Frenkel Excitons in Vacancy-Ordered Titanium Halide Perovskites (Cs$_2$TiX$_6$)

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Abstract

Low-cost, non-toxic and earth-abundant photovoltaic materials are a long-sought target in the solar cell research community. Perovskite-inspired materials have emerged as promising candidates for this goal, with researchers employing materials design strategies including structural, dimensional and compositional transformations to avoid the use of rare and toxic elemental constituents, while attempting to maintain high optoelectronic performance. These strategies have recently been invoked to propose Ti-based vacancy-ordered halide perovskites (A$_2$TiX$_6$; A = CH$_3$NH$_3$, Cs, Rb, K; X = I, Br, Cl) for photovoltaic operation, following the initial promise of Cs$_2$SnX$_6$ compounds. Theoretical investigations of these materials, however, consistently overestimate their band gaps — a fundamental property for photovoltaic applications. Here,
we reveal strong excitonic effects as the origin of this discrepancy between theory and experiment; a consequence of both low structural dimensionality and band localization. These findings have vital implications for the optoelectronic application of these compounds, while also highlighting the importance of frontier-orbital character for chemical substitution in materials design strategies.

Perovskite-inspired materials aim to replicate the exceptional optoelectronic performance of lead-halide perovskites (LHPs), while avoiding issues of toxicity and operational stability. For decades, the standard materials design approach for identifying novel inorganic semiconductors has been chemical substitution, where the undesirable elemental constituents (e.g. toxic Pb$^{2+}$ in LHPs) are replaced by more favorable counterparts, while retaining the same structural motifs. For example, in the diamond-cubic crystal family, research moved from Group IV elements Si and Ge to II-VI compounds like CdTe – to yield direct rather than indirect electronic band gaps – and then further splitting into the I-III-VI$_2$ (e.g. CuInSe$_2$) and I$_2$-II-IV-VI$_4$ families (e.g. Cu$_2$ZnSnS$_4$) – to give earth-abundant compositions. While strategies such as dimensional modification$^2$ and disorder engineering$^{3,4}$ have recently risen in popularity, elemental substitution remains the prevailing design approach.

Strategies to replace the divalent B-site cation in halide perovskites, while retaining the BX$_6$ octahedral motif, have led to the exploration of A$_2$BB’X$_6$ double perovskites with a pair of monovalent and trivalent cations at the B and B’ sites,$^{1,5,6}$ as well as the A$_3$B$_2$X$_9$ ‘vacancy-
ordered perovskites’, where a trivalent B cation is combined with a 1/3 vacancy of the B-site to satisfy electroneutrality.\textsuperscript{7–9} Issues of indirect and/or large band gaps in these materials has led to the emergence of A\textsubscript{2}BX\textsubscript{6} vacancy-ordered double perovskites (VODPs), where now the combination of a tetravalent cation and a 50\% vacancy of the B site is employed, giving a checkerboard arrangement (Fig. 1).\textsuperscript{10–12} Also known as defective or tetravalent perovskites, these compounds are actually one of the decomposition products of conventional ABX\textsubscript{3} perovskites, for example CsSnI\textsubscript{3} which breaks down to form Cs\textsubscript{2}SnI\textsubscript{6}.\textsuperscript{13}

A\textsubscript{2}BX\textsubscript{6} vacancy-ordered perovskites have shown promise for optoelectronic applications, with good stability under air, moisture, light and thermal stresses, as well as being solution-processable and non-toxic.\textsuperscript{11,14,15} As with the single and double perovskites, the frontier orbitals of the B-cation and X-anion govern the conduction and valence band-edge properties, respectively. This combination allows tunability in the energy gap, absorption profile and carrier effective masses for example. The A-site species, on the other hand, is a large monovalent cation such as Cs\textsuperscript{+} which behaves as a spectator, dictating the spacing between BX\textsubscript{6} octahedra but with no direct contribution to the band edges. A crucial difference to the ABX\textsubscript{3} perovskite template, is the lack of corner-sharing BX\textsubscript{6} octahedra caused by vacancy introduction. Consequently, the crystal structure is comprised of isolated octahedra and thus an effective zero-dimensional (0D) framework, with this dramatic reduction in connectivity being a key factor in the properties of this material family.\textsuperscript{10,11,14} Research efforts in this area initially focused on the Sn-based compounds (A\textsubscript{2}SnX\textsubscript{6}),\textsuperscript{16} but have since expanded so that a range of tetravalent species have successfully been implemented in A\textsubscript{2}BX\textsubscript{6} materials, including Te, Pd, Zr and Pt.\textsuperscript{17–20} While some of these compounds have shown promise as potential white-light and tunable emitters, it is the Sn and Ti-based materials which have shown the most promising results in the context of solar photovoltaic applications, and thus received the majority of research attention. Cs\textsubscript{2}SnI\textsubscript{6} was originally used as a hole-transporting layer in dye-sensitized solar cells, for instance, achieving efficiencies of 8 \%,\textsuperscript{16} while a Cs\textsubscript{2}TiBr\textsubscript{6} photovoltaic device demonstrated a modest efficiency of 3 \%.\textsuperscript{14} The poor performance of
these materials has been attributed to relatively weak visible light absorption and indirect band gaps.\textsuperscript{21}

