Organic-inorganic halide perovskites (OIHPS) have emerged as highly promising optoelectronic materials with applications in photovoltaics [1, 2], light-emitting diodes and low-threshold lasers [3]. All three applications rely on the slow radiative recombination rates of electrons and holes. In OIHPS, electrons (holes) exist as electronic polarons (EPs) [hole polarons (HPs)], excitons [4], free and trapped electrons (holes). Six kinds of collisions could lead to electron and hole annihilation: (i) a free electron and a free hole; (ii) the electron and hole in an exciton; (iii) a free electron (hole) with a HP (EP); (iv) a HP and an EP; (v) a free electron (hole) and a trapped hole (electron); and (vi) an EP (HP) and a trapped hole (electron). To conceive new materials, one has to know the radiative recombination rates and statistical weights of six collisions. Measurements on mobility [5–8] indicate [9] that the majority carriers in OIHPS are EPs and HPs [10–15]. Then, the radiative recombination involving polaron(s) [processes (iii,iv,vi)] are predominant [16].

To annihilate an EP (HP), the extra electron (hole) must escape from its distorted environment. The annihilation probability of an electron with a hole is significant only the average distance $d_{eh}$ between electron and hole is small (several Å), i.e. the electron wave function has enough overlap with the hole wave function. In MAPbI$_3$, the radius $R_p$ of a polaron is $\sim$28Å [15], which is much larger than the required ‘small’ $d_{eh}$ for recombination. If a free or trapped hole was at the boundary of an EP while the extra electron was at the center of EP, the annihilation probability would be negligible. Similarly, if an EP and a HP are in contact, while the extra electron (hole) was at the center of EP (HP), the annihilation probability would be negligible too. In addition, a band edge hole (electron) cannot enter a close neighbor of the extra electron (hole) inside an EP (HP) to annihilate. The reason is that the polarization produced by an electron is opposite to that produced by a hole, the barrier for an electron entering a HP is about two times of the polaron formation energy (~140meV) [15]. In normal operation condition, the concentration of photo-generated electrons (holes) is less than $10^{15}$cm$^{-3}$ [20], the electron gas is non-degenerate [15]. After cooling, the kinetic energy of a band edge electron (hole) is $\sim$3kBT/2, which is too low to enter a HP (EP). Therefore, to annihilate an EP (HP), the extra electron (hole) must break away from the distorted lattice, and move to a close neighbor of the counterpart hole (electron). The evolution of the state of the electron + lattice + hole system is driven by the effective Coulomb attraction $V_{eh}$ between electron and hole, the interaction $V_{nm}$ between electron (hole) and radiation field, and the interaction $h_{e-LO}$ between electron (hole) and longitudinal optical (LO) phonons. In OIHPS, $h_{e-LO}$ is larger than the kinetic energy of electron (hole) and the energy of LO phonon, conventional methods are not able to trace the radiative recombination involving polaron(s).

In this letter, we present a tractable scheme based on three observations: (1) If the average distance $d_{eh}$ between an electron and a hole is smaller than a critical distance $L$, the probabilities of such an electron-hole pair to dissolve into EP and HP, to be disassembled by thermal excitation, to become an exciton are small, while the annihilation probability is significant (a dying pair); (2) The extra electron (hole) in an EP (HP) can escape the distorted lattice either through tunneling or through thermal activation; (3) In the annihilation channel of each collision process, there is a certain probability to form a dying pair [9]. The annihilation probability per unit time (APPUT) of a collision process is a product of the formation probability of the dying pair in that process and the APPUT of the corresponding dying pair. Had we known the statistical weights of six kinds of collisions, the monomolecular annihilation rate $k_1$ is a weighted average.
of the APPUT of processes (ii,v,vi); the bimolecular annihilation rate \( k_2 \) is a weighted average of the APPUT of processes (i,iii,iv).

