Supplemental Material: Upconversion Theory Software Manual

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This is a manual for using the provided program to simulate photochemical upconversion/triplet-triplet annihilation augmented, third generation photovoltaic/solar cells. For updates, see `http://laszlofrazer.com`.

I. INTRODUCTION

The simulation algorithm is described in

> David Jefferies, Timothy W. Schmidt, and Laszlo Frazer (2019). Phys. Rev. Applied 12, 024023.
>
> doi:10.1103/PhysRevApplied.12.024023

Please cite this paper if you use the provided software.

II. WINDOWS GRAPHICAL INTERFACE

A. Installation

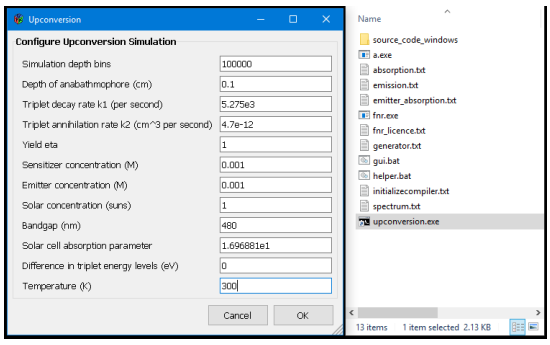
1. Install Zenity for Windows `https://github.com/kvaps/zenity-windows`.
2. Extract the provided .zip file.

B. Usage

1. Run the "upconversion.exe" shortcut.
2. Complete the twelve text boxes describing the parameters of the system you are simulating. The format of the number is according to the `atof()` standard. Example input is given in the screenshot.
   (a) "Simulation depth bins" controls the precision of the calculation. The value required depends on the other parameters. The absorption length of your sensitizer is the most important consideration. We recommend using 100 for quick testing and 10^5 for accurate results. Higher values will lead to a slower calculation. The number of samples simulated is 10^4 times the number of bins selected.
   (b) "Depth of the anabathmophore (cm)" is the thickness of the material which performs upconversion.
   (c) "Triplet decay rate k1 (per second)" is k_1.
   (d) "Triplet annihilation rate k2 (cm^3 per second)" is k_2.
   (e) "Yield eta" is η_c, the singlet yield of triplet annihilation, which should be between 0 and 1.
   (f) "Sensitizer concentration (M)" is $[S]$.
   (g) "Emitter concentration (M)" is $[E]$.
   (h) "Solar concentration (suns)" is the irradiance of the illumination source in units of $\mathrm{kW\,m^{-2}}$. This value is the number of suns only if the spectral irradiance file selected in step 4d is the solar spectrum.
   (i) "Bandgap (nm)" is the wavelength where the solar cell begins to absorb light. The model does not determine if the absorbed light becomes photocurrent. The bandgap must be within the range of the data files selected below.
   (j) "Solar cell absorption parameter" If using a solar cell with a sharp absorption onset, then entering a large value (10^9) will be sufficiently accurate. In Ref. [1],

$$(\alpha h\nu)^2 = A\,(h\nu - E_g)\,. \tag{1}$$

   If x is the thickness of the solar cell, then this parameter is defined to be $x\sqrt{A}$.
   (k) "Difference in triplet energy levels (eV)" is ΔE.
   (l) "Temperature (K)" is used to determine the Maxwell-Boltzmann distribution of triplet excitons between the sensitizer and emitter.



The example will calculate the value $(1 \times 10^{-3}\,\mathrm{M}, 0\,\mathrm{eV}, 5.8 \times 10^{-2}\,\mathrm{mA\,cm^{-2}})$ from main text Fig. 6.

3. Click "OK".

4. Select four spectrum files as prompted. The files you select will replace the files currently in the directory of the executable. There is no warning before replacing the files. Click cancel to use the files that are currently present.

   Example input files are included. Each file must be in tab separated value format. The first row gives the number of rows of data that follow. The data must be sorted by increasing wavelength and (for emission files) probability. Emission spectra must be presented as cumulative distribution functions. A cumulative distribution function is the integral of the emission spectrum, scaled so that the first value is zero and the last value is one.

