[†]ESI for Action spectrum experiment for the measurement of incoherent photon upconversion efficiency under sun-like excitation

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1 Model for TTA-UC system

The action spectrum experiment applied to TTA-UC records emitter fluorescence generated by triplet-sensitized upconversion and by direct photoexcitation of the emitter. Comparison of the responses due to the two fluorescence generation pathways provides the efficiency of the upconversion route compared to emitter fluorescence. A simple comparison of peak heights is sufficient to infer relative efficiency between homologous upconverter samples under the same bias conditions. But in order to obtain an absolute measure of the upconversion efficiency, modelling of the optical conditions and system photophysics is required. This section contains the full derivation of a one-dimensional model for TTA-UC generation and detection.

1.1 Upconversion portion of the action spectrum

Starting from the expression for the generation of emitter triplets within a volume element at a depth z within the sample, we assume the low-efficiency regime in which most triplets decay through the first-order channel:

$$k_{\phi} \mid_{z} N_{S} = k_{1} N_{T} \mid_{z}$$
$$\therefore N_{T} \mid_{z} = \frac{k_{\phi} \mid_{z} N_{S}}{k_{1}}, \qquad (1)$$

where $k_{\phi} \mid_{z}$ is the sensitiser excitation rate at depth *z*, *N*_S is the sensitiser concentration, and *N*_T \mid_{z} is the triplet-excited emitter concentration at depth *z*. The two concentrations are in units of cm⁻³.

The intensity of the upconversion response generated per volume element, $dI_{UC} |_z / dz$, depends on the population of singlet-excited emitters, which itself is determined by the square of the local triplet concentration and the second-order rate constant:

$$dI_{UC}|_{z} = 0.5 k_{2} N_{T}^{2}|_{z} \eta_{c} \Phi_{PL} dz.$$
(2)

The factor of 0.5 accounts for the 2 to 1 annihilation of triplets to singlets, η_c is the likelihood that emitter TTA yields the

singlet-excited state, and Φ_{PL} is the emitter fluorescence quantum yield. Combining these two expressions gives

$$dI_{UC}|_{z} = \frac{k_{2}k_{\phi}^{2}|_{z}N_{S}^{2}\eta_{c}\Phi_{PL}}{2k_{1}^{2}}dz,$$
(3)

which is the *in-situ* intensity of upconversion generated at depth z. To convert this to the measured quantity, we need to consider the sources of excitation, and the attenuation of light reaching depth z and returning to the cuvette surface.

The excitation rate has contributions from both the probe beam and the bias beam. The excitation rate at z depends on the attenuation of both beams on their path to that depth, while the intensity of the returned light depends on reabsorption:

$$dI_{UC}|_{z} = \frac{k_{2}N_{S}^{2}\eta_{c}\Phi_{PL}}{2k_{1}^{2}} \left[k_{\phi_{b}}|_{0}\exp(-\alpha_{b}z) + k_{\phi_{p}}|_{0}\exp(-\alpha_{p}z)\right]^{2}\exp(-\alpha_{pl}z)dz, \quad (4)$$

where α_p and α_b are the absorption coefficients of the probe and bias beams in the medium, which is given by the sum of the absorption coefficients of each absorbing species. Although the data reported in this work was collected using relatively broadband incoherent pumping, a single bias beam α value is used here for simplicity, and proved to be sufficient for the results reported. Very broadband biasing, with spectral components well away from the sensitiser peak absorption, may require additional terms to model the effect.

The term α_{pl} is the absorption coefficient of the medium at the detection wavelength. The single term here belies a more complex wavelength-dependent transmission of fluorescence through the medium, but because the detector is viewing only a narrow bandwidth of the fluorescence spectrum the approximation is good. We assume that reabsorbed fluorescence is not re-emitted into detectable paths, which considering the refractive index mismatch of the cuvette-air interface should be true in at least 87% of cases.