We show that two types of dying pair can be formed in OIHPs: (1) both electron and hole are movable (mobile dying pair); (2) electron (hole) is movable and hole (electron) is trapped by a trapping center (immobile dying pair). If \( d_{eh} \) is order of or smaller than the lattice constant \( a \), then there are a few ions between the electron and hole. The screening caused by the displacements of ions is negligible. Then, \( V_{eh} \) relates to the bare interaction by \( V_{eh} = V_{eh}^{bare}/\varepsilon_{\infty} \), where \( \varepsilon_{\infty} \) is the dielectric constant originated from the bound electrons. For an electron-hole pair with \( d_{eh} \lesssim a \), \( V_{eh} \) is the same order as the electron-nucleus interaction, the effective mass of electron and hole are the same as the mass \( m \) of a bare electron. If both electron and hole are mobile, the reduced mass \( m^\star = m/2 \); the binding energy \( B_m \) of a mobile pair is \( B_m = \varepsilon^2 m (Ke)^2/4\hbar^2 \), where \( K = (4\pi\epsilon_0)^{-1} \); the Bohr radius of the pair is \( L_m = \varepsilon/2\varepsilon_{\infty}m^2/(mKe)^2 \). Similarly, for a free electron (hole) and a trapped hole (electron), the reduced mass \( m^\star \) of an immobile pair is \( m^\star = m \); the binding energy \( B_i \) is \( B_i = 2B_m \), the Bohr radius is \( L_i = \varepsilon/2\varepsilon_{\infty}m^2/(mKe)^2 \). In MAPbI\(_3\), \( \varepsilon_{\infty} = 6.5 \) [21], then \( B_m = 162\)meV, \( L_m = 6.8\)\AA, \( B_i = 324\)meV, \( L_i = 3.4\)\AA. One can see that \( B_m \) and \( B_i \) are larger than the binding energy \( E_b \) of an exciton (16-50meV [22]), the thermal energy (300K=26meV) and the sum of formation free energies \( F_P(T) \) of an EP and a HP (80-140meV) [13]. Therefore, an electron-hole pair with \( d_{eh} < L_m \) (\( L_i \)) cannot disassemble into EP and HP, cannot be disassembled by thermal excitation, cannot become an exciton; its fate is annihilation. We should emphasize that a dying pair indicates all \( d_{eh} < L \) configurations not just the \( d_{eh} = L \) one [6]. In the annihilation channel of collision processes (i,ii,iii,iv), a mobile dying pair is formed; in the annihilation channel of process (v,vi), immobile dying pair is formed.

We first calculate the APPUT \( w_{2f} \) for a free electron and a free hole. By approximating their wave-functions with plane-waves, we can derive \( w_{2f} \) based on the second-order perturbation theory with the electron-phonon interaction and \( V_{fm} \) treated as perturbations [23] [25]:

\[
w_{2f} = \frac{e^2}{V4\pi\epsilon_0} \frac{n_{cell}h^2\omega_k}{m^22\epsilon^2\omega^4} \left( \frac{\epsilon_{\beta\sigma}k_{\beta\sigma}3}{\epsilon(\omega_k)} \right)^2 \tag{1}
\]

\[
\frac{\eta^q_q}{|E_{ck} + q - E_{ck}|^2 + |h\omega_q|^2} \frac{e^{-i\mathbf{q} \cdot \mathbf{r}}}{\sqrt{M_k}} \frac{G_0}{\epsilon_0^2} \frac{\epsilon_0^2}{\epsilon(\omega_k)^2},
\]

where the repeated indices are summed over; \( V \) is the volume of the sample; \( n_{cell} \) is the number of primitive cells per volume; \( M_k \) and \( z_k \) are the mass and effective nuclear charge of the \( k \)th atomic core. \( \mathbf{s}_k \) is the position vector of the \( k \)th atom relative to the center of the primitive cell. \( \mathbf{k} \) and \( \omega_k \) are the wave vector and frequency of emitted photon. \( \epsilon(\omega_k) \) is the dielectric constant at frequency \( \omega_k \). \( \epsilon_{\beta\sigma}k_{\beta\sigma} \) is the \( \beta \)th Cartesian component of the \( \sigma \)th polarization vector of photon. \( \mathbf{k}_1 \) is the electron wave vector in the conduction band, and \( E_{ck_1} \) is the energy of the electron in a state |\( \mathbf{k}_1 \rangle \) of the conduction band \( c \). \( \mathbf{k}_3 \) is the wave vector of the hole in the valence band. \( \mathbf{q} = \mathbf{k} + \mathbf{k}_3 - \mathbf{k}_1 \) is the phonon wave vector and \( g \) is the phonon branch index. \( \omega_q \) and \( \eta_q \) are the frequency and occupation number of the phonon in mode |\( g \rangle \).

