

Electronic Supplementary Information: THz Mobility and Polarizability: Impact of Transformation and Dephasing on the Spectral Response of Excitons in a 2D Semiconductor

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S1. DENSITY MATRIX FORMALISM

A. Excitonic Transition Dipole Moment

Charge displacement and transitions occur for relative wavefunction transitions only, when electron and hole alter their distance. We consider their relative movement in terms of the relative coordinate $\underline{\vec{\rho}} = \vec{r}_e - \vec{r}_h$. This should not be confused with the density matrix ρ used later. The non-stationary dipole moment of excitons will thus be expressed as

$$\vec{M}(t) = -q_e \vec{r}_e(t) + q_e \vec{r}_h(t) = -q_e \vec{r}_e(t) + q_e (\vec{r}_e(t) - \underline{\vec{\rho}}(t)) = -q_e \underline{\vec{\rho}}(t) \quad (\text{S1})$$

This quantity, however, is linked to the velocity of correlated, relative electron-hole-movement, which can be understood once we look at its derivative.

$$\frac{d\vec{M}(t)}{dt} = -q_e \frac{d\underline{\vec{\rho}}(t)}{dt} = -q_e \vec{v}_{rel}(t) \quad (\text{S2})$$

Dealing with quantum systems, however, a certain property is given as a matrix element resulting from an operator representing the property of interest. Here, we will be concerned with the expectation value of the dipole moment operator

$$\hat{M} = -q_e \hat{r} \quad \text{or in the excitonic formulation} \quad \hat{M}_X = -q_e \hat{\underline{\rho}}. \quad (\text{S3})$$

For the sake of clear readability we simply write M always implying vectorial properties, where necessary, depicting symbol visuals as readable as possible, although the operator always acts on the relative coordinate of an intraexcitonic wavefunction.

B. Equation of Motion under Perturbation

For a discussion of properties in the frequency domain, we have to establish the temporal behavior first. To do so, we resort to the von-Neumann equation describing the temporal evolution of a system's density matrix ρ .

$$\dot{\rho} = -\frac{i}{\hbar} [\hat{H}, \rho], \quad (\text{S4})$$

where \hat{H} is the Hamiltonian. For a proper description, we expand $\rho = \rho_0 + \Delta\rho$ to be a small perturbation around the unperturbed equilibrium state ρ_0 . For the cases of \hat{H} and ρ we skip writing them with their explicit time-dependence (t). In contrast we use $E(t)$ for the perturbing THz field, to distinguish it from the time invariant system Eigenenergies E_j of the excitonic series in first order perturbation theory, used later. Further $\vec{E}(t)$ and \hat{M} are considered to be parallel so that the scalar product reduces to a scalar multiplication.

Given the full Hamiltonian $\hat{H} = \hat{H}_0 - \hat{M} \cdot E(t) = \hat{H}_0 - q_e \hat{\rho} \cdot E(t)$ including the perturbation $\hat{M} \cdot E(t)$ given by the excitonic transition dipole moment $q_e \hat{\rho}$ expressed through the relative displacement operator $\hat{\rho}$. Inserting into Equation S4, we obtain

$$\Delta\dot{\rho} = -\frac{\dot{\hbar}}{\hbar} [\hat{H}_0 - \hat{M} \cdot E(t), \rho_0 + \Delta\rho]. \quad (\text{S5})$$

In the small perturbation limit, the terms $[\hat{H}_0, \rho_0]$ and $[\hat{M}, \Delta\rho]$ vanish. This is, because the unperturbed ground state ρ_0 and the ground state Hamiltonian H_0 commute and additionally $\Delta\rho$ does not further couple to the transition dipole moment. We arrive at

$$\Delta\dot{\rho} = -\frac{\dot{\hbar}}{\hbar} \{ [\hat{H}_0, \Delta\rho] - [\hat{M}, \rho_0] E(t) \} \quad (\text{S6})$$