Integrating Equation 4 over z gives the upconversion intensity emitted from the cuvette surface:

$$U_{UC} = \frac{k_2 N_S^2 \eta_c \Phi_{PL}}{2k_1^2} \int_0^\infty dz \left(k_{\phi_b^2} \Big|_0 \exp[-z(2\alpha_b + \alpha_{pl})] + k_{\phi_p}^2 \Big|_0 \exp[-z(2\alpha_p + \alpha_{pl})] + 2 k_{\phi_b} \Big|_0 k_{\phi_p} \Big|_0 \exp[-z(\alpha_b + \alpha_p + \alpha_{pl})] \right).$$
(5)

Evaluating the integral produces

$$I_{UC} = \frac{k_2 N_s^2 \eta_c \Phi_{PL}}{2k_1^2} \times \left[\frac{k_{\phi_b}^2}{2\alpha_b + \alpha_{pl}} + \frac{k_{\phi_p}^2}{2\alpha_p + \alpha_{pl}} + \frac{2k_{\phi_b}k_{\phi_p}}{\alpha_b + \alpha_p + \alpha_{pl}} \right] (6)$$

Up until this point it has been sufficient to specify an absorption coefficient of the medium, which encompasses all absorbing components within the upconverter. However, to simplify the excitation rate portion of the equation above, it is necessary to introduce terms that address absorption by the individual components – in this case, the sensitiser in the TTA-UC system. Hence Equation 6 is simplified using the following expressions for excitation rate:

$$k_{\phi_b} = \sigma_b^s I_b, \, k_{\phi_p} = \sigma_p^s I_p, \tag{7}$$

where σ^s is the absorption cross-section of the sensitiser at the bias beam (sub-script *b*) and probe beam wavelengths (sub-script *p*), in units of cm², and I_b and I_p is the flux intensity of the bias and probe beams, respectively, in units of cm⁻². Applying this to Equation 6 gives

$$I_{UC} = \frac{k_2 N_s^2 \eta_c \Phi_{PL}}{k_1^2} \times \left[\frac{I_b^2 \sigma_b^{s2}}{2\alpha_b + \alpha_{pl}} + \frac{I_p^2 \sigma_p^{s2}}{2\alpha_p + \alpha_{pl}} + \frac{I_b \sigma_b^s I_p \sigma_p^s}{\alpha_b^s + \alpha_p + \alpha_{pl}} \right] (8)$$

The first two terms in the brackets above represent the separate contributions to the upconversion signal generated by photons in the bias beam and the probe beam, respectively. The third term represents the effect of light-biasing; that is, the improved response of the probe due to the bias beam. By phase-locking to the probe beam the experiment's detection is insensitive to upconversion generated purely from the bias beam, hence the first term is ignored from here onwards. Additionally, since typically $I_b \gg I_p$, the detected signal is akin to the derivative of the upconversion response with respect to I_p :

$$\frac{\mathrm{d}I_{UC}}{\mathrm{d}I_p} = \frac{k_2 N_S^2 \eta_c \Phi_{PL}}{k_1^2} \left[\frac{2I_p \sigma_p^{s\,2}}{2\alpha_p + \alpha_{pl}} + \frac{I_b \sigma_b^s \sigma_p^s}{\alpha_b^s + \alpha_p + \alpha_{pl}} \right].$$
 (9)

Applying the Beer-Lambert law,

$$\alpha_b^s = \sigma_b^s N_S, \, \alpha_p^s = \sigma_p^s N_S \tag{10}$$

to relate the sensitiser absorption coefficient α^s to the sensitiser concentration, then using Equation 7 once more, we obtain

$$\frac{\mathrm{d}I_{UC}}{\mathrm{d}I_p} = \frac{k_2 N_S \eta_c \Phi_{PL}}{k_1^2} \left[\frac{2k_{\phi_p} \alpha_p^s}{2\alpha_p + \alpha_{pl}} + \frac{k_{\phi_b} \alpha_p^s}{\alpha_b + \alpha_p + \alpha_{pl}} \right]. \quad (11)$$

During the experiment, we measure one action spectrum with the bias beam completely blocked, which sets I_b to zero. Hence the response measured is represented by the first term in Equation 11, and we subtract this response from all other spectra measured at non-zero bias intensity. The modeled response is therefore given entirely by the second term above, wherein the probe and bias responses are inter-mingled.

