Electronic Supplementary Information

Refractive index change dominates transient absorption response of metal halide perovskite thin films in near infrared

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Contents

1 Substrate refractive index

Sellmeier dispersion formula was used to model refractive index spectrum of glass substrate:

$$n^2(\lambda) - 1 = \frac{B_1\lambda^2}{\lambda^2 - C_1} + \frac{B_2\lambda^2}{\lambda^2 - C_2} + \frac{B_3\lambda^2}{\lambda^2 - C_3} \quad (1)$$

with coefficients adopted provided fro Scott BK7 glass: $B_1 = 1.03961212$, $B_2 = 0.231792344$, $B_3 = 1.01046945$, $C_1 = 0.00600069867\ \mu^2$, $C_2 = 0.0200179144\ \mu^2$ and $C_3 = 103.560653\ \mu^2$.

2 Transmittance and reflectance of thin flat sample

We will use analytical theory developed by Barybin and Shapovalov,[1] and will apply it to the sample structure presented in Figure 1. Essential assumptions for for our case is that medium 1 (perovskite layer) is a thin homogeneous layer with thickness d_1 (d_1 is in order of magnitude of the wavelength), and medium 2 is a thick transparent substrate (thick means much larger than the wavelength). We will assume that only medium 1 is photo-active, meaning that upon excitation its complex refractive index may change in time $\tilde{n}_1(t) = n_1(t) + ik_1(t)$, or $n_1 = n_1(t)$ and $k_1 = k_1(t)$. The aim is to find relations between the measurable values, such as reflectance and transmittance coefficients, and parameters of interest, $n_1(t)$ and $k_1(t)$. First we will derive equations for the static transmittance $T = T(n_1, k_1)$ and reflectance $R = R(n_1, k_1)$ dependences, and then will analyse how a small change of n_1 and k_1 affects T and R.

2.1 Static transmittance and reflectance

A general equations for reflectance, R, and transmittance, T, are (eqs. (60) and (61) in Ref. 1). The measurements are carried our in air, therefore $n_0 = 1$ and $n_3 = 1$, and

$$R = \frac{L_- + M\cos(2\beta_1 d_1 + \varphi_-)}{L_+ + M\cos(2\beta_1 d_1 + \varphi_+)} \tag{2}$$

$$\begin{aligned} T &= \frac{16 n_0 |\tilde{n}_1|^2 |\tilde{n}_2|^2 n_3}{L_+ + M\cos(2\beta_1 d_1 + \varphi_+)} \\ &= \frac{16(n_1^2 + k_1^2) n_2^2}{L_+ + M\cos(2\beta_1 d_1 + \varphi_+)} \end{aligned} \tag{3}$$

where $\beta_1 = \frac{2\pi}{\lambda} n_1$ and λ is the wavelength. Other parameters in the equations are modulation coefficient M (following are the eqautions from Ref. 1 adopted to our case)

$$\begin{aligned} M(n_1) &= (n_0^2 - n_1^2)(n_1^2 - n_2^2)(n_2^2 + n_3^2) \\ &= (1 - n_1^2)(n_1^2 - n_2^2)(n_2^2 + 1) \end{aligned} \tag{4}$$

the phase angle $\varphi_\pm$ is given by

$$\tan\varphi_\pm = \frac{m_\pm}{M}\frac{k_1}{n_1} \tag{5}$$

with

$$\begin{aligned} m_\pm(n_1, k_1) &= 2n_1[-2(n_0^2 - n_1^2) n_2^2 n_3 \pm n_0 (n_1^2 - n_2^2)(n_2^2 + n_3^2)] \\ &= 2n_1[-2(1 - n_1^2) n_2^2 \pm (n_1^2 - n_2^2)(n_2^2 + 1)] \end{aligned} \tag{6}$$

In the near infra red (NIR) part of the spectrum one can use approximation of a slightly absorbing medium ($n_1^2 \gg k_1^2$), then eq. (5) can be simplified

$$\varphi_\pm(n_1, k_1) \simeq \frac{m_\pm(n_1)}{M(n_1)}\frac{k_1}{n_1} \tag{7}$$

