Methylammonium fragmentation in amines as source of localized trap levels and the healing role of Cl in Hybrid Lead-Iodide Perovskites

Pietro Delugas,1,2 Alessio Filippetti,2,∗ and Alessandro Mattoni2,†

1CompuNet, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
2Istituto Officina dei Materiali, CNR-IOM Cagliari SLACS, Cittadella Universitaria, I-09042 Monserrato (CA), Italy

Abstract

The resilience to deep traps and localized defect formation is one of the important aspects that qualify a material as suited photo-absorber in solar cell devices. Here we investigate by ab-initio calculations the fundamental physics and chemistry of a number of possible localized defects in hybrid methylammonium lead-iodide perovskites. Our analysis encompasses a number of possible molecular fragments deriving from the dissociation of methylammonium. In particular, we found that in stoichiometric conditions both ammonia and methylamine molecules present lone-pair localized levels well within the perovskite band gap, while the radical cation CH$_2$NH$_3^+$ observed by EPR after irradiation injects partially-occupied levels into the band gap but only in $p$-type conditions. These defects are thus potentially capable to significantly alter absorption and recombination properties. Amazingly, we found that additional interstitial Cl is capable to remove these localized states from the band gap. These results are consistent with the observed improvement of photoabsorption properties due to the Cl inclusion in the solution processing.

PACS numbers: 71.55.-i, 78.20.-e, 82.50.hb, 88.40.fh

Keywords: Density Functional Theory, Doping, Photovoltaics, Electronic structure, Recombination Centers, Traps

∗ Corresponding author: alessio.filippetti@dsf.unica.it
† Corresponding author: Alessandro.Mattoni@iom.cnr.it
I. INTRODUCTION

The outstanding photoconversion properties of CH$_3$NH$_3$PbI$_3$ perovskites (we will, from now on, abbreviate methylammonium as M and methylammonium lead iodide as MPbI$_3$) have been subject of an impressive number of experimental and theoretical studies in the last few years [1–6]. Nowadays, most of the key ingredients which characterize the photo-absorption properties of the system, at least in its bulk form, are understood: the large absorption coefficient in the important frequency range [7–11] the dominance of unbound electron-hole recombination over excitonic effects at room temperature [12, 13], the small band-to-band radiative recombination rate [8, 14], the long ($\approx 10^2 \div 10^3$ ns) lifetime and diffusion length (hundreds nm) [2, 12, 13, 15, 16]. In summary, the great appeal of this system stems from the fact that, while processed through low-cost solid solution as organic materials, it is nevertheless assignable, for what concerns photo-absorption properties, to the category of the best crystalline semiconducting absorbers (see Refs 7–9 for a detailed comparison with GaAs).

However, several aspects are still to be fully understood. One of them concerns the incidence and typology of native defects present in these materials. The fact that these films prepared at low thermal budgets have optimal optical absorption is a clear indication of the resilience of the electronic properties against structural defects and vacancies [17]. Experiments provide few specific indications about point defects and intra-gap electronic levels. Electronic Paramagnetic Resonance (EPR) measurements detect CH$_2$NH$_3^+$ cations and Pb$^0$ paramagnetic clusters in samples which had been irradiated with intense ultraviolet light [18]. Evidence of Pb metallic clusters in MPbI$_3$ is also given by X-ray Photo-emission Spectroscopy [19, 20]; ref. 19 reports also the presence of occupied (mainly in $n$-type conditions) or empty (mainly in $p$-type conditions) intra-gap electronic levels distributed at variable energies inside the gap. Indirect information about intra-gap electronic levels can also be drawn from photoluminescence (PL) experiments. As an example, a recent work [12] revealed that while transient PL spectroscopy in the high excitation density regime is dominated by unbound electron-hole radiative recombination, the steady-state PL intensity follows a 3/2-power law as a function of laser intensity (PL $\propto I^{3/2}$) which deviates from a purely radiative behavior (PL $\propto I$) and suggests the presence of intra-gap states. These intra-gap states can trap either electrons or holes, but not both of them simultaneously, thus indi-
cating that these traps should be either fully occupied or empty, but not partially filled. The trapping contribution is visible up to a injected carrier density of $\sim 10^{16} \div 10^{17}$ cm$^{-3}$, above which the radiative regime takes place and the linear behavior $\text{PL} \propto \text{I}$ is recovered. First-principles calculations are an extremely useful approach to evaluate the presence of defects in the systems. In several recent theoretical works [21–23] (see also Refs. 9 and 10 for a review) the most common point defects (vacancies, interstitials, substitutionals, and anti-sites) were thoroughly analyzed. It was found that the defects with the lowest formation energies (Pb vacancy and interstitial methylammonium, according to Ref. 15) are shallow acceptors and donors, respectively, thus coherently with the expectation of good $p$-type or $n$-type conductivity and recombination properties dominated by radiative processes. For some defects with larger formation energies (e.g. Pb interstitial and anti-site [15, 22, 24]) it is estimated by the very simplified transition-state argument that electronic levels lying well into the band gap could occur, but no explicit evidence of these defects was obtained from the calculated electronic properties. In the search for localized states evidenced by PL, in this work we use Density Functional Theory calculations to analyze a different scenario, i.e. the possibility of intra-gap electronic localization induced by the presence of interstitial molecules containing a C or N atom with a 2$p$ lone-pair. We will consider only molecules that derive from the methylammonium dissociation or deprotonation. In doing so, we assume the rather conservative viewpoint of including only moieties that respect the chemical composition and stoichiometry of the bulk perovskite. Apart from the dissociation processes, these and other physically similar impurities can be introduced in MPbI$_3$ accidently. Nicely, this limited set of cases is however sufficient to display a significant variety of defect states, whose characteristics are consistent with the PL analysis. In particular, we found that amine groups originating from the lone-pair of nitrogen molecules (e.g. ammonia and methylamine produced by M dissociation) have the general tendency to furnish trap states located well into the band gap.