As we will be concerned with specific elements of the matrix $\Delta\dot{\rho}$, say $\Delta\dot{\rho}_{j'j}$, they can be selected through $\langle j' | \dots | j \rangle$. Additionally, we implement relaxation mechanisms of population ($j' = j$) and polarization ($j' \neq j$) terms through $\gamma_{j'j} \Delta\rho_{j'j}$

$$\langle j' | \Delta\dot{\rho} | j \rangle = \Delta\dot{\rho}_{j'j} = -\frac{\dot{\hbar}}{\hbar} \{ \langle j' | [\hat{H}_0, \Delta\rho] | j \rangle - \langle j' | [\hat{M}, \rho_0] | j \rangle E(t) \} - \gamma_{j'j} \Delta\rho_{j'j}. \quad (\text{S7})$$

Once the commutators get expanded, the operator products can be resolved by inserting the identity matrix through a full basis $\mathbb{1} = \sum_k |k\rangle \langle k|$. The expression then reads

$$\Delta\dot{\rho}_{j'j} = -\frac{\dot{\hbar}}{\hbar} \sum_k \{ H_{0,j'k} \Delta\rho_{kj} - \Delta\rho_{j'k} H_{0,kj} - (M_{j'k} \rho_{0,kj} - \rho_{0,j'k} M_{kj}) E(t) \} - \gamma_{j'j} \Delta\rho_{j'j} \quad (\text{S8})$$

To further simplify, we invoke the implications of small perturbation theory, namely

$$\Delta\rho_{j'j} = \begin{cases} 0 & j' = j, & \text{population remains constant} \\ \Delta\rho_{j'j} & j' \neq j \end{cases}$$

This will later eliminate contributions from population relaxation to any expectation value, leading to dephasing being the only relevant relaxation parameter.

$$\rho_{0,j'j} = \begin{cases} \rho_{0,j'j} & j' = j, & \text{initial population} \\ 0 & j' \neq j, & \text{initial polarization} \end{cases}$$

$$H_{0,j'k} = \begin{cases} E_{j'} & j' = k, & \text{ground state energy of } j' \\ 0 & j' \neq k, & \text{initial} \end{cases}$$

$$M_{j'k} = \begin{cases} 0 & j' = k, & \text{transitions require changing states} \\ q_e \rho_{j'k} & j' \neq k, \end{cases}$$

where, again, ρ is the relative e-h-displacement operator, describing the state of relative excitonic motion. Regarding these sets of implications, the sum over k can be reduced, to obtain the final equation

$$\Delta\dot{\rho}_{j'j} = -\frac{\dot{\hbar}}{\hbar} \{ (E_{j'} - E_j) \Delta\rho_{j'j} - (\rho_{0,jj} - \rho_{0,j'j'}) M_{j'j} E(t) \} - \gamma_{j'j} \Delta\rho_{j'j} \quad (\text{S9})$$

Finally, we use $(E_{j'} - E_j)/\hbar = E_{j'j}/\hbar = \omega_{j'j}$ and reduce the expression

$$\Delta\dot{\rho}_{j'j} = -(\dot{\hbar} \omega_{j'j} + \gamma_{j'j}) \Delta\rho_{j'j} + \frac{\dot{\hbar}}{\hbar} (\rho_{0,jj} - \rho_{0,j'j'}) M_{j'j} E(t) \quad (\text{S10})$$

C. Detailed Derivation of Equation 9

In the following discussion we derive how the polarizability translates into mobility for excitons. We calculate the transition dipole moment of the exciton in the linear excitation regime (precisely: the net transition dipole moment over all transitions within the intraexcitonic series). In the density matrix formalism, an expectation value is given as the trace of the product between the time-dependent density matrix ρ and the operator matrix (here M). We skip writing them with an explicit time-dependence. In contrast we use $E(t)$ for the perturbing THz field, to distinguish it from the time invariant system Eigen-energies E_j of the excitonic series in first order perturbation theory.

