

Frenkel Excitons in Vacancy-ordered Titanium Halide Perovskites (Cs_2TiX_6)

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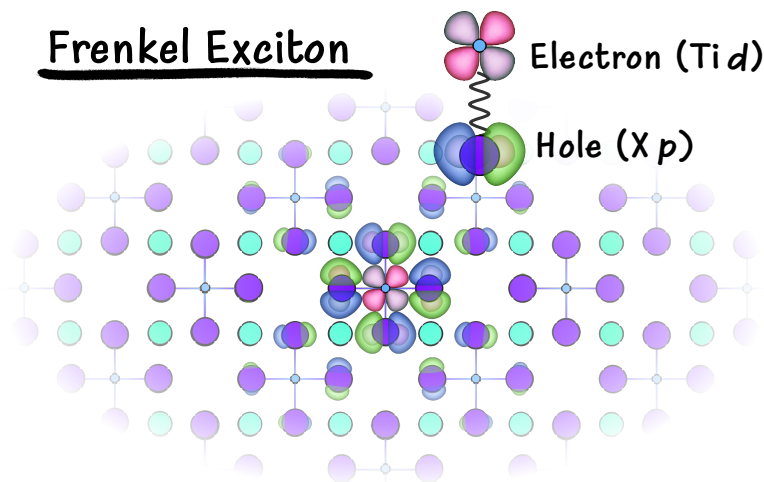
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Abstract

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_2TiX_6 ; $\text{A} = \text{CH}_3\text{NH}_3$, Cs, Rb, K; $\text{X} = \text{I}, \text{Br}, \text{Cl}$) for photovoltaic operation, following the initial promise of Cs_2SnX_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.¹ 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-VI₂ (e.g. CuInSe_2) and I₂-II-IV-VI₄ families (e.g. $\text{Cu}_2\text{ZnSnS}_4$) – to give earth-abundant compositions. While strategies such as dimensional modification² and disorder engineering³ 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 $A_2BB'X_6$ double perovskites with a pair of monovalent and trivalent cations at the B and B' sites,^{1,4,5} as well as the $A_3B_2X_9$ ‘vacancy-ordered perovskites’, where a trivalent B cation is combined with a 1/3 vacancy of the B-site to satisfy electroneutrality.^{6–8} Issues of indirect and/or large band gaps in these materials has led to the emergence of A_2BX_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).^{9–11} Also known as defective or tetravalent perovskites, these compounds are actually one of the decomposition products of conventional ABX_3 perovskites, for example $CsSnI_3$ which breaks down to form Cs_2SnI_6 .¹²

A_2BX_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.^{10,13,14} 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^+ which behaves as a spectator, dictating the spacing between BX_6 octahedra but with no direct contribution to the band edges. A crucial difference to the ABX_3 perovskite template, is the lack of corner-sharing BX_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.^{9,10,13} Research efforts in this area initially focused on the Sn-based compounds (A_2SnX_6),¹⁵ but have since expanded so that a range of tetravalent species have successfully been implemented in A_2BX_6 materials, including Te, Pd, Zr and Pt.^{16–19} 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_2SnI_6 was originally used as a hole-transporting layer

in dye-sensitized solar cells, for instance, achieving efficiencies of 8%,¹⁵ while a Cs₂TiBr₆ photovoltaic device demonstrated a modest efficiency of 3%.¹³ The poor performance of these materials has been attributed to relatively weak visible light absorption and indirect band gaps.²⁰

As issues of defect intolerance and operational instability becoming apparent for Cs₂SnI₆,²¹ there is growing interest in the Ti-based compounds. The effects on structure, stability and electronic properties in going from the Group 14 $d^{10}s^0$ Sn⁴⁺ to Group 4 d^0s^0 Ti⁴⁺ cations have been probed,^{9,10,22} 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,¹⁰ a major discrepancy exists for the d^0 Ti-based compounds,^{9,13,20,22–28} with severe overestimation of the experimental band gap by both hybrid Density Functional Theory (DFT) and Green’s function (*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.