Fragments containing a carbon 2$p$ lone-pair instead are generally unstable and tend to form bonded complexes with I ions. In this case all the localized electronic states are well below the valence band. This behavior is significantly influenced by the Fermi level position. For example in $p$-type conditions the CH$_2$NH$_3$ fragment yields one electron to (captures one hole from) the valence band and loosens its bond with iodine. The hole remains thus localized on a C(2$p$) state of the fragment. This intragap half filled level has been actually observed
by EPR [18].

Considering these defected perovskites as starting point, we then include interstitial Cl doping in the analysis (previous calculations [25] only considered Cl as I-substitutional in the bulk perovskite, and as such, hardly capable to change on any significant extent the photo-absorption properties of the perovskite). Here we give evidence that additional inclusion of 2% interstitial Cl in the perovskite (thus corresponding to p-type conditions) is capable to remove a corresponding fraction of N-derived localized states from the gap without including any additional charge localization in its own. Our results provide a clear evidence of the beneficial action of Cl in removing electronic localized states from the gap, and furnish a possible explanation to the increase of an order of magnitude in lifetime and diffusion length observed after Cl inclusion in solution.

II. COMPUTATIONAL METHODS

The electronic and structural properties of the defects were computed using the Density Functional Theory within Local Density Approximation, as implemented in the ESPRESSO package [26] which is a well known plane-wave plus ultrasoft pseudopotential [27] code. Pseudopotentials for I, C and N have projectors on s and p channels. For C and N the valence reference states are 2s and 2p, and 5s and 5p for Iodine. The Pb pseudopotentials have projectors in the s, p and d channels; with reference valence states 6s, 6p and 5d.

All calculations were done by using a plane-waves basis set cut-off of 35 Ry. All the reported results are inherent to the same $2\sqrt{2} \times 2\sqrt{2} \times 2$ supercell (i.e. 16 MPbI3 cubic units), which is the $2 \times 2 \times 1$ repetition of the Tetragonal P4/mbm [28] unit cell. Periodic boundary conditions are imposed along a tetragonal body centered lattice with vectors $(a, -a, c), (a, a, c), (-a, -a, c)$, where $a = 8.712 \, \AA$ and $c/a = 1.41$ are the lattice parameters obtained by the theoretical optimization of bulk unit cell and in good agreement with those reported in Ref. 28 for the tetragonal phase which is most stable at room temperature.

An accurate treatment of Pb 6p states in the conduction band would require the inclusion of Spin-Orbit Coupling [29] (SOC). SOC has nonetheless small influence on energetics, structure and electronic properties of valence band and defects and represents a major increase of the computational load. For this reason, similarly to what done in many other works on this subject [15, 21–23] we choose to discard SOC. One additional advantage deriving from
FIG. 1. (Color on line.) A: Density of states of bulk MPbI₃, Valence Band Top is set to 0. To better visualize the molecular levels, they are plotted in separate panels, one for each atomic type. Top panel: total DOS (green). Bottom panels: projected DOS on atomic states of methylammonium molecule. HC and HN are hydrogens bound to C and N, respectively; black and red lines refer to s-type and p-type states. B: scheme of methylammonium orbital levels, as inferred for the calculated DOS.

this choice is the quite realistic value for band gap yielded by LDA (albeit as a consequence of a fortuitous error cancelation).

The integrations in the Brillouin Zone during self consistency uses a 3 × 3 × 3 Monkhorst-Pack mesh. For the density of states calculation we have used the linear tetrahedron method on a 8 × 8 × 8 k-space mesh.

III. RESULTS AND DISCUSSION

A. Bulk perovskites

In defect-free bulk perovskites, the M¹⁺ electronic states are well localized in space, as seen from the calculated DOS in Figure 1.

The electronic structure of methylammonium embedded in the perovskite is not dissimilar to that of the isolated molecule, showing (from bottom, relatively to the Valence Band Top(VBT)) a singlet (at −19.2 eV) derived from N(2s)-H(1s) hybridized states; another
singlet at $-12.4$ eV from C(2s)-H(1s) hybridization; a N(2p)-H(1s) doublet at $-8.8$ eV, and another singlet at about $-7$ eV derived from N(2p)-C(2p) states. Finally, the C(2p)-H(1s) doublet at $-4.8$ eV is the HOMO. Since this states are located well below the VBT, no molecular level interferes directly with the band gap region. The same holds for the empty molecular states (not shown here) being the LUMO well above the Conduction Band Bottom (CBB). This decoupling of extended bands (derived from Pb and I states) with respect to the molecular states does not necessarily holds anymore if we consider configurations with methylammonium broken in C-based or N-based fragments. In the following, we will examine all the possible stoichiometric processes obtained by the fragmentation of methylammonium, giving rise to stable molecules.

B. Methylammonium fragmentation

A neutral M (i.e. not the M$^{1+}$ state of the bulk perovskite) lacks one H to be dissociated in a couple of NH$_3$ and CH$_4$ molecules, which would be both stable and neutral. It follows that, forcing a starting configuration with two separated C- and N-based complexes, one of them (the one lacking an hydrogen) will tend to form covalent bonding with neighboring ions, while the most stable will remain located nearby the perovskite A-site. For completeness we also include in the analysis the deprotonation processes. Five types of decomposition leaving at least one stable product can be hypothesized: a) CH$_3$NH$_3$ $\rightarrow$ CH$_3$ + NH$_3$; b) CH$_3$NH$_3$ $\rightarrow$ CH$_4$ + NH$_2$; c) 2 x CH$_3$NH$_3$ $\rightarrow$ CH$_3$NH$_2$ + NH$_4$ + CH$_3$; d) CH$_3$NH$_3$ $\rightarrow$ CH$_3$NH$_2$ + H; e) CH$_3$NH$_3$ $\rightarrow$ CH$_2$NH$_3$ + H.