$$\langle M \rangle = Tr \{ M \rho \} = \sum_{j',j} M_{jj'} \rho_{j'j} = \sum_{j',j} (-q_e \rho_{jj'} \rho_{j'j}) = \sum_{j',j} M_{j'j}(t) \quad (\text{S11})$$

expanding the density matrix as before ($\rho = \rho_0 + \Delta\rho$) we rewrite Equation S11 by directly applying Equation S3

$$\langle M \rangle = Tr \{ M \rho_0 \} + Tr \{ M \Delta\rho \} = \underbrace{\sum_{j',j} (-q_e \rho_{jj'} \rho_{0,j'j})}_{\sum_{j',j} \tilde{M}_{0,jj'}} + \underbrace{\sum_{j',j} (-q_e \rho_{jj'} \Delta\rho_{j'j})}_{\sum_{j',j} \tilde{M}_{jj'}(t)} \quad (\text{S12})$$

and identify the stationary dipole moment intrinsic to the equilibrium state $\sum_{j',j} \tilde{M}_{0,jj'}$ as well as the time-dependent dipole moment $\sum_{j',j} \tilde{M}_{jj'}(t)$ containing the response through polarizability as will become clear later. Going back to the discussion from the main text and Equation S2 above, we establish the time derivative of $\langle M \rangle$ to find a link to $\langle v_{rel} \rangle$. We evaluate $d\langle M \rangle / dt$ and find according to Equation S12

$$\langle \dot{M} \rangle = \sum_{j',j} M_{jj'} \Delta\dot{\rho}_{j'j} = -q_e \sum_{j',j} \rho_{jj'} \Delta\dot{\rho}_{j'j} = -q_e \langle \dot{\rho} \rangle = -q_e \langle v_{rel} \rangle \quad (\text{S13})$$

We remark, that in time-dependent 1st order perturbation the transition dipole moments ($-q_e \rho_{jj'}$) are time independent, while the time dependence is reflected in the density matrix ρ . Simultaneously, the equation above immediately suggests to insert Equation S10, which delivers

$$\langle \dot{M} \rangle = \sum_{j',j} (i\omega_{jj'} + \gamma_{jj'}) M_{jj'} \Delta\rho_{j'j}. \quad (\text{S14})$$

It should be noted, that the second term of Equation S10 can not sustain in Equation S13, since the double sum j, j' (running through all indices twice) invoked by the definition of the expectation value is generating $(\rho_{0,jj} - \rho_{0,j'j'})$ and $(\rho_{0,j'j'} - \rho_{0,jj})$ in pairs canceling each other. This is also not abrogated by simultaneously running through the $M_{j'j}$, since the matrix M is symmetric (as ρ is a multiplicative operator).

In Equation S13 this expectation value is linked to the velocity, which we can also write as

$$\langle v_{rel} \rangle = \sum_{j',j} v_{rel,jj'} \Delta\rho_{j'j}. \quad (\text{S15})$$

So, unifying the relations established, we can deduce

$$\boxed{
\begin{aligned}
\langle \dot{M} \rangle &= -q_e \langle v_{rel} \rangle \\
&\Updownarrow \\
\sum_{j',j} (\mathrm{i}\omega_{jj'} + \gamma_{jj'}) \underbrace{M_{jj'} \Delta \rho_{j'j}}_{\tilde{M}_{jj'}(t)} &= -q_e \sum_{j',j} \underbrace{v_{rel,jj'} \Delta \rho_{j'j}}_{\tilde{v}_{rel,jj'}(t)}
\end{aligned}
} \tag{S16}$$

Now, this relation holds in the time as well as frequency domain. In the time domain, both dipole moment M as well as the relative velocity v_{rel} are tied to their response functions, the polarizability α [1] and mobility μ [2] via convolution (\otimes) with the external perturbation field $E(t)$. To write down an equivalent expression in the frequency domain, a Fourier Transformation (\mathcal{FT}) is necessary.

$$\boxed{
\begin{aligned}
\tilde{M}(t) = \alpha(t) \otimes E(t) & \quad \tilde{v}_{rel}(t) = \mu(t) \otimes E(t) \\
& \Updownarrow \mathcal{FT} \\
\tilde{M}(\omega) = \alpha(\omega) \cdot E(\omega) & \quad \tilde{v}_{rel}(\omega) = \mu(\omega) \cdot E(\omega)
\end{aligned}
}$$

These relations can also be applied to Equation S16. Once the fourier transformed excitation fields $E(\omega)$ are dropped on both sides, Equation 2 from the main text is recovered:

$$\sum_{j',j} (\mathrm{i}\omega_{jj'} + \gamma_{jj'}) \alpha_{jj'}(\omega) = -q_e \sum_{j',j} \mu_{jj'}(\omega) = -q_e \mu_X(\omega) \tag{S17}$$