As issues of defect intolerance and operational instability becoming apparent for Cs\textsubscript{2}Sn\textsubscript{I\textsubscript{6}},\textsuperscript{22} there is growing interest in the Ti-based compounds. The effects on structure, stability and electronic properties in going from the Group 14 \textit{d}\textsuperscript{10}s\textsuperscript{0}Sn\textsuperscript{4+} to Group 4 \textit{d}\textsuperscript{0}s\textsuperscript{0}Ti\textsuperscript{4+} cations have been probed,\textsuperscript{10,11,23} however the performance limits of these materials remains an open question. Notably, while theoretical methods are found to successfully reproduce the experimental electronic structure of the Te- and Sn-based compounds,\textsuperscript{11} a major discrepancy exists for the \textit{d}\textsuperscript{0}Ti-based compounds,\textsuperscript{10,14,21,23–29} with severe overestimation of the experimental band gap by both hybrid Density Functional Theory (DFT) and Green’s function (\textit{GW}) methods. So extreme is the error, that these theoretical methods actually yield qualitatively incorrect relative band gap energies for the Sn vs Ti compounds, as we show in this study.

Through in-depth computations including explicit electron-hole interactions via the Bethe-Salpeter equation (BSE), we resolve the Ti perovskite discrepancy and reveal strong excitonic effects as the origin. Electron-hole interactions result in significant renormalization of the lowest-energy electronic excitation, as well as qualitative reshaping of the optical absorption spectrum, finally reconciling computational predictions with experimental measurements. We elucidate the origins of this behavior, and highlight the implications of strong exciton binding for applications of these materials in optoelectronic devices.

The crystal structure of the Cs\textsubscript{2}BX\textsubscript{6} (B = Sn, Ti; X = Cl, Br, I) family of vacancy-ordered perovskites is shown in Fig. 1. The low structural dimensionality of this family is expected to produce similar behavior to the corresponding [BX\textsubscript{6}]\textsuperscript{2−} molecular salts.\textsuperscript{16,24} One consequence of this ‘molecular’ crystal structure is the possibility for intermolecular interactions, such as London dispersion, between the localized octahedra. Table 1 corroborates this hypothesis, showing contraction of the calculated lattice parameters upon inclusion of dispersion corrections in the model, demonstrating the presence of important van der Waals
Figure 1: a. Crystal structure of Cs$_2$BX$_6$ vacancy-ordered perovskites, in the conventional cubic unit cell (space group: Fm$ar{3}$m). Cs atoms in green, M-cations in blue, and halide anions (X) in purple.

(vdW) bonding contributions. Indeed, geometry optimization with hybrid DFT excluding dispersion corrections consistently overestimates the experimental lattice parameters by $\sim 3\%$, whereas inclusion of vdW effects gives lattice constants with errors $< 1\%$ in all cases. Semi-local DFT including dispersion corrections (PBE+D3) was also found to accurately reproduce the experimental lattice constants (Table S1). The change in lattice parameter ($\Delta a_{D3}$) is consistent within each halide subclass, irrespective of the B-site identity (Sn or Ti), reflecting the expected inter- (BX$_6$–BX$_6$) rather than intra-octahedral (B–X) origin of these vdW interactions. Moreover, we demonstrate the importance of dispersion interactions between the BX$_6$ molecular blocks on the electronic properties, showing the calculated energy band gap to shift by $0.04 – 0.31$ eV in the optimized crystal structure. There is an increasing sensitivity of the band gap to the lattice parameter as we move down the halogen group (Cl $\rightarrow$ Br $\rightarrow$ I), as the through-space B–X and X–X interactions in the conduction and valence bands strengthen with larger X $p$ orbitals, also explaining the reduced band gap shifts for B = Ti due to the more localized $d$ orbitals. We further note a sensitivity of the
electronic band gap on the DFT functional choice for *geometry optimization*, with a band gap 0.4 eV lower (−40%) obtained for Cs₂SnI₆ using semi-local DFT (PBEsol) for structure relaxation.³⁰ Hybrid DFT including dispersion corrections was employed for all further DFT calculations in this study.

Table 1: Calculated cubic lattice parameters and electronic band gap shifts (ΔE₉,D₃) for Cs₂BX₆ (B = Sn, Ti; X = Cl, Br, I) using hybrid DFT including spin-orbit coupling (HSE06+SOC), with and without explicit inclusion of vdW dispersion interactions (D3 correction). Lattice parameter errors (Δa) given with respect to experimental values.