These five processes conserve the perovskite bulk stoichiometry so that it is possible to estimate their energetic cost by direct comparison of total energies. The results for the completely separated fragments are reported in Table I. The computations show that the CH$_3$–I fragment has a significant binding energy with NH$_3$ (0.4 eV) and CH$_3$NH$_2$ (0.5 eV).

We should notice that our structures are product of atomic relaxations which sample a limited portion of the potential energy profile. Thus, we cannot exclude that the same final products could be arranged in a more energetically convenient way than that found in our final state.

As one can see in Table I the formation energies $\Delta E$ substantially reflect the average bond enthalpy $\Delta H$ of the C-N bond in case of a) and b) configurations (see the Table), and
TABLE I. Energetic cost of the fragmentation processes (∆E) examined in this work. The energies are calculated with respect to an equivalent bulk MPbI₃ supercell with 16 cubic perovskite units. The corresponding Average bond dissociation enthalpies (∆H) are reported, as a comparison with the corresponding dissociation.

| Configuration                        | ∆E (eV) | ∆H (eV) |
|--------------------------------------|---------|---------|
| NH₃ + CH₃–I                          | 2.03    | 3.17    |
| CH₄ + NH₂–I                          | 1.90    | 3.17    |
| CH₃NH₂I + NH₄ + CH₃–I                | 2.30    | 3.17    |
| CH₃NH₂I + H–I                        | 2.66    | 4.03    |
| CH₂NH₃–I + H–I                       | 3.22    | 4.28    |

of the N-H bond in case of c). Since the dissociation products are stable molecules, they gain some stability at the end of the process, thus ∆E are actually sizably smaller than ∆H. These large formation energies are indeed coherent with the low concentration of localized defects indicated by the experiments. However, this should not lead to the conclusion that the final products of dissociation are unlikely, since they could form during non-equilibrium solution processing, and not necessarily through the actual thermodynamic dissociation of methylammonium. Further, as reported in Ref. 18 deprotonated fragments are formed upon ultraviolet irradiation and, once created, they are stable. Finally notice that these results should not be compared with those calculated for point defects in Refs. 9, 15, and 16: in that case non-stoichiometric defects are considered (e.g. vacancies, interstitials, substitutionals) thus a suited choice of atomic chemical potentials can always favor the formation of specific defects. In the present case, all the configurations are stoichiometric, and no chemical reservoir is assumed. The resulting energies depend only on the actual energetic cost of the dissociation mechanism and do not depend on adjustable parameters. In the following we will analyze structural and electronic properties of the fragments.

C. Dissociation of methylammonium in ammonia and iodomethane

Following the mechanism (a) we forced the separation of one M in NH₃ (ammonia) and CH₃. The former remains close to the starting M position (i.e. the A-site of the perovskite)
FIG. 2. *(Color on line)* Atomic and electronic structure of the perovskite after CH$_3$NH$_3$ → CH$_3$ + NH$_3$ a) dissociation process. **A)** Atomic structure in close-by configuration: CH$_3$ migrates onto a PbI$_4$ plaquette to form a iodomethane molecule (CH$_3$I, the CI dimer indicated by cyan and red balls), while NH$_3$ remains close to the initial A-site of the perovskite. **B)** corresponding DOS. Upper panel: total DOS (green); lower panels: atom-resolved DOS for CH$_3$I and NH$_3$ molecules (orbital contribution labels are the same as the DOS in Figure 1). Zero energy is fixed at the VBT.

and fairly stable in its ground state, with three electrons distributed in an equal number of N-H bonds, and other two in a lone-pair HOMO of N(2p) orbital character. On the other hand, CH$_3$ is in a highly electronegative state, it migrates toward an I atom (also in the need of an electron to fill the valence hole, assuming a neutral M at the start) After structural optimization, a stable CH$_3$–I complex (*“methyl-iodide”*, also called *“iodomethane”*) is established, with the C-I axis lying nearly parallel to the PbI$_4$ square and a bond length of 2.17 Å. The key feature, for what concern the photo-absorption properties, is that the N(2p) HOMO level of NH$_3$ is high enough in energy to overcome the whole I(5p)-Pb(6s) valence band manifold (spanning a 3.6 eV wide energy interval) and intrudes well within the band gap. Thus, a doubly occupied donor appears 0.17 eV above the VBT. For iodo-methane, on the other hand, the HOMO state is a highly stable I(5p)-C(2p) σ-bond lying well below the valence band manifold, thus ineffective for what concerns the band gap region. The detailed properties of this configuration are shown in Figure 2.
D. Dissociation of methylammonium in methane and iodoamine

Following mechanism (b) we separate methylammonium in \( \text{CH}_4 \) (methane) and \( \text{NH}_2 \), the behavior of C and N is exchanged with respect to the previous case: the stable methane molecule remains nearby the starting M site, while \( \text{NH}_2 \) migrates toward a I ion and forms a \( \text{NH}_2\text{I} \) (iodoamine) molecule again placed at the interstice of the perovskite’s octahedral cage. The electronic structure of \( \text{CH}_4 \) (shown in Figure 3) is quite close to that of an isolated methane molecule, indicating small interaction with the inorganic surroundings. However, the electronic levels of this fragment remain far from the important energy region of photoabsorption. The interstitial \( \text{NH}_2\text{I} \) fragment also shows an electronic structure substantially similar to that of the isolated iodo-amine molecule, with the LUMO given by a \( \text{N}(2p)\text{-I}(5p) \) hybridized state lying just at the bottom of the conduction band. Thus, this state is a deep acceptor, but with a binding energy too small to be effective as recombination center.