D. ω scaling of polarizability

In the following, we want to rewrite the Equation S17 above and motivate Equation 17 for excitonic mobility from the main text.

$$\mu_X(\omega) = -\frac{1}{q_e} \sum_{j',j} (\mathrm{i}\omega_{j'j} + \gamma_{j'j}) \alpha_{j'j}(\omega) = -\mathrm{i} \frac{\omega}{q_e} \sum_{j',j} \alpha_{j'j}(\omega), \tag{S18}$$

At first, we have to stress the fact, that the second equality relation can only hold pairwise, i.e. for transition pairs $j \rightarrow j' + j' \rightarrow j$. This, in turn, means the following inequation holds

$$-\frac{1}{q_e} (\mathrm{i}\omega_{j'j} + \gamma_{j'j}) \alpha_{j'j}(\omega) \neq -\mathrm{i} \frac{\omega}{q_e} \alpha_{j'j}(\omega), \tag{S19}$$

but becomes an equation, as soon as both, the corresponding down- or upwards-transition are considered, i.e. a pair of resonant and anti-resonant transition, identified in the summed terms on the left and right hand side of the equation. We can state

$$-\frac{1}{q_e} \{ (\mathrm{i}\omega_{j'j} + \gamma_{j'j}) \alpha_{j'j}(\omega) + (\mathrm{i}\omega_{jj'} + \gamma_{jj'}) \alpha_{jj'}(\omega) \} = -\mathrm{i} \frac{\omega}{q_e} \{ \alpha_{j'j}(\omega) + \alpha_{jj'}(\omega) \}. \tag{S20}$$

So we are left to prove this alternative equation. It is clear, that this proof can only be comprehensible, considering the specific form of $\alpha(\omega)$. For that matter, we resort to Equation 1 from the main text

$$\alpha_{j'j}(\omega) = \frac{(b_{j'} - b_j)}{\hbar} |\langle j' | \hat{M} \cdot \vec{e} | j \rangle|^2 \cdot \frac{1}{\omega - \omega_{j'j} + i\gamma_{j'j}}, \quad (\text{S21})$$

Proofing Equation S20 to be true, requires to plug Equation S21 in Eq. S20, first on the left and then on the right hand side. We spare the lengthy mathematical conversion steps and find, that both sides come down to

$$\mu_{j'j} = -\frac{(b_{j'} - b_j)}{\hbar q_e} |\langle j' | \hat{M} \cdot \vec{e} | j \rangle|^2 \omega \left\{ \frac{\gamma_{j'j} - \gamma_{jj'} + i(\omega_{j'j} - \omega_{jj'})}{(\omega - \omega_{j'j} + i\gamma_{j'j})(\omega - \omega_{jj'} + i\gamma_{jj'})} \right\}, \quad (\text{S22})$$

which in turn immediately reveals, that our new full quantum mechanical transformation formula in fact captures the explicit ω scaling, however, assuming that transition pairs are concerned. Still, although it is necessary to stress this fact, it poses no constraint, since the entirety of up- and downwards transitions (i.e. resonant and anti-resonant) within the intraexcitonic series has to be considered anyway. The ω scaling remains, once the summation over all j', j of the exciton series is performed in Equation S18.

S2. MODELING OF EXCITONS

We model two-dimensional Wannier-Mott excitons in CdSe NPLs. As we have shown in our previous work [3, 4], NPLs are characterized by robust excitons with high binding energy in the order of hundreds meV due to the reduced dielectric screening, the high effective electron and hole masses and the confinement into a few layer. In this case the Coulomb attraction between electron and hole creates bound exciton states, showing a strong correlated motion of both particles. Hence, as the excitons form correlated states, excitation of the hole from a single THz-photon in the valance band (VB) simultaneously implies a similar electron transition in the conduction band (CB). As the calculation of either polarizability or mobility requires knowledge about exciton transition energies and dipole moments, we first determine the exciton energies and wavefunctions for different states taking selection rules into account.

