Determining the Recombination Rates of Solar Cell Materials

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Introduction

In the field of solar energy, solar panels are constructed from semiconductors due to the structure of their energy bands (Fig. 1). Energy bands are clusters of energy levels that electrons in the material are allowed to occupy. Under standard conditions, electrons fill up the valence band, but when light hits the material, the photons can be absorbed, exciting the electrons from the valence band up into a higher energy band, the conduction band. The energy of these free electrons can be collected when the material is incorporated into a solar panel. The charge carrier lifetime, a measure of how long on average electrons remain excited before recombining to the valence band, helps determine whether a semiconductor can make an efficient solar cell. In order to calculate the lifetime precisely, the rate that electrons recombine at must be known. The goal of this project was to construct a program that takes time-resolved terahertz spectroscopy (TRTS) data and finds the recombination rate constants of the inspected semiconductor. In testing our program, we used data we collected in the spring on perovskites, a promising group of organic-inorganic materials that has emerged fairly recently as a potential contender in the field of solar cell technology.

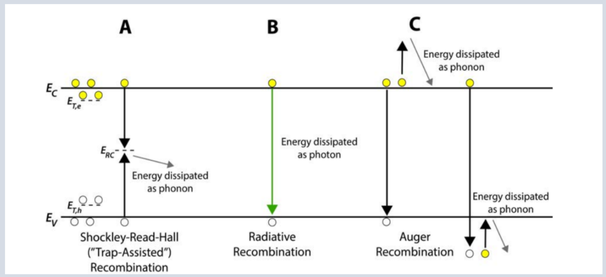

Fig. 1: Visual representation of the band structure of a semiconductor and the three types of recombination. Figure adapted from Ref [1].

Recombination Rates

The rate at which electrons recombine is governed by the recombination equation:[2]

Eq. 1: $$\frac{dn}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n$$

Each of the three terms on the right hand side are associated with one of the ways that an electron can recombine (Fig. 1). In the equation, n stands for the number density of charge carriers in the conduction band, in other words the number of excited electrons per unit of volume, t stands for time, while k_1, k_2, and k_3 are the recombination rate constants. Our lab's TRTS setup does not directly measure number density, it measures the transmission of terahertz (THz) waves through a sample with respect to the time after an excitation, and the density of charge carriers can be calculated by:[3]

Eq. 2: $$n(t) \approx \left(\frac{1+N}{Z_0 d e \mu}\right)\left(-\frac{\Delta T}{T_0}\right)$$

The first term is made up of known constants. The second term, $-\Delta T/T_0$, is how much THz transmission drops when travelling through an excited sample ($-\Delta T$) normalized by the peak value of THz transmission through an unexcited sample (T_0). Eq. 2 can be rewritten in a simpler form:

$$\alpha = \left(\frac{1+N}{Z_0 d e \mu}\right),\ x(t) = -\frac{\Delta T}{T_0}$$

$$n(t) = \alpha x(t)$$

The recombination equation can now be written solely in terms of $-\Delta T/T_0$:

Eq. 3: $$\frac{dx}{dt} = -k_3 \alpha^2 x^3 - k_2 \alpha x^2 - k_1 x$$

Now a parameter fit can be performed on our $-\Delta T/T_0$ data directly, though the constants being solved for are now k_1, αk_2, and $\alpha^2 k_3$, which from this point forward will be referred to generally as the altered constants.

Parameter Fitting

We created a program in MATLAB that models recombination dynamics and uses nonlinear least squares curve fitting to extract recombination rates from spectroscopy data. The curve used for fitting is the numerical solution to Eq. 3, the recombination equation in terms of $-\Delta T/T_0$. The three altered constants and the initial value of $-\Delta T/T_0$ are allowed to vary. It should be noted that in our experimental conditions, $k_1 n$ is much smaller than $k_2 n^2$ and $k_3 n^3$, so we cannot determine k_1 through our data fitting. A typical k_1 value for perovskites determined by a different experimental method is on the order of 10^7 s^{-1}.[2] We tested our program on TRTS measurements of a hybrid methylammonium formamidinium (MAFA) perovskite sample.

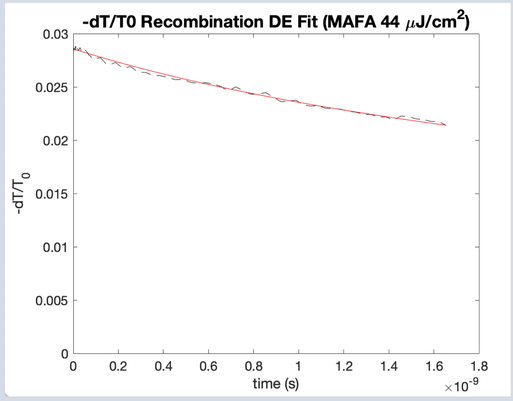

Fig. 2: Curve fitting performed using data obtained from an MAFA perovskite sample, with a pump fluence of 44 μJ/cm² and with pump wavelengths centered around 400 nm.