E. Formation of ammonium, iodomethane and methylamine.

Following dissociation process (c), specularly to path (b), we separate the methylammonium in \( \text{NH}_4 \) and \( \text{CH}_2 \) fragments. Again the stable \( \text{NH}_4 \) remains at the A-site and the unstable fragment is attracted by one I ion. In this case the \( \text{CH}_2 \) not only binds to a I ion but—as it has to stabilize two 2\( p \) one pairs—captures also one H from a close-by methylammonium (thus ending up to a methylamine) and forms a stable \( \text{CH}_3\text{I} \) iodo-methane complex. This result confirms that the formation of 2\( p \) lone pair on N is energetically more favorable with respect to C.

Structural and electronic properties of methylamine and iodo-metane are illustrated in the discussion of dissociation paths (b) and (d), respectively. The 4 electronic levels stemming from ammonium valence states are all well below the I(5\( p \)) valence band. 1 level at about \(-20 \text{ eV}\) and 3 almost degenerate levels at about \(-10 \text{ eV}\) with respect to the VBT.

F. Dissociation of methylammonium in hydrogen iodide and methylamine.

The methylamine can also form directly from the deprotonation process of path (d). The detached H migrates toward the PbI\(_6\) octahedron and binds to a I to form a HI molecule (hydrogen iodide). The deprotonated \( \text{CH}_3\text{NH}_2 \) (methylamine) molecule is stable (structural
FIG. 3. (Color on line.) Structural optimization of the CH$_3$NH$_3$ → CH$_4$ + NH$_2$ dissociation c); A) NH$_2$ migrates into a PbI$_4$ plaquette to form a iodoamine like complex (NH$_2$–I), and methane (CH$_4$) remains stuck to the starting M-site. B): corresponding DOS, and atomic projected DOS. Orbital types and labels are the same as in Figure 2. C and D): schemes of the molecular levels, as inferred from the atomic-projected DOS.

and electronic properties are shown Figure 4) and thus remains in a substitutional position at the A-site. At variance with M, methylamine is neutral, thus the I(5p) valence band manifold remains nominally hole-doped. Our calculations show that this hole is compensated by the HI formation, which produces localized s–p states, thus formally subtracting one I to the Pb-I bands. But the most interesting aspect is that the filled methylamine HOMO and the empty hydrogen iodide LUMO are both located well within the band gap.
For what concerns methylamine, its 14 electrons fill 7 doubly-occupied localized levels. The second-highest in energy (a C-H bond at \(-2.9\) eV) falls well within the I(5p) valence manifold an it is slightly broadened and barely visible on the same scale of the other levels of the molecule (see the DOS enlargement in a small energy region around the band gap in Figure 4-panel C). The highest occupied state of methylamine is a N(2p) lone-pair, located \(1.17\) eV above the VBT; thus, as in the case of the the ammonia molecule, we have a stable molecule whose HOMO, derived by a lone-pair of N(2p) character, is high enough in energy to emerge above the VBT. For what concerns the HI molecule, it presents a I(5p)-H(1s) singlet at \(-6.2\) eV, and a I(5p)-H(1s) doublet at \(-3.9\) eV. Interestingly, its first empty state is another I(5p)-H(1s) bond below the CBB. To highlight the characteristics of these in-gap states we also calculated the band dispersion along the \(\Gamma - Z\) direction (Fig. 4–D): while the \(\text{CH}_3\text{NH}_2\) HOMO is quite flat through the whole region, the HI LUMO is characterized by a substantial broadening (\(\approx 0.1\) eV), remaining however separated from the CBB by \(\sim 50\) meV. The presence of these fully occupied and empty in-gap states is a potentially relevant feature for what concern photo-absorption and photo-emission, since they represent sources of strong non-radiative electron-hole recombination processes.

G. Dissociation of methyl-ammonium in hydrogen iodide and \(\text{CH}_2\text{NH}_3\)–I

Following process (e) the deprotonation occurs at the C side. We have again the formation of an H-I dimer which implies the transfer of one electron to the I(5p) valence band. The deprotonated methyl-ammonium fragment is thus neutral. At variance with the \(\text{CH}_3\text{NH}_2\) fragment, \(\text{CH}_2\text{NH}_3\) binds to an I ion and forms a stable complex which is in many aspects analogous to the \(\text{CH}_3\)–I complex seen above. Also the computed bond length (2.17 Å) is the same as we obtained for the iodo-methane complex. All of the 14 electrons of this fragment are localized in molecular levels whose energies are well below the valence band (see Figure 5). With respect to the valence band top (VBT) we have 3 distinct levels at \(-14\) eV, \(-9.5\) eV and \(-6\) eV; we have 4 more electronic levels that are organized in two doublets at \(-9\) eV and at \(-4.8\) eV. The electronic orbitals relative to the doublet at \(-4.8\) eV are the bond orbitals of the complex showing a strong hybridization between I(5p) and C(2p) atomic orbitals.
FIG. 4. (*Color on line.*) Simulation of the \( \text{CH}_3\text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2 + \text{H}^-\text{I} \) dissociation: one H migrates into a PbI\(_6\) octahedron to form hydrogen iodide (HI), leaving a stable methylamine molecule (\( \text{CH}_3\text{NH}_2 \)) close to the original M-site. A): atomic resolved DOS in the full energy range. Orbital types and labels are the same as in Figure 1-A. B) DOS in a small energy interval around the band gap, to better visualize the molecular levels overlapping with the valence bands (see text). C): band structure along the Γ–Z direction. The flat red band is due to the N(2p) lone-pair levels of methylamine. The blue band is related to H-I empty levels. The dashed line indicates the level of the Conduction Band Bottom.