We model the properties of the excitons in CdSe NPLs using the slowly-varying envelope approximation of two-dimensional Wannier excitons. According to the effective mass theory, the exciton hamiltonian is given by [3, 5]:

$$H_X = \frac{\mathbf{p}_e^2}{2m_e} + \frac{\mathbf{p}_h^2}{2m_h} + V_{conf}(\mathbf{r}_e) + V_{conf}(\mathbf{r}_h) + V_c(\mathbf{r}_e - \mathbf{r}_h) \quad (\text{S23})$$

where $V_{conf}(\mathbf{r}_{e(h)})$ is the electron (hole) confinement potential and $V_c(\mathbf{r}_e - \mathbf{r}_h)$ is the Coulomb interaction. 2D NPLs are strongly confined in z-direction, allowing for the

exciton Hamiltonian to be separated into in-plane (IP) and z-oriented parts [3, 5].

$$\begin{aligned} & \left(H(z_e, z_h) + H_X^{IP}(\rho_e, \rho_h) \right) \overbrace{|\Psi_X^z\rangle |\Psi_X^{IP}\rangle}^{\Psi_X} = \\ & \left(E_{conf} + E_X^{IP} \right) |\Psi_X^z\rangle |\Psi_X^{IP}\rangle, \end{aligned} \quad (\text{S24})$$

where ρ_i describes the particle coordinate in the x-y-plane, E_{conf} and $\Psi_X^z(z_e, z_h)$ are the confinement energy and wavefunction resulting from solving the single electron (hole) Schrödinger Equation in the z-direction. E_X^{IP} and $\Psi_X^{IP}(\rho_e, \rho_h)$ are the in-plane excitonic energy and wavefunction obtained by numerically solving the in-plane (IP) Hamiltonian H_X^{IP} . Based on ref [3, 6] in the weak confinement regime, using relative and center-of-mass (COM) coordinates ($\vec{\rho} = \vec{\rho}_e - \vec{\rho}_h$ and $\vec{R}_X = \frac{m_e \vec{\rho}_e + m_h \vec{\rho}_h}{m_X}$) allows for further separation of the in-plane wavefunction. In this case, the exciton will be described by center-of-mass and relative motion.

$$\begin{aligned} & \overbrace{\left(H_X^{rel}(\vec{\rho}) + H_X^{COM}(\vec{R}_X) \right)}^{H_X^{IP}(\vec{\rho}, \vec{R}_X)} \overbrace{|\Psi_X^{rel}\rangle |\Psi_X^{COM}\rangle}^{|\Psi_X^{IP}\rangle} = \\ & \left(E_X^{rel} + E_X^{COM} \right) |\Psi_X^{rel}\rangle |\Psi_X^{COM}\rangle, \end{aligned} \quad (\text{S25})$$

where $\Psi_X^{rel}(\vec{\rho})$ ($\Psi_X^{COM}(\vec{R}_X)$) and E_X^{rel} (E_X^{COM}) are the wavefunction and energy of the relative and center-of-mass Hamiltonian, respectively. The system and its solutions have been described in detail in [3].

The coupling between exciton and THz-photon depends on the dipole charge displacement $\vec{\rho}_e - \vec{\rho}_h$, ($H' = \vec{M}_X \cdot \vec{e} E(t) = -q_e(\vec{\rho}_e - \vec{\rho}_h) \cdot \vec{e} E(t)$) and the corresponding expectation value for the transition dipole moment can be calculated as follows:

$$-q_e \langle \Psi_X^f | (\vec{\rho}_e - \vec{\rho}_h) \cdot \vec{e} | \Psi_X^i \rangle = -q_e \langle \Psi_X^{z,f} | \Psi_X^{z,i} \rangle \langle \Psi_X^{COM,f} | \Psi_X^{COM,i} \rangle \langle \Psi_X^{rel,f} | \vec{\rho} \cdot \vec{e} | \Psi_X^{rel,i} \rangle \quad (\text{S26})$$

