Excitonic luminescence upconversion in a two-dimensional semiconductor

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Supplementary Figures:

Supplementary Figure 1

Figure S1 | Polarization-Resolved Luminescence Up-Conversion. a-d Data from four additional samples. Upper and bottom rows show spectra under $\sigma^+$ and vertically polarized excitation, respectively. The conservation of circular, but not linear, polarization implies the up-converted exciton inherits the valley properties of the negatively charged exciton.
Supplementary Figure 2

Figure S2 | Fine Structure of Negatively Charged Exciton in WSe$_2$ on Boron Nitride. Photoluminescence spectrum of boron nitride supported monolayer WSe$_2$, clearly showing a split negatively charged exciton ($X^-$) peak. Blue lines denote a bi-Lorentzian fit to the doublet. Inset: microscope image of the device, with boron nitride appearing light blue.

Supplementary Figure 3

Figure S3 | Overlap of Reverse PLE Spectrum with $X_0$ in Additional Samples. Blue lines show bi-Gaussian peaks fit to the doublet structure of the negatively charged exciton ($X^-$) in standard PL spectra (black data). Red data are the integrated $X^0$ luminescence intensity for varying laser excitation energy. In all instances, the luminescence up-conversion follows the high-energy $X_{(2)}^0$ peak, with maximal efficiency occurring near its peak energy. The ratios of standard $X^0$ PL to peak reverse PL intensity shown here are 20, 25, 10, 61, 77, and 41 for samples a-f, respectively. The variation in efficiency likely comes from different doping levels and sample quality.
Supplementary Figure S4

**Figure S4 | Negatively Charged Exciton Doublet at Varying Excitation Energies.** a, Polarization resolved photoluminescence spectra as a function of excitation energy with $\sigma^+$ polarized excitation. Black and red curves represent co-circular and cross circular detection. These data show that the $X^-$ doublet has a strong excitation wavelength and polarization dependence. When the excitation energy moves from far above $X^0$ to lower energy, the intensity of $X^-_{12>}$ relative to $X^-_{12<}$ increases concomitantly with $X^0$. In the limit of resonant $X^0$ excitation, the $X^-$ emission is almost entirely composed of the higher energy state $X^-_{12>}$, as shown in b, Overlay of charged exciton spectrum for excitation resonant with the neutral exciton (blue) with PL spectrum for excitation above the neutral exciton (black). (also see Figs. 2c and d).

Supplementary Figure S5

**Figure S5 | $X^-_{12} - X^-_{11}$ Peak Splitting in Additional Samples.** a, The doublet splitting from 14 monolayer WSe$_2$ samples. The distribution yields a mean splitting of 6.9 ± 0.5 meV. b, Extracted doublet splitting of a single sample from 20 K to 80 K, showing constant $X^-_{12} - X^-_{11}$ splitting. Due to linewidth broadening, we cannot obtain reliable peak fitting for temperatures above 80 K.
Supplementary Text

I. The coupling of the $A_1'$ and $E'$ phonon to the $\pm K$-valley exciton

From ab initio results, the $A_1'$ phonon mode has a rather strong deformation potential coupling with the $\pm K$-valley electron \(^1\). From the viewpoint of symmetry considerations \(^2,3\), the out-of-plane $A_1'$ phonon mode preserves the lattice symmetry while the in-plane $E'$ mode breaks the lattice symmetry. Thus, an electron at the $\pm K$ point which has the symmetry of the lattice can emit/absorb an $A_1'$ $\Gamma$-phonon, while emission/absorption of the $E'$ $\Gamma$-phonon is forbidden exactly at the $\pm K$ point. Consequently, we expect the coupling strength of $E'$ to be much weaker than $A_1'$ for low energy electrons/holes and excitons in $\pm K$ valleys.

