

Electronic supplementary information on Rashba effect and indirect electron-hole recombination in hybrid organic-inorganic perovskites

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1 Electric dipole matrix elements in the presence of Rashba effect

The conduction bands of HOIPs are comprised of Pb p orbitals, which, due to the strong spin-orbit coupling (SOC), are characterized by the total angular momentum $\mathbf{j} = \mathbf{l} + \mathbf{s}$ with \mathbf{l} and \mathbf{s} being orbital and spin angular momenta. The SOC and crystal field split the conduction bands into three bands, which, in the descending order in energy, are described by $(j, j_z) = (3/2, \pm 1/2)$, $(j, j_z) = (3/2, \pm 3/2)$, and $(j, j_z) = (1/2, \pm 1/2)$, respectively¹. The most relevant processes to photovoltaics in HOIPs occur in the lowest conduction band, which has the basis functions of Eq. (1) in the main text.

The Rashba effect lifts the spin degeneracy and splits the lowest conduction band into an upper band and a lower band with energy dispersions

$$E_{\mathbf{c}\mathbf{k}}^{\pm} = \frac{\hbar^2}{2m_e} [(k_{\perp} \pm k_0)^2 + k_z^2], \quad (1)$$

and the eigenstates for each \mathbf{k} are

$$\tilde{c}_{\mathbf{k}\pm} = \frac{1}{\sqrt{2}} (e^{-i\phi/2} c_+ \mp i e^{i\phi/2} c_-) e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (2)$$

The valence band in HOIPs is made of s orbital and has basis functions of $v_{\uparrow(\downarrow)} \equiv S \uparrow(\downarrow)$. When the smaller Rashba effect in the valence band is included,

$$E_{\mathbf{v}\mathbf{k}} = -E_g - \frac{\hbar^2}{2m_h} (k_x^2 + k_y^2 + k_z^2) + \lambda_v (k_y \sigma_x - k_x \sigma_y), \quad (3)$$

the band is also split into an upper band and a low band with energy dispersions

$$E_{\mathbf{v}\mathbf{k}}^{\pm} = -E_g - \frac{\hbar^2}{2m_h} [(k_{\perp} \pm \tilde{k}_0)^2 + k_z^2], \quad (4)$$

where $\tilde{k}_0 = \lambda_v m_h / \hbar^2$. The eigenstates at \mathbf{k} are

$$\tilde{v}_{\mathbf{k}\pm} = \frac{1}{\sqrt{2}} (e^{-i\phi/2} v_{\uparrow} \pm i e^{i\phi/2} v_{\downarrow}) e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (5)$$

To evaluate the electric-dipole matrix moment between conduction and valence states, we start from the matrix element between the basis functions,

$$\langle c_+ | \mathbf{e} \cdot \mathbf{p} | v_{\uparrow} \rangle = -\frac{mP_{\parallel} \sin \xi}{\hbar} \mathbf{e}_z, \quad (6)$$

$$\langle c_+ | \mathbf{e} \cdot \mathbf{p} | v_{\downarrow} \rangle = -\frac{mP_{\perp} \cos \xi}{\hbar} \mathbf{e}_-, \quad (7)$$

$$\langle c_- | \mathbf{e} \cdot \mathbf{p} | v_{\uparrow} \rangle = -\frac{mP_{\perp} \cos \xi}{\hbar} \mathbf{e}_+, \quad (8)$$

$$\langle c_- | \mathbf{e} \cdot \mathbf{p} | v_{\downarrow} \rangle = \frac{mP_{\parallel} \sin \xi}{\hbar} \mathbf{e}_z. \quad (9)$$

It is straightforward to obtain the electric-dipole matrix elements between the conduction and valence bands,

$$\langle \tilde{c}_{\mathbf{k}-} | \mathbf{e} \cdot \mathbf{p} | \tilde{v}_{\mathbf{k}+} \rangle = \frac{m}{2\hbar} [ie^{-i\phi} P_{\perp} \cos \xi \mathbf{e}_+ - ie^{i\phi} P_{\perp} \cos \xi \mathbf{e}_-], \quad (10)$$

$$\langle \tilde{c}_{\mathbf{k}-} | \mathbf{e} \cdot \mathbf{p} | \tilde{v}_{\mathbf{k}-} \rangle = \frac{m}{2\hbar} [-2P_{\parallel} \sin \xi \mathbf{e}_z + ie^{-i\phi} P_{\perp} \cos \xi \mathbf{e}_+ + ie^{i\phi} P_{\perp} \cos \xi \mathbf{e}_-]. \quad (11)$$