As we can clearly see, the dipole will act only on the relative motion leaving unity between the equal initial and final states of the center-of-mass (COM) and z-related products, respectively, that can not be addressed by THz-photons. Hence, COM wavefunctions do not interact with the THz-field and the actual exciton movement does not transport charge. Instead, transitions only occur within the series of relative wavefunctions, when electron and hole alter their distance. Excitons in two-dimensional materials experience pronounced dielectric screening, leading to a non-hydrogenic Rydberg series, where for example no degeneracy between states with the same principal quantum number n but different orbital angular momentum m occurs [5]. Our calculation is based on ref. [3] and the there mentioned formalism and material constants. The coulomb interaction in bound electron-hole-pairs is treated using the Rytova-Keldysh potential V_c , a widely accepted approach. This takes the dielectric screening of the exciton wave function due to the dielectric contrast between the semiconductor NPLs and the surrounding ligands

and solvent properly into account [3, 7, 8].

$$V_c(\rho) = \frac{-\pi e^2}{2\epsilon r_s} \left[H_0 \left(\frac{\rho}{r_s} \right) - Y_0 \left(\frac{\rho}{r_s} \right) \right], \quad (\text{S27})$$

where r_s is the screening length, H_0 and Y_0 are the Struve and Neumann functions of order 0, respectively. In contrast to the interaction potential for the simple 2D hydrogen model, this non-locally-screened interaction potential can only be treated numerically. In this case, the relative wave function

$$\Psi_{X,n,m}^{rel}(\rho) = \sum_{\tilde{n}, |\tilde{m}| < \tilde{n}} C(\tilde{n}, \tilde{m}) \varphi_{\tilde{n}, \tilde{m}}(\rho, \theta) \quad (\text{S28})$$

is scaled by the reduced effective band mass $m_r = \frac{m_e m_h}{m_e + m_h}$ and modified by the non-local dielectric screening potential. They are expanded in terms of 2D hydrogenic states

$$\varphi_{\tilde{n}, \tilde{m}}(\rho, \theta) = \sqrt{\frac{1}{2\pi}} \sqrt{\left(\frac{2}{(2\tilde{n}-1)a_b} \right)^2 \frac{(\tilde{n} - |\tilde{m}| - 1)!}{(\tilde{n} + |\tilde{m}| - 1)!(2\tilde{n} - 1)}} e^{i\tilde{m}\theta} \left(\frac{4\rho}{(2\tilde{n}-1)a_b} \right)^{|\tilde{m}|} e^{-\frac{2\rho}{(2\tilde{n}-1)a_b}} L_{\tilde{n}-|\tilde{m}|-1}^{2|\tilde{m}|} \left(\frac{4\rho}{(2\tilde{n}-1)a_b} \right), \quad (\text{S29})$$

where $L_n^\alpha(x)$ are the orthogonal associated Laguerre polynomials, $\tilde{n} = 1, 2, 3..$ is the principal quantum number, $\tilde{m} = \pm 1, \pm 2, \pm 3.. \pm n - 1$ is the angular momentum number. The states are labeled s for $\tilde{m}=0$, and p for $\tilde{m} = \pm 1$, d for $\tilde{m} = \pm 2$. a_b is the effective exciton Bohr radius and the coefficients $C(\tilde{n}, \tilde{m})$ are obtained by solving the matrix problem with the eigenfunctions $\varphi_{\tilde{n}, \tilde{m}}(\rho, \theta)$. n and m , as also used in the main text, represent the quasi hydrogenic series obtained for the exciton using a Rytova–Keldysh potential. Within this framework, we compute in Table S1, the energy separation and the intra excitonic transition matrix elements according to Equation S26 for all allowed transitions within the 1st to 5th shell. Notably, the angular part of the transition dipole matrix element creates transition selection rules among the intra excitonic series, for instance, allowing processes that obey $\Delta m = \pm 1$. We note that for a purely coulombic potential, states with the same quantum number n , yet different orbital angular moment m (e.g. $2s$ and $2p$) are degenerate. As shown in table S1, the non-local dielectric screening clearly removes this degeneracy, producing separation between these states and thus leading to a non-hydrogenic Rydberg series.

TABLE S1: Transition energies and -dipole matrix elements for different allowed state couples within the intra excitonic series.

