ACS Energy LETTERS
Cite This: ACS Energy Lett. 2017, 2, 2713-2714
http://pubs.acs.org/journal/aelccp

H-Center and V-Center Defects in Hybrid Halide Perovskites

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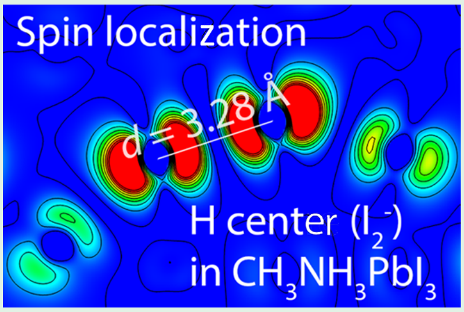
Supporting Information



ABSTRACT: The self-trapping of holes with the formation of a molecular X_2^- anion is a well-established process in metal halide (MX) crystals, but V-center ($2X^- + h^+ \rightarrow X_2^-$) and H-center ($X^- + X_i^- + h^+ \rightarrow X_2^-$) defects have not yet been confirmed in halide perovskite semiconductors. The I_2^- split-interstitial defect is predicted to be a spin radical in $CH_3NH_3PbI_3$ with an optically excited state in the semiconductor band gap.

The behavior of point defects in lead halide perovskites, such as $CH_3NH_3PbI_3$, is challenging to classify according to standard models. The rapid transport of ions at room temperature suggests a high concentration of mobile point defects, while the intrinsic conductivity and slow nonradiative recombination rates suggest a low concentration of electrically active defect centers.[1] Identifying the key point defects and means to control them remains a major challenge in the field, even for the highest-performing solar cells.[2]

Elementary thermodynamics ensures there are no "defect-free" crystalline materials.[3] The enthalpic cost of perturbing the long-range bonding in a crystal is offset by the gain in configurational entropy. Usually, defect levels in a semiconductor band gap correspond to the energy required to change charge state, i.e., the cost of adding (or removing) electrons from the defect center to the valence or conduction band of the host material. However, certain point defects can act as color centers, with charge-conserving optically excited states. For example, the color (F) centers consisting of an electron trapped at a vacant lattice site in alkali halides, or self-trapped holes in heteropolar crystals that are termed V-centers.[4]

V-centers have been studied in metal halide crystals since the 1950s, including F_2^- impurities in CaF_2 and LiF, where F^- anions are normally present at specific lattice sites.[5,6] Related molecular halide impurities have also been characterized in metal chlorides, bromides, and iodides.[7] They are unusual point defects as they involve *no* missing or extra atoms. A hole is introduced into a pristine lattice, and the charge induces the formation of a bond between two nearest-neighbor halide ions, producing an open-shell dihalide species, $2X^- + h^+ \rightarrow X_2^-$. In contrast to the V-center, the H-center is where hole-capture and dimer formation involves excess halide (for example, an interstitial) interacting with a lattice site, $X^- + X_i^- + h^+ \rightarrow X_2^-$. It has been shown that H-centers can be thermally converted into V-centers, and the two defects have similar but distinguishable optical and electronic signatures.[5] The local structures are illustrated in Figure 1.

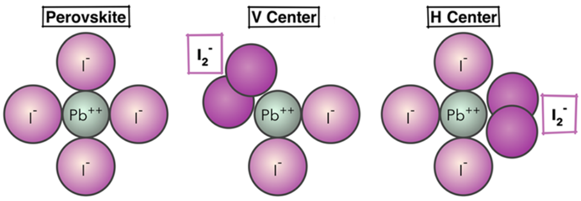


Figure 1. Change in local equatorial environment around Pb in a lead halide perovskite upon hole (h^+) capture leading to the formation of a V-center and H-center defect. In the V-center, two lattice iodides form a dimer, while in the H-center the dimer is formed from a lattice iodide and interstitial iodide. The I−I interatomic spacing of ca. 4.5 Å in the perfect lattice decreases to a bond length of 3.3 Å upon dimer formation (calculated value for the H center).