The transition amplitude of a radiative recombination exponentially decreases with the increase of \( d_{eh} \) [14] [18]. Then, in the collisions of a free electron and a free hole, the annihilation primarily happens for those wave-packets with \( d_{eh} < L_m \), i.e. through a mobile dying pair. In other words, in the annihilation channel of the free-electron-hole free collision, the formation probability of a mobile dying pair almost equals one, \( w_{2f} \) approximately equals the APPUT of a mobile dying pair. Later on, we take the APPUT of a mobile dying pair as \( w_{2f} \).

For the electron and hole in an exciton, the formation probability of mobile dying pair is \( V[\psi(0)]^2 \), where \( \psi(0) \) represents the wave-function of the electron at the position of the hole [17] [18]. According to the Hydrogenic model of excitons, \( |\psi(0)|^2 = (\pi r_{ex}^3)^{-1} \), where \( r_{ex} = h(2m_ex E_b)^{-1/2} \) is the radius of the exciton: \( m_ex \) is the reduced mass of the electron and hole pair. Thus, the APPUT of an exciton is \( w_{ex} = Vw_{2f}/(\pi r_{ex}^3) \).

To annihilate an EP (HP) with a free hole (electron), the electron (hole) of EP (HP) must first break free from the surrounding lattice, facilitated by thermal activation or quantum tunneling. The tunneling probability is the greatest if the free hole is in contact with the EP. In this case, the Coulomb attraction between them is \( E_{con} = Ke^2[R_{P}(\varepsilon(0,T))^{-1}] \), where \( \varepsilon(0,T) \) is the static dielectric function at temperature \( T \). The probability that an EP and a free hole are in contact is \( p_{con}^{\prime} = (eE_{con}^{\prime}k_bT - 1)/(eE_{con}^{\prime}k_bT + 1) \). By means of the Molecular Orbital theory, the probability \( P_{tun}^{\prime} \) that the extra electron in EP tunnels to a point which its distance to the contacted hole is \( L_m \) is:

\[
P_{tun}^{\prime} = \frac{R_{P}}{E_{P}(B_m - E_{P})} e^{2KE_{con}^{\prime}/k_bT} e^{-(E_{con}^{\prime}/k_bT - 1)/2(1/E_{con}^{\prime}/k_bT + 1)}. \tag{2}
\]

where \( E_{P} \) is the formation energy of the polaron [13]. Hence the formation probability of the mobile dying pair via tunneling is \( P_{tun}^{\prime}p_{con}^{\prime} \). The same electron can also escape from the surrounding lattice distortion via thermal activation, and the formation probability of the dying pair by thermal activation is \( e^{-F_{P}/k_bT} \). The formation probability of the mobile dying pair in EP-free hole collision is:

\[
P_{tun}^{\prime}p_{con}^{\prime} + e^{-F_{P}/k_bT}. \]

Finally, the APPUT \( w_{2f} \) of
for free electron (hole)-HP (EP) collision is:

\[ w_{Pt} = |P_{tun}P_{econ} + e^{-F_T/k_BT}]w_{2f}. \quad (3) \]

The formation probability of the mobile dying pair in the EP-HP collision can be found similarly. The attraction energy \( E_{con} \) of an EP with a close contacted HP is \( E_{con} = Ke^2/2R_{ep}\epsilon(0,T) \). At temperature \( T \), the probability that EP and HP is in contact is \( p_{con} = (e^{E_{con}/k_BT} - 1)/(e^{E_{con}/k_BT} + 1) \). Under the influence of \( V_{eh} \), the electron in EP can tunnel to a close neighbor of the hole in HP and form a mobile dying pair. The probability \( P_{tun} \) that electron tunnels into a HP and forms a mobile dying pair is:

\[ P_{tun} = \frac{4\epsilon^{-2F_T/L_{mNP}}}{L_{mNP}} \left[ B - e^{F_T} \right]^2. \quad (4) \]