|                | Cs₂SnCl₆ | Cs₂SnBr₆ | Cs₂SnI₆ | Cs₂TiCl₆ | Cs₂TiBr₆ | Cs₂TiI₆ |
|----------------|----------|----------|----------|----------|----------|----------|
| a₁HSE06        | 10.65 Å  | 11.15 Å  | 11.95 Å  | 10.51 Å  | 10.99 Å  | 11.76 Å  |
| ∆a₁HSE06       | 2.8%     | 3.5%     | 2.7%     | 2.6%     | 2.9%     | 2.3%     |
| a₁HSE06+D3     | 11.03 Å  | 11.78 Å  | 11.54 Å  | 10.18 Å  | 10.62 Å  | 11.32 Å  |
| ∆a₁HSE06+D3    | −0.4%    | −0.1%    | −0.9%    | −0.6%    | −0.6%    | −1.5%    |
| a₁Exp          | 10.36 Å  | 10.77 Å  | 11.64 Å  | 10.24 Å  | 10.68 Å  | 11.5 Å   |
| ∆a₁D3          | −0.33 Å  | −0.37 Å  | −0.41 Å  | −0.33 Å  | −0.37 Å  | −0.44 Å  |
| ∆E₉,D3         | −0.14 eV | −0.23 eV | −0.31 eV | −0.04 eV | −0.08 eV | −0.15 eV |

*Experimental values taken from Refs: Cs₂SnCl₆,³¹,³² Cs₂SnBr₆,³²,³³ Cs₂SnI₆,³⁰,³²,³⁴–³⁶ Cs₂TiCl₆,²³,³⁷ Cs₂TiBr₆,²¹,²³,³⁷ Cs₂TiI₆,³⁸ matching with our measured values (Section S1.6).*

The electronic band structures, density of states and charge densities at the valence band maximum (VBM) and conduction band minimum (CBM) for Cs₂TiI₆ and Cs₂SnI₆ are shown in Figs. 2 and 3. While Cs₂SnX₆ exhibit direct electronic band gaps at Γ, Cs₂TiX₆ have indirect gaps with the CBM at the X high-symmetry k-point and the VBM remaining at Γ – in agreement with experimental studies.¹⁵,²¹ The direct/indirect gap energy difference (Δ) is relatively small however, with Δ = 0.06 eV, 0.07 eV and 0.04 eV for the I, Br and Cl isomorphs respectively calculated using HSE06+SOC. As previously noted,¹⁰,¹¹ the VBM and CBM electronic levels follow that predicted by BX₆²⁻ crystal-field splitting molecular orbital diagrams, with a t₂g(π) Ti d – X p CBM for Cs₂TiX₆ (dₓᵧ, dₓz, dᵧz; threefold degenerate at Γ) and an e₃g(σ) band just above (dₓ² & dₓ₋ᵧ²), a single a₁g(σ) Sn s – X p CBM for
Figure 2: a. Electronic band structure of Cs$_2$TiI$_6$ calculated with hybrid DFT including spin-orbit coupling (HSE06+SOC), alongside a vertical plot of the orbital-projected electronic density of states. Faded gray and green arrows indicate the lowest-energy symmetry-forbidden and allowed electronic transition ($\Delta E_{t^1_u/t^1_u} = 0.02$ eV), respectively. Valence band in blue, conduction band in orange, and valence band maximum (VBM) set to 0 eV. Ti $d$ conduction bands are labeled with their crystal field orbital symmetries. Charge densities at the (b.) conduction band minimum (CBM) and (c.) VBM. Unoccupied states in yellow, occupied states in blue.

Cs$_2$SnX$_6$, and non-bonding X $p$ $t_{2g}(\pi)$ states at the VBM in all cases (Figs. 2 and 3 c). The centrosymmetric crystal structure and equal (gerade) parity with respect to inversion for the VBM and CBM states (Figs. 2 and 3 b,c) results in a dipole-forbidden transition at the direct band gap. Consequently, the symmetry-allowed direct band gap ($E_{g, \text{Allowed}}$) corresponds to the vertical transition from the second-highest valence band at $\Gamma$ ($t_{1u}$ ($\Gamma_{15}$) symmetry; $\psi_{\text{VBM-1}}$) to the CBM.

The halide $p$ valence band is similar for both compounds, though with a slightly wider bandwidth ($\sim$0.5 eV) for the Ti analogues (Figs. 2 and 3 & Figs. S3 to S8) due to a significantly reduced anion-anion distance ($d_{\text{I-I}} = 4.03$ Å vs 3.87 Å for Cs$_2$SnI$_6$ vs Cs$_2$TiI$_6$) and wider interaction range between the cation valence orbitals (Ti $s$ and $d$) with anion $p$ states in the lower valence band, compared to Sn $p$. This is a consequence of reduced M-X bond lengths (2.73 Å vs 2.85 Å) and lattice parameters for B = Ti vs Sn (Table 1) — aided by
Figure 3: a. Electronic band structure of Cs$_2$SnI$_6$ calculated with hybrid DFT including spin-orbit coupling (HSE06+SOC), alongside a vertical plot of the orbital-projected electronic density of states. Faded gray and green arrows indicate the lowest-energy symmetry-forbidden and allowed electronic transition ($\Delta E_{t_{1g}/t_{1u}} = 0.38$ eV), respectively. Valence band in blue, conduction band in orange, and VBM set to 0 eV. Charge densities at the (b.) conduction band minimum (CBM) and (c.) valence band maximum (VBM), using the same isosurface levels as for Cs$_2$TiI$_6$. Unoccupied states in yellow, occupied states in blue.