There have been multiple reports of defect formation energies and levels in $CH_3NH_3PbI_3$ based on first-principles quantum mechanical procedures. Defect processes are sensitive to the theoretical treatment, requiring the calculation of small energy differences and the simultaneous description of extended and localized electronic states. Quantitative defect level calculations with density functional theory (DFT) require nonlocal (hybrid) exchange-correlation functionals and an account for spin−orbit coupling (SOC). Du studied the interstitial iodine defect using

Received: October 12, 2017
Accepted: November 1, 2017

DOI: 10.1021/acsenergylett.7b00995

DFT in $CH_3NH_3PbI_3$ and highlighted the stability of several charge states and favorable I–I interactions.[8] The influence of electrons and holes on Frenkel defects (iodine vacancy and interstitials) have also been studied by DFT,[9] in addition to trapping of holes by iodine interstitial defects in molecular dynamics simulations.[10]

The management of iodine precursors has been the focus of the latest advances in perovskite solar cells. An I-rich precursor was proposed to be necessary to fully convert I-deficient intermediate phases during crystallization.[2] It has also been shown that postsynthetic annealing in iodine vapor shifts the Fermi level closer to the valence band, either through the creation of acceptors (iodine interstitial) or the annihilation of donors (iodine vacancy).[11] We find that the I_2^- split-interstitial defect forms an iodide dimer with highly localized spin ("H-center"), as shown in the opening image. Because of the radical nature of the trapped hole, the presence of V- and H-centers in perovskite samples could be confirmed using spin-sensitive techniques such as electron–spin resonance (ESR) or electron–nuclear double resonance (ENDOR).

Following the "molecule in crystal" approach[7] with dielectric embedding, we computed the optically excited states of the Cl_2^-, Br_2^-, and I_2^- defect centers as a function of bond lengths using time-dependent DFT (see Figure 2) including relativistic effects.

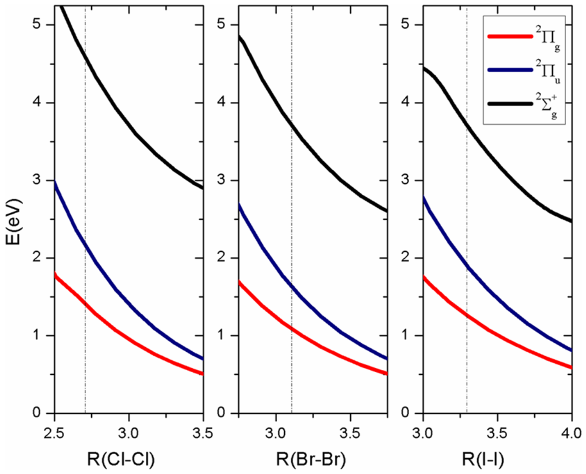


Figure 2. Optical excitation energies for halide dimers (found for V- and H-center defects) as a function of the interatomic spacing (in units of angstroms) from time-dependent DFT calculations including spin–orbit coupling. The ground-state electronic configuration is $^2\Sigma_u^+$, which corresponds to $(\sigma_g)^2$ $(\pi_u)^4$ $(\pi_g)^4$ $(\sigma_u)^1$, and the excited states involve the hole moving from σ_u to higher-binding energy orbitals. The vertical lines correspond to the dimer bond lengths of 2.7 Å (Cl), 3.1 Å (Br), and 3.3 Å (I).[7]

The ground-state electronic configuration is $^2\Sigma_u^+$, which corresponds to $(\sigma_g)^2$ $(\pi_u)^4$ $(\pi_g)^4$ $(\sigma_u)^1$. The lowest excited state involves moving the hole from the highest occupied σ_u level to higher binding-energy molecular orbitals. For the bond lengths found in the methylammonium lead iodide perovskite host (calculated to be 3.28 Å), the three lowest excited states occur at 1.26 eV (symmetry-allowed), 1.90 eV (forbidden), and 3.70 eV (symmetry-allowed). Two optically allowed transitions fall in the visible–ultraviolet range, and a sub-band gap absorption band at ca. 1.3 eV should be observable in long-wavelength absorption measurements if present in sufficient concentration.

While band transport is the predominant conduction mechanism in the lead halides, we suggest that the V- and H-centers could be acting as traps for photogenerated holes. The molecular iodide defects discussed here are not necessarily static carrier traps, because the halides that form the corner-sharing perovskite framework support reasonable rates of ion transport. Room-temperature diffusion is expected for the V-center, which could proceed in a pathway akin to vacancy-mediated diffusion. Transport of the H-center would require an interstitialcy mechanism, which has also been predicted to be low energy in halide perovskites.[12] The slow motion of trapped holes would add a further layer to the complexity of the temporal response of perovskite solar cells to light soaking and bias voltages (also evident in quantum dot photovoltaics[13]). Given the polyanion nature of iodine (e.g., charged I_2 up to I_{16} complexes) and the flexibility of the perovskite structure, the formation of larger charged molecular aggregates is also possible for the iodide perovskites. Such polyanion inclusions in a crystal would be redox active and could facilitate additional electron or hole trapping, which is a fertile line of research for future studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00995.

Computational details and data access information (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the EPSRC (Grants EP/M009580/1, EP/L01551X/1, and EP/K016288/1) and the Royal Society. Via our membership of the UK's HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202), this work used the ARCHER Supercomputing Service.

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