Results & Discussion

The crystal structure of the Cs₂BX₆ (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 [BX₆]²⁻ molecular salts.^{15,23} One consequence of this ‘molecular’ crystal structure is the possibility for intermolecular interactions, such as

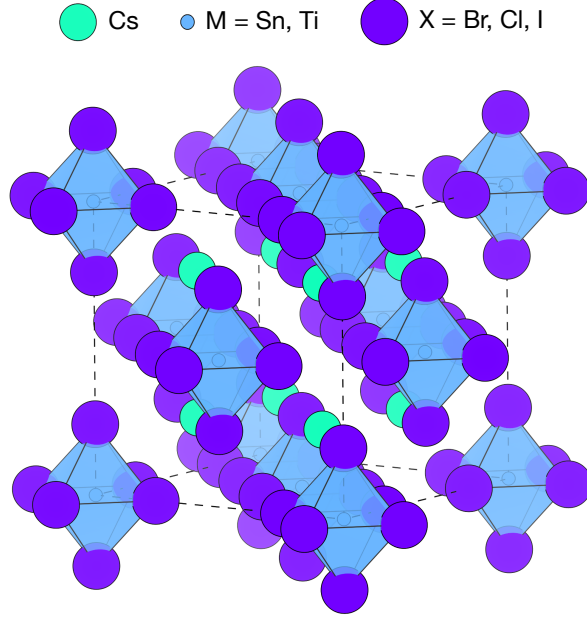


Figure 1: **a.** Crystal structure of Cs_2BX_6 vacancy-ordered perovskites, in the conventional cubic unit cell (space group: $Fm\bar{3}m$). Cs atoms in green, M-cations in blue, and halide anions (X) in purple.

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 (vdW) bonding contributions. Indeed, geometry optimization without dispersion corrections consistently overestimates the experimental lattice parameters by $\sim 3\%$ in this material class, whereas inclusion of vdW effects gives lattice constants with errors $< 1\%$ in all cases. The change in lattice parameter ($\Delta a_{w/D3}$) is consistent within each halide subclass, irrespective of the B-site identity (Sn or Ti), reflecting the expected *inter-* ($\text{BX}_6\text{-BX}_6$) 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 $B = \text{Ti}$ 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 Cs_2SnI_6 using semi-local DFT (PBEsol) for structure relaxation.²⁹ 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 ($\Delta E_{g, w/D3}$) for Cs_2BX_6 ($B = \text{Sn, Ti}$; $X = \text{Cl, Br, I}$) 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.^a

	Cs_2SnCl_6	Cs_2SnBr_6	Cs_2SnI_6	Cs_2TiCl_6	Cs_2TiBr_6	Cs_2TiI_6
a_{HSE06}	10.65 Å	11.15 Å	11.95 Å	10.51 Å	10.99 Å	11.76 Å
Δa_{HSE06}	2.8 %	3.5 %	2.7 %	2.6 %	2.9 %	2.3 %
$a_{\text{HSE06+D3}}$	10.32 Å	10.78 Å	11.54 Å	10.18 Å	10.62 Å	11.32 Å
$\Delta a_{\text{HSE06+D3}}$	-0.4 %	0.1 %	-0.9 %	-0.6 %	-0.6 %	-1.5 %
a_{Exp}	10.36 Å	10.77 Å	11.64 Å	10.24 Å	10.68 Å	11.5 Å
$\Delta a_{w/D3}$	-0.33 Å	-0.37 Å	-0.41 Å	-0.33 Å	-0.37 Å	-0.44 Å
$\Delta E_{g, w/D3}$	-0.14 eV	-0.23 eV	-0.31 eV	-0.04 eV	-0.08 eV	-0.15 eV

^a Experimental values taken from Refs: Cs_2SnCl_6 ,^{30,31} Cs_2SnBr_6 ,^{31,32} Cs_2SnI_6 ,^{29,31,33-35} Cs_2TiCl_6 ,^{22,36} Cs_2TiBr_6 ,^{20,22,36} Cs_2TiI_6 ,³⁷ 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 Cs_2TiI_6 and Cs_2SnI_6 are shown in Figs. 2 and 3. While Cs_2SnX_6 exhibit direct electronic band gaps at Γ , Cs_2TiX_6 have indirect gaps with the CBM at the \mathbf{X} high-symmetry k -point and the VBM remaining at Γ – in agreement with experimental studies.^{14,20} The direct/indirect gap energy difference (Δ) is relatively small however, with $\Delta = 0.06$ eV, 0.07 eV and 0.04 eV for the I, Br and Cl isomorphs respectively calculated using HSE06+SOC. As previously noted,^{9,10} the VBM and CBM electronic levels follow that predicted by BX_6^{2-} crystal-field splitting molecular orbital diagrams, with a $t_{2g}^*(\pi)$ Ti $d - X$ p CBM for Cs_2TiX_6 (d_{xy} , d_{xz} , d_{yz} ; threefold degenerate