Another consequence is that, in contrast to the electron masses, the hole effective masses are actually larger for Cs$_2$SnX$_6$ than for Cs$_2$TiX$_6$ (Table 2). Unlike conventional perovskites and many other ‘perovskite-inspired’ materials which retain the partially-oxidized, filled valence subshell of the B cation (yielding antibonding character at the VBM$^{1,39,40}$), the fully-oxidized B$^{4+}$ in A$_2$BX$_6$ means we have a less dispersive, non-bonding VBM$^4$, yielding heavier hole masses (particularly for X = Br, Cl) and aiding carrier localization. In contrast, the conduction band of the Sn analogues is relatively disperse with low electron effective masses (Table 2) due to strong mixing and delocalization of the Sn $s$ and X $p$ states, while extremely flat bands are found for B = Ti due to weak Ti $d$ - X $p$ mixing and localized, isolated Ti $d$ states. The band structures of the bromide and chloride isomorphs are in-
cluded in Figs. S3 to S8, showing similar results, though with larger band gaps and reduced
dispersion as X changes from I to Br to Cl. Further analysis of the electronic structure is
provided in Section S2.

The electronic properties of the $\text{Cs}_2\text{BX}_6$ family are tabulated in Table 2. In order to
illustrate the expected trends in exciton binding based on band structure and dielectric
screening, the Wannier-Mott model binding energies are also included, calculated using the
average carrier effective masses ($m_e/m_h$) and high-frequency dielectric constants ($\varepsilon_\infty$) from
hybrid DFT (HSE06+SOC) according to:\(^{41}

$$E_{\text{ex}} = -\frac{\mu}{m_0\varepsilon_\infty^2}\text{Ry}$$

where $\mu = (m_e \times m_h)/(m_e + m_h)$ is the reduced mass of the electron-hole pair, Ry is the
Rydberg energy (13.6 eV) and $m_0$ is the electron rest mass.

Table 2: Calculated direct ($E_g$, Direct) and direct-allowed band gaps ($E_g$, Allowed), effective
masses ($m_e$)\(^a\), high-frequency dielectric constants ($\varepsilon_\infty$) and Wannier-Mott model exciton
binding energies ($E_{\text{ex, Wannier}}$) for $\text{Cs}_2\text{BX}_6$ ($B = \text{Sn}, \text{Ti}; X = \text{Cl}, \text{Br}, \text{I}$) using hybrid DFT
including spin-orbit coupling (HSE06+SOC). Comparison given to experimentally-reported
band gap ranges.\(^b\)

|                | $\text{Cs}_2\text{SnCl}_6$ | $\text{Cs}_2\text{SnBr}_6$ | $\text{Cs}_2\text{SnI}_6$ | $\text{Cs}_2\text{TiCl}_6$ | $\text{Cs}_2\text{TiBr}_6$ | $\text{Cs}_2\text{TiI}_6$ |
|----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $E_g$, Direct   | 4.10 eV                     | 2.39 eV                     | 0.71 eV                     | 3.68 eV                     | 2.75 eV                     | 1.69 eV                     |
| $E_g$, Allowed  | 4.38 eV                     | 2.70 eV                     | 1.09 eV                     | 3.79 eV                     | 2.84 eV                     | 1.71 eV                     |
| $E_g$, Exp      | 4.4-4.9 eV                  | 2.7-3.3 eV                  | 1.25-1.3 eV                 | 2.8-3.4 eV                  | 1.8-2.3 eV                  | 1.0-1.2 eV                  |
| $m_e$           | 0.55 $m_0$                  | 0.38 $m_0$                  | 0.26 $m_0$                  | 3.5 $m_0$                   | 2.7 $m_0$                   | 1.8 $m_0$                   |
| $m_h$           | 2.2 $m_0$                   | 1.3 $m_0$                   | 0.78 $m_0$                  | 2.2 $m_0$                   | 0.90 $m_0$                  | 0.55 $m_0$                  |
| $\varepsilon_\infty$ | 2.86                        | 3.37                        | 4.54                        | 3.26                        | 3.84                        | 5.08                        |
| $E_{\text{ex, Wannier}}$ | 0.73 eV                     | 0.35 eV                     | 0.13 eV                     | 1.73 eV                     | 0.62 eV                     | 0.22 eV                     |

\(^a\) $m_e$ are computed from the harmonic mean over directions and light/heavy bands for the effective
masses. Values greater than 1 are given to 1 decimal place.

