Fingerprints of Iodoplumbate Chains in the Optical Absorption of Lead-Halide Perovskite Solution Precursors

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Abstract

Solvent-solute interactions in precursor solutions of lead halide perovskites (LHP) critically impact the quality of solution-processed materials, as they lead to the formation of a variety of polyiodide plumbates that act as building blocks for LHP. The formation of $[\text{PbI}_{2+n}]^n^−$ complexes is often expected in diluted solutions while coordination occurring at high concentrations is not well understood yet. In a combined $ab\initio$ and experimental work, we demonstrate that the optical spectra of the quasi-one-dimensional iodoplumbate chains $\text{PbI}_2(\text{DMSO})_4$, $\text{Pb}_2\text{I}_4(\text{DMSO})_6$, and $\text{Pb}_3\text{I}_6(\text{DMSO})_8$ formed in dimethyl sulfoxide solutions are compatible with the spectral fingerprints measured at high concentrations of lead iodide. This finding suggests that the optical spectra of LHP precursor solutions at high concentration should be interpreted accounting for the presence of iodoplumbate chains as well.
Lead halide perovskites (LHPs) are considered among the most promising solution-processed materials for the next generation of optoelectronic devices. The impressive progress in terms of device efficiency achieved within the last decade has established the success of these systems and consolidated their popularity among solar cell materials. Similarly to other solution-processed materials, the quality of hybrid perovskites is dictated by solvent-solute interactions, structures of the intermediate solvate phases, and the processing conditions of precursor solutions. Therefore, open-ended questions regarding material formation range from the evolutionary process from solution complexes to thin films, the peculiar coordination of lead and iodine atoms, to the role of residual solvent molecules in altering the overall performance of LHPs. Numerous experimental studies have reported the formation of coordination complexes in LHP precursor solutions.

Radicchi et al. recently rationalized experimental spectral features of iodoplumbate complexes \([\text{PbI}_m\text{Sol}_n]^{2-m}\) (with \(m = 0 - 4\), \(n = 0 - 6\)) in a number of common solvent molecules (Sol) with ab initio calculations. The absorption spectrum of LHP precursor solution was interpreted through the red-shift of absorption bands as the number of coordinated iodide ions \((m)\) in \([\text{PbI}_m\text{Sol}_n]^{2-m}\) increases from 2 to 4. Similarly to other reports, the LHP solution chemistry and, more specifically, the formation of \([\text{PbI}_m\text{Sol}_n]^{2-m}\) iodoplumbate complexes was demonstrated in diluted solutions of lead iodide with the addition of large excess of iodide ions (1:150). However, in highly concentrated precursor solutions with 1:1 ratio of PbI\(_2\) to I\(^-\), which are typically used for material deposition, the coordination processes may differ dramatically from those considered previously. Therefore, the formation of only mono-nuclear polyhalido plumbates cannot be used for the rationalization of chemical interactions in the precursor solutions used for material deposition. During crystallization of precursor solutions, the formation of intermediate perovskite phases with inclusions of solvent molecules and lead-halide chains \([e.g., (\text{DMSO})_2(\text{MA})_2\text{Pb}_3\text{I}_8]\) has been experimentally observed. In addition, the formation of polymeric polyiodide plumbates in concentrated solutions of PbI\(_2\) has been hypothesized recently. Therefore, further assoc-
tion/agglomeration of iodoplumbate complexes into quasi-one-dimensional (1D) chains is conceivable at high concentration of precursors in the solution.

The formation of quasi-one-dimensional polyiodoplumbate chains has been previously observed in coordination compounds of PbI$_2$ with different organic ligands. Typi
cally, the increase of coordination in low-dimensional materials leads to a red-shift of the optical absorption due to the combination of enhanced screening and quantum confinement. Such a behavior has been discussed in relation to a number of diverse systems, including organic semiconductors, graphene nanostructures, and nanoparticles. Therefore, the formation of these polymeric chains can also affect the optical properties of LHP precursor solutions.

To verify this hypothesis and corroborate the interpretation of the UV-vis spectra of complexes formed in solution, we evaluate herein the impact of chain length on the absorption spectra of polymeric iodoplumbates formed in solutions of PbI$_2$ in dimethyl sulfoxide (DMSO). To this end, we investigate from first principles a set of neutral compounds with the chemical formula \([\text{PbI}_2(\text{DMSO})_4]_N\) \((N = 1 - 3)\). Through the calculation of the electronic structure and the optical absorption spectra from state-of-the-art many-body perturbation theory \(^{55}\) (GW approximation and Bethe-Salpeter equation), we quantify the red-shift induced by the increasing Pb - I coordination and determine the spatial distribution across solute and solvent of the excitations involved. We also provide an in-depth analysis of the nature of the excitations that appear in the spectra, which is useful to assess the impact of residual solvent molecules in LHPs.