Experiments in Ref. \(^4\) have shown that the $A_1'$ Raman mode is more intense than $E'$ when the exciting laser energy lies near the resonance of the A or B exciton ($X^0$). Meanwhile, in our experiment, Stokes Raman emission at $X^0$ preserves both circular and linear polarization of the excitation laser, signaling that the involved phonon scattering preserves both valley polarization and coherence. Combined with observations that the $A_1'$ phonon preserves both circular and linear polarization while the $E'$ phonon is cross-polarized (un-polarized) for circular (linear) polarization\(^5,6\), we conclude that the $A_1'$ phonon should dominate the resonant anti-Stokes emission observed here. Our experimental observations are in agreement with the above theoretical analysis.

II. Phonon induced coupling between a negatively charged exciton and a neutral exciton

Here, we use the convention that the electron center-of-mass (COM) wave vector is measured from the band edge $\pm K$ point, while that of the neutral exciton $X^0$ is measured from its energy minimum. We denote $\hat{\epsilon}_q$ as the electron annihilation operator with wave vector $k$, $\hat{X}_{0,k}$ ($\hat{P}_{0,q}$) as the $X^0$ (negatively charged exciton $X^-$) annihilation operator with COM wave vector $k$. We also write $\hat{P}_{k,q} \equiv \hat{\epsilon}_q \hat{m}_{e,k} \hat{X}_{0,q} + \hat{m}_{e,k} \hat{P}_{0,q}$ as the annihilation operator of an unbound electron-$X^0$ pair with COM wave vector $k$ and relative wave vector $q$. The system Hamiltonian can be written as $\hat{H} = \hat{H}_0 + \hat{H}_{e-ph}$, with the non-interacting Hamiltonian

$$\begin{align*}
\hat{H}_0 &= \sum_{q,k} \left( E_{X^0} + \frac{\hbar^2 k^2}{2M_-} + \frac{\hbar^2 q^2}{2\mu} \right) \hat{P}_{k,q} \hat{P}_{k,q}^\dagger + \sum_k \left( E_{X^-} + \frac{\hbar^2 k^2}{2M_-} \right) \hat{\epsilon}_k \hat{\epsilon}_k^\dagger + \sum_Q \hbar \omega_Q \hat{b}_Q \hat{b}_Q^\dagger .
\end{align*}$$

Here the $1^{st}$ term describes the energy of an unbound electron-$X^0$ pair with COM wave vector $k$ and relative wave vector $q$. The $2^{nd}$ term describes the energy of $X^-$ (bound electron-$X^0$ pair) with COM wave vector $k$, and the $3^{rd}$ term denotes the energy of $A_1'$ optical phonons. The $X^0$ (electron) effective mass is estimated as $M_0 \approx 0.6m_0$ ($m_e \approx 0.4m_0$), while $M_- = M_0 + m_e$ is the $X^-$ effective mass.

We write the electron-phonon interaction Hamiltonian

$$\begin{align*}
\hat{H}_{e-ph} &= \sum_{kq} \frac{\mathcal{g}_q}{\sqrt{A}} \hat{\epsilon}_{k+q} \hat{\epsilon}_k \left( \hat{b}_Q^\dagger + \hat{b}_Q \right) .
\end{align*}$$

Here $\hat{b}_Q$ is the $A_1'$ phonon annihilation operator, and $\frac{\mathcal{g}_q}{\sqrt{A}}$ is the coupling parameter with quantized area $A$. 

We assume a bath of $A_1$ optical phonons in the monolayer described by: $|b\rangle \equiv \bigotimes_{\mathbf{Q}} |N_{\mathbf{Q}}\rangle_{\mathbf{Q}}$. Here $|N_{\mathbf{Q}}\rangle_{\mathbf{Q}}$ is the number state of the phonon mode with wavevector $\mathbf{Q}$ where the occupation number is $N_{\mathbf{Q}}$. The $A_1$ phonon has a nearly flat dispersion which can be neglected here for simplicity, i.e. we take $\omega_{\mathbf{Q}} = \omega_{\text{ph}}$ for all $\mathbf{Q}$ values. The average phonon occupation number is given by the Bose distribution $\bar{N} = \left(\exp(h\omega_{\text{ph}}/k_B T_L) - 1\right)^{-1}$, where $T_L$ is the lattice temperature (often distinct from the carrier temperature).

