

molecular orientation

Absorption probability (referred to electric dipolar absorption) for a molecular transition with its electric transition (dipole) moment at an angle θ with the electric vector of the light is proportional to $\cos^2 \theta$. For the whole sample it is proportional to the orientation factor $K_\theta = \langle \cos^2 \theta \rangle$, averaged over all sample molecules. This average is 1 for a sample with all transition moments perfectly aligned along the electric vector of the light, 1/3 for an isotropic sample and 0 for a sample where all transition moments are perpendicular to the electric vector.

Note 1: The directional cosines provide, especially for uniaxial samples, a simple description of exactly those orientation properties of the sample that are relevant for light absorption. With the principal coordinate system (x, y, z) , forming angles $\theta = \alpha, \beta, \gamma$ with the light electric vector in the z direction, all orientation effects induced by light absorption are contained in $K_{\theta\theta} = K_\theta$. Since the sum of K_θ for three perpendicular molecular axes is equal to 1, only two independent parameters are required to describe the orientation effects on light absorption.

Note 2: A related, commonly used description is based on diagonalized Saupe matrices:

$$S_\theta = (3 K_\theta - 1) / 2$$

The principal (molecular) coordinate system (x, y, z) forming angles $\theta = \alpha, \beta, \gamma$ with the light electric vector should be chosen such that the matrix K and the tensor S_θ are diagonal.

To describe processes involving two or more photons, such as luminescence of a uniaxial, aligned sample, an expansion of the directional cosines to the fourth power is required.

Note 3: Order parameters (related to Wigner matrices) are an alternative to the directional cosine-based description of molecular alignment. Order-parameter methods also work well for non-uniaxial samples and provide a seemingly more complex, but in other ways convenient, description of molecular orientation distributions. Wigner matrices are used as a basis set for an expansion of the orientation-distribution function.

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