A final two expressions for upconversion in the low-intensity regime are used to re-cast the model into experimentally-amenable terms:

$$N_T|_0 = \frac{k_{\phi} N_S}{k_1}, \qquad (12)$$
and

$$f_2|_0 \simeq \frac{k_2 N_T|_0}{k_1} \,. \tag{13}$$

where $f_2|_0$ is the fraction of emitter triplets undergoing bimolecular decay at the front of the cuvette. Applying Equations 12 then 13 to the second term in Equation 11 gives

$$\frac{\mathrm{d}I_{UC}}{\mathrm{d}I_p} = f_2|_0 \eta_c \Phi_{PL} \left[\frac{\alpha_p^s}{\alpha_b + \alpha_p + \alpha_{pl}} \right] \tag{14}$$

$$=\Phi_{TTA}\Phi_{PL}\left[\frac{\alpha_p^s}{\alpha_b+\alpha_p+\alpha_{pl}}\right],\qquad(15)$$

where Φ_{TTA} is the likelihood of triplet-excited emitters by the cuvette surface decaying through the bimolecular channel and yielding the emissive singlet-excited state. Note the difference here between this formulation of Φ_{TTA} and that of the strict quantum yield, which is typically defined to have a maximum value of 0.5.

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1.1.1 Direct excitation portion of the action spectrum Equation 15 alone is insufficient to determine Φ_{TTA} from an action spectrum, since the experiment scaling factor is undetermined. The direct emitter excitation region of the action spectrum provides the necessary reference. This response is linear and independent of the bias beam, which simplifies the model of the response.

Prompt fluorescence generated per volume element at depth z, dI_f/dz will reach the cuvette surface with intensity

$$dI_f = N_E \Phi_{pL} \left[k_{\phi_p} \exp(-\alpha_p z) \exp(-\alpha_{pl}^e z) \right] dz \qquad (16)$$

$$= N_e \Phi_{PL} \left[k_{\phi_p} \exp(-z(\alpha_p + \alpha_{pl})) \right] dz$$
(17)

where N_e is the emitter concentration, and α_p is once more the absorption coefficient of the medium and the probe wavelength. As before, the model of reabsorption used here is a simplification, but justified by the narrow detection bandwidth used. Integrating over z gives

$$I_f = \frac{N_E k_{\phi_p} \Phi_{PL}}{\alpha_p + \alpha_{pl}} \,. \tag{18}$$

Applying Equations 7 and 10 gives

$$I_f = \frac{I_p \alpha_p^e \Phi_{PL}}{\alpha_p + \alpha_{pl}}, \qquad (19)$$

which yields the derivative with respect to probe intensity,

$$\frac{\mathrm{d}I_f}{\mathrm{d}I_p} = \frac{\alpha_p^e \Phi_{_{PL}}}{\alpha_p + \alpha_{_{Pl}}}\,.$$
(20)

Thus we obtain a model for the prompt component of the action spectrum.

1.1.2 Fitting function The fitting function is produced by combining the upconversion and prompt fluorescence portions of the model (Equations 15 and 20, respectively). It is note-worthy that upon combining the expressions, Φ_{PL} is subsumed into the scale factor *A*, removing that variable from the evaluation of upconverter performance.

Two free parameters are used in fitting the just-derived model to action spectra: the scale factor, and Φ_{TTA} . In generating the model, only the absorption cross-section and chromophore concentrations are required. More complex optical systems will likely require greater complexity, but at least in this simple case of a bulk liquid upconverter there is a pleasing scarcity of parameters. The completed model is thus:

$$f(\lambda) = A \left[\frac{\alpha_p^e(\lambda)}{\alpha_p(\lambda) + \alpha_{pl}} + \Phi_{TTA} \frac{\alpha_p^s(\lambda)}{\alpha_b + \alpha_p(\lambda) + \alpha_{pl}} \right], \quad (21)$$

2 The problems with relative actinometry for upconversion

A comprehensive review of recently-reported TTA-UC efficiencies by Moth-Poulsen and coworkers shows that actinometry is by far the most commonly-reported method of measuring TTA-UC efficiency.¹ The technique is based on the following equation: ^{1,2}

$$\Phi_{UC} = \frac{A_{ref}}{A_{unk}} \frac{E_{unk}}{E_{ref}} \frac{\eta_{unk}^2}{\eta_{ref}^2} \Phi_{PL} , \qquad (22)$$

where A is the sample absorbance at the excitation wavelength, E is the integrated measured emission spectrum (the subscript r denotes the reference sample), η is the sample refractive index, and Φ_{PL} is the luminescence quantum yield of the reference. In many ways this approach is a single-wavelength relative EQE measurement, and aside from allowing for differing absorbance, treats the upconverter as a black box. In this section, we show that this approach is fraught with problems.