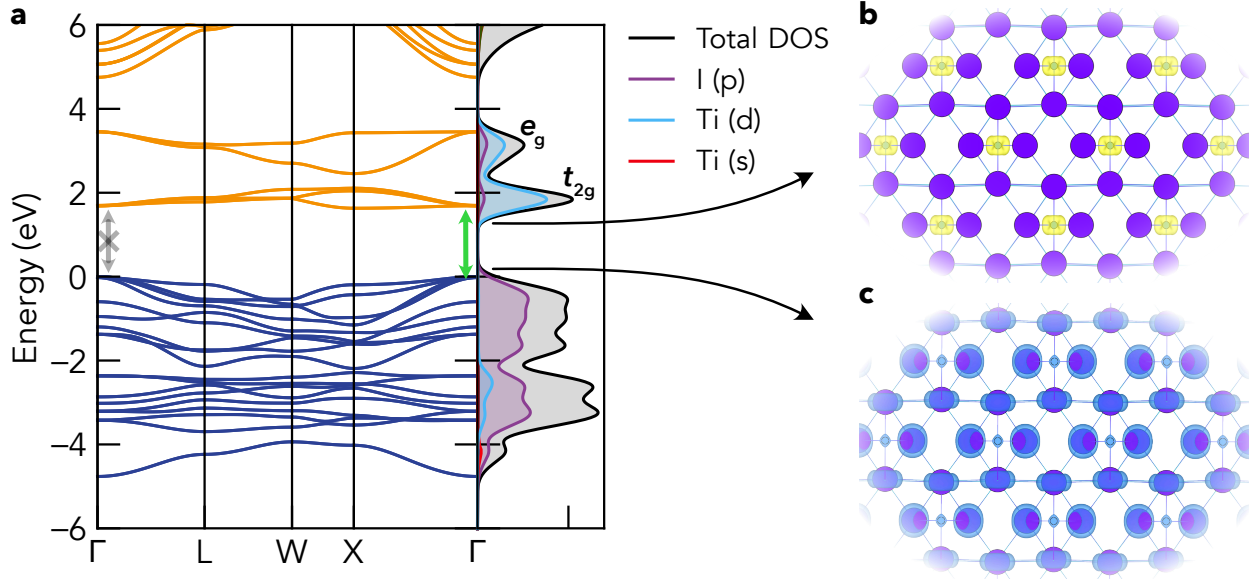


Figure 2: **a.** Electronic band structure of Cs_2TiI_6 calculated with hybrid DFT including spin-orbit coupling (HSE06+SOC), alongside a vertical plot of the orbital-projected electronic density of states. Faded gray and green arrows indicate the lowest-energy symmetry-forbidden and allowed electronic transition ($\Delta E_{t_{1g}/t_{1u}} = 0.02 \text{ eV}$), 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.

at Γ) and an $e_g^*(\sigma)$ band just above (d_{z^2} & $d_{x^2-y^2}$), a single $a_{1g}^*(\sigma)$ Sn $s - X p$ CBM for Cs_2SnX_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 apparent optical band gap corresponds to the vertical transition from the second-highest valence band at Γ (t_{1u} (Γ_{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 ($\sim 0.5 \text{ eV}$) for the Ti analogues (Figs. 2 and 3 & Figs. S3 to S8) due to a significantly reduced anion-anion distance ($d_{\text{I-I}} = 4.03 \text{ \AA}$ vs 3.87 \AA for Cs_2SnI_6 vs Cs_2TiI_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