The formation probability of mobile dying pair through thermal activation is given by \( e^{-F_T/k_BT} \). Thus the APPUT \( w_{2P} \) in an EP-HP collision is:

\[ w_{2P} = |P_{tun}P_{econ} + e^{-2F_T/k_BT}]w_{2f}. \quad (5) \]

Let us consider the annihilation between a free electron (hole) and a trapped hole (electron). We approximate the wave-function of the trapped hole as \( \phi_h = \pi^{-1/2}a_0^{-3/2}e^{-r/a_0} \), where \( a_0 = \epsilon_\infty h^2/(m_eK^2) \) is the Bohr radius of the hole, and \( z_t \) is the effective nuclear charge of the trap. We can show that the APPUT \( w_{tt} \) of the free electron-trapped hole collision is [17] [18]:

\[ w_{tt} = \frac{\hbar \omega e^2}{V2\pi m_e^3 e_0} \int \frac{d^3k_2}{(2\pi)^3} \frac{ik_{2\beta}}{\epsilon_{\infty e_0}} |k_2 - k_1|^2, \quad (6) \]

where \( k_1 \) is the wave vector of the free electron, and \( \omega \) is the photon frequency. Here \( w_{tt} \) should be understood as an average over various initial states on the right hand side of Eq. (6). In the collision of a free electron (hole) and a trapped hole (electron), the annihilation mainly comes from those wave-packets with \( d_{eh} < L_t \), i.e. an immobile dying pair. To put it another way, in the annihilation channel of the free electron (hole)-trapped hole (electron) collision, the formation probability of immobile almost equals one, the APPUT of an immobile dying pair approximately equals \( w_{tt} \).

We consider the collision between an EP (HP) and a trapped hole (electron). Because the overall charge of trapped hole (electron) and trapping center is neutral, there is no attraction between the trapped hole (electron) and the EP (HP). Thus, the extra electron (hole) cannot escape from EP (HP) through tunneling, and the escape can only occur by thermal activation. Therefore, the formation probability of the immobile dying pair is \( e^{-F_T/k_BT} \), and the APPUT \( w_{Pt} \) of the EP (HP)-trapped hole (electron) is

\[ w_{Pt} = e^{-F_T/k_BT}w_{tt}. \quad (7) \]

Let us calculate the statistical weight of each collision. Since radiative recombination is slower than the dissociation of excitons and polarons, we assume that electrons (holes), excitons and EPs (HPs) are in thermal equilibrium with each other. Exciton and polaron were not able to broken by thermal energy, the fraction of free carriers, excitons, and polarons would be \( f_1 = 1 + e^{E_X/k_BT} + e^{E_P/k_BT} \), \( f_2 = e^{E_X/k_BT} \), and \( f_3 = e^{E_P/k_BT} \). respectively. However, exciton and polaron can be broken by thermal energy. Therefore, the percentages of electrons (or holes), excitons and EPs (HPs) are \( p_e = f_1^0 = f_1 + f_Xe^{E_X/k_BT} + f_Pe^{E_P/k_BT} \), \( p_{ex} = f_0^0 = f_0(1 - e^{-E_X/k_BT}) \), and \( p_p = f_0^0 = f_0(1 - e^{-E_P/k_BT}) \). Therefore, the statistical weight of the four collisions concerning the mobile dying pairs is: \( p_{2f} = p_1^2, p_{ex}, p_{py} = p_0p_p, \) and \( p_{2P} = p_2^2 \). Let \( E_{tra} \) be the trap energy defined relative to the edge of the valence (conduction) band for the hole (electron) [26], then the probability that a carrier is trapped is \( 1 - e^{-E_{tra}/k_BT} \). Thus the statistical weight of free electron (hole)-trapped hole (electron) collision is \( p_{tt} = p_t(1 - e^{-E_{tra}/k_BT}) \), the statistical weight of EP (HP)-trapped hole (electron) collision is \( p_{Pt} = p_0(1 - e^{-E_{tra}/k_BT}) \).