First we analyze the $X^0/X^-$ phonon interplay under resonant excitation at the $X^-$ resonance. In this case, we consider the initial state of the $X^0/X^-$ phonon system as: $|i\rangle_{\mathbf{k}} \equiv |T\rangle_{\mathbf{k}} \otimes |b\rangle$ with energy $E_i = E_{X^-} + \hbar \omega_{\mathbf{k}}^2$, i.e. $X^-$ with COM wave vector $\mathbf{k}$ ($|T\rangle_{\mathbf{k}} \equiv \hat{T}_{\mathbf{k}}|0\rangle$) plus the phonon bath. After absorbing a $\mathbf{Q}$-wave vector phonon from the bath, $X^-$ can be discharged into an unbound $X^0$-electron pair $|P_{\mathbf{q}}\rangle_{\mathbf{k}+\mathbf{Q}} \equiv \hat{P}_{\mathbf{k}+\mathbf{Q},\mathbf{q}}|0\rangle$ with COM wave vector $\mathbf{k} + \mathbf{Q}$ and relative wave vector $\mathbf{q}$ (Fig. S6 (a)). This final state can be written as

$$|\mathbf{Q}, \mathbf{q}\rangle_{\mathbf{k}} \equiv |P_{\mathbf{q}}\rangle_{\mathbf{k}+\mathbf{Q}} \otimes \hat{b}_{\mathbf{q}}|b\rangle,$$

which has the energy $E_k(\mathbf{Q}, \mathbf{q}) = E_{X^0} + \hbar \omega_{\mathbf{Q}}^2 + \hbar \omega_{\text{ph}}^2 - \omega_{\text{ph}}$. Here $\hat{b}_{\mathbf{q}}|b\rangle$ is the phonon state where a phonon with wavevector $\mathbf{Q}$ is removed from the initial bath $|b\rangle$. Momentum conservation puts no constraints on the relative momentum $\mathbf{q}$, so there is a continuum of final states starting from $E_{X^0} - \omega_{\text{ph}}$.

Alternatively, when the applied laser is resonant with the $X^0$ state, we consider the initial state $|i\rangle \equiv \hat{X}_{\mathbf{k}}^+|eB\rangle \otimes |b\rangle$ with $|eB\rangle$ denoting an electron bath. For the final state, we have $|\mathbf{Q}, \mathbf{q}\rangle \equiv \hat{T}_{\mathbf{q}}^+ \hat{e}_{\mathbf{q}+\mathbf{Q}}|eB\rangle \otimes \hat{b}_{\mathbf{q}}^+|b\rangle$, where $\hat{e}_{\mathbf{q}}|eB\rangle$ denotes extraction of a $\mathbf{q}$ wave vector electron from the electron bath, $\hat{b}_{\mathbf{q}}^+|b\rangle$ indicates the addition of a phonon of wavevector $\mathbf{Q}$ to the phonon bath, and $\hat{T}_{\mathbf{q}}^+$ creates $X^-$ with COM wave vector $\mathbf{q}$. The state $|\mathbf{Q}, \mathbf{q}\rangle$ has an energy

$$E(\mathbf{Q}, \mathbf{q}) = \frac{\hbar \omega_{\mathbf{Q}}^2}{2m_e} - \frac{\hbar \omega_{\mathbf{Q}}^2}{2m_\text{ph}} + E_{X^-} + \omega_{\text{ph}},$$

Again, as momentum conservation puts no constraint on the value of $\mathbf{q}$, the possible $|\mathbf{Q}, \mathbf{q}\rangle$ states form a continuum near the energy $E_{X^-} + \omega_{\text{ph}}$.

