
FIG. 3: Partial densities of state from a QSGW calculation including spin orbit coupling. A Mulliken projection of the total DOS is made onto Pb 6s and 6p, and I 5s and 5p. The valence band is shown to be almost pure I 5p, as would be expected from a tight-binding picture. However, the intermediate and conduction bands are not purely of Pb 6p character, as would be predicted by atomic orbital arguments. This suggests that transitions between the intermediate and conduction band are not symmetry forbidden, as would be the case if they were both composed wholly of identical orbital angular momentum states. A more complete understanding requires calculation of explicit dipole matrix-elements, which will require custom codes.

In the equivalent circuit of an IBSC, the VB to IB and IB to CB transition are connected in series by the conservation of electron charge; forming equivalent circuit of a two-lead tandem solar cell. Therefore an efficient device requires the current flux between the two processes to be balanced. This depends on the details of the band structure, including the bandgap, density of states, and the strength of the optical transitions (transition matrix elements). The critical factor for hybrid perovskites, which is not present in tetrahedral semiconductors such as GaAs, is the reduced electron-hole recombination rates due to Rashba splitting. As discussed above, these will affect CB → VB and IB → VB transitions, due to a momentum offset between thermalised populations of electrons and holes. Our prior analysis has shown that the direct radiative recombination rate is reduced by a factor of 350X under one sun illumination. This will ensure significant steady state population of electrons in the IB under working conditions.

In summary, we have proposed a novel route to achieve intermediate band solar cells based on spin-split indirect-gap materials such as hybrid perovskites. According to the calculations presented herein, with suitable contacts CH$_3$NH$_3$PbI$_3$ should make a working device, with all transitions in the visible, and accessible in the laboratory. In order to quantitatively predict whether a device with efficiencies beyond the SQ limit is achievable will require more detailed device simulations that takes into account the unusual band physics, including the asymmetry in absorption and recombination between the three band system (VB, IB and CB).

Beyond CH$_3$NH$_3$PbI$_3$, in looking for spin-split materials to make high power conversion efficiency IBSC devices, we want to identify materials with a lower bandgap than the SQ matched 1.5 eV. Searches of novel materials for photovoltaics often discard such low-gap materials. An exciting prospect of using a bulk, band structure engineered, material for IBSC is the relatively low cost of making the devices, compared to engineering real-space heterojunctions.

**Acknowledgement** We thank Jenny Nelson and N. J. Ekins-Daukes (NED), for stimulating discussion. We acknowledge membership of the UK’s HPC Materials Chemistry Consortium, which is funded by EPSRC grant EP/F067496. J.M.F is funded by EPSRC Grant EP/K016288/1, the KCL group acknowledges support from EPSRC Grant EP/M009602/1. A.W. acknowledges support from the Royal Society. The authors declare no competing financial interests.

1 A. Luque and A. Martí, Physical Review Letters 78, 5014 (1997).
2 Y. Okada, N. J. Ekins-Daukes, T. Kita, R. Tamaki, M. Yoshida, A. Pusch, O. Hess, C. C. Phillips, D. J. Farrell, K. Yoshida, N. Alsan, Y. Shoji, T. Sogabe, and J.-F. Guillemoles, Applied Physics Reviews 2, 021302 (2015).

| Band | $\Delta E_{Rashba}$ (meV) | $m_e^*$ (meV) | $m_h^*$ (meV) | $m_e^*$ (meV) |
|------|------------------|--------------|--------------|--------------|
| VB   | 9.5              | -0.1420      | -0.2410      | -0.8920      |
| IB   | 63.7             | 1.250        | 0.1530       | 0.1280       |
| CB   | 19.5             | 0.5830       | 0.2900       | 0.1910       |

**TABLE II**: Rashba energy depth (from extremal point to high-symmetry saddle location) in meV and effective mass ($m^*$ in units of $m_e$) calculated around the Rashba extremal location for the three bands.
FIG. 4: Many-body electronic band structure of CH$_3$NH$_3$PbI$_3$ from QSGW. The Red-dashed line shows the band structure without a spin-orbit contribution, the three $p$ orbital conduction bands are near 3.0 eV, split in a two-fold and singly degenerate level.

Including spin-orbit (Black, full), the energies are significantly renormalised with the singly-occupied band shifting down to 1.6 eV, and the spin-channels Rashba split into two (IB) and four (CB) mutually inequivalent minima.

FIG. 5: A 3D render of the Rashba pockets of the VB (red), IB (green) and CB (blue), located around the high symmetry R locations. The ellipsoids are generated from the sampled effective mass tensors.

---

3M. Yoshida, N. J. Ekins-Daukes, D. J. Farrell, and C. C. Phillips, Appl. Phys. Lett. 100, 263902 (2012).
4P. Azarhoosh, S. McKechnie, J. M. Frost, A. Walsh, and M. van Schilfgaarde, APL Mater. 4, 091501 (2016).
5A. M. A. Leguy, P. Azarhoosh, M. I. Alonso, M. Campoy-Quiles, O. J. Weber, J. Yao, D. Bryant, M. T. Weller, J. Nelson, A. Walsh, M. van Schilfgaarde, and P. R. F. Barnes, Nanoscale 8, 6317 (2016).
6“Questaal,” https://lordcephei.github.io/, accessed: 2016-11-22.
7F. Brivio, K. T. Butler, A. Walsh, and M. van Schilfgaarde, Phys. Rev. B 89 (2014), 10.1103/physrevb.89.155204.
8A. N. Chantis, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. 96, 086405 (2006).