Linearity in the space of the reaction rates

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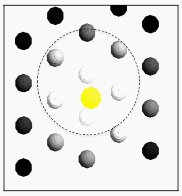
Why fluorescence decays are complex in solids ?

Rates depending on distance



The decay by 0 or 1quencher ≠ 0.5 quencher

Time dependant reaction rates

Radiative Rate Constant

$$\frac{d[S]}{dt} = -[Q_o]k_Q(t)[S] - k_f[S]$$

Time dependant Rate Coefficient

Example of time dependant rate :

a) Distance, orientation, nature dependant rate constant.

For a single pair of exciton/quencher The quenching rate is a constant. But for an ensemble :

According to Berberan Santos 2005 :

$$Ln(I_f(t)/I_f(0)) = -k_f t - \langle n \rangle Ln\left(\int_0^\infty H(k_Q)\exp(-k_Q t)dk_Q\right)$$

According to Tachiya 1992 :

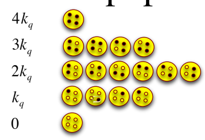
$$Ln(I_f(t)/I_f(0)) = -k_f t - \langle n \rangle \int_0^\infty (1-\exp(-k(r)t))4\pi r^2 dr$$

A general linear equation :

$$Ln\left(\frac{I_f(t)}{I_f(0)}\right) = -k_f t + \langle n \rangle \left\{\exp\left(-\int_0^t k_Q(u)du\right) - 1\right\}$$

Quenching rate rates are proportional to concentration <n>.

Binomial distribution of populations :



The total decay :

$$I_f(t) = I_f(0)\sum_{n=0}^{m} C_m^n p^n (1-p)^n \exp(-k_f t - n k_Q t)$$

Summation on n the number of occupied sites

$$I_f(t) = I_f(0)\exp(-k_f t)\left((1-p) + p\exp(-k_Q t)\right)^m$$

If p ->0

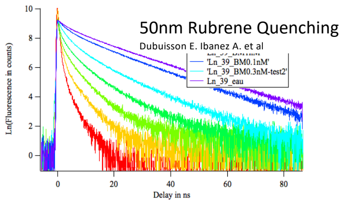
$$Ln(I_f(t)/I_f(0)) \to -k_f t + mp(\exp(-k_Q t) - 1)$$

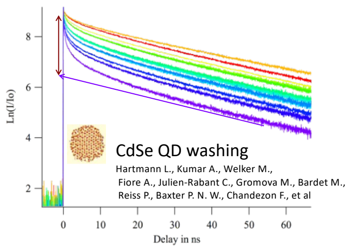
If p ->1

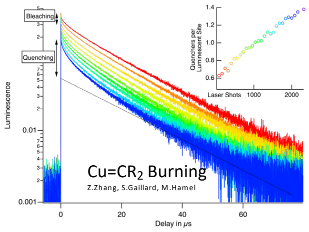
$$Ln(I_f(t)/I_f(0)) \to -k_f t + m\exp(-k_Q t)$$

Examples :

Qualitative analysis



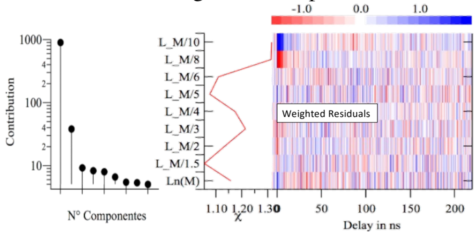




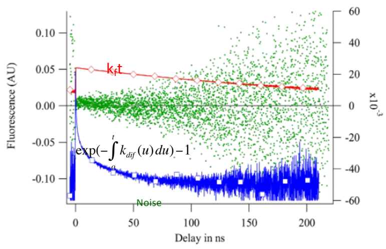
- The drop at short time is the averaged number of quencher per emitter.
- The long lived component is that of the unquenched population.

Quantitative analysis by PCA

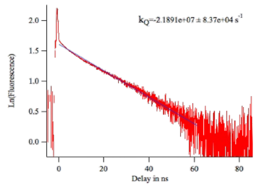
Two components are enough for a good description



Extraction of the time dependant quenching rates

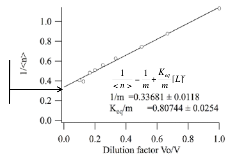


Utilisation

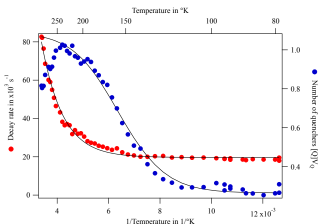


50nm Rubrene crystals detect 1 MB molecule

Conclusion :
m =2.97±0.1
r=1



The maximum number of defects at the surface of CeSe QD is 3



Quenching volume of Singlet and Triplet states of Cu=CR2

Conclusion :

- The decays in solid reveal the corpuscular nature of quenchers following Perrin models.