**H. Effects of the \( p \)-type doping.**

In the stoichiometric dissociation processes described above the loss of a neutral M leaves the I(5p) valence band manifold with one electronic vacancy. This hole is compensated when a dissociation fragment binds to a I atom (forming \( \text{H}^-\text{I} \), \( \text{CH}_3^-\text{I} \), \( \text{NH}_3^-\text{I} \), or \( \text{CH}_2\text{NH}_3^-\text{I} \) complexes) so that no holes are present at the VBT. Starting from these stoichiometric configurations, in order to explore the effect of \( p \)-doping on the intra-gap localized states, we further enforced \( p \)-type conditions by subtracting electron charges from the supercell. Surprisingly, in the case of methylamine or ammonia, the filled lone pair is not ionized by \( p \)-doping, instead it shifts down in energy below the Fermi level and out of the band gap. If, by an increase of hole concentration, we shift further down the Fermi level, the lone-pair remains below the Fermi level undergoing rigidly to the same energy shift. An outstanding consequence then results from our simulations: amine lone-pair levels can stay in the gap as long as they are fully occupied or empty, but not if partially occupied, since in this case they regain full occupancy by shifting in energy below the VBT and thus taking one electron charge from the I(5p) valence bands. According to these results thus it is impossible
FIG. 5. (Color on line.) A) Structure of the CH$_2$NH$_3$–I complex. The I ion is displaced from its equilibrium position to bind to the deprotonated fragment. B) electronic structure of the CH$_2$NH$_3$–I complex, illustrated by the DOS projected on CH$_2$NH$_3$ and I sites. States are filled up to the Valence Band Minimum (VBM). Except for the H-I peak close to the conduction band there are no other defect states within the gap. Five distinct peaks (see text) are present in the projected DOS of CH$_2$NH$_3$; C-derived $s$–$p$ states are strongly hybridized with the I 5$p$ states.

to have N(2$p$) lone-pair levels with partial filling. As previously mentioned, the lack of in-gap partially filled states is in agreement with the arguments based on PL experiments of Refs. 12 and 19. A different situation is obtained by $p$-doping path (e) leading to the formation of the CH$_2$NH$_3$–I complex: the HOMO doublet of this complex, which in intrinsic conditions is a strongly covalent superposition of C(2$p$) and I(5$p$) orbitals, in consequence of $p$-doping splits in a fully occupied C(2$p$) singlet –laying about 5 eV below the VBT –and in a half-filled localized state inside the band gap– at about 1.4 eV above the VBT. This result is coherent with EPR measurements in irradiated MPbI$_3$ [18] which indicate the presence of half-filled electronic orbitals derived by CH$_2$NH$_3^+$ ions.

In summary, according to our results N-derived and C-derived localized in-gap states behaves quite differently: the former can never stay partially occupied in the band gap, and subtract electrons from the valence band if $p$-doping conditions are enforced; the latter, on the other hand remains well within the band gap even if half-occupied. We can understand this difference on the basis of the very high electronegativity of $p$-doped N-H group. In comparison, the electronegativity of C-H molecules is much lower and these latter have thus the
FIG. 6. (Color on line.) Scheme of the stable fragments considered in the present work under stoichiometric conditions. For each configuration the molecular levels closer to the band gap region are also indicated. In particular, amine groups display localized lone-pair HOMO and LUMO orbitals well into the band gap which are eventually removed after addition of interstitial Cl.

tendency to form hybridized bonds with I ions or alternatively strip H from neighboring M molecules. Finally, the total energy comparison between perovskites including methylamine and CH$_2$NH$_3^+$ in the same p-type conditions (thus directly comparable having the same number of atoms in the simulation supercell) shows that the latter is 0.46 eV/f.u. higher in energy. Thus, the dissociation of methylammonium in methylamine should be regarded as the most probable source of in-gap localized defects in the perovskite.

I. Role of Cl in perovskites.

A major conundrum concerns the capability of Cl to enhance the photoconversion properties of the perovskite; since the very first work revealing the solar cell efficiency of these systems [1], the presence of Cl in solution with the reactants of the perovskite was highlighted as a key ingredient to obtain power conversion efficiency (PCE) greater than 10%.
FIG. 7. (Color on line.) Density of states close to the VBT for two MPbI₃ supercells containing one methylamine at different hole doping concentrations. Top-panel: a bulk MPbI₃ with one methylammonium substituted by one methylamine (i.e. one H subtracted) in the 192-atom supercell. This corresponds to a hole doping concentration of $2.74 \times 10^{20}$ cm$^{-3}$. Bottom panel: a bulk MPbI₃ plus a M-vacancy plus a M-to-methylamine substitution (2 holes per supercell).