Experimental results motivating the \textit{ab initio} study presented herein are shown in Figure 1. The absorption spectra of lead iodide solutions in dimethylsulfoxide (DMSO) as a function of PbI$_2$ concentration are shown in Figure 1a. Low concentration lead iodide solutions \((C = 0.1 - 1 \text{ mM})\) exhibit absorption bands above 4.96 eV \((i.e., \text{less than 250 nm})\) and 4.39 eV \((282 \text{ nm})\), that are characteristic of dissociated PbI species - \([\text{Pb(Sol)}_6]^{+2}\) and \([\text{PbI(Sol)}_5]^{+1}\), respectively. Increasing the PbI$_2$ solution concentration to 5 mM leads to an
Figure 1: a) Optical absorption spectra of PbI$_2$ in DMSO measured as a function of PbI$_2$ concentration, C(PbI$_2$). b) Fitted absorption spectra (red symbols) of 0.25 mM PbI$_2$ solution with addition of MAI (1:120 PbI$_2$: MAI) in DMSO (top) and 500 mM PbI$_2$ solution in DMSO (bottom). The fitted Gaussian functions indicate the positions of the absorption bands assigned to the polyiodide plumbate species [PbI]$^{+1}$, [PbI$_2$]$^0$, [PbI$_3$]$^{-1}$, and [PbI$_4$]$^{-2}$ respectively.

increase of the absorption at 4.39 eV and an appearance of a shoulder at 3.85 eV (325 nm). This can be attributed to the formation of [PbI$_2$(Sol)$_4$]$^0$. Further incrementing the PbI$_2$ concentration in solution results in the increase of the peak strength at 3.85 eV, and in the appearance of another feature/shoulder at 3.48 eV (357 nm) that can be attributed to [PbI$_3$(Sol)$_3$]$^{-1}$. The solution with the highest concentration of PbI$_2$ in DMSO (500 mM) shows, in addition to the absorption band at 3.48 eV, an increase of absorption in the range of photon energy below 3.1 eV (> 400 nm).

Interestingly, the absorption bands observed in the solutions with a high concentration of PbI$_2$ in DMSO closely resemble the absorption spectrum of PbI$_2$ solutions with the addition of iodide ions. Figure 1b, top panel, shows the absorption spectra of PbI$_2$ with the addition of methylammonium iodide (MAI) (1:120 PbI$_2$ : MAI), and the 500 mM PbI$_2$ solution in DMSO is shown in the bottom panel. The absorption spectra are fitted with Gaussian functions, as shown in Figure 1b. In the presence of an excess of MAI, the absorption bands at 3.48 eV and 2.98 eV were previously ascribed to the absorption of [PbI$_3$(Sol)$_3$]$^{-1}$ and
Using the same peak positions with a significant peak broadening, the Gaussian functions are fitted to the absorption spectrum of pure PbI₂. The position of the absorption bands of the concentrated PbI₂ solution indicates the presence of solution species that exhibit spectroscopic features similar to those previously correlated with the [PbI₃]⁻¹ and [PbI₄]⁻² species. However, in the solutions of pure PbI₂, this observation cannot be simply rationalized by the formation of lead-halide solution complexes, as in the absence of positively charged MA⁺ ions the charge neutrality of the solution species has to be preserved via interaction with other positively charged ions such as [Pb⁺²Sol₆] and [PbI₁Sol₅]⁺₁. Previously, this effect was ascribed to the presence of polymeric polyiodide plumbates formed in solution. We interpret the broader absorption features around 3.48 eV of the highly concentrated PbI₂ solution to indicate the interaction of lead halide species and the formation of polymeric iodoplumbate chains. Polycomplexes with two or three lead-halide-solvent units, such as [PbI₂(DMSO)₅]₃, hereafter referred to as dimers (D) and trimers (T), are critical initials steps in the formation of solid state perovskite semiconductors.