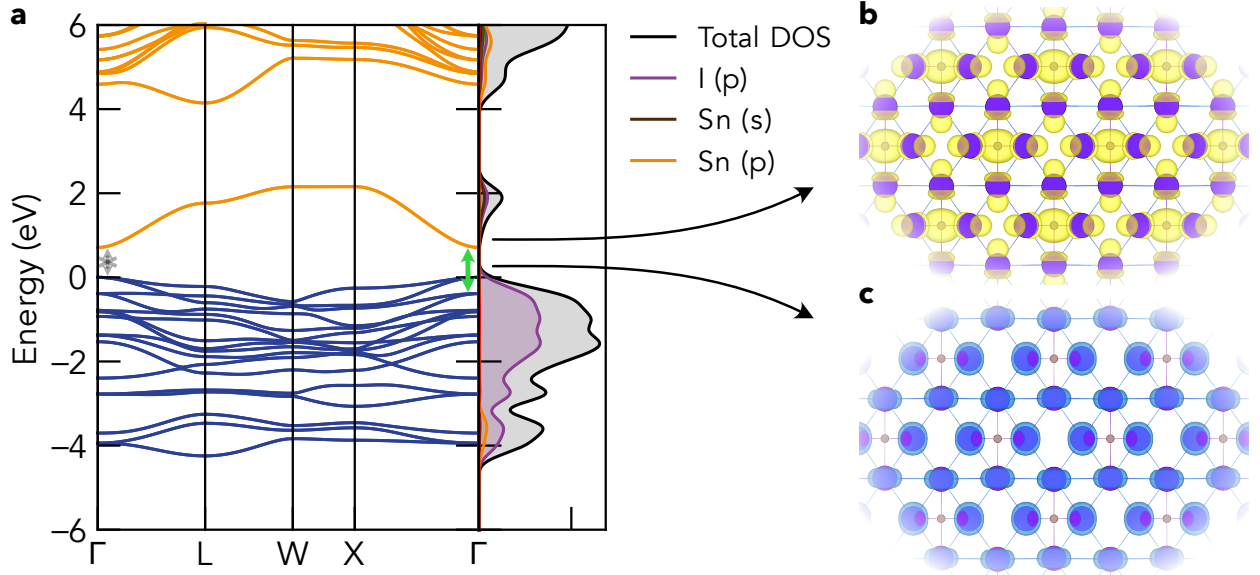


Figure 3: **a.** Electronic band structure of Cs_2SnI_6 calculated with hybrid DFT including spin-orbit coupling (HSE06+SOC), alongside a vertical plot of the orbital-projected electronic density of states. Faded gray and green arrows indicate the lowest-energy symmetry-forbidden and allowed electronic 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_2TiI_6 . Unoccupied states in yellow, occupied states in blue.

lengths (2.73 \AA vs 2.85 \AA) and lattice parameters for $B = \text{Ti}$ vs Sn (Table 1) — aided by the reduced ionic radius of Ti^{4+} vs Sn^{4+} — resulting in a much lower energy difference between the t_{1g} ψ_{VBM} and t_{1u} $\psi_{\text{VBM}-1}$ for $B = \text{Ti}$ vs Sn , with $\Delta E_{t_{1g}/t_{1u}} = 0.02 \text{ eV}/0.38 \text{ eV}$, $0.07 \text{ eV}/0.30 \text{ eV}$ and $0.07 \text{ eV}/0.07 \text{ eV}$ for $B = \text{Ti}/\text{Sn}$; $X = \text{I}, \text{Br}, \text{Cl}$ (using HSE06+SOC). Another consequence is that, in contrast to the electron masses, the hole effective masses are actually larger for Cs_2SnX_6 than for Cs_2TiX_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^{1,38,39}), the fully-oxidized B^{4+} in $A_2\text{BX}_6$ means we have a less dispersive, non-bonding VBM; yielding heavier hole masses (particularly for $X = \text{Br}, \text{Cl}$) 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 $B = \text{Ti}$ due to weak Ti d - X p mixing and localized, iso-

lated Ti d states. The band structures of the bromide and chloride isomorphs are included 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 Cs_2BX_6 family are tabulated in Table 2, where the Wannier free exciton binding energies are calculated using the average carrier effective masses ($\overline{m}_{e/h}$) and high-frequency dielectric constants (ε_∞) from hybrid DFT (HSE06+SOC) according to:⁴⁰

$$E_{ex} = -\frac{\mu}{m_0\varepsilon_\infty^2}\text{Ry} \quad (1)$$

where $\mu = (\overline{m}_e \times \overline{m}_h)/(\overline{m}_e + \overline{m}_h)$ 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 ($E_{g, \text{Direct}}$) and ‘optical’ band gaps ($E_{g, \text{Optical}}$)^a, effective masses (\overline{m}_x)^b, high-frequency dielectric constants (ε_∞) and Wannier model exciton binding energies ($E_{ex, \text{Wannier}}$) for Cs_2BX_6 (B = Sn, Ti; X = Cl, Br, I) using hybrid DFT including spin-orbit coupling (HSE06+SOC). Comparison given to experimentally-reported band gap ranges.^c