The 1-body annihilation comes from processes (ii,v,vi). Hence the monomolecular recombination rate \( k_1 \) is given by:

\[ k_1(T) = p_{ex}w_{ex} + 2p_{ht}(Vn_tw_{tt}) + 2p_{Pt}(Vn_tw_{Pt}), \quad (8) \]

where \( n_t \) is the density of the traps. Similarly, 2-body annihilation comes from processes (i,iii,iv). Then the bimolecular recombination rate \( k_2 \) is read as

\[ k_2(T) = p_{2f}(Vw_{2f}) + 2p_{f_P}(Vw_{2f}) + p_{2P}(Vw_{2P}). \quad (9) \]

The slow radiative recombination rate is caused by the small formation probability of dying pairs in the collisions involving polaron(s) [8].

We apply Eqs. (5,9) to MAPbI_3. The materials parameters used are: \( R_p = 28\AA, E_p = 70 \text{ meV} \), \( r_{ex} = 49 \AA, m_{ex} = 0.1m, k_{ex} = 1, n_t = 3 \times 10^{16} \text{cm}^{-3} \), \( \epsilon(0,T) \) is taken from [32]. In Fig.1 and Fig.2 we compare the measured \( k_1(T) \) and \( k_2(T) \) with Eqs. (5,9). The theory reproduces the general experimental trends [8] that \( k_1 \) increases monotonically while \( k_2 \) decreases first and then increases with increasing temperature. For the three collision processes contributing to \( k_1 \), only the annihilation between a HP (EP) and a trapped electron (hole) depends sensitively on \( T \). Because the trapped hole is overall charge neutral, there is no Coulomb attraction.
The most populated EP level is \( c_b - g < 310 \text{K}) \) owing to the fact that \( F_p \approx 40 \text{ - 70 meV} \) is greater than thermal energy \((300 \text{K}=26 \text{meV})\). Below 310 K, as \( T \) increases, the probability that the two polarons (or a polaron and a free carrier) are in a close proximity necessary for tunneling is reduced, thus \( k_2 \) decreases as \( T \). Above 310 K, the thermal activation of polarons dominates and \( k_2 \) increases as \( T \).

We estimate the peak frequency \( \omega_{\text{PL}} \) of PL spectrum. Since large polarons are dominant carriers in OIHPS under normal conditions, the PL spectrum is primarily determined by polaron recombination. \( h\omega_{\text{PL}} \) approximated equals to the energy difference between the most populated EP level and the most populated HP level. The most populated EP level is \( c_b - g < F_p(T) \), where \( c_b \) is the bottom of the conduction band. \( g = \epsilon F[1 - (\pi k_B T/2\epsilon F)^2/3] \) is the chemical potential of polaron gas at temperature \( T \). \( \epsilon F = h^2(3\pi^2 n_e)^{2/3} / 2m_p \) is the Fermi energy of the polaron gas. \( n_e \) is the density of photo-generated electrons, where \( \omega \) is the excitation frequency, \( \phi \) is the quantum yield efficiency, \( c \) is the speed of light in vacuum, and \( I \) is the incident flux \([6]\). Similarly, the most populated HP level is \( v_i - g + F_p(T) \), with \( v_i \) being the top of the valence band. Therefore,

\[
h\omega_{\text{PL}}(T) = (c_b - v_i - 2F_p(T) + 2\epsilon F[1 - (\pi k_B T/2\epsilon F)^2].
\]

In Fig. 3(a) we plot \( \omega_{\text{PL}} \) as a function of incident light flux \( \phi \) for MAPbI\(_3\). The agreement with the experimental data is very good. Furthermore, the temperature dependence of \( \omega_{\text{PL}} \) expected from Eq. \((10)\) compare very well to the experimental measurements \([5, 33]\), as shown in Fig. 3(b).

FIG. 3. (a) PL peak frequency \( \omega_{\text{PL}} \) of MAPbI\(_3\) as a function of the incident flux \( \phi \): the experimental data (cross) is taken from \([5]\) and the solid line is calculated from Eq. \((10)\). (b) \( \omega_{\text{PL}} \) as a function of temperature: the solid lines are calculated from Eq. \((10)\) and the experimental values (circles) are taken from \([5]\), and (diamonds) taken from \([33]\).