$L_{\pm}$ are the losses parameters introduced as

$$\begin{aligned} L_{\pm}(n_1, k_1) &= a_{\pm} \cosh(2\alpha_1 d_1) + b_{\pm} \sinh(2\alpha_1 d_1) \\ &= a_{\pm}(n_1) \cosh\left(\frac{4\pi d_1}{\lambda} k_1\right) + b_{\pm}(n_1) \sinh\left(\frac{4\pi d_1}{\lambda} k_1\right) \end{aligned} \tag{8}$$

where d_1 is the thickness of photo-active layer, and

$$\begin{aligned} a_{\pm}(n_1) &= (n_0^2 + n_1^2)(n_1^2 + n_2^2)(n_2^2 + n_3^2) \pm 8 n_0 n_1^2 n_2^2 n_3 \\ &= (1 + n_1^2)(n_1^2 + n_2^2)(n_2^2 + 1) \pm 8 n_1^2 n_2^2 \end{aligned} \tag{9}$$

$$\begin{aligned} b_{\pm}(n_1) &= 2n_1[2(n_0^2 + n_1^2)n_2^2 n_3 \pm n_0(n_1^2 + n_2^2)(n_2^2 + n_3^2)] \\ &= 2n_1[2(1 + n_1^2)n_2^2 \pm (n_1^2 + n_2^2)(n_2^2 + 1)] \end{aligned} \tag{10}$$

For optically transparent medium, e.g. in the NIR, one can notice that ϕ is a small value, $\phi = \frac{4\pi d_1}{\lambda} k_1 \to 0$, and can use approximation $\cosh(\phi) \simeq 1$ and $\sinh(\phi) \simeq \phi$, which gives

$$L_{\pm}(n_1, k_1) \simeq a_{\pm}(n_1) + b_{\pm}(n_1) \frac{4\pi d_1}{\lambda} k_1 \tag{11}$$

However, in practice this means $k_1 < 0.01 \frac{\lambda}{d_1}$ and since for our sample $\frac{\lambda}{d_1} \approx 1$, we come to the relation $k_1 < 0.01$. This is satisfied at $\lambda > 800$ nm reasonably well but not at shorter wavelengths, in which case eq. (8) must be used. At this point we have two criteria for "slightly absorbing" or "optically transparent" medium, one comes from comparison of $n_1^2 \gg k_1^2$ and another from a small phase shift $\phi \approx 0$. The former is less restrictive since in the visible part of the spectrum $n_1 > 2$ and $k_1 \approx 0.2$ at 700 nm which means that $n_1^2 > 100\ k_1^2$ and this approximation should be reasonably accurate even in the visible part of the spectrum.

All the above equations were taken from Ref. 1 with the assumption of $n_0 = 0$ and $n_3 = 0$, or the measurements carried out in air. The wavelength dependence is hidden under parameters $\beta_1 = \frac{2\pi}{\lambda} n_1(\lambda)$ and $\tilde{n}_1 = n_1(\lambda) + i k_1(\lambda) = n_1(\lambda) + i \frac{1}{2\pi} \lambda \alpha_1(\lambda)$, or there are three wavelength dependent parameters $n_1(\lambda)$, $k_1(\lambda)$ and $n_2(\lambda)$. These equations were used to calculate transmission and reflection coefficients and absorbance spectra of the sample from known spectra of $n_1(\lambda)$, $k_1(\lambda)$ and $n_2(\lambda)$ by adjusting the perovskite layer thickness, d_1 as presented in Figure 2.

2.2 Transient reflectance and transmittance

Next we will use these are equations to analyse the effect of changing absorption or refractive index of the perovskite layer (medium 1) or both on reflectance, R, and transmittance, T. The functional dependence on n_1 and k_1 is

$$R(n_1, k_1) = \frac{L_-(n_1, k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda} n_1 + \frac{m_-(n_1)}{M(n_1)}\frac{k_1}{n_1}\right)}{L_+(n_1, k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda} n_1 + \frac{m_+(n_1)}{M(n_1)}\frac{k_1}{n_1}\right)} \tag{12}$$

$$T(n_1, k_1) = \frac{16(n_1^2 + k_1^2)n_2^2}{L_+(n_1, k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda} n_1 + \frac{m_+(n_1)}{M(n_1)}\frac{k_1}{n_1}\right)} \tag{13}$$

Expressions for R and T have the same denominator, therefore it is reasonable to introduce

$$\begin{aligned} A &= L_+(n_1, k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda} n_1 + \frac{m_+(n_1)}{M(n_1)}\frac{k_1}{n_1}\right) \\ &= L_+(n_1, k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda} n_1 + \varphi_+\right) \end{aligned} \tag{14}$$

and

$$\begin{aligned} B &= L_-(n_1, k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda} n_1 + \frac{m_-(n_1)}{M(n_1)}\frac{k_1}{n_1}\right) \\ &= L_-(n_1, k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda} n_1 + \varphi_-\right) \end{aligned} \tag{15}$$

which gives simple forms for R and T:

$$R = \frac{B}{A} \tag{16}$$

$$T = \frac{16(n_1^2 + k_1^2)n_2^2}{A} \tag{17}$$

Experiments are carried out with low excitation density, therefore we can limit our consideration by small changes of the refractive index real psrt $n_1(t) = n_1 + \triangle n_1(t)$ and imaginary part $k_1(t) = k_1 + \triangle k_1(t)$ (not that absorption coefficient is $\alpha = 2\pi k_1/\lambda$). Thus we can expect only a small change of the reflectance and transmittance, and within the linear approximation this gives