	Cs_2SnCl_6	Cs_2SnBr_6	Cs_2SnI_6	Cs_2TiCl_6	Cs_2TiBr_6	Cs_2TiI_6
$E_{g, \text{Direct}}$	4.1 eV	2.4 eV	0.7 eV	3.7 eV	2.8 eV	1.7 eV
$E_{g, \text{Optical}}$	4.5 eV	2.9 eV	1.2 eV	4.0 eV	3.0 eV	1.9 eV
$E_{g, \text{Exp}}$	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
\overline{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
\overline{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
ε_∞	2.86	3.37	4.54	3.26	3.84	5.08
$E_{ex, \text{Wannier}}$	0.73 eV	0.35 eV	0.13 eV	2.23 eV	0.62 eV	0.22 eV

^a ‘Optical band gaps’ determined from Tauc fits of the calculated absorption, assuming direct gaps.

^b \overline{m}_x 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.

^c Experimental band gap values taken from Refs: Cs_2SnCl_6 ,^{30,31,41,42} Cs_2SnBr_6 ,^{31,34,35,41-43} Cs_2SnI_6 ,^{15,16,30,31,34,41,44} Cs_2TiCl_6 ,^{22,36} Cs_2TiBr_6 ,^{13,14,20,22,23,36,37,45} Cs_2TiI_6 .^{23,36}

From Table 2, we witness the typical trend of larger band gap with smaller and more electronegative halogen anions ($E_g(\text{Cl}) > E_g(\text{Br}) > E_g(\text{I})$), as observed across the perovskite(-inspired) family.^{1,9} Typically, the smaller the B-site atom, the smaller the band gap in the

A_2BX_6 family.^{9,46} 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 $X = Cl$). While the optical gap predicted by hybrid DFT is in good agreement with experiment in all cases for Cs_2SnX_6 as previously noted,¹⁰ a consistent severe overestimation of the experimental band gap is found for each Cs_2TiX_6 isomorph. Notably, screened hybrid DFT (HSE06) tends to slightly *underestimate* rather than overestimate semiconductor band gaps, with this underestimation typically worsening with larger band gaps.^{47,48} The error in predicted band gaps for Cs_2TiX_6 results in *qualitatively* incorrect relative band gap energies for Cs_2SnX_6 vs Cs_2TiX_6 ($X = I, Br$).

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,⁴⁸⁻⁵⁰ though this only slightly reduced the hybrid DFT gap for Cs_2TiI_6 by 0.04 eV ($\alpha_{SCF} = 24\%$), 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,⁵¹ the calculated quasiparticle gaps in fact show far worse overestimation (both for Cs_2TiX_6 — as previously noted by Cucco et al.,⁹ and Cs_2SnX_6 ; Section S3). These observations, in contrast to the good performance of hybrid DFT for the Sn analogues, suggest the presence of physical interactions in Cs_2TiX_6 which are not captured in these single-particle electronic models.

This major experiment-theory discrepancy is witnessed in reported values across the literature,^{9,13,20,22-28} but has not been addressed until now. In many cases, semi-local DFT (known to severely underestimate semiconductor band gaps)⁴⁷ 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_2SnI_6 to be metallic for example; Table S2), alongside incorrect absorption spectra, thus being unsuitable for modeling the electronic structure of A_2BX_6

compounds.

Using the Wannier effective mass model (Table 2),⁵² 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 binding energies, isolated octahedra, low dielectric screening and highly-localized d orbitals suggests that strongly-bound excitons may be formed for Cs_2TiX_6 .⁴⁰ 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.

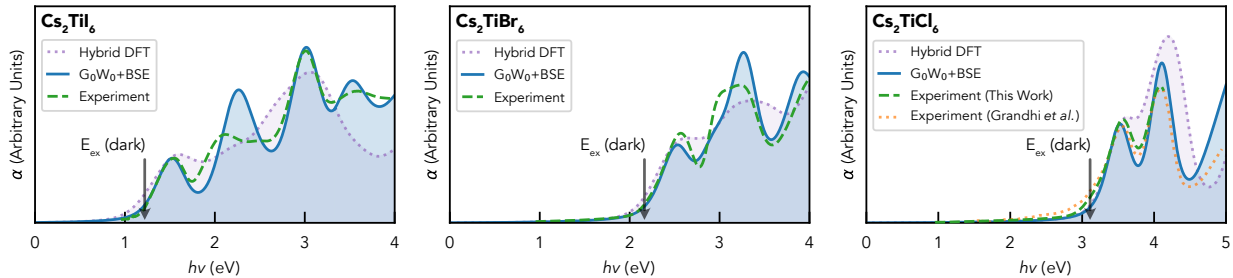


Figure 4: Optical absorption spectra of (left to right) Cs_2TiI_6 , Cs_2TiBr_6 and Cs_2TiCl_6 , calculated with both hybrid DFT (dotted violet) and the G_0W_0+BSE method (solid blue), alongside the experimental data from UV-Vis spectroscopy (dashed green). Calculated curves have been rigidly shifted to match the experimental absorption onset (unshifted results shown in Section S3).