Simple problems arising from Eqn. 22 are the requirement of a luminescent reference sample with an accurately known quantum yield that absorbs in the same region as the upconversion sensitizer, and the need to take account of the detector responsivity at the detection wavelengths of the unknown and reference samples (an implicit assumption in Equation 22). Both problems are potentially tedious, but not in themselves difficult.

Much more serious are problems relating to linear absorption, and generation profile. The former refers to the A_r/A term in Eqn. 22, which implies the number of photons absorbed from the excitation beam scales linearly with absorbance. This is only so in the limit of low absorbance. For a beam of intensity I_0 incident on a bulk sample, $I = I_0 \exp(-\alpha z)$, where α is the absorption coefficient and z is the sample penetration depth. The number of photons absorbed is given by ΔI , where

$$\Delta I = I_0 - I$$

= $I_0 \left(1 - e^{-\alpha z} \right)$
= $I_0 \left(1 - \left[1 - \alpha z - \frac{\alpha^2 z^2}{2} - \dots \right] \right),$ (23)

where the exponential function has been Taylor-expanded in the final line. Clearly, $\Delta I \approx \alpha_z I_0$ only when α_z , that is, the absorbance, is small. The optimum concentration range for a TTA-UC system is, in our experience, typically high, and greater than that required to satisfy the low optical density requirement. Equation 22 is thus of doubtful usefulness in assessing samples operating near their optimum efficiency. The

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upconversion efficiency cannot be expected to remain the same when the concentrations are changed to such an extent, given its sensitivity to the triplet concentration.

Even if, however, absorption at high optical density is properly accounted for, and TTA-UC samples with optimized concentrations are measured according to Equation 22, we must now consider the differing generation profiles of the upconversion sample and the fluorescent reference, and the effect of this difference on the collection efficiency of the detector. Whatever the detection geometry in the measuring system, whether 90° off-axis detection (as in a standard fluorometer) or otherwise, the veracity of Equation 22 relies upon two further conditions:

- 1. The unknown sample and the reference sample, once excited, must contain a similar distribution of excited centers throughout the sample (i.e. equivalent generation profiles), and
- 2. These two distributions should have equal proportions of the emitted photons reaching the detector (i.e. equal reabsorption losses and collection efficiency).

Direct excitation of emitters produces a generation profile that decays according to $e^{-\alpha z}$, as per the Beer-Lambert law. But at low excitation intensity $I_{UC} \propto N_t^2$, and the generation profile of singlet-excited emitters resulting from sensitiser excitation decays quadratically, according to $e^{-2\alpha z}$. Hence the upconversion generation profile can be dramatically foreshortened compared to that of the direct emitter fluorescence, depending on the absorbance of the two species, and condition 1 is violated.

The TTA-UC sample and the reference must have identical reabsorption properties if condition 2 is to be satisfied at high optical density, which is improbable. Furthermore, controlling for differing rates of signal loss due to reabsorption in the upconversion emitter and in the fluorescence standard is also required. To be clear, given the right standard and sufficiently careful measurements it is not impossible to return an accurate measure of Φ_{UC} based on Eqn. 22 alone. But we argue that, given the numerous potential shortfalls, it is a far from ideal method of quantifying upconverter performance, and should not be used without accounting for the issues described here.

To our knowledge, no report of upconversion efficiency using the relative actinometry technique has satisfactorily addressed all the issues outlined here. On this point, we advocate for the adoption of a more rigorous method of evaluating and reporting upconverter performance. The upconverter action spectrum experiment is, hopefully, a first step in this direction.

References

 V. Gray, D. Dzebo, M. Abrahamsson, B. Albinsson and K. Moth-Poulsen, *Physical Chemistry Chemical Physics*, 2014, 16, 10345–10352. 2 T. N. Singh-Rachford and F. N. Castellano, *Journal of Physical Chemistry Letters*, 2010, 1, 195–200.