\(^b\) Experimental band gap values taken from Refs: $\text{Cs}_2\text{SnCl}_6,$\(^{31,32,42,43}$ $\text{Cs}_2\text{SnBr}_6,$\(^{32,35,36,42-44}$ $\text{Cs}_2\text{SnI}_6,$\(^{16,17,31,32,35,42,45}$ $\text{Cs}_2\text{TiCl}_6,$\(^{23,37}$ $\text{Cs}_2\text{TiBr}_6,$\(^{14,15,21,23,24,37,38,46}$ $\text{Cs}_2\text{TiI}_6.$\(^{24,37}$

From Table 2, we witness the typical trend of larger band gap with smaller and more elec-
tronegative halogen anions ($E_g(\text{Cl}) > E_g(\text{Br}) > E_g(\text{I})$), as observed across the perovskite(-
inspired) family. Typically, the smaller the B-site atom, the smaller the band gap in the $A_2BX_6$ family. This is the case experimentally here, with all Ti isomorphs having smaller experimentally-measured band gaps than their Sn counterparts. The opposite trend is found in the computed band gaps, for which hybrid DFT incorrectly predicts larger gaps for the Ti compounds (except for $X = \text{Cl}$). While the direct-allowed gaps computed by hybrid DFT mostly coincide with the lower end of experimental ranges for $\text{Cs}_2\text{SnX}_6$, neglecting Wannier-Mott predicted exciton binding, the entirely opposite trend is found for each $\text{Cs}_2\text{TiX}_6$ isomorph, with a consistent severe overestimation of the experimental band gap. Notably, screened hybrid DFT (HSE06) tends to slightly underestimate rather than overestimate semiconductor band gaps, with this underestimation typically worsening with larger band gaps. The error in predicted band gaps for $\text{Cs}_2\text{TiX}_6$ results in qualitatively incorrect relative band gap energies for $\text{Cs}_2\text{SnX}_6$ vs $\text{Cs}_2\text{TiX}_6$ ($X = \text{I, Br}$).

A dielectric-dependent hybrid functional approach was also tested, which can improve the description of dielectric screening from hybrid DFT with fixed exchange (e.g. HSE06) and give reduced band gap prediction errors, though this only slightly reduced the hybrid DFT gap for $\text{Cs}_2\text{TiI}_6$ by 0.04 eV ($\alpha_{\text{SCF}} = 24\%$), still giving a significantly over-estimated band gap with a relative error $\Delta E_g = \sim 70\%$. Even using the computationally-intensive GW approximation, typically a gold standard for predicting band gaps, the calculated quasiparticle gaps in fact show far worse overestimation (both for $\text{Cs}_2\text{TiX}_6$ — as previously noted by Cucco et al., and $\text{Cs}_2\text{SnX}_6$; Section S3). These observations suggest the presence of physical interactions in $\text{Cs}_2\text{TiX}_6$ which are not captured in these single-particle electronic models.

This major experiment-theory discrepancy is witnessed in reported values across the literature, but has not been addressed until now. In many cases, semi-local DFT (known to severely underestimate semiconductor band gaps) has been employed in order to yield fortuitous error cancellation and thus theoretical values closer to experiment. As we show in this work, however, semi-local DFT predicts qualitatively incorrect relative
band gaps (even finding Cs$_2$SnI$_6$ to be metallic for example; Table S3), alongside incorrect absorption spectra, thus being unsuitable for modeling the electronic structure of A$_2$BX$_6$ compounds.

Using the Wannier-Mott effective mass model (Table 2),$^{54}$ we find large exciton binding energies, particularly for the Ti compounds (due to flat bands and heavy carrier masses), suggesting strong electron-hole interactions in these materials. Moreover, the large Wannier-Mott binding energies, isolated octahedra, low dielectric screening and highly-localized $d$ orbitals suggests that strongly-bound excitons may be formed for Cs$_2$TiX$_6$.$^{41}$ To explore this hypothesis, we extend our model using GW to calculate quasiparticle eigenvalues and include electron-hole interactions via the Bethe-Salpeter equation (BSE). The optical absorption spectrum calculated with this approach, alongside that obtained from hybrid DFT and the experimental data, is shown in Fig. 4.

![Figure 4: Optical absorption spectra of (left to right) Cs$_2$TiI$_6$, Cs$_2$TiBr$_6$ and Cs$_2$TiCl$_6$, calculated with both hybrid DFT (dotted violet) and the $G_0W_0 + BSE$ method (solid blue), alongside the experimental data from UV-Vis spectroscopy (dashed green). To directly compare the spectral shapes, calculated curves have been rigidly shifted to match the experimental absorption onset (unshifted results shown in Section S3).](image-url)