The oscillator strength of these transitions are

$$\sum_q |\langle \tilde{c}_{\mathbf{k}-} | \mathbf{e} \cdot \mathbf{p} | \tilde{v}_{\mathbf{k}+} \rangle|^2 = \frac{m^2}{2\hbar^2} P_{\perp}^2 \cos^2 \xi, \quad (12)$$

$$\sum_q |\langle \tilde{c}_{\mathbf{k}-} | \mathbf{e} \cdot \mathbf{p} | \tilde{v}_{\mathbf{k}-} \rangle|^2 = \frac{m^2}{2\hbar^2} [2P_{\parallel}^2 \sin^2 \xi + P_{\perp}^2 \cos^2 \xi], \quad (13)$$

which are similar in magnitude since $\cos^2 \xi / \sin^2 \xi \simeq 5$ and $P_{\parallel} \simeq P_{\perp}$ in $\text{CH}_3\text{NH}_3\text{PbI}_3$,¹ and their average is identical to p_{cv} defined in the main text. Hence the Rashba effect does not significantly suppress the electric-dipole matrix elements or the oscillator strengths of transitions between the conduction and valence bands. This is because the conduction band is made of $j_z = \pm 1/2$ states, which contain both up- and spin-components.

2 Polar couplings in the conduction and valence bands

The polar coupling in HOIPs was derived in Ref.³, which is an extension of the well-known Fröhlich Hamiltonian². For electron

$$H_{\text{ep}}^{\text{e}} = -i \sum_{\mathbf{q}} \left(\frac{4\pi\alpha_{\text{ej}}}{\Omega} \right)^{1/2} \frac{\hbar\omega_{l_j}}{q} \left(\frac{\hbar}{2m_{\text{e}}\omega_{l_j}} \right)^{1/4} (b_{\mathbf{q}}c_{\mathbf{k}+\mathbf{q}\tau}^{\dagger}c_{\mathbf{k}\tau} - b_{\mathbf{q}}^{\dagger}c_{\mathbf{k}\tau}^{\dagger}c_{\mathbf{k}-\mathbf{q}\tau}), \quad (14)$$

and for hole,

$$H_{\text{ep}}^{\text{h}} = i \sum_{\mathbf{q}} \left(\frac{4\pi\alpha_{\text{hj}}}{\Omega} \right)^{1/2} \frac{\hbar\omega_{l_j}}{q} \left(\frac{\hbar}{2m_{\text{h}}\omega_{l_j}} \right)^{1/4} (b_{\mathbf{q}}c_{\mathbf{k}+\mathbf{q}\tau}^{\dagger}c_{\mathbf{k}\tau} - b_{\mathbf{q}}^{\dagger}c_{\mathbf{k}\tau}^{\dagger}c_{\mathbf{k}-\mathbf{q}\tau}), \quad (15)$$

where the dimensionless polar coupling strength is defined as

$$\alpha_{\text{e(h)}j} = \frac{e^2}{\hbar} \left(\frac{m_{\text{e}}}{2\hbar\omega_{l_j}} \right)^{1/2} \frac{1}{\epsilon_{\infty}} \left(1 - \frac{\omega_{l_j}^2}{\omega_j^2} \right) \prod_{i \neq j} \left| \frac{\omega_{l_j}^2 - \omega_{l_i}^2}{\omega_{l_j}^2 - \omega_{l_i}^2} \right| \equiv \frac{e^2}{\hbar} \left(\frac{m_{\text{e(h)}}}{2\hbar\omega_{l_j}} \right)^{1/2} \frac{1}{\epsilon_{s_j}}. \quad (16)$$

In the calculations presented in the main text, we consider only the Pb-X stretching mode with phonon energy $E_p \equiv \hbar\omega_{l_1}$ and neglect its dispersion. The polar coupling is then

$$V_q^{\text{e(h)}} = \left(\frac{4\pi\alpha_{\text{e(h)}}}{\Omega} \right)^{1/2} \frac{E_p}{q} \left(\frac{\hbar^2}{2m_{\text{e(h)}}E_p} \right)^{1/4} \equiv \frac{U_{\text{e(h)}}}{\sqrt{\Omega}q}, \quad (17)$$

where Ω is the material's volume and $\alpha_{\text{e}}/\alpha_{\text{h}} = (m_{\text{e}}/m_{\text{h}})^{1/2}$.