Although polarons are dominant carriers in OIHPS, a line width model of PL spectrum based on free electrons (holes) \([55, 30]\) works well \([37]\). This contradiction can be resolved: for each collision process, annihilation is realized via dying pair where electron and hole are no longer confined by lattice distortion. According to Eq. \((11)\), the recombination time of the mobile dying pair is in the order of \( 10^{-3}s \), which is much larger than the timescale \((\sim 10^{-13}s) \) of absorbing and emitting LO phonons \([38, 39]\). The coupling of the “free” electron (hole) with LO phonons is the dominant process for determining the line width \([9]\).

In conclusion, six kinds of binary collision could lead to radiative recombination via dying pair. The annihilation probability per unit time of a collision process is a product of the formation probability of the dying pair in the annihilation channel and the annihilation probability per unit time of the dying pair. In a recombination process involving EP, the Coulomb attraction between the extra electron in EP and the counterpart hole helps the extra electron in EP to escape the distorted lattice either by tunneling or by thermal excitation. The escaped electron and counterpart hole form a dying pair. The ansatz is applicable to all ionic and strong polar semiconductors where large polarons are the majority of carriers.
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Supplemental Material for
Radiative recombination of large polarons in halide perovskites

Polarons as the majority of carriers

If a beam of light is shed on a halide perovskite, electrons and holes are produced. It is well-known that in an ionic crystal, an extra electron (hole) usually exists as large electronic (hole) polaron [1]. Applying theory of polaron [10] to MAPbI₃, one can estimate the formation energy of polaron is $E_P = 70$ meV, the formation free energy $F_P$ is 40–70meV [15]. The binding energy $E_b$ of an exciton is 15meV [22]. If $T < E_b/k_B$ (174K), carriers mainly exist as polarons and excitons. If $E_b/k_B < T << F_P$, excitons eventually disappear and become polarons. Further increasing temperature, the majority of carriers are still polarons, the percentage of free electrons (holes) increases, $\sim 10\%$ at 300K [15]. If temperature is too high such that lattice distortion cannot follow the motion of electron, polarons cannot exist [11].

Three behaviors of mobility $\mu$ indicate that the majority of carriers are polarons. (1) $\mu$ depends on temperature $T$ as $\mu \propto T^{-3/2}$ [8, 15], which implies that (a) the strong 1-phonon interaction $V_{e-LO}$ of electron (hole) with longitudinal optical phonons does not appear. Otherwise the temperature dependence of $\mu$ will be different; (b) the change in distribution function is caused by the interaction $V_{e-LO}$ of carrier with longitudinal acoustic phonons. (2) $\mu$ is insensitive to defects [11, 12], which means that (c) the carrier is massive than a bare electron, otherwise the change in wave vector will be too large in the elastic scattering with defects; (d) the size or de Broglie wave length of carrier is larger than a typical bond length. (3) $\mu$ depends on the concentration $n$ of photo-generated carriers as $\mu \propto n^{-1}$ [8, 15], which is possible only when (e) the gas of carriers is non-degenerate and the number of carriers is fixed by the incident flux. Combination of (1) and (3) requires that (f) the effective interaction $V_{e-LO}$ is screened by a Curie-Weiss type of dielectric function [15]. Features (a-f) can only be explained by assuming that the majority of carriers are large polarons [15].

Dying pairs

A dying pair means that the average distance $d_{eh}$ between electron and hole $d_{eh} \leq L$. Denote the formation probability for the dying pairs in the interval $(d_{eh}, d_{eh} + \delta d_{eh})$ as $q(d_{eh})\delta d_{eh}$, one has

$$\int_0^L \delta d_{eh} \cdot q(d_{eh}) = 1.$$  

Denote the annihilation probability per unit time for pairs with $(d_{eh}, d_{eh} + \delta d_{eh})$ as $A(d_{eh})$. Because any dying pair with $d_{eh} \leq L$ cannot be broken by thermal activation, become an exciton or dissolve into polaron, $A(d_{eh})$ is not very sensitive to $d_{eh}$, $A(d_{eh}) \approx A(L)$. The total annihilation probability per unit time for all pairs $0 \leq d_{eh} \leq L$ is

$$\int_0^L \delta d_{eh} \cdot q(d_{eh}) \cdot A(d_{eh}) \approx A(L).$$  

(11)

Eq. (11) means that one can use the annihilation rate for the $d_{eh} = L$ dying pair to approximate the total annihilation rate for all $d_{eh} \leq L$ dying pairs.