Electron-hole interactions are found to dramatically redshift (Tables S2 and S3 and Fig. S10) and qualitatively alter the absorption spectra for Cs$_2$TiX$_6$, now yielding excellent agreement with the peaked experimental spectra. Analysis of the electronic states reveals the lowest energy *bright* exciton peak to originate from the $t_{1u}(\pi + \sigma) \rightarrow t_{2g}(d)$ electronic transition as expected, i.e. from the second-highest valence band ($\psi_{\text{VBM}-1}$) at $\Gamma$ (Fig. 2) to the CBM. The lowest energy *dark* excitonic state, indicated by the arrows in Fig. 4 and located
0.3-0.4 eV below the first bright peak, corresponds to the symmetry-forbidden $t_{1g}(\pi) \psi_{\text{VBM}} \rightarrow t_{2g}(d) \psi_{\text{CBM}}$ transition mentioned previously. While improved agreement with the experimental spectra is found for all Cs$_2$TiX$_6$ isomorphs, smaller changes in the spectral shapes are noticed for X = Br, Cl. This results from the low band dispersion in these compounds (demonstrated by the large effective masses in Table 2), resulting in similar strong excitonic downshifting of the low-energy excitations; $t_{1u}(\pi + \sigma) \rightarrow t_{2g}(d)$ and $t_{2u}(\pi) \rightarrow t_{2g}(d)$ corresponding to $\langle \psi_{\text{VBM} - 1}|H'|\psi_{\text{CBM}}\rangle$ and $\langle \psi_{\text{VBM} - 2}|H'|\psi_{\text{CBM}}\rangle$ transitions. Indeed in their recent paper, Grandhi et al.\textsuperscript{37} refer to the absorption onset of Cs$_2$TiBr$_6$ as an exciton peak, with our calculations revealing in fact both low-energy peaks to be excitonic in nature. This strong renormalization of the low-energy excitations and lack of a band-like absorption onset rules out standard spectrum fitting techniques (such as the Tauc and Elliott models) for extracting band gap and exciton binding energies.\textsuperscript{55,56} Notably, the experimental spectra for TiBr$_6^{2-}$ and TiCl$_6^{2-}$ salts reported in Brisdon et al.\textsuperscript{57} closely resemble the results for Cs$_2$TiBr$_6$ and Cs$_2$TiCl$_6$ reported here and in the literature,\textsuperscript{37,38} evidencing the conclusion of molecular crystal behavior, the orbital assignments of the absorption peaks and the presence of strong electron-hole interactions. Improved agreement between the calculated and experimental spectra is also found for the Sn compounds upon inclusion of electron-hole interactions, as weaker exciton interactions modify transition intensities and shift spectral weights to give more peak-like absorption onsets. The small residual mismatch in some cases between the $GW$+BSE and experimental spectra could be a result of temperature effects (vibrations can lower the symmetry-restriction of dark excitonic transitions in this range), quasiparticle lifetime broadening or the neglect of higher order terms in $GW$.\textsuperscript{56,58,59}

We highlight that the low-energy absorption peaks for Cs$_2$TiX$_6$ correspond to charge-transfer Frenkel excitons, with the electron wavefunction localized on the Ti $t_{2g}$ d orbitals ($d_{xy}$, $d_{xz}$, $d_{yz}$) and the hole localized on the surrounding X p orbitals of the BX$_6$ octahedron. This form of exciton is commonly witnessed in organic and molecular crystals,\textsuperscript{60} and has been well-established in other $3d^0$ (Ti$^{4+}$, Sc$^{3+}$, Ca$^{2+}$) halides,\textsuperscript{61} arising here as a consequence
Figure 5: Optical absorption spectra of (left to right) Cs$_2$SnI$_6$, Cs$_2$SnBr$_6$ and Cs$_2$SnCl$_6$, calculated with both hybrid DFT (dotted violet) and the $G_0W_0+BSE$ method (solid blue), alongside the experimental data from UV-Vis spectroscopy (dashed green). To directly compare the spectral shapes, calculated curves have been rigidly shifted to match the experimental absorption onset (unshifted results shown in Section S3). For Cs$_2$SnCl$_6$, the absorption spectrum recorded by Karim et al.$^{32}$ is also shown for comparison (downshifted by 0.5 eV as discussed in Section S3.4).

of the 0D polyhedral connectivity. The strongly-bound nature of these excitons is further demonstrated by the band contributions (‘fatband plot’) shown in Fig. 6, where the delocalization of the exciton wavefunctions in reciprocal space for the Ti compounds corresponds to real space localization of the exciton wavepacket.$^{41}$ The large Stokes shifts ($\sim$0.5 eV) and broad PL emission observed for this family of materials in both this and other studies$^{15,21,23}$ is another characteristic result of localized bound excitons, as well as strong exciton-phonon coupling and low-energy dark excitons, with the photogenerated electron-hole pair readily localizing within the lattice to yield emissive self-trapped exciton (STE) states.