In either of the two resonant excitation scenarios discussed above, we can model the $X^- \leftrightarrow X^0$ coupling as a discrete state $|i\rangle$ coupled to a continuum $|f\rangle$ (Fig. S6 (b)). Such a model has already been thoroughly discussed in Ref. 7. In order to analyze the dynamics of the initial state, below we give an estimate of the coupling strength and how it varies with the final state energy in the continuum.
Fig. S6 | (a) X− with wave vector k− can absorb a Q-wave vector phonon and become an unbound electron-X0 pair, and vice versa. (b) This is equivalent to a model in which a single state |i⟩ couples with an energy continuum |f⟩, with the coupling strength dependent on the energy E.

III. Up-conversion (X− → X0)

We consider the initial state of X− with wave vector k ≈ 0, dropping its k-subscript. As shown in the previous section, the final states of an unbound X0-electron pair are characterized by the state |Q, q⟩ with an energy \( E(Q, q) = E_{X0} - \omega_{ph} + \frac{\hbar^2 q^2}{2M_e} + \frac{\hbar^2 q^2}{2M} \) which forms a continuum. The \( X^- \rightarrow X^0 \) coupling strength is then \( \langle Q, q | \hat{H}_{e-ph} | i \rangle \). In order to calculate \( \langle Q, q | \hat{H}_{e-ph} | i \rangle \), the \( X^- \) state is expanded using the basis of unbound \( X^0 \)-electron pairs: \( |T⟩ = \frac{2\pi}{\sqrt{N}} \sum_q \phi^-(q) |P_q⟩ \). In the expansion, \( X^0 \) excited states (2p orbitals etc.) are dropped as they are hundreds of meV above the ground state and are not substantially mixed into \( X^- \) by the Coulomb binding. The electron-phonon interaction Hamiltonian \( \hat{H}_{e-ph} \) is taken to have the deformation potential coupling form

\[
g_q = \sqrt{\frac{\hbar}{2\rho_{ph}}} M_q \sim 300 \text{ meV} \cdot \text{Å},
\]

where we have used \( \hbar \omega_{ph} = 30 \text{ meV} \) for WSe2, while the mass density \( \rho = 3.1 \times 10^{-7} \text{ g/cm}^2 \) and electron-phonon coupling matrix element \( M_q=0 = 4.8 \text{ eV/Å} \) are taken from the \textit{ab initio} values of MoS2 (we expect these values to have the same order of magnitude for WSe2). We then have

\[
\langle Q, q | \hat{H}_{e-ph} | i \rangle = \frac{2\pi}{A} \sqrt{N} g_q \phi^-(q - \frac{M_e}{M} Q).
\]

The spectral density for the coupling of |i⟩ with the continuum is then

\[
\Gamma(E) = \sum_{Q,q} \delta (E(Q, q) - E) \left| \langle Q, q | \hat{H}_{e-ph} | i \rangle \right|^2
\]

\[
= \int \frac{dQ dq}{(2\pi)^2} \delta(E(Q, q) - E) N_Q \left| g_q \phi^-(q - \frac{M_e}{M} Q) \right|^2.
\]