In the conduction bands, because of the Rashba effect, the polar coupling between the eigenstates are

$$\langle \tilde{c}_{\mathbf{k}'+} | V_q^{\text{e}} | \tilde{c}_{\mathbf{k}+} \rangle = \langle \tilde{c}_{\mathbf{k}'-} | V_q^{\text{e}} | \tilde{c}_{\mathbf{k}-} \rangle = \frac{U_{\text{e}}}{\sqrt{\Omega}q} \cos \frac{\phi' - \phi}{2}. \quad (18)$$

$$\langle \tilde{c}_{\mathbf{k}'+} | V_q^{\text{e}} | \tilde{c}_{\mathbf{k}-} \rangle = -\langle \tilde{c}_{\mathbf{k}'+} | V_q^{\text{e}} | \tilde{c}_{\mathbf{k}-} \rangle = i \frac{U_{\text{e}}}{\sqrt{\Omega}q} \sin \frac{\phi' - \phi}{2}. \quad (19)$$

3 Evaluation of integrals

Equations (16) and (17) in the main text involve 6-fold integrals, which are numerically challenging if not analytically simplified. To take advantage of the symmetry in the conduction- and valence-band dispersions, we use the cylindrical and spherical coordinates for the conduction and valence bands, respectively,

$$\int d^3k \int d^3k' = \int k_{\perp} dk_{\perp} dk_z d\phi \int k'^2 dk' \sin \theta' d\theta' d\phi' \quad (20)$$

From the energy conservation in the δ -function, we can fix k' . Since the integrands in Eqs. (16) and (17) depend only the difference $\phi - \phi'$, we can set $\phi' = 0$ and integrals become four-fold.

For Eq. (16), we can analytically integrate over ϕ and θ' and obtain

$$I_{\pm}^h = \frac{U_h^2}{(2\pi)^4} \frac{1}{2} \left(\frac{2m_h}{\hbar^2} \right)^{3/2} \int k_{\perp} dk_{\perp} dk_z \frac{\left(\hbar\omega \pm E_p - E_g - \frac{\hbar^2}{2m_e} [(k_{\perp} - k_0)^2 + k_z^2] \right)^{1/2}}{\left[E_g + \frac{\hbar^2}{2m_e} [(k_{\perp} - k_0)^2 + k_z^2] + \frac{\hbar^2}{2m_h} k^2 - \hbar\omega \right]^2} \times \frac{1}{kk'} \log \frac{(2\sqrt{c(a+b_1+c)} + 2c + b_1)(2\sqrt{c(a+b_2+c)} + 2c + b_2)}{(2\sqrt{c(a+b_1+c)} - 2c + b_1)(2\sqrt{c(a+b_2+c)} - 2c + b_2)}, \quad (21)$$

$$a = (k^2 + k'^2)^2 - 4k_{\perp}^2 k'^2, \quad b_1 = -4k_z k' (k^2 + k'^2), \quad c = 4k^2 k'^2, \quad b_2 = -b_1, \quad (22)$$

which is a two-fold integral and can be reliably evaluated numerically. Numerically, in order to avoid the resonance when $\hbar\omega$ approaches Δ_m , we include an energy broadening Γ^2 in the energy denominator,

$$[\Delta_{\mathbf{k}} - \hbar\omega]^2 \rightarrow [\Delta_{\mathbf{k}} - \hbar\omega]^2 + \Gamma^2, \quad (23)$$

where $\Delta_{\mathbf{k}} \equiv [E_g + \frac{\hbar^2}{2m_e} [(k_{\perp} - k_0)^2 + k_z^2] + \frac{\hbar^2}{2m_h} k^2]$ and $\Gamma = 0.01$ eV is fixed in the calculations. It should be note that $\Delta_{\mathbf{k}} > \hbar\omega$ since the PA absorption is limited to $\hbar\omega < \Delta_m \leq \Delta_{\mathbf{k}}$ in our calculations.

For Eq. (17), the integration over ϕ involves expressions

$$I_1 = \int_0^{2\pi} d\phi \frac{1 + \cos\phi}{A - B \cos\phi} \quad \text{and} \quad I_2 = \int_0^{2\pi} d\phi \frac{1 - \cos\phi}{A - B \cos\phi}, \quad (24)$$

where $A = k^2 + k'^2 - 2k_z k' \cos\theta'$ and $B = 2k_{\perp} k' \sin\theta'$. I_1 and I_2 can be analytically worked out,

$$I_1 = 2\pi \left[-\frac{1}{B} + \frac{A+B}{B} \frac{1}{\sqrt{A^2 - B^2}} \right], \quad (25)$$

$$I_2 = 2\pi \left[\frac{1}{B} + \frac{B-A}{B} \frac{1}{\sqrt{A^2 - B^2}} \right]. \quad (26)$$

However, the integration over θ' can be expressed in a closed form and the final integral to be numerically evaluated is three-fold.

References

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