In contrast, the reduced effective masses of Cs$_2$SnX$_6$ yield a weakly-bound exciton as expected, demonstrated by dominant band contributions at the $\Gamma$ point to the first bright exciton state. Fig. 6 also illustrates the differing trends in band structure for $B =$ Sn/Ti, as X changes from I to Br to Cl, with a greater band gap increase and reduction in conduction band dispersion for Cs$_2$SnX$_6$ than Cs$_2$TiX$_6$ (such that the relative band gap energies of $B =$ Sn/Ti changes from $X =$ I ($E_g, \text{Sn} < E_g, \text{Ti}$) to $X =$ Cl ($E_g, \text{Ti} < E_g, \text{Sn}$)), due to the greater localization of the Ti $d$ states. As discussed in Section S3, quasiparticle band gaps and thus exciton binding energies from $GW(+BSE)$ remain overestimated for these vacancy-ordered compounds, consistent with recent studies which attribute this behavior to under-screening.
Figure 6: Band contributions to the brightest exciton state at the absorption onset in Cs$_2$SnX$_6$ (top) and Cs$_2$TiX$_6$ (bottom), calculated using the BSE approach. Band eigenvalues are indicated by the black dots, with filled circles weighted by their contributions to the exciton state and gray interpolating bands. The average of the three degenerate brightest states at the absorption onset is used, with the sum area of the filled circles normalized across all compositions. Hole and electron states are shown in blue and orange, respectively, and the VBM is set to 0 eV.
errors within the Random Phase Approximation (RPA) employed within GW.\textsuperscript{10,62–64} As such, to avoid this issue and obtain a reasonable estimate of the exciton binding energies in these systems, we also employed a constrained-supercell approach in which an exciton state is generated by controlling spin initialisation and band occupation. Here we calculate the exciton binding energy using hybrid DFT for multiple supercell sizes up to 972 atoms, then extrapolate to the dilute limit using the relevant scaling relationship to avoid supercell-size effects.\textsuperscript{65,66} With this approach, we obtain localised Frenkel exciton states as expected for each Cs\textsubscript{2}TiX\textsubscript{6} (Fig. S13, TOC), with extrapolated binding energies of 0.44 eV, 0.52 eV and 0.72 eV for X = I, Br, Cl (Fig. S14), which when subtracted from the HSE06+SOC direct-allowed transition energies in Table 2 brings the hybrid DFT optical transition energy into agreement with the experimental values in each case. For Cs\textsubscript{2}SnX\textsubscript{6}, the electron and hole remain delocalised across the supercell with this approach (under a maximum cell length of 23.1 Å; Fig. S13), yielding extrapolated binding energies close to zero (Fig. S15). Further details provided in Section S3.3.

Crucially, these results demonstrate the presence of qualitatively different electronic behavior in the Cs\textsubscript{2}SnX\textsubscript{6} and Cs\textsubscript{2}TiX\textsubscript{6} families, where despite retaining the same cation valence, the change in frontier orbital character upon substitution of Sn\textsuperscript{4+} with Ti\textsuperscript{4+} dramatically alters the electronic structure and optical absorption. From the band structures in Fig. 6 and values in Table 2, it is clear that the electron effective masses (\(m_e\)) dictate the exciton behavior in this family, with the weak dispersion and strong real-space localization of the flat \(d\) orbital conduction bands in Cs\textsubscript{2}TiX\textsubscript{6}, aided by the zero-dimensional crystal structure, yielding strong electron-hole interactions. This strong excitonic renormalization of the optical absorption in Cs\textsubscript{2}TiX\textsubscript{6} explains the origin of longstanding discrepancies between experiment and theoretical models of their electronic structure. Moreover, these findings serve as a warning of the changes that can occur when employing ionic substitution as a materials design approach, when such strategies involve changes in valence orbital character.

The presence of strong excitonic interactions in this material family is unsurprising, given
the low structural and electronic dimensionality (Figs. 1 and 2), weak band dispersion and
large carrier effective masses (Table 2) discussed above. We find the exciton binding strength
to be governed by the conduction band character in these compounds, giving the expectation
for similar strongly-bound Frenkel excitons in \( \text{A}_2\text{BX}_6 \) compounds with isoelectronic \((d^0)\) \( \text{B}^{4+} \) cations, such as Zr and Hf. Indeed, strong excitonic interactions have been recently been
reported in \( \text{Cs}_2\text{ZrX}_6 \) — promising white-light emitters,\(^\text{20}\) and a distinct excitonic feature is
seen at the absorption onset in \( \text{Cs}_2\text{HfCl}_6 \)\(^\text{67,68}\) — which has emission and radiation detection
applications. Moreover, the bound excitonic behavior in this material class is very similar to
that witnessed in the double perovskites,\(^\text{55,69,70}\) which despite a greater structural connect-
tivity, exhibit a low \emph{effective} electronic dimensionality due to orbital mismatch between the
\( \text{B} \)-site cations.\(^\text{5,71}\) Likewise, extension of theoretical models to include explicit electron-hole
interactions was required in order to reproduce the experimental spectrum,\(^\text{55,70,72}\) explaining
the excitonic origin of the direct absorption onset.

In conclusion, by revealing strongly-bound excitonic behavior in the caesium titanium
halide vacancy-ordered perovskites \( \text{Cs}_2\text{TiX}_6 \), we reconcile longstanding discrepancies be-
tween theoretical predictions and experimental measurements for this material class. While
previous theoretical studies have found semi-local DFT to yield band gaps matching ex-
periment, we show this to be the result of fortuitous error cancellation with qualitatively
incorrect absorption spectra and relative band gaps for \( \text{Cs}_2\text{SnX}_6 \) vs \( \text{Cs}_2\text{TiX}_6 \) \((\text{X} = \text{I, Br})\).
Our results show that electron-hole interactions are crucial to obtaining the correct polar-
izability and dielectric screening between octahedra within many-body perturbation theory
(MBPT) in these low-electronic-dimensionality systems. A range of optical, photoelectron
and polarization spectroscopies could be employed to further study the behavior of excitons
in this material class, including Stark spectroscopy, temperature-dependent optical measure-
ments, excitation-dependent THz and electromodulation spectroscopies.\(^\text{58,61,69,73}\) Moreover,
the majority of previous theoretical studies have not included vdW dispersion interactions
when modeling these systems, yet here we demonstrate their importance in obtaining ac-
curate crystal and electronic structure predictions, calling for their inclusion in future computational studies of these and related low-dimensional and ‘molecular’ crystals such as the $A_4BX_6$ family.