Electron-hole interactions are found to dramatically redshift (Tables S1 and S2 and Fig. S10) and qualitatively alter the absorption spectra for Cs_2TiX_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 Γ (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 exper-

imental spectra is found for all Cs_2TiX_6 isomorphs, smaller changes in the spectral shapes are noticed for $\text{X} = \text{Br}, \text{Cl}$. 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.³⁶ refer to the absorption onset of Cs_2TiBr_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.^{53,54} Notably, the experimental spectra for TiBr_6^{2-} and TiCl_6^{2-} salts reported in Brisdon et al.⁵⁵ closely resemble the results for Cs_2TiBr_6 and Cs_2TiCl_6 reported here and in the literature,^{36,37} 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.

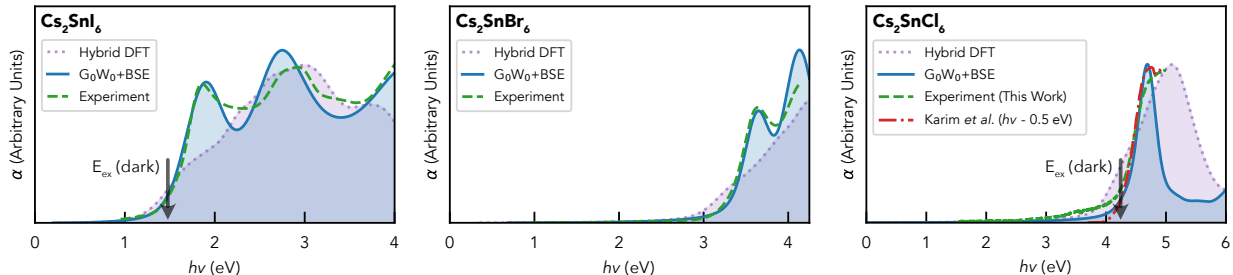


Figure 5: Optical absorption spectra of (left to right) Cs_2SnI_6 , Cs_2SnBr_6 and Cs_2SnCl_6 , calculated with both hybrid DFT (dotted violet) and the $G_0W_0 + BSE$ method (solid blue), alongside the experimental data from UV-Vis spectroscopy (dashed green). Calculated curves have been rigidly shifted to match the experimental absorption onset (unshifted results shown in Section S3). For Cs_2SnCl_6 , the absorption spectrum recorded by Karim et al.³¹ is also shown for comparison (downshifted by 0.5 eV as discussed in Section S3.3).

We highlight that the low-energy absorption peaks for Cs_2TiX_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,⁵⁶ and has been well-established in other $3d^0$ (Ti^{4+} , Sc^{3+} , Ca^{2+}) halides,⁵⁷ arising here as a consequence 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.⁴⁰ The large Stokes shifts (~ 0.5 eV) and broad PL emission observed for this family of materials in both this and other studies^{14,20,22} 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_2SnX_6 ($X = \text{I}, \text{Br}$) yield a weakly-bound exciton as expected, demonstrated by dominant band contributions at the Γ point to the first bright exciton state, while Cs_2SnCl_6 exhibits intermediate behavior. Fig. 6 also illustrates the differing trends in band structure for $B = \text{Sn}/\text{Ti}$, as X changes from I to Br to Cl, with a greater band gap increase and reduction in conduction band dispersion for Cs_2SnX_6 than Cs_2TiX_6 (such that the relative band gap energies of $B = \text{Sn}/\text{Ti}$ changes from $X = \text{I}$ ($E_{g, \text{Sn}} < E_{g, \text{Ti}}$) to $X = \text{Cl}$ ($E_{g, \text{Ti}} < E_{g, \text{Sn}}$)), due to the greater localization of the Ti d states. Crucially, these results demonstrate the presence of *qualitatively* different electronic behavior in the Cs_2SnX_6 and Cs_2TiX_6 families, where despite retaining the same cation valence, the change in frontier orbital character upon substitution of Sn^{4+} with Ti^{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 (\overline{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_2TiX_6 , aided by the zero-dimensional crystal structure, yielding strong electron-hole interactions. This strong excitonic renormalization of the optical absorption in