$$R(t) \simeq R + \frac{dR}{dn_1}\triangle n_1(t) + \frac{dR}{dk_1}\triangle k_1(t) = R + R'_n\triangle n_1(t) + R'_k\triangle k_1(t) = R + \triangle R \tag{18}$$

$$T(t) \simeq T + \frac{dT}{dn_1}\triangle n_1(t) + \frac{dT}{dk_1}\triangle k_1(t) = T + T'_n\triangle n_1(t) + T'_k\triangle k_1(t) = T + \triangle T \tag{19}$$

where R'_n, R'_k, T'_n and T'_k are derivatives of R and T over n_1 and k_1, respectively. Therefore, next we need to calculate the derivatives. Starting with eqs. (16) and (17)

$$R'_n = \frac{dR}{dn_1} = \frac{d\frac{B}{A}}{dn_1} = \frac{B'_n A - BA'_n}{A^2} \tag{20}$$

$$T'_n = \frac{d}{dn_1}\left[\frac{16(n_1^2 + k_1^2)n_2^2}{A}\right] = 16n_2^2\frac{2n_1A - (n_1^2 + k_1^2)A'_n}{A^2} \tag{21}$$

where

$$A'_n = \frac{dA}{dn_1} = \frac{d}{dn_1}\left[L_+(n_1,k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_+\right)\right] \tag{22}$$
$$= L'_{+n} + M'_n \cos\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_+\right) - M\sin\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_+\right)\left(\frac{2\pi d_1}{\lambda} + \varphi'_{+n}\right)$$

$$B'_n = \frac{dB}{dn_1} = \frac{d}{dn_1}\left[L_-(n_1,k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_-\right)\right] \tag{23}$$
$$= L'_{-n} + M'_n \cos\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_-\right) - M\sin\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_-\right)\left(\frac{2\pi d_1}{\lambda} + \varphi'_{-n}\right)$$

and

$$R'_k = \frac{dR}{dk_1} = \frac{d\frac{B}{A}}{dn_1} = \frac{B'_k A - BA'_k}{A^2} \tag{24}$$

$$T'_k = \frac{d}{dk_1}\left[\frac{16(n_1^2+k_1^2)n_2^2}{A}\right] = 16n_2^2 \frac{2k_1 A - (n_1^2+k_1^2)A'_k}{A^2} \tag{25}$$

where

$$A'_k = \frac{dA}{dk_1} = \frac{d}{dk_1}\left[L_+(n_1,k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_+\right)\right] \tag{26}$$
$$= L'_{+k} - M\sin\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_+\right)\varphi'_{+k}$$

$$B'_k = \frac{dB}{dk_1} = \frac{d}{dk_1}\left[L_-(n_1,k_1) + M(n_1)\cos\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_-\right)\right] \tag{27}$$
$$= L'_{-k} - M\sin\left(\frac{4\pi d_1}{\lambda}n_1 + \varphi_-\right)\varphi'_{-k}$$

and $L'_{\pm n}$, $L'_{\pm k}$, M'_n, M'_k, $\varphi'_{\pm n}$ and $\varphi'_{\pm k}$ are corresponding derivatives.

$$
\begin{aligned}
M'_n = \frac{dM}{dn_1} &= \frac{d[(1-n_1^2)(n_1^2-n_2^2)(n_2^2+1)]}{dn_1} \\
&= -2n_1(n_1^2-n_2^2)(n_2^2+1) + 2n_1(1-n_1^2)(n_2^2+1) \\
&= 2n_1(n_2^2+1)(n_2^2+1-2n_1^2)
\end{aligned} \tag{28}
$$

$$
\begin{aligned}
m'_{\pm n} = \frac{dm_\pm}{dn_1} &= 2\frac{d}{dn_1}n_1[-2(1-n_1^2)n_2^2 \pm (n_1^2-n_2^2)(n_2^2+1)] \\
&= 2\{-2(1-n_1^2)n_2^2 \pm (n_1^2-n_2^2)(n_2^2+1) + n_1[4n_1n_2^2 \pm 2n_1(n_2^2+1)]\} \\
&= 2[2n_1^2n_2^2 - 2n_2^2 + 4n_1^2n_2^2 \pm (n_1^2n_2^2 + n_1^2 - n_2^4 - n_2^2 + 2n_1^2n_2^2 + 2n_1^2)] \\
&= 2[6n_1^2n_2^2 - 2n_2^2 \pm (3n_1^2 + 3n_1^2n_2^2 - n_2^4 - n_2^2)]
\end{aligned} \tag{29}
$$