Direct transition and indirect transition

The slow charge recombination in OIHs has been explained by the formation of indirect band gap originated from spin-orbit coupling [42–46] and/or lattice distortion [47, 48]. Denote $q$ as the relative shift between the bottom of the conduction band and the top of the valence band in reciprocal space. To conserve momentum, one has an indirect transition. A phonon with wave vector $q$ has to be involved. For a direct band gap material, phonon assistance is not necessary for radiative recombination. In this case, $q = 0$, and $w_{2f}$ becomes $w_{2f}^{d}$ defined below:

$$w_{2f}^{d} = \frac{e^2}{\sqrt{4\pi\varepsilon_0 m^2\varepsilon_1}} \frac{2\hbar\omega_k}{\varepsilon(\omega_k)} |k_x| |k_y| |k_z|^2.$$  

(12)

Denote $R_{q\alpha} = w_{2f} / w_{2f}^{d}$. For $|q| \ll \pi/a$, one can show that if an acoustic phonon is involved:

$$R \approx \frac{|k_1|^2 n_{cell} m k_B T}{|q|^3 M \sigma \varepsilon_0 \hbar^2 c_s^4},$$

(13)

where $k_1$, $v_g$, and $m$ are the wave vector, a typical group velocity and the mass of electron, $c_s$ is speed of sound, $M$ is the mass of a typical atom. If an optical phonon is involved:

$$R \approx \frac{n_{cell} m k_B T}{|q|^3 M \sigma \varepsilon_0 \hbar^2 c_s^4} |k_1|^2 |z_n|^2.$$  

(14)

It has been shown that $|q| < 0.1$ Å $\ll \pi/a$ [42 [48]. Using Eqs. (13) [14], one can estimate that $w_{2f} / w_{2f}^{d} \approx 0.1 - 0.3$. If the charge carriers were “free” electrons and holes as opposed to large polarons, their recombination rates would be slowed down by a factor of 3 to 10 relative to a direct band gap material, owing to the shift of the extremes of bands in reciprocal space.

Eqs.(3,5,7) in text give the ratios of the annihilate rates involving polaron(s) to the annihilation rates of bare electrons and holes. For MAPbI₃, $R_P = 28\ A, E_P = 70$ meV, $F_P = 40-70$ meV [15], $\varepsilon(0, T)$ is given in [32]. $L_m = 6.8$ Å,
which is not taken into account here. The uncertainties of initial state and final state. If the EP-HP line width of PL spectrum is determined by the energy picture does not reject a possible change in (1) exciton is neutral; and (2) in halide perovskites, the slow radiative recombination rate is not caused by the small shift of band extremes, but is caused by the small formation probability of dying pairs in the collisions involving polaron(s).

Deviations of model from measurements

There are apparent discrepancies between the theory and experimental values of $k_1$ and $k_2$ around 310 K. A sharp decrease of $k_2$ just below 310 K may be attributed to strong ferroelectric fluctuation [49, 50] which could separate mobile positive and negative charges across the domains.

The 1-body annihilation is caused by three collisions: exciton, free electron (hole)-trapped hole (electron), and EP(HP)-trapped hole (electron). The electric field produced by ferroelectric fluctuation cannot affect the spatial distribution of excitons and the trapped electrons (holes), because (1) exciton is neutral; and (2) in MAPbI$_3$, the largest ‘shallow’-trap energy $E_{tra}$ for electron is 0.192eV, the largest ‘shallow’-trap energy $E_{tra}$ for hole is 0.128eV [26]. That is why $k_1$ is not affected by the ferroelectric fluctuation below 310K.