Group Number	k_1 (s^{-1})	k_2 (cm^3 s^{-1})	k_3 (cm^6 s^{-1})
1	3000	2×10^{-12}	1.2×10^{-30}
2	3000	7.6×10^{-18}	1.4×10^{-30}
3	150	1.5×10^{-11}	4.4×10^{-32}

Table 1: A sampling of k_1, k_2, and k_3 values found from the fitting for an MAFA perovskite sample.

For the analyses performed on this data set, the output values for the fit constants were highly sensitive to the values of the guesses inputted by the user (Table 1). Depending on the guess, the values of some parameters can vary up to six orders in magnitude, yet graphically the curves are so close together that it is impossible to distinguish which constants result in a better fit (Fig. 3), suggesting that there are a number of combinations of parameters that result in a decent fit. With the current data we have, it would be difficult to improve the accuracy of the fitting. However, we plotted out the numerical solutions to Eq. 3 with the constants from Table 1, and discovered that as we increased the initial $-\Delta T/T_0$ value, the curves started to separate.

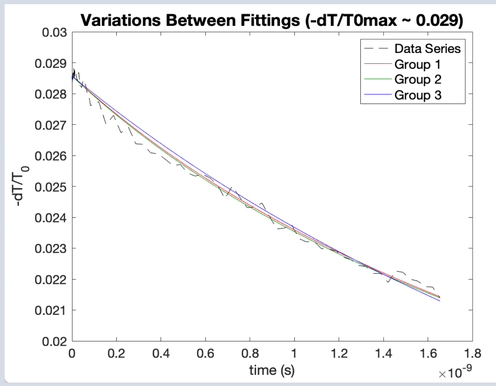

Fig 3: Numerical solutions for the recombination rate equation using the three MAFA parameter groups found in Table 1, with a maximum $-\Delta T/T_0$ value of about 0.029. Plotted above the TRTS data obtained from an MAFA perovskite sample with a pump fluence of 44 μJ/cm²

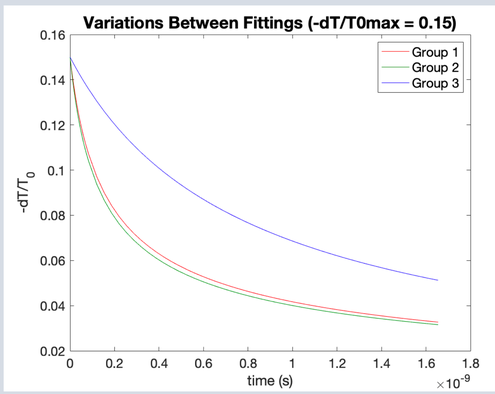

Fig 4: Numerical solutions for the recombination rate equation using the three MAFA parameter groups found in Table 1, with a maximum $-\Delta T/T_0$ value of 0.15. Simulates what these fittings would look like at higher pump fluences.

The three parameter groups all produce relatively similar solutions to the differential equation when the initial $-\Delta T/T_0$ value is around 0.029, as in Fig. 3, but the solutions start to vary noticeably from each other when the initial $-\Delta T/T_0$ value is set higher, as in Fig. 4. In our experimental setup, a higher maximum $-\Delta T/T_0$ value can be reached by increasing the laser's pump power, so these results suggest that collecting TRTS data with a larger pump power and including it in our analysis will improve the accuracy of our results. One way to incorporate these higher fluence data would be to perform a global fit, where the program would take several sets of data with different pump powers into account at once when fitting the recombination rates. Notably, variations in k_3 at higher fluences are more visually obvious than variations in k_2, and as a result a global fit may be better at finding precise k_3 values than precise k_2 values.

Conclusions

- We wrote a fitting in MATLAB to extract the higher order recombination rates of solar cell materials.
- Further exploration suggested that our program will be more effective if we integrate data of higher fluences into our analysis.
- Moving forward, our lab will perform TRTS measurements on samples with several higher pump fluences, and incorporate the multiple sets of data into the calculation of the recombination constants using a global fitting.

Works Cited

[1] Blinick, George A., *The development of long timescale terahertz spectroscopy techniques to measure lifetimes of photovoltaic materials*, Masters Thesis, 2020.
[2] Rehman, Waqaas, et al., *Charge-Carrier Dynamics and Mobilities in Formamidinium Lead Mixed-Halide Perovskites*, Advanced Materials, 2015.
[3] Hegmann, Frank A., et al., *Probing Organic Semiconductors with Terahertz Pulses*, 2005.