or

$$
m'_{+n} = 2(6n_1^2n_2^2 - 2n_2^2 + 3n_1^2 + 3n_1^2n_2^2 - n_2^4 - n_2^2) = 2(9n_1^2n_2^2 + 3n_1^2 - 3n_2^2 - n_2^4) \tag{30}
$$

$$
m'_{-n} = 2(6n_1^2n_2^2 - 2n_2^2 - 3n_1^2 - 3n_1^2n_2^2 + n_2^4 + n_2^2) = 2(3n_1^2n_2^2 - 3n_1^2 - n_2^2 + n_2^4) \tag{31}
$$

$$
\begin{aligned}
a'_{\pm n} = \frac{da_\pm}{dn_1} &= \frac{d}{dn_1}[(1+n_1^2)(n_1^2+n_2^2)(n_2^2+1) \pm 8n_1^2n_2^2] \\
&= 2n_1(n_1^2+n_2^2)(n_2^2+1) + 2n_1(1+n_1^2)(n_2^2+1) \pm 16n_1n_2^2 \\
&= 2n_1(n_2^2+1)(2n_1^2+n_2^2+1) \pm 16n_1n_2^2
\end{aligned} \tag{32}
$$

or

$$
a'_{+n} = \frac{da_+}{dn_1} = 2n_1[(n_2^2+1)(2n_1^2+n_2^2+1) + 8n_2^2] \tag{33}
$$

$$
a'_{-n} = \frac{da_-}{dn_1} = 2n_1[(n_2^2+1)(2n_1^2+n_2^2+1) - 8n_2^2] \tag{34}
$$

$$b'_{\pm n} = \frac{db_\pm}{dn_1} = \frac{d}{dn_1} 2n_1[2(1+n_1^2)n_2^2 \pm (n_1^2+n_2^2)(n_2^2+1)]$$

$$\begin{aligned} &= 4(1+n_1^2)n_2^2 \pm 2(n_1^2+n_2^2)(n_2^2+1) + 2n_1[4n_1n_2^2 \pm 2n_1(n_2^2+1)] \\ &= 4n_2^2(1+3n_1^2) \pm 2(n_2^2+1)(3n_1^2+n_2^2) \\ &= 2[2n_2^2 + 6n_1^2n_2^2 \pm (3n_1^2n_2^2 + n_2^4 + 3n_1^2 + n_2^2)] \end{aligned} \tag{35}$$

or

$$b'_{+n} = \frac{db_+}{dn_1} = 2(3n_2^2 + 9n_1^2n_2^2 + n_2^4 + 3n_1^2) \tag{36}$$

$$b'_{-n} = \frac{db_-}{dn_1} = 2(n_2^2 + 3n_1^2n_2^2 - n_2^4 - 3n_1^2) \tag{37}$$

Parameter $L_\pm$ depends on both n_1 and k_1, and in small absorption approximation of eq. (11)

$$\begin{aligned} L'_{\pm n} = \frac{dL_\pm(n_1,k_1)}{dn_1} &\simeq \frac{da_\pm(n_1)}{dn_1} + \frac{4\pi d_1 k_1}{\lambda}\frac{db_\pm(n_1)}{dn_1} \\ &= a'_{\pm n} + \frac{4\pi d_1 k_1}{\lambda} b'_{\pm n} \end{aligned} \tag{38}$$

$$L'_{\pm k} = \frac{L_\pm(n_1,k_1)}{dk_1} \simeq a_\pm(n_1) + b_\pm(n_1)\frac{4\pi d_1}{\lambda} \tag{39}$$

Otherwise (eq. (8))

$$L'_{\pm n} = \frac{dL_\pm(n_1,k_1)}{dn_1} = a'_{\pm n}\cosh\left(\frac{4\pi d_1}{\lambda}k_1\right) + b'_{\pm n}\sinh\left(\frac{4\pi d_1}{\lambda}k_1\right) \tag{40}$$

and

$$L'_{\pm k} = \frac{L_\pm(n_1,k_1)}{dk_1} = \frac{4\pi d_1}{\lambda}\left[a_\pm(n_1)\sinh\left(\frac{4\pi d_1}{\lambda}k_1\right) + b_\pm(n_1)\cosh\left(\frac{4\pi d_1}{\lambda}k_1\right)\right] \tag{41}$$

Another parameter which depends on both n_1 and k_1 is $\varphi_\pm$:

$$\varphi'_{\pm k} = \frac{d\varphi_\pm(n_1,k_1)}{dk_1} \simeq \frac{m_\pm(n_1)}{M(n_1)n_1} \tag{42}$$

$$\begin{aligned}\varphi'_{\pm n} = \frac{d\varphi_\pm}{dn_1} &\simeq k_1 \frac{Mn_1\frac{dm_\pm}{dn_1} - m_\pm\left[n_1\frac{dM}{dn_1} + M\right]}{M^2n_1^2} \\ &= \frac{k_1}{M^2n_1^2}\left[Mn_1m'_\pm - m_\pm n_1 M' - m_\pm M\right] \\ &= \frac{k_1}{M(n_1)n_1}\left[m'_{\pm n}(n_1) - \frac{m_\pm(n_1)}{M(n_1)}M'_n(n_1) - \frac{m_\pm(n_1)}{n_1}\right]\end{aligned} \tag{43}$$

Though one can notice that in the small absorption limit $\frac{d\varphi_\pm(n_1,k_1)}{dn_1} \simeq 0$. However this approximation has to be used with caution as was discussed above.