where we have changed the summation to an integral: \( \sum_q (\ldots) = \frac{A}{(2\pi)^2} \int dq (\ldots) \).
Below we analyze the behavior of $\Gamma(E)$ as a function of $E$. For $E$ slightly above the threshold energy $E_{X0} - \omega_{ph}$ (that is, small $\Delta E \approx \hbar^2 q^2 / 2M - \hbar^2 q^2 / 2\mu$), both $Q$ and $q$ are close to zero so $g_Q$ and $\phi^-(q - \frac{M_0}{M}Q)$ are nearly constant, leaving $\Gamma(E) \approx N_Q |g_Q = 0| \phi^-(q = 0)|^2 \frac{\mu M}{\hbar^2} \Delta E$ which increases linearly with $E$. On the other hand, when $\Delta E \approx \hbar^2 q^2 / 2M - \hbar^2 q^2 / 2\mu$ is large, either $Q$ or $q$ becomes large, so we need to analyze the behavior of $|g_Q|^2$ and $|\phi^-(Q)|^2$. From the ab initio calculation in Ref. 1, $g_Q$ is almost independent of the $Q$-direction, and attains a maximal value $\approx 300 \text{ meV} \cdot \text{Å}$ for $Q = 0$, and then decays with increasing $Q$. The half-width half-maximum is $\sim 0.2 \text{ Å}^{-1}$. $\phi^-(Q)$ and also decays with $Q$. Numerical estimations have shown average electron-hole separations in $X^{-}$ of $\sim a_B$ and $\sim 2.5a_B$ 9, giving the half-width of $\phi^-(Q)$ to be $\sim 1/25a_B \sim 0.03 \text{ Å}^{-1}$. Thus $\phi^-(Q)$ decays much faster than $g_Q$, and for a rough estimation we can approximate $|\phi^-(q - \frac{M_0}{M}Q)|^2$ by $\delta(q - \frac{M_0}{M}Q)$ and replace the phonon occupation with its thermal average $N_Q \approx \bar{N} = (e^{\hbar\omega_{ph}/k_B T} - 1)^{-1}$, yielding

$$\Gamma(E) \approx \frac{\bar{N}}{(2\pi)^2} \int dQ |g_Q|^2 \delta(E \left(Q, \frac{M_0}{M}Q\right) - E) \approx \bar{N} \frac{m_e}{2\pi\hbar^2} |g_Q|_{q = \frac{\bar{N}}{2m_e \Delta E}}^2,$$

which means $\Gamma(E) \to 0$ when $E$ is significantly higher than the threshold energy $E_{X0} - \omega_{ph}$. So $\Gamma(E)$ shows a single peak (Fig. S6 (b)). The expression above leads to an estimation of a half width half maximum $w \sim 100 \text{ meV}$.

The height (maximum value) of the spectral density $\Gamma(E)$ can be estimated as

$$\max(\Gamma) \sim \frac{1}{w} \int \Gamma(E)dE = \frac{1}{w} \int \frac{dQ dQ}{(2\pi)^2} \left( \int dE \delta(E(Q, Q) - E) \right) N_Q |g_Q \phi^-(q - \frac{M_0}{M}Q)|^2 \approx \frac{\bar{N}}{(2\pi)^2} \int dQ |g_Q|^2 \sim \bar{N} \times \frac{100 \text{ (meV)}^2}{w} \sim \bar{N} \times 1 \text{ meV} \ll w.$$

Above the threshold energy $E_{X0} - \omega_{ph}$, the spectral density of the final states continuum has an approximately linear rising $\Gamma(E) \sim 0.1\bar{N} \times \Delta E$, reaching the same order (few meV) as the peak value for $\Delta E$. Since $\max(\Gamma) \sim E_{X0} - \omega_{ph}$, the effective decay rate is well described by Fermi’s Golden rule: $\frac{2\pi}{\hbar} \Gamma(E_i) \sim \frac{2\pi}{\hbar} \bar{N} \times 1 \text{ meV}$. One shall also keep in mind that the above threshold energy will be blurred by the finite linewidth of $X^{-}$ and $X^{0}$. For $\Gamma(E_i) \sim \max(\Gamma)$ and assuming a lattice temperature $T_L \sim 100 \text{ K}$, then $\bar{N} \sim 0.03$ and we estimate an effective $X^{-} \to X^{0}$ up-conversion rate $\frac{2\pi}{\hbar} \Gamma(E_i) \approx 0.03 \text{ ps}^{-1}$. On the other hand, if the $X^{-}$ energy is well below the threshold energy $E_{X0} - \omega_{ph}$ (by a detuning much larger than the $X^{-}$ and $X^{0}$ linewidths), it will experience a small red shift instead of decaying to the continuum. This is consistent with the observation that up-conversion is efficient only for the higher energy peak and not the lower energy one in the $X$-doublet.

