emission anisotropy

Also contains definitions of: degree of (polarization) anisotropy, luminescence anisotropy

Also contains definition of: time-resolved anisotropy, $r(t)$

Used to characterize luminescence (fluorescence, phosporescence) polarization resulting from photoselection. Defined as:

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2\,I_{\perp}}$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensities measured with the linear polarizer for emission parallel and perpendicular, respectively, to the electric vector of linearly polarized incident electromagnetic radiation (which is often vertical). The quantity $I_{\parallel} + 2\,I_{\perp}$ is proportional to the total fluorescence intensity I.

Notes:

1. Fluorescence polarization may also be characterized by the polarization ratio, also called the degree of polarization p,

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

   For parallel absorbing and emitting transition moments the (theoretical) values are $(r, p) = (2/5, 1/2)$; when the transition moments are perpendicular, the values are $(r, p) = (-1/5, -1/3)$. In many cases, it is preferable to use emission anisotropy because it is additive; the overall contribution of n components r_i, each contributing to the total fluorescence intensity with a fraction $f_i = I_i/I$, is given by:

$$r = \sum_{i=1}^{n} f_i\, r_i \text{ with } \sum_{i=1}^{n} f_i = 1$$

2. On continuous illumination, the measured emission anisotropy is called steady-state emission anisotropy ($\bar{r}$) and is related to the time-resolved anisotropy by:

$$\bar{r} = \frac{\displaystyle\int_0^{\infty} r(t)\, I(t)\,\mathrm{d}t}{\displaystyle\int_0^{\infty} I(t)\,\mathrm{d}t}$$

   where $r(t)$ is the anisotropy and $I(t)$ is the radiant intensity of the emission, both at time t following a δ-pulse excitation.

3. Luminescence polarization spectroscopy, with linear polarizers placed in both beams, is usually performed on isotropic samples, but it may also be performed on oriented anisotropic samples. In the case of an anisotropic, uniaxial sample, five linearly independent luminescence spectra, instead of the two available for an isotropic sample, may be recorded by varying the two polarizer settings relative to each other and to the sample axis.

4. The term fundamental emission anisotropy describes a situation in which no depolarizing events occur subsequent to the initial formation of the emitting state, such as those caused by rotational diffusion or energy transfer. It also assumes that there is no overlap between differently polarized transitions. The (theoretical) value of the fundamental emission anisotropy, r_0, depends on the angle α between the absorption and emission transition moments in the following way:

$$r_0 = \; <3\cos^2\alpha - 1>\big/_5$$

where $<\,>$ denotes an average over the orientations of the photoselected molecules. r_0 can take on values ranging from $-1\big/_5$ for $\alpha = 90\,°$ (perpendicular transition moments) to $2\big/_5$ for $\alpha = 0\,°$ (parallel transition moments). In spite of the severe assumptions, the expression is frequently used to determine relative transition-moment angles.

5. In time-resolved fluorescence with δ-pulse excitation, the theoretical value at time zero is identified with the fundamental emission anisotropy.

Source:
PAC, 2007, *79*, 293 *(Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006))* on page 332