2.3 The measured values

Our pump-probe instrument saves data assuming measurements in transmission mode and recalculating the result to the change of optical density. If the optical density changes by $\triangle OD$ then the monitoring light intensity is

$$I = I_{in}10^{-(OD+\triangle OD)} = I_{in}10^{-OD}10^{-\triangle OD} = I_0 10^{-\triangle OD} \tag{44}$$

where I_0 is he monitoring light intensity after non-excited sample. Thus the program saves

$$\triangle OD = -\log\left(\frac{I}{I_0}\right) = -\log\left(1 + \frac{\triangle I}{I_0}\right) \tag{45}$$

In transmittance mode monitoring intensity changes as $I = I_{in}(T + \triangle T) = I_0 + I_{in}\triangle T = I_0(1 + \frac{\triangle T}{T})$. Therefore, relation between $\triangle OD$ and $\triangle T$ is

$$\triangle OD(\triangle T) = -\log\left(1 + \frac{\triangle T}{T}\right) \tag{46}$$

Similarly, in reflection mode

$$\triangle OD(\triangle R) = -\log\left(1 + \frac{\triangle R}{R}\right) \tag{47}$$

In both cases a relative change of either transmittance or reflectance can be restored from the measured data, for reflectance one obtains

$$\frac{\triangle R(t,\lambda)}{R(\lambda)} + 1 = \frac{R + \triangle R}{R} = 10^{-\triangle OD(t,\lambda)} \tag{48}$$

Denominator can be modeled by eq. (18), thus

$$\triangle R = R\left(10^{-\triangle OD_R} - 1\right) = R'_n \triangle n_1 + R'_k \triangle k_1 \tag{49}$$

and similarly for transmittance mode

$$\triangle T = T\left(10^{-\triangle OD_T} - 1\right) = T'_n \triangle n_1 + T'_k \triangle k_1 \tag{50}$$

where $\triangle OD_R$ and $\triangle OD_T$ are saved measurements in reflectance and transmittance modes, respectively.

Eqs. (49) and (50) present a simple system of two linear equations which can be solved. Determinant of the system is $R'_n T'_k - T'_n R'_k$, and solutions are

$$\triangle n_1 = \frac{\triangle R T'_k - \triangle T R'_k}{R'_n T'_k - T'_n R'_k} \tag{51}$$

$$\triangle k_1 = \frac{\triangle T R'_n - \triangle R T'_n}{R'_n T'_k - T'_n R'_k} \tag{52}$$

Here $\triangle R = R(10^{-\triangle OD_R} - 1)$ and $\triangle T = T(10^{-\triangle OD_T} - 1)$ are composed of "purely" experimental data, $\triangle OD_R$ and $\triangle OD_T$ spectra, and "model" spectra, R and T, though R and T can be measured, and at least T can be measured with reasonably high accuracy. However, derivatives R'_n, R'_k, T'_n and T'_k are "purely" model values, but can be calculated using equations derived above.

In conclusion, at each wavelength we have to measured values, $\triangle OD_R$ and $\triangle OD_T$, and we calculate two values of our interest, $\triangle n_1$ and $\triangle k_1$, using eqs. (51) and (52), for which we first calculate derivatives R'_n, R'_k, T'_n and T'_k, which, in turn, depends on "static" values n_1 and k_1, and d_1. In this study we used previously reported values of n_1 and k_1 (these are experimentally available values), and we did some fine tuning of d_1 as explained in the main text. But calculations were done at each wavelength independently by solving system of two linear equations, meaning that these are exact solutions.

3 Pump-probe measurements

3.1 Measurements, data presentation and dispersion correction

The raw transient absorption data after group velocity dispersion compensation are presented in Figures S1.