The iodoplumbate chains in DMSO solution corresponding to the monomer (M), dimer (D), and trimer (T) structures introduced above are modeled by the chemical formula [PbI₂(DMSO)₄]ₙ, where n runs from 1 to 3, respectively (see Figure 2 insets). Each PbI₂ unit is coordinated with 4 DMSO molecules to ensure charge neutrality. The resulting structures are obtained via force minimization in the framework of density-functional theory (DFT) including explicitly van der Waals interactions (further details in the Section Theoretical Methods and Computational Details below). Interestingly, the dimer and trimer exhibit the polyhedral coordination of the polymeric iodoplumbate chains reported in Ref. A close inspection on the optimized model structure in the inset of Figure 2 reveals their quite distorted backbone (see Supporting Information, Figure S1 and related discussion), which was not reported in previous works. We ascribe this behavior to our choice of simulating the iodoplumbate chains as isolated compounds interacting atomistically with DMSO solvent molecules linked to the Pb atoms through the available O lone pair. Addi-
tionally, we consider these compounds in vacuo, in order to focus on the explicit quantum-mechanical interactions between solute and solvent without additional contributions from implicit media. As a consequence of these choices, we anticipate a sizable and systematic overestimation of the excitation energies with respect to the experimental ones reported in Figure 1. However, we do not expect the physical picture provided by our first-principles results to be altered by this quantitative discrepancy.

Figure 2: Optical absorption spectra of the monomer, dimer, and trimer structures PbI$_2$(DMSO)$_4$, Pb$_2$I$_4$(DMSO)$_6$, and Pb$_3$I$_6$(DMSO)$_8$ respectively. Vertical bars indicate the energy and oscillator strength of the calculated excitations. A Lorentzian broadening of 500 meV is applied to all spectra.

The optical absorption spectra computed for these model compounds (see Figure 2) show a significant red-shift at increasing coordination length of the PbI$_2$ units. All three systems exhibit a smooth absorption onset characterized by a bright but relatively weak lowest-energy excitation, labeled $E_I$. In the monomer, $E_I^M$ is found at 5.13 eV, in the dimer $E_I^D$ is at 4.67 eV, and in the trimer $E_I^T$ appears at 4.58 eV. The oscillator strength (OS) calculated for $E_I$ decreases from the monomer to the trimer (see Figure 2 and Table S1 in the Supporting Information for further details). These results clearly indicate that the energy of the first excitation decreases at increasing chain length, hinting at a similar behavior as the inverse
power law $1/l$ ($l$ is the effective length of the system). The latter is a common behavior of quantum-confined nanosystems observed also, for example, in the context of carbon-based nanostructures. This given, the overall intensity associated to the onset appears similar in all spectra, due to the presence of additional excitations in the spectra of the dimer and trimer, which are energetically to the first one.

Beyond the onset, the absorption increases steeply in all spectra (see Figure 2). In the spectrum of the monomer, only two excitations appear beyond the first one, which we label $E_{II}$ and $E_{III}$. In the spectra of dimer and trimer, many more excited states and absorption maxima characterize the energy region between 4.8 eV and 5.5 eV. From the analysis of these excitations in terms of single-particle transitions, we identify two maxima that can be associated with $E_{II}$ and $E_{III}$. From these results, we can also calculate hole and electron densities that quantify their spatial distribution across solute and solvent:

$$
\rho_h^\lambda(r) = \sum_{\alpha\beta} A^\lambda_{\alpha\beta}|\phi_\alpha(r)|^2
$$  

and

$$
\rho_e^\lambda(r) = \sum_{\alpha\beta} A^\lambda_{\alpha\beta}|\phi_\beta(r)|^2,
$$

respectively, where $\phi_\alpha$ and $\phi_\beta$ are the occupied and unoccupied molecular orbitals included in the transition space, and $A^\lambda_{\alpha\beta}$ are the absolute squares of the normalized BSE coefficients, which act as weighting factors of $\phi_\alpha$ and $\phi_\beta$ for the $\lambda$-th excitation.

The results summarized in Figure 3 offer important insight for the overall understanding of the optical excitations in iodoplumbate precursors of LHPs in solution. First of all, it is evident that upon photoexcitation both the electron and the hole are essentially localized on the Pb-I backbone with very little contribution from the DMSO solvent molecules. This is a very relevant result, as it is proves that regardless of the formed complex structure between solute and solvent molecules, the latter essentially do not participate in the optical absorption. From this finding we can speculate that the presence of residual solvent molecules
Figure 3: Hole and electron densities of the first bright excitation $E_I$, $E_{II}$ and $E_{III}$ in the monomer (M), dimer (D), and trimer (T). Isosurfaces are plotted with a cutoff of 0.002 Å⁻³.

in processed LHP films will not prejudice its light-harvesting performance. The second important evidence emerging from the results in Figure 3 is the increasing delocalization of the electron and hole densities across the molecular backbone as the latter increases in size. In the monomer, a non-negligible portion of the electron density and, to a lower extent, also of the hole density are spilled-over onto the oxygen atom ($E_{M,I}$) and also on the sulphur atoms ($E_{M,II}$ and $E_{M,III}$). This characteristic is closely connected with the character and the spatial distribution of the molecular orbitals contributing to these excitations (see Supporting Information, Table S1 and Figure S2).