We note that the above analysis focuses only on the process of $X^{-}$ to $X^{0}$ conversion, while the luminescence up-conversion or spontaneous anti-Stokes relies also on the interconversion of photons with $X^{-}$ and $X^{0}$. The latter processes happens only within the appropriate light cones. $X^{-}$ can be efficiently created only when the laser frequency is within $E_{X^-} \pm \Gamma_{X^-}$, where $\Gamma_{X^-}$ is the
linewidth of the \(X^-\) absorption peak. If the \(X^-\) energy is much higher than \(E_{X0} - \omega_{ph} + \Gamma_{X0}\) (\(\Gamma_{X0}\), being the linewidth of the \(X^0\) luminescence peak), after phonon induced discharging, the resultant \(X^0\) has a large kinetic energy and is dark, i.e. well outside the light cone. This also leads to the double resonant condition for luminescence up-conversion (spontaneous anti-Stokes), i.e. the two broadened resonances \(E_{X-} \pm \Gamma_{X-}\) and \(E_{X0} - \omega_{ph} \pm \Gamma_{X0}\) will have significant overlap. The enhancement at doubly resonant conditions comes from energy conservation of all three consecutive steps: photon to \(X^-\), \(X^-\) to \(X^0\), \(X^0\) to photon.

Finally, we emphasis that the discussions and estimation of the up-conversion rate here are for a 2D system where the in-plane translational invariance requires momentum conservation of both the \(X^-\) to \(X^0\) conversion and their interconversion with photons. In reality, the trapping of \(X^-\) and \(X^0\) by local potential fluctuations will relax the momentum conservation constraint, which will help to enhance the efficiency of the spontaneous anti-Stokes process.

IV. Down-conversion under resonant excitation of \(X^0\) \((X^0 \rightarrow X^-)\)

When the \(X^0\) state is resonantly excited, the generated bright \(X^0\) with zero COM wavevector can combine with a free electron to become \(X^-\), accompanied by the emission of a phonon (Fig. S6 (a)). We write the initial state as \(|i\rangle \equiv \hat{X}^+_0|eB\rangle \otimes |b\rangle\) with \(|eB\rangle\) an electron bath and \(|b\rangle\) the phonon bath, and the final state as \(|Q, q\rangle \equiv \hat{T}_q \hat{e}_{q+Q}|eB\rangle \otimes \hat{b}_q^+|b\rangle\), where \(\hat{e}_q|eB\rangle\) denotes annihilation of a \(q\)-wave vector electron from the electron bath and \(\hat{T}_q^+\) corresponds to \(X^-\) with COM wave vector \(q\). This state \(|Q, q\rangle\) has an energy

\[
E(Q, q) = \frac{\hbar^2 q^2}{2m_e} - \frac{\hbar^2 (Q + q)^2}{2m_e} + E_{X-} + \omega_{ph},
\]

All \(|Q, q\rangle\) states form a continuum near the energy \(E_{X-} + \omega_{ph}\). We expand \(\hat{T}_q^+\) with the unbound electron-\(X^0\) pair as \(\hat{T}_q^+ = \frac{2\pi}{\mathcal{V}} \sum_k \phi_k^{-} (k) \hat{e}_{k+\frac{m_e}{M}q}^+ \hat{X}^+_0, k_{0}, k_{0} - k, k_{0} - k, k_{0} - k_{0} - q\). The matrix element \(\langle Q, q|\hat{R}_{e-\text{ph}}|i\rangle = \frac{2\pi}{\mathcal{V}} n_{q+Q} \int \frac{dQdq}{(2\pi)^2} \delta(E(Q, q) - E)n_{q+Q} \left| \phi_q^{-} (M_{0}/M - q) \right|^2\), with \(n_{q+Q} \equiv \langle eB|\hat{e}_{q+Q}^+ \hat{e}_{q+Q}|eB\rangle = 0\) or 1 the electron occupation number in the initial electron bath \(|eB\rangle\).