FIG. 8. (Color on line.) A) Atomic structure of the CH$_2$NH$_3^+$–I complex in $p$-type conditions. B) Electronic structure of the complex illustrated by the DOS projected on the atomic orbitals of the molecules.
This is somewhat surprising since on the one hand, the actual amount of Cl included in the perovskite was revealed to be not larger than few percent and possibly accumulated at the interfaces [30, 31]; on the other, it was realized that the isovalent Cl-I substitution could bring little effect on the fundamental electronic properties of the system [25]; in fact, several PL studies highlighted the fact that Cl could increase the lifetime and the related diffusion length of the perovskite by an order of magnitude [2], a result hardly understandable in terms of a few-percent I → Cl substitutions. These considerations have motivated a thorough search of the possible mechanisms which could explain the role of Cl in the perovskites. At the present, one of the most credited hypothesis focuses on the role of the interfaces where a significant concentration of Cl could be confined, thus effectively changing the photoabsorption properties [30, 31]. An alternative explanation, very interesting in its simplicity, is based on the hypothesis that a certain amount of native defects present in the undoped stoichiometric perovskite could be removed from the gap by the inclusion of interstitial Cl, acting as a p-type dopant. An estimate based on purely radiative band-to-band recombination [7] showed that a reduction of defect concentration of about one order of magnitude can justify an increase of lifetime of the order of that found in PL experiments. This scenario implies that: i) native doping in the perovskite is n-type; ii) interstitial Cl doping is somehow capable to eliminate the defect states laying in the band gap. In our description of methylammonium dissociations, we found that condition i) is actually realized by two configurations characterized by HOMO levels well into the band gap (see a summary of results in Figure 6). In the following we will show that even the hypothesis ii) is absolutely justified by our calculations, i.e. the inclusion of interstitial Cl always acts in a way to compensate the trap states and remove them from the band gap. We have simulated the inclusion of a Cl atom in the perovskite, together with the most interesting end-products of methylammonium, for various Cl starting positions. The inclusion of one Cl in our 16 f.u. supercells corresponds to a 2% additional concentration with respect to the I atoms, in line with the PL estimates of defect concentration. Interestingly, we found a rather universal behavior for the interstitial Cl, i.e. scarcely dependent on the initial atomic configurations: in all the cases, Cl migrates into the octahedral cage, bonding with one Pb and distorting the Pb-I octahedral cage; in Figure 9 A) and B) we report the final structure for two different simulations, one with an additional Cl atom included in the bulk MPbI$_3$ perovskite, and the other with a Cl included together with CH$_3$NH$_2$ and HI as products of the methylam-
FIG. 9. (Color on line.) **A)** Atomic structure obtained upon structural optimization after inclusion of one Cl in a bulk-like MPbI$_3$ supercell; **B)** atomic structure upon structural optimization with Cl included in a supercell after M dissociation in methylamine plus hydrogen iodide. In both cases, Cl ends up in the octahedral cage, binding with Pb atoms. **C)** DOS relative to the system displayed in **B**). The upmost panel is the total DOS, lower panel the DOS of the methylamine molecule, resolved per atoms. As usual red and black colors represent $p$ and $s$ states. **D)**: band structure for the same system along $\Gamma$–$Z$. The green line is the HOMO of methylamine, the blue line a HI state, both laying within the band gap before Cl inclusion (Fig. 5-D).

Mononium dissociation. The two atomic structures in the region around Cl are quite similar, with Cl moving close to a Pb and sharing the ligand position with one I ion. In this way Cl($3p$) states are hybridized with the I($5p$) valence states, thus effectively decreasing the $n$-type concentration by one electron per Cl. In Figure 9 we report DOS and band energies relative to the relaxed structure with one CH$_3$NH$_2$ plus HI plus Cl. The HOMO state of methylamine, which in absence of Cl was well into the band gap, is now located just below the VBT, i.e. the inclusion of Cl cleans up the band gap from its occupied localized states.

This *cleaning* mechanism is rather transparent: Cl grabs an electron from the in-gap
lone-pair, which then falls down in energy as a consequence of the subtracted electrostatic repulsion. Furthermore, the \( p \)-type states of Cl spreads through the I(5\( p \)) valence band region, without introducing any relevant change in the total DOS, i.e. the basic electronic properties of the perovskite are not disrupted by the interstitial Cl, at least for the 2\% concentration examined here. We emphasize that this mechanism is quite general: any \( n \)-type dopant, whatever the source, will be compensated by an equal concentration of interstitial Cl subtracting one electron from the valence band manifold.

IV. CONCLUSIONS

In summary, we have studied by First-Principles calculations the effect in the perovskites of various molecular defects. We have focused our analysis on those which can be obtained by the dissociation or fragmentation of methylammonium. For these defects the formation energies calculated by total energy differences range from about 2 eV up to 3.2 eV. Accordingly their concentration is expected to be low under thermal equilibrium conditions, but it can eventually increase out of equilibrium, i.e. during synthesis or as a result of chemical contamination. Our results demonstrate that some of these defects form (either completely filled or empty) localized levels inside the band gap, in particular those related to N(2\( p \)) lone pairs present in ammonia and methylamine molecules derived from methylammonium dissociation. An overall account of these defects is schematically summarized in Figure 6: while the electronic states of the M\(^{1+}\) molecule in the bulk perovskite lie far beyond or above the relevant band gap extremes, these molecules display either HOMO or LUMO states well within the band gap (specifically, the ammonia HOMO 0.17 eV above the VBT, and the methylamine HOMO and LUMO 1.17 eV and 1.48 eV above VBT, respectively).

Also, we have shown that the amine lone-pair localized in the band gap are always either full or empty, since any attempt to extract an electron from the in-gap HOMO state results in a sudden falling of this state below the VBT. In other words, their fractionally occupied states are never stable within the band gap. This result is in striking agreement with the interpretations of the steady-state PL experiments carried out in Ref. 12.