$n, m \rightarrow n', m'$	$E_{n', m'} - E_{n, m}$ (meV)	M/q_e (Å)
1s→2p	77.80	1.89
1s→3p	128.00	0.77
1s→4p	142.00	0.45

1s→5p	146.00	0.31
2p→2s	23.80	18.62
2p→3d	39.12	11.44
2p→3s	57.07	4.08
2p→4d	63.44	2.91
2p→4s	66.01	2.54
2p→5d	68.22	2.13
2p→5s	68.65	2.08
2s→3p	26.41	16.30
2s→4p	40.43	7.80
2s→5p	44.56	5.65
3d→3p	11.09	39.26
3d→4f	21.44	21.45
3d→4p	25.11	17.30
3d→5f	28.04	14.80
3d→5p	29.24	13.98
3p→3s	6.85	48.39
3p→4d	13.22	35.40
3p→4s	15.80	30.20
3p→5d	18.00	26.29
3p→5s	18.43	25.79
3s→4p	7.17	47.40
3s→5p	11.30	38.90
4f→4d	2.87	65.30
4f→5d	7.65	46.08
4d→4p	0.80	114.00
4d→5f	3.73	59.50
4d→5p	4.93	53.80
4p→4s	1.78	80.20
4p→5d	3.98	57.30
4p→5s	4.41	56.30
4s→5p	2.35	73.00
5f→5p	0.15	160.00
5p→5s	0.28	145.00

S3. THERMAL DISTRIBUTION OF STATES

As our 2D excitons are bosons they obey a Bose-Einstein distribution among the states of the excitonic series at finite temperature. This results in a finite population of excited states at elevated temperatures. The exciton ground state is ~ 200 meV [3, 4] below the continuum, so that a number of states can be occupied at room temperature. According to Bose-Einstein distribution

$$B(E_j - \mu_{cp}) = \frac{1}{e^{E_j - \mu_{cp}/k_B T} - 1}, \quad (\text{S30})$$

with μ_{cp} the chemical potential of state j . We define $B_{jj'} = B(E_j - \mu_{cp}) - B(E_{j'} - \mu_{cp})$ and the occupation difference between initial and final state of the THz transition. According to Ref. [9] the polarizability is proportional to this population difference, so that we obtain from Equation 1 in the main text

$$\alpha_{j'j}(\omega) = \frac{1}{N_X} \frac{(B_{j'} - B_j)}{\hbar} |\langle j' | \hat{M} \cdot \vec{e} | j \rangle|^2 \cdot \frac{1}{\omega - \omega_{j'j} + i\gamma_{j'j}}, \quad (\text{S31})$$

where $N_X = \int_0^\infty D(E)B(E - \mu_{cp})\delta(E - E_j)dE$ is the number of excitons in the nanoplatelet, considered as 1 in our calculations. This equation reflects the well known fact, that a

system becomes transparent as it approaches equal occupation of initial and final state, i.e. $b_{jj'} = 0$. Occupation number B and probability b relate by $B_j/N_X = b_j$. As the Bose distribution changes with increasing temperature, the polarizability becomes temperature dependent, and hence the polarizability is altered due to varying population differences between the states, which have non zero matrix element.

S4. APPROACHING EXPERIMENTAL THZ DATA

As discussed in the main text, Equation (2) can not only be seen as an instruction, how to extract mobility from modeled polarizability, but also as a tool to recover information about polarizability from the experimentally accessible conductivity and mobility data, respectively. The flow chart in Figure S1 is a proposed guiding thread on how to treat experimental data, which can be fit in a final step using the state energies and transition matrix elements, obtained from modeling of the nanosystem in a first step. The thermal population of states has to be taken into account for any experiments at room temperature. Using the above-mentioned system parameters and constants the polarizability of each transition can be summed up to a spectrally-dependent trial function, which still depends on the dephasing $\gamma_{j'j}$, a parameter which may be treated with an initial guess (e.g. from calculation on the exciton-phonon interaction or from other methods like four wave mixing). Then the fit routine optimizes the trial function spectrum in a least square routine to fit the experimental data and obtain the polarizabilities.