   (a) Sensitizer absorption 'absorption.txt': sensitizer molar absorptivity (/M/cm) as a function of wavelength (nm). The first column contains a wavelength (nm). The second contains a corresponding molar absorptivity (/M/cm).

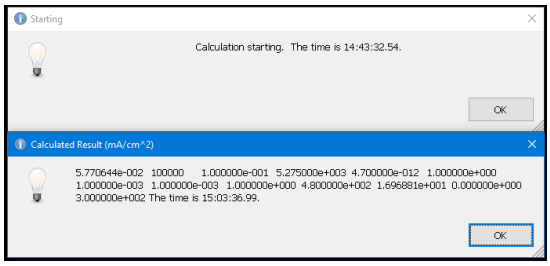
   (b) Emitter absorption 'emitter_absorption.txt': emitter molar absorptivity (/M/cm) as a function of wavelength (nm). The first column contains a wavelength (nm). The second contains a corresponding molar absorptivity (/M/cm)

   (c) Emitter emission 'emission.txt': cumulative distribution function of the emitter fluorescence. The first column contains a probability between 0 and 1, inclusive. The second contains a corresponding wavelength (nm). The range of wavelengths in this file must be within the ranges of the wavelengths in the absorption spectra.

   (d) Illumination 'spectrum.txt': cumulative distribution function of the illumination. The first column contains a number between 0 and 1 inclusive. The second contains a corresponding wavelength (nm).

5. A dialog will appear indicating that your calculation has begun.

6. A dialog will appear indicating the results. The first number is the figure of merit in $\mathrm{mA\,cm^{-2}}$.



7. The remaining numbers indicate the input values provided in Step 2. Finally, the time when the calculation completed is displayed.

III. COMMAND LINE INTERFACE

There are 12 command line arguments. These are identical to the twelve parameters entered into the graphical interface. Make sure all inputs are separated by a space. The four input files are read from the current directory with the assumption that they have the file names listed above.

The output of the program will be 13 columns separated by tabs. The first column will be the figure of merit (mA/cm2). The remaining 12 columns will be 12 command line arguments in the same order.

To calculate current once: Run 'make.sh.' Edit 'test.sh' and run it. The output will be printed to the screen. Note you will have to manually calculate k_1.

Testing was performed with MinGW/GCC 6.3 and 8.2 using Debian and Windows 10.

IV. FREQUENTLY ASKED QUESTIONS

- How do I convert the result of the simulation to the power output of the complete system in sunlight?

  Measure the external quantum efficiency spectrum of the solar cell without the anabathmophore using rear illumination. Multiply the simulated upconversion figure of merit by the external quantum efficiency of the solar cell at the emitter molecule's emission wavelength, the cell area, and the voltage at maximum power point. Add the power output of the solar cell under front illumination.

- My solar cell is opaque below the bandgap. Will it work?

  No.

- What is the solar cell absorption parameter, abbreviated "sctA" in the source code?

  In Ref. [1],

$$(\alpha h\nu)^2 = A\,(h\nu - E_g)\,. \tag{2}$$

  If x is the thickness of the solar cell, then this parameter is defined to be $x\sqrt{A}$.

- Where are gasdev.c, spline.c, and splint.c?

  We do not have a license to distribute these files from Numerical Recipes in C. Most university libraries have a copy.

- I get an error like "Assertion '2147483647==RAND_MAX' failed."

  You are using libraries that have a different value of RAND_MAX, such as those provided by Windows. A larger value may give more precise results. You can edit ran1.c to remove the error message.

- My anabathmophore thickness is 1 cm or more, or my concentration is high. Why does the simulation do a bad job?

  Increase the number of bins until the bin size is much less than the absorption length.

- My sensitizer does not absorb much light. How do I get accurate results?

  Increase the number of bins to increase the number of samples you simulate. This will increase the chance that enough samples are absorbed.

- Where can I get help?

  Email `laszlo@laszlofrazer.com`.

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[1] B. D. Viezbicke, S. Patel, B. E. Davis, and D. P. Birnie III, Evaluation of the Tauc method for optical absorption edge determination: ZnO thin films as a model system, physica status solidi (b) **252**, 1700 (2015).