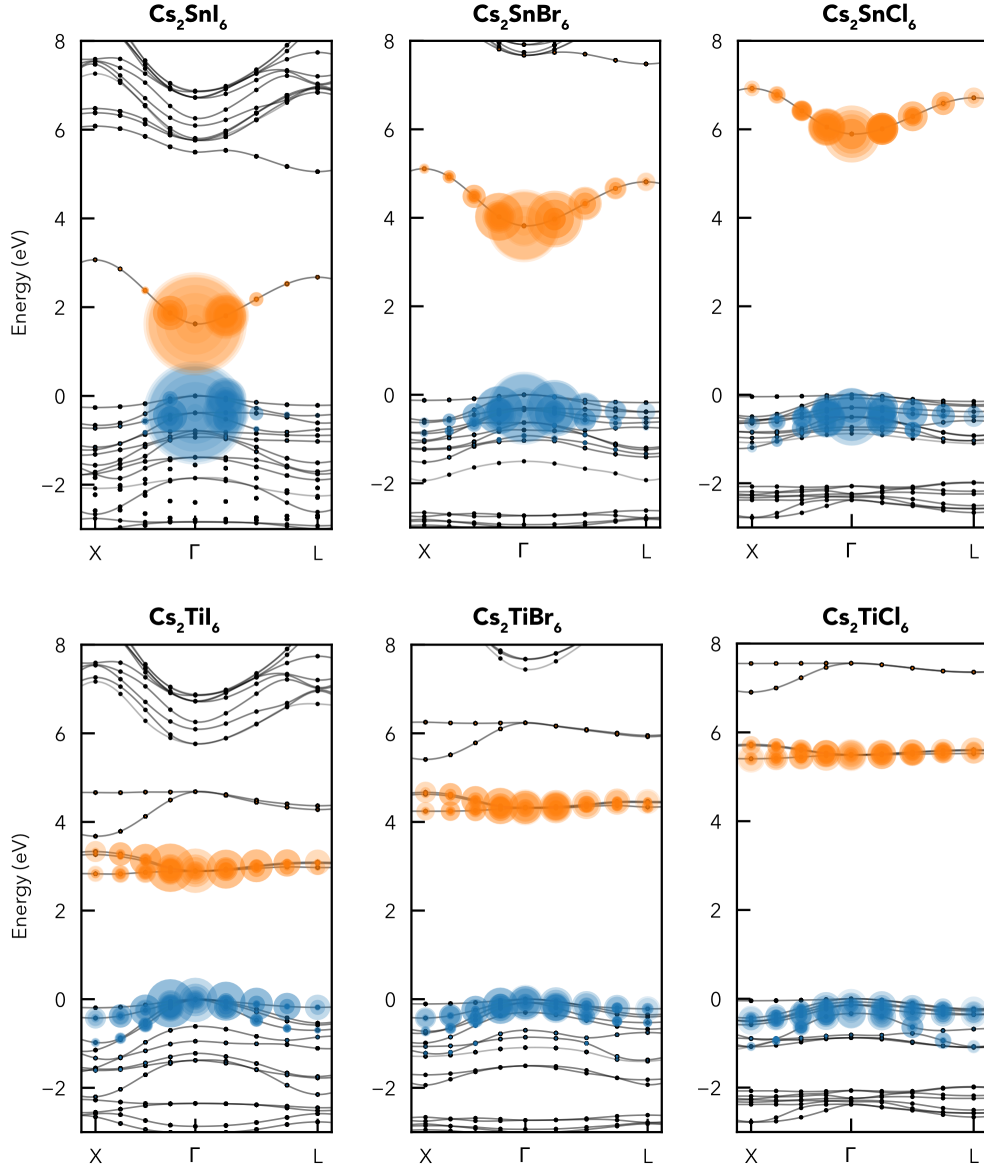


Figure 6: Band contributions to the brightest exciton state at the absorption onset in Cs_2SnX_6 (**top**) and Cs_2TiX_6 (**bottom**), calculated using the *BSE* approach. Band eigenvalues are indicated by the black dots, with filled circles weighted by their contributions to the exciton state and gray 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.