At variance with amines, fragments having a C(2\( p \)) lone-pair like CH\(_2\)NH\(_3\) or CH\(_3\) can form stable complexes by binding to I ions, but, as long as stoichiometric conditions are retained, their HOMO levels always remain well below the VBT. However, in \( p \)-type con-
FIG. 10. (Color on line.) Schematic representations of the effects of $p$-type doping; (left) the molecular level of the methyl-type fragment is able to trap one hole and it forms a singly occupied level right in the gap; (right) the lone pair of the methylamine fragment is always doubly occupied, and shifts below the Fermi level in $p$-type conditions.

Conditions the orbital related to C-I bond remains singly occupied thus moving into the band gap; this is in agreement with EPR evidences, reported in Ref. 18, of half-filled orbitals derived by the CH$_2$NH$_3$ radical. Results for p-type conditions are summarized in Figure 10. Furthermore, we have analyzed the inclusion of interstitial Cl in the perovskite. Our results show that an amount of 2% interstitial Cl is capable to remove from the band gap from an equal amount of N-derived lone-pair HOMO states of methylamine or ammonia, and at the same time does not disrupt the fundamental electronic properties of the perovskite. Our results build a sound conceptual fundament to the observed enhancement of lifetime and diffusion length caused by the inclusion of Cl in the solution processing of the perovskite.
ACKNOWLEDGMENTS

The Authors acknowledge financial support by CompuNet, Istituto Italiano di Tecnologia (IIT), by Regione Autonoma della Sardegna under L. R. 7/2007 (CRP-24978 and CRP-18013), by Consiglio Nazionale delle Ricerche (Progetto Premialit RADIUS), by Fondazione Banco di Sardegna Projects n. 5794 and n. 7454. They also acknowledge computational support by CINECA (Casalecchio di Reno, Italy) and CRS4 (Loc. Piscina Manna, Pula, Italy).

[1] Michael M Lee, Joël Teuscher, Tsutomu Miyasaka, Takurou N Murakami, and Henry J Snaith, “Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites.” Science (New York, N.Y.) 338, 643–7 (2012).

[2] Samuel D Stranks, Giles E Eperon, Giulia Grancini, Christopher Menelaou, Marcelo J P Alcocer, Tomas Leijtens, Laura M Herz, Annamaria Petrozza, and Henry J Snaith, “Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber.” Science (New York, N.Y.) 342, 341–4 (2013).

[3] Guichuan Xing, Nripan Mathews, Shuangyong Sun, Swee Sien Lim, Yeng Ming Lam, Michael Grätzel, Subodh Mhaisalkar, and Tze Chien Sum, “Long-range balanced electron- and hole-transport lengths in organic-inorganic CH$_3$NH$_3$PbI$_3$.” Science (New York, N.Y.) 342, 344–7 (2013).

[4] Julian Burschka, Norman Pellet, Soo-Jin Moon, Robin Humphry-Baker, Peng Gao, Mohammad K Nazeeruddin, and Michael Grätzel, “Sequential deposition as a route to high-performance perovskite-sensitized solar cells.” Nature 499, 316–9 (2013).

[5] Guichuan Xing, Nripan Mathews, Swee Sien Lim, Natalia Yantara, Xinfeng Liu, Dharani Sabba, Michael Grätzel, Subodh Mhaisalkar, and Tze Chien Sum, “Low-temperature solution-processed wavelength-tunable perovskites for lasing.” Nat Mater 13, 476–480 (2014).

[6] Edoardo Mosconi, Anna Amat, Md. K. Nazeeruddin, Michael Grätzel, and Filippo De Angelis, “First-Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications,” The Journal of Physical Chemistry C 117, 13902–13913 (2013).

[7] A. Filippetti and A. Mattoni, “Hybrid perovskites for photovoltaics: Insights from first prin-
ciples,” Physical Review B 89, 125203 (2014).

[8] Alessio Filippetti, Pietro Delugas, and Alessandro Mattoni, “Methylammonium Lead-Iodide Perovskite: Recombination and Photoconversion of an Inorganic Semiconductor Within a Hybrid Body,” The Journal of Physical Chemistry C 118, 24843 (2014).

[9] Wan-Jian Yin, Tingting Shi, and Yanfa Yan, “Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance.” Advanced materials (Deerfield Beach, Fla.), 4653–4658 (2014).

[10] Wan-Jian Yin, Ji-Hui Yang, Joongoo Kang, Yanfa Yan, and Su-Huai Wei, “Halide Perovskite Materials for Solar Cells: A Theoretical Review,” J. Mater. Chem. A (2014), 10.1039/C4TA05033A.

[11] Stefaan De Wolf, Jakub Holovsky, Soo-Jin Moon, Philipp Lper, Bjoern Niesen, Martin Ledinsky, Franz-Josef Haug, Jun-Ho Yum, and Christophe Ballif, “Organometallic halide perovskites: Sharp optical absorption edge and its relation to photovoltaic performance,” The Journal of Physical Chemistry Letters 5, 1035–1039 (2014), http://dx.doi.org/10.1021/jz500279b.

[12] Michele Saba, Michele Cadelano, Daniela Marongiu, Feipeng Chen, Valerio Sarritzu, Nicola Sestu, Cristiana Figus, Mauro Aresti, Roberto Piras, Alessandra Geddo Lehmann, Carla Cannas, Anna Musinu, Francesco Quochi, Andrea Mura, and Giovanni Bongiovanni, “Correlated electron-hole plasma in organometal perovskites.” Nature communications 5, 5049 (2014).

[13] Valerio D’Innocenzo, Giulia Grancini, Marcelo J P Alcocer, Ajay Ram Srimath Kandada, Samuel D Stranks, Michael M Lee, Guglielmo Lanzani, Henry J Snaith, and Annamaria Petrozza, “Excitons versus free charges in organo-lead tri-halide perovskites.” Nature communications 5, 3586 (2014).