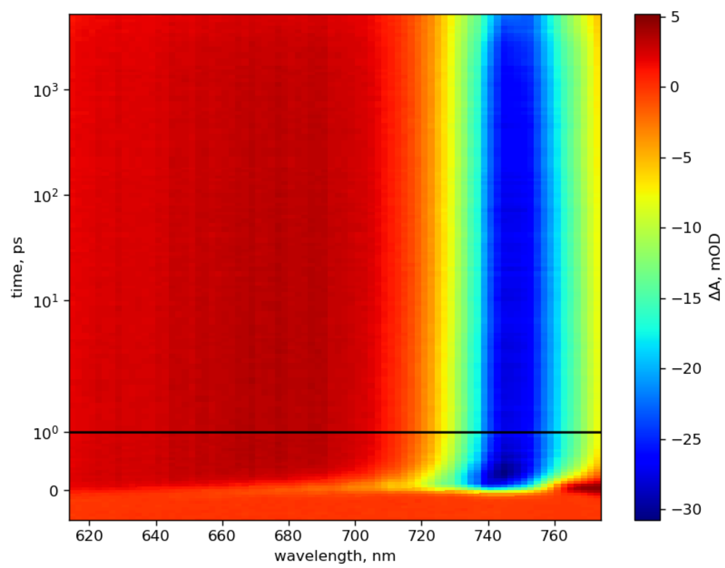

Figure S1: Color map presentation of the transient absorption responses of the sample measured in transmittance mode in the red part of the spectrum. Excitation wavelength was 600 nm. The time scale is linear till 1 ps and logarithmic after that.

3.2 Excitation density dependence

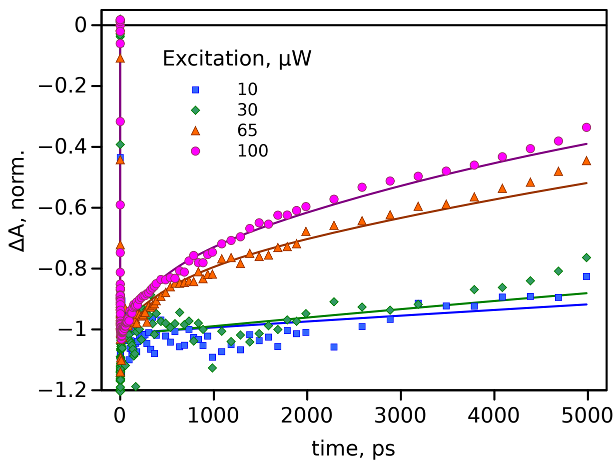

Figure S2: Color map presentation of the transient absorption responses of the sample measured in transmittance mode in the red part of the spectrum. Excitation wavelength was 600 nm. The time scale is linear till 1 ps and logarithmic after that.

There excitation density dependence was studied by using gray filters to attenuate excitation energy and repeating pump-probe measurements in the band gap region. The average excitation power was measured to control the excitation power density. The normalized transient absorption decays at 750 nm are shown in Figure S2. The excitation energy range for this data is 10–100 μW. There is no change in the lifetime up to 30 μW excitation intensity. The excitation repetition rate was 1 kHz and the excitation spot size was roughly 1 mm^2. Thus excitation energy density corresponding to 30 μW power is 3 μJ cm^{-2}.

4 Fresnel equations and transfer matrix method

Wavevectors before and after air-perovskite interface:

$$k_1^2 = \frac{\omega^2}{c^2} n_1^2 \tag{53}$$

$$k_2^2 = \frac{\omega^2}{c^2} n_2^2 \tag{54}$$

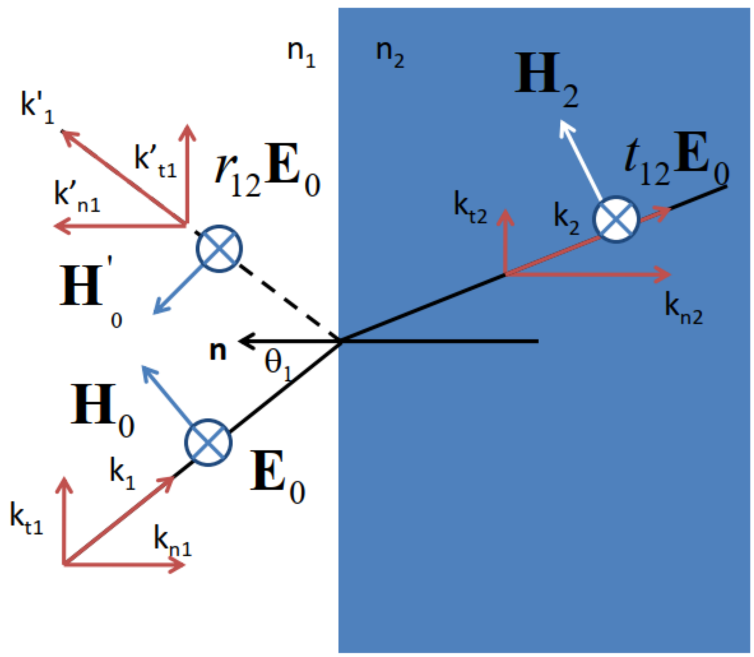

Figure S3: Wavevectors before and after interface

where ω is angular frequency, c is speed of light in vacuum and n is refractive index. Relation of wavevector to refractive index and extinction coefficient κ is

$$k = \frac{2\pi(n + i\kappa)}{\lambda_0} \tag{55}$$

where λ_0 is wavelength in vacuum.

