

## magic angle

Upon excitation of an 'isotropic' sample (assuming an ultra short excitation pulse) the relationship between the fluorescence intensity detected at a time  $t$  and through a polarization analyser oriented at an angle  $\beta$  with respect to the electric polarization of the exciting beam is given by

$$I(t, \beta) \propto N(t) [1 + (3 \cos^2 \beta - 1) R(t)]$$

where  $R(t)$  is the degree of alignment of the emitting transition dipole in the laboratory frame and  $N(t)$  is the excited-state population, both at time  $t$ . For  $\beta = 54.7^\circ$  (the magic angle), the dipole-alignment contribution vanishes and  $I(t, \beta = 54.7^\circ) \propto N(t)$ .

Notes:

1. This concept also applies for time-resolved absorption measurements in cases in which photoselection occurs because the detected species do not freely rotate fast enough to make the measurement isotropic within the time of the experiment.
2. Applies for steady-state measurements on fixed samples. In this case

$$I(\beta) \propto N [1 + (3 \cos^2 \beta - 1) R]$$

with  $I(\beta)$  the intensity of the effect observed at an analyser angle  $\beta$  with respect to the electric polarization of the exciting beam,  $N$  the excited-state population at steady-state equilibrium, and  $R$  the degree of alignment of the transition (dipole) moment of the excited molecular entity.

3. The term magic angle is also used in NMR spectroscopy.

### Source:

PAC, 2007, 79, 293 (*Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006)*) on page 367