[14] Kristofer Tvingstedt, Olga Malinkiewicz, Andreas Baumann, Carsten Deibel, Henry J Snaith, Vladimir Dyakonov, and Henk J Bolink, “Radiative efficiency of lead iodide based perovskite solar cells,” Sci. Rep. 4 (2014).

[15] Arianna Marchioro, Joel Teuscher, Dennis Friedrich, Marinus Kunst, Roel van de Krol, Thomas Moehl, Michael Gratzel, and Jacques-E. Moser, “Unravelling the mechanism of photoinduced charge transfer processes in lead iodide perovskite solar cells,” Nat Photon 8, 250–255 (2014).

[16] V. Roiati, S. Colella, G. Lerario, L. De Marco, A. Rizzo, A. Listorti, and G. Gigli, “Investi-
gating charge dynamics in halide perovskite-sensitized mesostructured solar cells,” Energy & Environmental Science 7, 1889 (2014).

[17] Jongseob Kim, Sung-Hoon Lee, Jung Hoon Lee, and Ki-Ha Hong, “The Role of Intrinsic Defects in Methylammonium Lead Iodide Perovskite,” The Journal of Physical Chemistry Letters 5, 1312–1317 (2014).

[18] Ilya A. Shkrob and Timothy W. Marin, “Charge trapping in photovoltaically active perovskites and related halogenoplumbate compounds,” The Journal of Physical Chemistry Letters 5, 1066–1071 (2014), http://dx.doi.org/10.1021/jz5004022.

[19] Tomas Leijtens, Samuel D. Stranks, Giles E. Eperon, Rebecka Lindblad, Erik M. J. Johansson, Ian J. McPherson, Hkan Rensmo, James M. Ball, Michael M. Lee, and Henry J. Snaith, “Electronic properties of meso-superstructured and planar organometal halide perovskite films: Charge trapping, photodoping, and carrier mobility,” ACS Nano 8, 7147–7155 (2014), pMID: 24949826, http://dx.doi.org/10.1021/nn502115k.

[20] Bert Conings, Linny Baeten, Christopher De Dobbelaere, Jan D’Haen, Jean Manca, and Hans-Gerd Boyen, “Perovskite-based hybrid solar cells exceeding 10film sandwich approach,” Advanced Materials 26, 2041–2046 (2014).

[21] Wan-Jian Yin, Tingting Shi, and Yanfa Yan, “Unusual defect physics in CH3NH3PbI3 perovskite solar cell absorber,” Applied Physics Letters 104, 063903 (2014).

[22] Andrei Buin, Patrick Pietsch, Jixian Xu, Oleksandr Voznyy, Alexander H Ip, Riccardo Comin, and Edward H Sargent, “Materials Processing Routes to Trap-Free Halide Perovskites.” Nano letters (2014), 10.1021/nl502612m.

[23] Hsin-Sheng Duan, Huanping Zhou, Qi Chen, Pengyu Sun, Song Luo, Tze-Bin Song, Brion Bob, and Yang Yang, “The identification and characterization of defect states in hybrid organic-inorganic perovskite photovoltaics,” Phys. Chem. Chem. Phys. (2014), 10.1039/C4CP04479G.

[24] M. H. Du, “Efficient carrier transport in halide perovskites: theoretical perspectives,” Journal of Materials Chemistry A 2, 9091 (2014).

[25] Silvia Colella, Edoardo Mosconi, Paolo Fedeli, Andrea Listorti, Francesco Gazza, Fabio Orlando, Patrizia Ferro, Tullio Besagni, Aurora Rizzo, Gianluca Calestani, Giuseppe Gigli, Filippo De Angelis, and Roberto Mosca, “MAPbI 3-x Cl x Mixed Halide Perovskite for Hybrid Solar Cells: The Role of Chloride as Dopant on the Transport and Structural Properties,” Chemistry of Materials 25, 4613–4618 (2013).
[26] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sclauzero, Ari P Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M Wentzcovitch, “QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials.” Journal of physics: Condensed matter 21, 395502 (2009).

[27] David Vanderbilt, “Soft self-consistent pseudopotentials in a generalized eigenvalue formalism,” Phys. Rev. B 41, 7892–7895 (1990).

[28] Tom Baikie, Yanan Fang, Jeannette M. Kadro, Martin Schreyer, Fengxia Wei, Subodh G. Mhaisalkar, Michael Graetzel, and Tim J. White, “Synthesis and crystal chemistry of the hybrid perovskite (CH3NH3)PbI3 for solid-state sensitised solar cell applications,” Journal of Materials Chemistry A 1, 5628 (2013).

[29] Jacky Even, Laurent Pedesseau, Jean-Marc Jancu, and Claudine Katan, “Importance of spinorbit coupling in hybrid organic/inorganic perovskites for photovoltaic applications,” The Journal of Physical Chemistry Letters 4, 2999–3005 (2013), http://dx.doi.org/10.1021/jz401532q.

[30] Silvia Colella, Edoardo Mosconi, Giovanna Pellegrino, Alessandra Alberti, Valentino L. P. Guerra, Sofia Masi, Andrea Listorti, Aurora Rizzo, Guglielmo Guido Condorelli, Filippo De Angelis, and Giuseppe Gigli, “Elusive Presence of Chloride in Mixed Halide Perovskite Solar Cells,” The Journal of Physical Chemistry Letters 5, 3532–3538 (2014).

[31] Edoardo Mosconi, Enrico Ronca, and Filippo De Angelis, “First-Principles Investigation of the TiO 2 /Organohalide Perovskites Interface: The Role of Interfacial Chlorine,” The Journal of Physical Chemistry Letters 5, 2619–2625 (2014).