The sudden rises of $k_1$ and $k_2$ at 310 K may be due to the fact that at higher temperatures, the electrons are too fast for the lattice deformation to follow [13, 41], and thus the carriers can escape from the surrounding lattice without resorting to tunneling or thermal activation.

Temperature dependence of peak frequency

In the present work, the blue shift of $\omega_{PL}$ with increasing temperature is attributed to the decrease of formation free energies $F_P(T)$ of EP and HP with increasing temperature [12]. Assuming electrons (holes) do not form EPs (HPs) but exist as free electrons (holes), there are attempts [51, 52] to understand $\omega_{PL}(T)$ from the changes of CBM and VBM with $T$, a qualitative agreement with the observed $\omega_{PL}(T)$ has been obtained. The polaron picture does not reject a possible change in $(c_b - v_t)$ with $T$ which is not taken into account here.

Line width of PL spectrum

According to the general theory of line width [53], the line width of PL spectrum is determined by the energy uncertainties of initial state and final state. If the EP-HP recombination goes through activation path, the energy uncertainty will be

$$\Gamma_1 = e^{-2F_p/k_BT}(F_p + k_BT e^{-F_p/k_BT}). \quad (15)$$

The number in bracket is less than 70meV, $e^{-2F_p/k_BT} < 0.05$, $\Gamma_1 < 3.5$meV. If EP-HP annihilation goes through tunneling path, the energy uncertainty is

$$\Gamma_2 = \rho_{con}\frac{e^2}{4\pi\varepsilon_0 2R_p \varepsilon(0, T)} + \frac{\hbar^2}{mR_p^2}. \quad (16)$$

The number in bracket is less than 20meV, $\rho_{con} < 0.4$, $\Gamma_2 < 8$meV.

Since the recombination of a bare electron and a bare hole is much slower than emitting or absorbing phonons, the energy levels of the breaking away electron and hole are further broadened by the electron (hole)-LO phonon interaction. In an ionic crystal, the coupling of electron (hole) with LO phonon is strongest. The energy uncertainty is

$$\Gamma_3 = g_{LO} n_B(\omega_{LO}), \quad (17)$$

where

$$g_{LO} \sim \frac{\hbar \omega_{LO}}{2\varepsilon_0} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right)^{1/2} \frac{k \cdot e_k}{k^2},$$

$\Omega = a_x^3$ is volume of a primitive cell, $a_x$ is the length of basis vector along x-direction, $k = |k|$ is length of wave vector $k$, $e_k$ is polarization vector of LO phonon [54]. Using data $\varepsilon_0 = 70$, $\varepsilon_\infty = 6.5$ [32], $\hbar \omega_{LO} \sim 11.5$meV [37], $a_x = 6.3A$ for MAPbI$_3$, one has $g_{LO} \sim 50$meV. For most of temperature range $k_B T > \hbar \omega_{LO}$, then $n_B(\omega_{LO})$ is number larger than 1. Therefore, $\Gamma_3$ is much larger than $\Gamma_1$ and $\Gamma_2$.

Non-radiative transition not important

Because the deep trap centers are rare in the middle of band gap [26], the intervals between available intermediate states are much larger than $\hbar \omega_{LO}$, non-radiative transition by multi-phonon emitting is improbable. By perturbation theory, one can show the probability $w_n$ of a $n$-phonon emitting process per unit time is $w_n \sim (u/a)^n w_1$, where $u$ is the displacement of atom, $a$ is lattice constant, $w_1$ is the emitting probability per unit time for a single phonon. For halide perovskites $w_1 \sim 10^{12}$s$^{-1}$ for LO phonon, $u/a \sim 10^{-2}$. Then the transition probability per unit time for a 3-phonon emitting process is $10^9$s$^{-1}$, which is already slower than any radiative recombination process. The energy change in a 3-phonon process is only 50meV, while the intervals between mid-gap states is much larger than 50meV [26]. Therefore, non-radiative transition is not important in
halide perovskites. The nonadiabatic molecular dynamics predicts that the life time of non-radiative transition is $\sim 1-5\text{ps}$\textsuperscript{[55, 57]}, which is contradict to the observed long life time of carrier (hundreds of ns)\textsuperscript{[5, 6, 39, 57]).

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