Cs_2TiX_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 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 .^{54,58,59} We note that the quasiparticle band gaps and thus exciton binding energies from $GW(+BSE)$ remain overestimated (discussion in Section S3), consistent with recent studies which attribute this behavior to under-screening errors within the Random Phase Approximation (RPA) employed within GW .⁶⁰⁻⁶²

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 A_2BX_6 compounds with isoelectronic (d^0) B^{4+} cations, such as Zr and Hf. Indeed, strong excitonic interactions have been recently been reported in Cs_2ZrX_6 — promising white-light emitters,¹⁹ and a distinct excitonic feature is seen at the absorption onset in Cs_2HfCl_6 ^{63,64} — 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,^{53,65,66} which despite a greater structural connectivity, exhibit a low *effective* electronic dimensionality due to orbital mismatch between the B-site cations.^{4,67} Likewise, extension of theoretical models to include explicit electron-hole interactions was required in order to reproduce the experimental spectrum,^{53,66,68} explaining the excitonic origin of the direct absorption onset.

Conclusions

In conclusion, by revealing strongly-bound excitonic behavior in the caesium titanium halide

vacancy-ordered perovskites (Cs_2TiX_6), we reconcile longstanding discrepancies between theoretical predictions and experimental measurements for this material class. While previous theoretical studies have found semi-local DFT to yield band gaps matching experiment, we show this to be the result of fortuitous error cancellation with qualitatively incorrect absorption spectra and relative band gaps for Cs_2SnX_6 vs Cs_2TiX_6 ($X = \text{I}, \text{Br}$). Our results show that electron-hole interactions are crucial to obtaining the correct polarizability 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 measurements, excitation-dependent THz and electromodulation spectroscopies.^{57,58,65,69} 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 accurate 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.

Methods

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).⁷⁰ Scalar-relativistic pseudo-potentials were employed to describe the interaction between core and valence electrons, via the projector-augmented wave (PAW) method.⁷¹ Specifically, the `Cs_sv`, `Sn_d`, `Ti_pv`, `I`, `Br` and `Cl` VASP PAW potentials were used. The choice of Ti pseudopotential was found not to significantly affect the computed electronic band gap ($\Delta E_g < 0.1$ eV), thus ruling it out as a possible explanation of the systematic band gap overestimation in Cs_2TiX_6 .

Initial guesses for the crystal structures were obtained from the Materials Project, before relaxing the geometry using the HSE06 screened hybrid DFT functional.⁷² The plane-wave energy cutoff and Γ -centered k -point mesh were sequentially increased using `vaspup2.0`⁷³ 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 \AA^{-3} in reciprocal space) respectively. During structural optimization, a convergence criterion of 0.01 eV/ \AA 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)⁷⁴ on the structural relaxation was tested and shown to be important; and so the HSE06+D3 (using the recommended PBE0+BJ parameterizations)⁷⁵ relaxed unit cells were used for all further calculations in this work.

Electronic band structures 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 Section S4). For density of states (DOS) and optical calculations, the k -point mesh for the primitive unit cell was increased to $8 \times 8 \times 8$ (reciprocal space density of 0.12 \AA^{-3}), and the tetrahedron smearing method was used. The number of virtual states in the optical calculations was increased using `vaspup2.0`⁷³ until the high-frequency dielectric constant ϵ_∞

was converged to a precision of 0.01. Electronic band structure diagrams and photoemission spectra (Figs. S18 and S19) were generated using the `sumo`⁷⁶ and `Galore`⁷⁷ packages respectively. Carrier effective masses were determined using non-parabolic fitting of the band edges through the `effmass`⁷⁸ package.

Wavefunctions calculated using HSE06+SOC were used as input orbitals for the $G_0W_0(+BSE)$ 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 numbers 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 G_0W_0+BSE calculations, a $3 \times 3 \times 3$ mesh (for the 9-atom primitive unit cell, equivalent to a k -point density of 0.33 \AA^{-1} in reciprocal space) was the maximum tractable k -point mesh for Cs_2BX_6 with our computational resources. While converged for the Br and Cl compounds, the greater band dispersion of the iodides (Cs_2BI_6) means the spectra are not well converged for this k -point density, thus the ‘model BSE’ approach^{79,80} was employed to reach converged k -point meshes of $4 \times 4 \times 4$ and $8 \times 8 \times 8$ for Cs_2TiI_6 and Cs_2SnI_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

Computational Methods; Data produced during this work is freely available at: [10.5281/zenodo.6906620](https://doi.org/10.5281/zenodo.6906620).

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