Wavevectors normal to interface (tangential components k_{t1} and k_{t2} are equal):

$$k_{n1}^2 = k_1^2 \cos^2(\theta_1) \tag{56}$$

$$k_{n2}^2 = k_2^2 - k_1^2 \sin^2(\theta_1) \tag{57}$$

where θ_1 is the angle of incidence.

Reflection and transmission coefficients[2] for TE polarization are

$$r_{12} = \frac{k_{n1} - k_{n2}}{k_{n1} + k_{n2}} \tag{58}$$

$$t_{12} = \frac{2k_{n1}}{k_{n1} + k_{n2}} \tag{59}$$

and for TM polarization

$$r_{12} = \frac{n_1^2 k_{n2} - n_2^2 k_{n1}}{n_1^2 k_{n2} + n_2^2 k_{n1}} \tag{60}$$

$$t_{12} = \frac{2n_1 n_2 k_{n1}}{n_1^2 k_{n2} + n_2^2 k_{n1}} \tag{61}$$

With small angle of incidence the difference between TE and TM polarization is also small.

Transfer matrix of 1) air-perovskite interface, 2) propagation in perovskite, 3) perovskite-glass interface is

$$M = \frac{1}{t_{12}} \begin{bmatrix} 1 & r_{12} \\ r_{12} & 1 \end{bmatrix} \begin{bmatrix} e^{jk_n L} & 0 \\ 0 & e^{-jk_n L} \end{bmatrix} \frac{1}{t_{23}} \begin{bmatrix} 1 & r_{23} \\ r_{23} & 1 \end{bmatrix} \tag{62}$$

$$M = \frac{1}{t_{12}t_{23}} \begin{bmatrix} e^{jk_n L} + r_{12}r_{23}e^{-jk_n L} & r_{12}e^{-jk_n L} + r_{23}e^{jk_n L} \\ r_{12}e^{jk_n L} + r_{23}e^{-jk_n L} & e^{-jk_n L} + r_{12}r_{23}e^{jk_n L} \end{bmatrix} \tag{63}$$

where L is the thickness of the perovskite layer and r_{23} and t_{23} are coefficients of perovskite-glass interface.

Reflectance and transmittance coefficients of the whole system are

$$r = \frac{M_{21}}{M_{11}} \tag{64}$$

$$t = \frac{1}{M_{11}} \tag{65}$$

and the reflectance and transmittance of the perovskite film on infinite glass substrate are

$$R_p = |r|^2 \tag{66}$$

$$R_p = \left| \frac{r_{12} e^{jk_n L} + r_{23} e^{-jk_n L}}{e^{jk_n L} + r_{12} r_{23} e^{-jk_n L}} \right|^2 \tag{67}$$

$$T_p = \frac{n_2 \sqrt{1 - n_2/n_1 \sin\theta_1}}{n_1 \cos\theta_1} |t|^2 \tag{68}$$

$$T_p = \frac{n_2 \sqrt{1 - n_2/n_1 \sin\theta_1}}{n_1 \cos\theta_1} \left| \frac{t_{12} t_{23}}{e^{jk_n L} + r_{12} r_{23} e^{-jk_n L}} \right|^2 \tag{69}$$

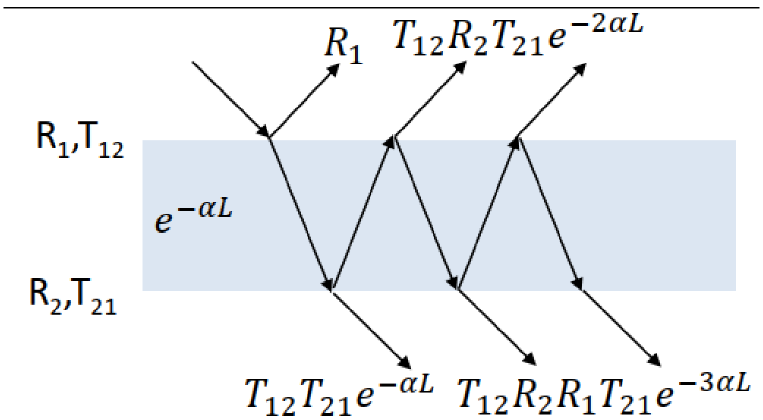

Figure S4: Reflection from substrate

With finite substrate taken into account the reflectance and transmittance are

$$R = R_p + R_g \frac{(1 - R_p)(1 - R_g) e^{-2\alpha L}}{1 - R_p R_g e^{-2\alpha L}} \tag{70}$$

$$T = \frac{(1 - R_p)(1 - R_g) e^{-\alpha L}}{1 - R_p R_g e^{-2\alpha L}} \tag{71}$$

where R_p is previously calculated reflectance from perovskite film and R_g is reflection of glass-air interface:

$$R_g = |r_{34}|^2 \tag{72}$$

and α is absorbance coefficient of perovskite (glass is assumed to have no absorbance).