Following the treatment in the previous section, we write the coupling spectral density as

\[
\Gamma(E) = \sum_{Q, q} \delta(E(E(Q, q) - E)|\langle Q, q|\hat{R}_{e-\text{ph}}|i\rangle|^2
\]

\[
= \int dQdq(2\pi)^2 \delta(E(Q, q) - E)n_{q+Q} \left| \phi_q^{-} (M_{0}/M - q) \right|^2.
\]

We approximate the electron occupation by its thermal average \(n_{q+Q} \approx \left(e^{(\frac{\hbar^2 (q+Q)^2}{2m_e} - \mu)/k_B T + 1}\right)^{-1}\) with \(\mu\) the chemical potential. For small or moderate electron density, \(n_{q+Q}\) is only significant when \(\frac{\hbar^2 (q+Q)^2}{2m_e} \lesssim k_B T\). Also \(\left| \phi_q^{-} (M_{0}/M - q) \right|^2\) decays to its half-maximum when \(q \sim 0.05 \text{ Å}^{-1}\), so we expect \(\Gamma(E)\) to be significant when

\[
E_0 - k_B T \leq E_0 - \frac{\hbar^2 (q+Q)^2}{2m_e} \leq E \leq E_0 + \frac{\hbar^2 q^2}{2m_e} \leq E_0 + 10 \text{ meV}.
\]

So \(\Gamma(E)\) bears the shape of a peak with half width \(\sim 10 \text{ meV}\) (Fig. S6 (b)).
We approximate the electron occupation by its thermal average \( n_{q+q} |\phi_q^{(-M_0/M_\pi)q}|^2 \) is significant only when \( |q + Q| \leq \sqrt{2m_e k_B T} \approx 0.03 \, \text{Å}^{-1} \) and \( q \approx 0.05 \, \text{Å}^{-1} \). For such a \( Q \) value, \( g_Q \approx g_{q=0} \) is almost a constant, so the maximum spectral density

\[
\text{max}(\Gamma) \approx \frac{1}{w} \int \Gamma(E) dE \approx \frac{|g_{q=0}|^2}{(2\pi)^2 w} \int dQ dQ n_{q+q} |\phi_q^{(-M_0/M_\pi)q}|^2 \\
= \frac{|g_{q=0}|^2}{(2\pi)^2 w} \left( \int dQ n_Q \right) \left( \int dQ |\phi_q^{(-M_0/M_\pi)q}|^2 \right) \\
= \frac{\rho_e}{(2\pi)^2 w} \left( \frac{M_-}{M_0} \right)^2 \int dQ n_Q \sim \frac{\rho_e}{w} \times 6400 \, (\text{meV} \cdot \text{Å})^2.
\]

Here \( \rho_e = \int dQ n_Q \) is the electron density. For \( \rho_e \approx 10^{13} \, \text{cm}^{-2} \approx 10^{-3} \, \text{Å}^{-2} \) or lower density, \( \text{max}(\Gamma) \ll w \approx 10 \, \text{meV} \). In this parameter regime, the population of the initial \( X^0 \) state \( \{i\} \) will irreversibly decay to the \( X^- \) continuum (Fermi’s golden rule regime), with an effective decay rate \( \frac{2\pi}{h} \Gamma(E_i) \approx \frac{2\pi}{h} \rho_e \times 600 \, \text{meV} \cdot \text{Å}^2 \). Assuming a doping with electron density \( \rho_e = 10^{12} \, \text{cm}^{-2} \approx 10^{-4} \, \text{Å}^{-2} \), then the decay rate \( \frac{2\pi}{h} \Gamma(E_i) \approx \frac{1}{16 \, \text{ps}} \).