In the monomer, the relatively small spatial extension of the molecular backbone enhances the hybridization between solute and solvent also in the orbitals closest to the fundamental gap. The first excitation, $E_{M,I}$, stems entirely from the transition from the highest-occupied molecular orbital (HOMO) to the lowest-unoccupied orbital (LUMO). Also $E_{M,II}$ corresponds to a transition from the HOMO mainly targeting the LUMO+1. Finally, the highest-energy of the examined excitations, $E_{M,III}$, is formed by a mixture of different transitions, including the one from the HOMO to the LUMO+2, as well as from the HOMO-1 to the LUMO+1.
Because of their similar composition in terms of single-particle transitions, $E_{II}^M$ and $E_{III}^M$ exhibit very similar electron and hole densities. In the dimer, the first excitation, $E_{II}^D$, also stems from the HOMO→LUMO transition, although the contribution from HOMO-1→LUMO is non-negligible (see Table S1). $E_{III}^D$ exhibit a similar composition as in the monomer, while $E_{III}^D$ has a strongly mixed character, given by a number of transitions between the HOMO and the first few lowest-unoccupied orbitals. Notably, all the virtual states involved are largely delocalized along the iodoplumbate backbone (see Figure S2), as testified by the corresponding electron distribution in Figure 3. The longer extension of the iodoplumbate chain in the trimer, enhances the number of molecular orbitals contributing to the low-energy excitations. In $E_{T}^I$, contributions from the HOMO-1→LUMO and the HOMO→LUMO transitions can still be identified, while both $E_{II}^T$ and $E_{III}^T$ stem from a huge number of transitions reported in Table S2.

It is worth noting that the mixing of single-particle transitions is a signature of correlation effects that are quantitatively captured by the adopted ab initio many-body approach. The spatial distribution of the electron and hole densities, as analyzed above, is consistent with the relative OS of the corresponding excitations. In particular, the large overlap between electron and hole components combined with their extension along almost the entire chain length is responsible for the enhanced absorption with increasing number of iodoplumbate units. Even larger yield is expected in extensively coordinated LHP films.

After the analysis of the ab initio results, we can go back to the experimental spectra shown in Figure 1 and critically discuss our hypothesis, that the observed red-shift of the peaks at increasing solute concentration is related to the formation of iodoplumbate chains. Similarly to the experimental data, the spectra computed for the three modeled structures [PbI$_2$DMSO$_4$]$_N$ indeed exhibit a spectral shift to lower energies, as $N$ increases from 1 to 3. The iodoplumbate chains exhibit similar optical properties to previously reported polyiodide plumbate complexes formed in LHP precursor solutions (Figure 1). This observation is consistent with the fact that calculated hole and electron densities of polymeric iodoplumbate
chains are mainly localized on Pb and I atoms with only negligible contributions from solvent molecules. Thus, our results confirm the hypothesis that the absorption bands observed at high concentration of lead iodide solutions indeed correspond to the presence of polymeric iodoplumbate chains. It is important to note that most of the previously reported studies used a large excess of I\(^-\) (e.g., 1:150 ratio of PbI\(_2\):MAI) to generate spectroscopically detectable amounts of \([\text{PbI}_4\text{Sol}_2]^{2-}\) complexes, whilst 500 mM solution PbI\(_2\) has already showed a considerable amount of trimer species.\(^{31,33,34}\) Hence, in LHP precursor solutions with 1:1 ratio of PbI\(_2\) : MAI, the formation of polymeric iodoplumbates becomes quite likely. This fact suggests that the absorption spectrum of LHP precursor solutions at high concentration cannot be considered in terms of polyiodide plumbate (\([\text{PbI}_{2+n}\text{Sol}_m]^{n-}\)) complexes only. The presence of plumbate chains should be accounted for as well, when analyzing optical data of solutions.

In summary, we were able to reproduce experimental absorption spectra of LHP precursors in solutions from \textit{ab initio} many-body simulations of the optical response of iodoplumbate chains of increasing length atomistically interacting with solvent molecules. These findings confirm that these species exist in solution and have similar optical properties than plumbate complexes that are usually considered as LHP solution complexes. Our results demonstrate that, especially at high concentrations, the absorption spectrum of lead iodide-based solutions cannot be analyzed only in terms of “cluster-like” complexes: The presence of iodoplumbate chains should be considered as well. Further studies are required to establish possible connections between these chains and intermediate LHP structures formed during the crystallization of thin films.

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Supporting Information Available

Experimental and computational procedures, as well as additional details about the calculated structural, electronic, and optical properties of the considered iodoplumbate complexes are reported in the Supporting Information. References [68][72] are cited therein.
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