However, it has to be mentioned, that optical excitation of colloidal semiconductor nanoparticle samples in a time-resolved THz-probe experiment will typically lead not only to excitons, but also to quasi-free electrons and holes. Unless designed otherwise, one has to separate the specific contributions of each particle by e.g. comparing different pump-probe delay times, certain sample dimensions, temperature or by a priori entering information about the electronic system of photoexcited electrons and holes before using the suggested steps above for retrieving α_X from μ_X .

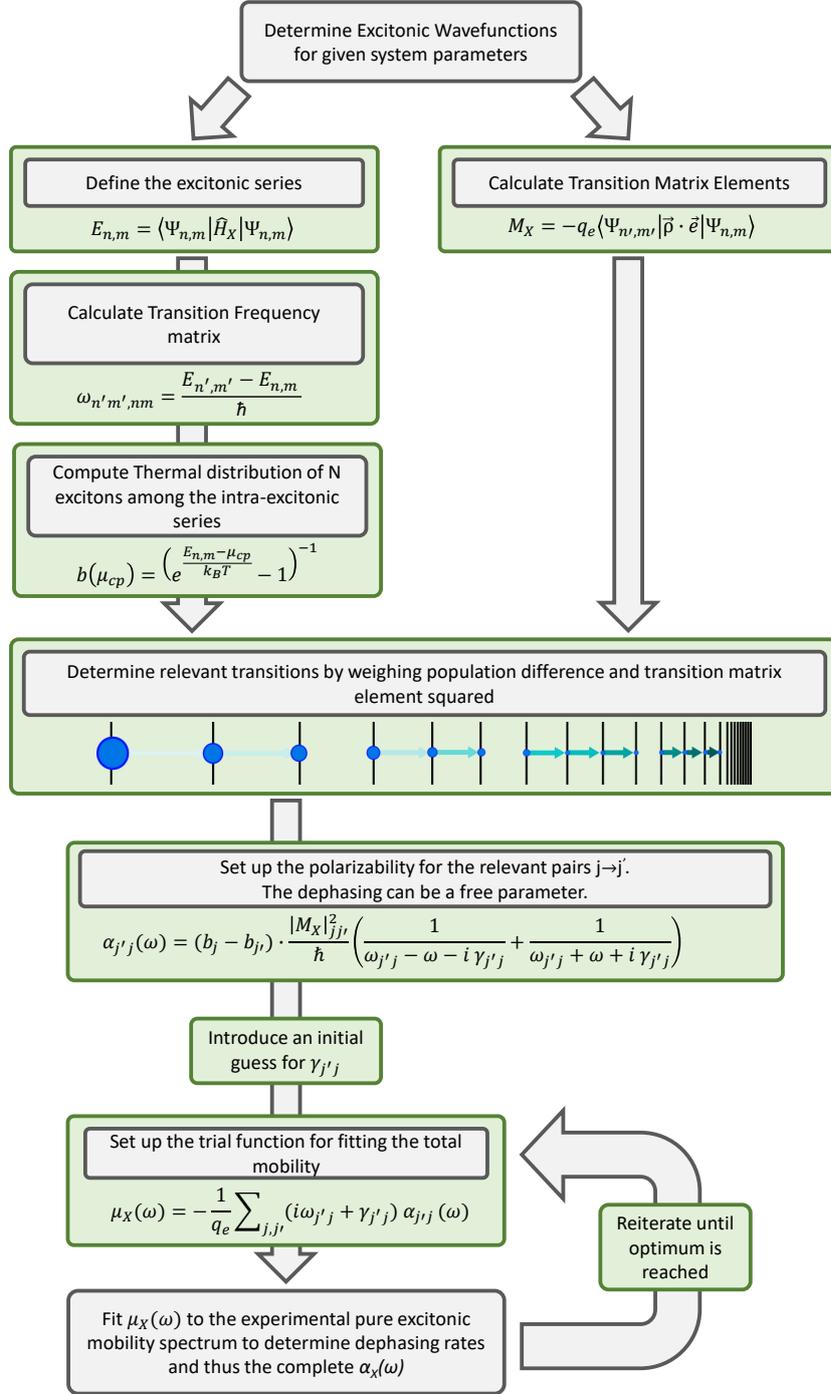


FIG. S1. Flow Chart proposing, how to extract the excitonic polarizability from a given experimental mobility spectrum.

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