V. Temperature-dependence

First, we focus on the up-conversion case (reverse PL). When resonantly exciting \( X^- \), the up-converted exciton PL is determined by three factors:

1. The conversion rate from \( X^- \) to an electron-\( X^0 \) pair, which is proportional to the phonon occupation \( \bar{N} \equiv (e^{\hbar \omega_{ph}/k_B T} - 1)^{-1} \). This conversion rate increases when raising the temperature.

2. The \( X^- \) absorption rate. An electron at wavevector \( k_e \) is optically coupled to \( X^- \) with the same COM wave vector, which introduces finite absorption at the energy of \( E_{X^-} - M_0 E_{e,k} \) (where \( E_{e,k} \equiv \frac{\hbar^2 k_e^2}{2m_e} \)) with the absorption proportional to the electron occupation at kinetic energy \( E_{e,k} \). For low doping levels and relatively high \( T \), the electron has a thermal distribution \( n_k \propto \frac{1}{k_B T} e^{E_{e,k}/k_B T} \). Assuming the CW excitation laser energy is at \( E_{X^-} \), the \( X^- \) absorption then scales as \( \sim 1/T \).

3. The \( X^0 \) radiative decay rate. The kinetic energy of \( X^0 \) will follow a thermal distribution, but only carriers inside the light cone, whose kinetic energy lies close to 0, can radiatively recombine. So the \( X^0 \) effective radiative decay rate \( \Gamma_r \) is proportional to the \( X^0 \) thermal population in the light cone which is \( \propto 1/T \). On the other hand, the nonradiative decay rate \( \Gamma_{nr} \) is usually much larger than \( \Gamma_r \), giving an exciton PL intensity proportional to \( \Gamma_r/(\Gamma_r + \Gamma_{nr}) \approx \Gamma_r/\Gamma_{nr} \propto 1/T \).

Combining the above three factors, the temperature dependence of the reverse PL is \( \propto T^{-2}/(e^{\hbar \omega_{ph}/k_B T} - 1) \), as shown in Fig. S7a.

Below, we discuss the temperature dependence of the standard PL, where an excitation laser with energy \( \approx 0.2 \, \text{eV} \) higher than the \( X^0 \) resonance is applied to generate \( X^0 \) and \( X^- \). The large excess laser energy can facilitate the dynamical equilibrium between \( X^0 \) and \( X^- \), so we assume...
that $X^0$ and $X^-$ populations satisfy the mass action law. Then the equilibrium exciton density $n_0$, $X^-$ density $n_-$, and electron density $n_e$ within the system satisfy:

$$\frac{n_0 n_e}{n_-} = \frac{4 M_0 m_e}{\pi \hbar^2 M_-} k_B T \exp \left( - \frac{E_c}{k_B T} \right) \equiv n_T.$$ 

Here, $E_c = 30$ meV is the $X^-$ binding energy. We also write $n_B \equiv n_- + n_e$ as the total background electron density and $n_L \equiv n_- + n_0$ as the total laser excitation. Then

$$n_- = \frac{n_L + n_B + n_T - \sqrt{(n_L + n_B + n_T)^2 - 4 n_L n_B}}{2},$$

$$n_0 = \frac{n_L + n_B - n_T + \sqrt{(n_L + n_B + n_T)^2 - 4 n_L n_B}}{2}.$$

Obviously $n_0$ and $n_-$ depend on several parameters: background electron density $n_B$, laser excitation density $n_L$, and the temperature $T$. In Fig. S7b we show the exciton PL ($\propto n_0/T$) as a function of $T$. Note that in Fig. 3d of the main text, the standard PL intensity remains nearly constant below 50 K. We consider this behavior to be a potential signature of laser heating from the $\sim 0.2$ eV excess photon energy.

![Fig. S7](image-url) (a) Estimated reverse PL intensity as a function of temperature. (b) Standard exciton PL intensity as a function of temperature, for background electron density $n_B = 10^{12}$ cm$^{-2}$ & total excitation density $n_L = 10^{12}$ cm$^{-2}$).