The changes of reflectance and transmittance by excitation are in percentages

$$\Delta R = \frac{R_2 - R_1}{R_1} \cdot 100\% \tag{73}$$

$$\Delta T = \frac{T_2 - T_1}{T_1} \cdot 100\% \tag{74}$$

where R_1, T_1 are reflectance and transmittance before excitation and R_2, T_2 after excitation. Conversion to mOD units:

$$\Delta R[mOD] = -log10(\frac{\Delta R}{100} + 1) \cdot 1000 \tag{75}$$

$$\Delta T[mOD] = -log10(\frac{\Delta T}{100} + 1) \cdot 1000 \tag{76}$$

References

(1) Barybin, A.; Shapovalov, V. Substrate Effect on the Optical Reflectance and Transmittance of Thin-Film Structures. *Intern. J. Optics* **2010**, 137572.

(2) Yariv, A.; Yeh, P. *Photonics: Optical Electronics in Modern Communications*, 6th ed.; Oxford University Press, 2007.

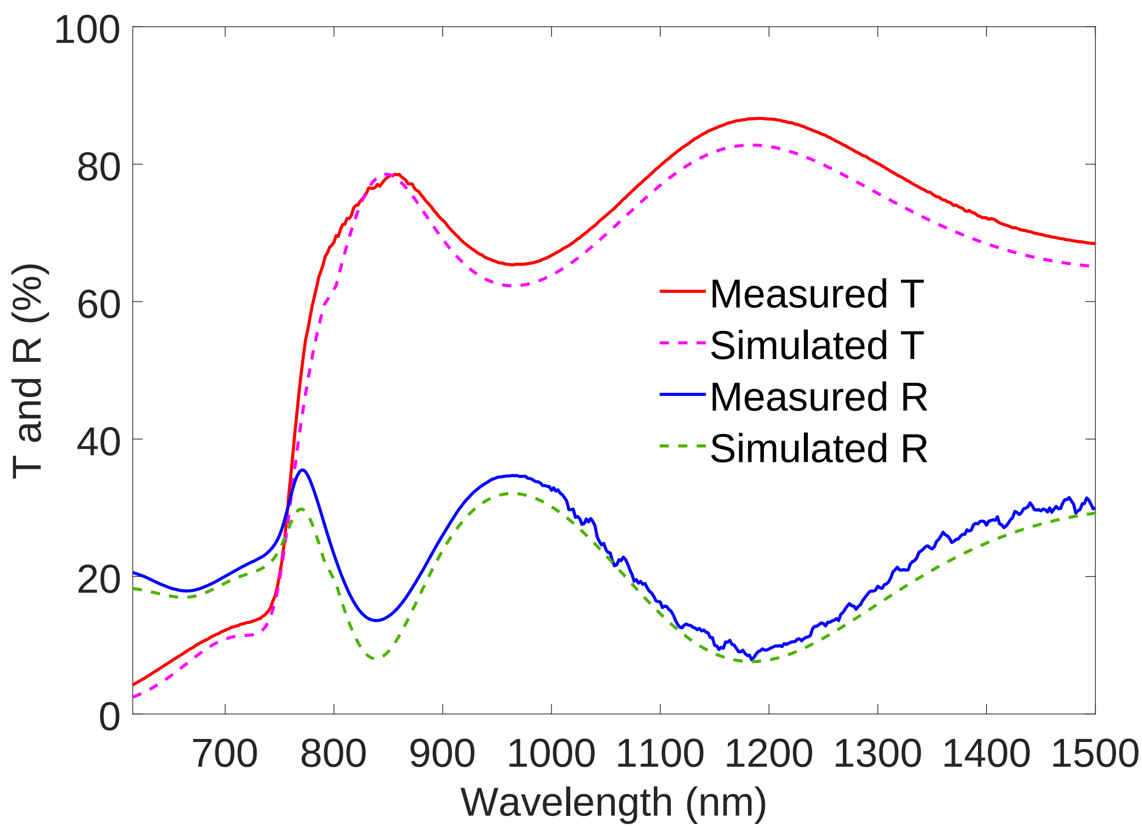

Figure S5: Simulated steady-state transmittance and reflectance from perovskite thin film on glass. Perovskite thickness was 522nm, angle of incidence 8° and polarization TM for the simulations