These findings have important implications for optoelectronic applications. Strong exciton binding can significantly reduce charge separation and open-circuit voltages ($V_{oc}$) in solar cells, likely one of the key origins of the poor photovoltaic performance achieved thus far in this material class. Our results show the key role of structural dimensionality and octahedral connectivity, alongside orbital chemistry, in determining the effective electronic dimensionality and optoelectronic properties of inorganic perovskite-inspired materials. More generally, these findings illustrate the importance of considering frontier orbital character when employing atomic substitution in materials engineering and design strategies – here resulting in qualitatively different electronic behavior despite equal cation valence and similar band gaps.

Calculations were performed using both Density Functional Theory (DFT) and quasiparticle Green’s function (GW) approaches within periodic boundary conditions, through the Vienna Ab Initio Simulation Package (VASP). Scalar-relativistic pseudo-potentials were employed to describe the interaction between core and valence electrons, via the projector-augmented wave (PAW) method. Specifically, the Cs\textsubscript{sv}, Sn\textsubscript{d}, Ti\textsubscript{pv}, I, Br and Cl VASP PAW potentials were used. The effect of pseudopotential choice and DFT starting point (semi-local vs hybrid) on the GW results was tested and found to give qualitatively similar results, with the same large overestimation of bandgaps relative to experiment (details in Section S3).

Initial guesses for the crystal structures were obtained from the Materials Project, before relaxing the geometry using the HSE06 screened hybrid DFT functional. The plane-wave energy cutoff and $\Gamma$-centered $k$-point mesh were sequentially increased using \texttt{vaspup2.0} until total energies from static calculations were converged to 0.1 meV/atom – giving values of 300 eV and $3 \times 3 \times 3$ (for the 9-atom primitive unit cell, equivalent to a $k$-point density...
of 0.33 Å⁻¹ in reciprocal space) respectively. During structural optimization, a convergence
criterion of 0.01 eV/Å was imposed on the forces on each atom, and the plane-wave energy
cutoff was increased to 500 eV, as well as re-relaxing the final geometries, to avoid Pulay stress
effects. As discussed at the beginning of the results section, the effect of dispersion corrections
(Grimme’s D3) on the structural relaxation was tested and shown to be important; and so
the HSE06+D3 (using the recommended PBE0+BJ parameterizations) relaxed unit cells
were used for all further calculations in this work.

Electronic band structures and and independent-particle optical absorption spectra were
initially calculated with the HSE06 hybrid DFT functional, including spin-orbit coupling
effects (HSE06+SOC) due to the presence of heavy-atom elements (see Results and Sec-
tion S4). For density of states (DOS) and optical calculations, the k-point mesh for the
primitive unit cell was increased to 8 × 8 × 8 (reciprocal space density of 0.12 Å⁻¹), and
the tetrahedron smearing method was used. The number of virtual states in the optical
calculations was increased using vaspup2.0 until the high-frequency dielectric constant
ε∞ was converged to a precision of 0.01. Electronic band structure diagrams were generated
using sumo. Carrier effective masses were determined using non-parabolic fitting of the
band edges through the effmass package.

Wavefunctions calculated using HSE06+SOC were used as input orbitals for the G0W0(+BSE)
calculations. While only having a modest effect on the band gap energies, SOC was found
to have a relatively significant effect on the spectral shape above the absorption onset, as
shown in Section S4. Convergence with respect to the number of virtual states / empty
bands, imaginary frequency and time grid points, and electron-hole excitation pairs was
confirmed in each case. Given the lack of symmetry reduction, requirement for large num-
bers of virtual states / empty bands (particularly when including spin-orbit coupling effects)
and rapid scaling of computational cost (memory) with k-point density in the G0W0+BSE
calculations, a 3 × 3 × 3 mesh (for the 9-atom primitive unit cell, equivalent to a k-point
density of 0.33 Å⁻¹ in reciprocal space) was the maximum tractable k-point mesh for Cs₂BX₆
with our computational resources. While converged for the Br and Cl compounds, the greater band dispersion of the iodides (Cs$_2$BI$_6$) means the spectra are not well converged for this k-point density, thus the ‘model BSE’ approach$^{82,83}$ was employed to reach converged k-point meshes of $4 \times 4 \times 4$ and $8 \times 8 \times 8$ for Cs$_2$TiI$_6$ and Cs$_2$SnI$_6$ respectively. Further details on the $G_0W_0$+BSE calculations are given in Section S3.

Details of the experimental synthesis and absorption measurements are provided in Section S1.

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Supporting Information Available

Experimental Methods; DFT Functional Dependence of Lattice Parameters; Additional Electronic Structure Analysis; Further GW Calculation Details & Analysis; Spin-Orbit Coupling (SOC) Analysis. Data produced during this work is freely available at: 10.5281/zenodo.6906620.

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