

# Photoselection of Luminescent Molecules in Anisotropic Media in the Case of Two-Photon Excitation.

## Part I. Theoretical Considerations

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Photoselection of elongated luminescent molecules oriented in a stretched polymer film is considered theoretically for the case of two- and three-photon excitation, having in mind the employment of this phenomenon for determining the angle between the absorption and emission transition moments. Two-photon photoselection provides information on electronic excited states which are not detectable by conventional one-photon spectroscopy due to selection principles.

### 1. Introduction

Photoselection of luminescent molecules (LM) in isotropic rigid media upon one-photon excitation is well-known and has extensively been discussed in a number of monograph papers [1–5]. The maximum value of the fluorescence emission anisotropy (the so-called fundamental anisotropy) in this case, at an excitation with linearly polarized light in the long-wave absorption region is  $2/5$  (corresponding to a polarization of  $1/2$ ). In order to obtain a much higher emission anisotropy, anisotropic rigid media are used, such as cellophane, polyethylene or polyvinyl alcohol (PVA) [6]. The LM's thus oriented in an anisotropic rigid solvent bring about the enhancement in the emission anisotropy (above  $2/5$ ). Orientation of molecules (the so-called Jablonski [7–9] method) can be attained by dissolving the investigated LM in an anisotropic cellophane or polymer film, as well as in a nematic liquid crystal host which may be easily aligned by electric or magnetic fields or by simply rubbing the cell surfaces in contact with the solution. Hence, for rigid anisotropic media one can determine angles between the absorption and emission transition moments and study the molecular dynamics and local orientational order in liquid-crystalline systems (e.g., oriented membranes and lipid vehicles).

As recently demonstrated, a markedly higher steady-state limiting anisotropy can be observed in two-photon than in one-photon excitation [10–12]. The fluorescence emission anisotropies obtained at

two- and three-photon excitation are  $4/7$  and  $2/3$ , respectively, compared to  $2/5$  measured upon one-photon excitation [12]. In this case, the higher limiting emission anisotropy is indicative of a better degree of orientation due to photoselection.

If an anisotropic (stretched) PVA film is used instead of an isotropic solution (e.g. unstretched PVA film), a still higher emission anisotropy is obtained upon two- or three-photon excitation.

In the present paper, photoselection of LM's embedded in anisotropic media is considered for two- and three-photon excitation, having in mind possible employment of this phenomenon in determining transition moment directions.

### 2. Theory

The theory of two-photon excitation of luminescence, worked out by Feofilov [13], assumes the existence of intermediate states, in general of various nature, in the excited system. The excitation of the emitting states can be accomplished either by a stepwise absorption of two photons, or by the cumulation of energies of two interacting excited particles by one of them due to a cooperative process [14, 15]. The intermediate states may also be virtual, due to the existence of non-resonance states, among them some quite distant, but in principle realizable excited states [13, 16].

In the case of linearly polarized light, the emission anisotropy is defined as [17]

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \frac{3}{2} \frac{I_{\parallel}}{I} - \frac{1}{2}, \quad (1)$$

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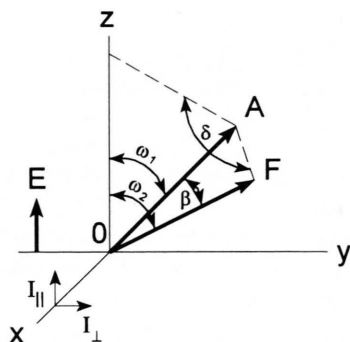


Fig. 1. Geometry of the system. The exciting light  $E$  is polarized in the  $Z$  direction. The fluorescence intensity is observed along  $X$ . Vectors  $A$  and  $F$  represent the directions of the absorption- and fluorescence transition moment.  $\delta$  is the angle between the planes formed by the  $(OZ, A)$  and  $(A, F)$  directions. The positions of the angles  $\omega_1$ ,  $\omega_2$ , and  $\beta$  are evident from the figure.

where  $I = I_{||} + 2I_{\perp}$  is the total emission intensity,  $I_{||}$  and  $I_{\perp}$  are the intensity components parallel and perpendicular to the electric vector  $E$  of the exciting light, respectively, and  $E$  is parallel to the  $z$ -axis of the reference system (Figure 1). The observation is along the  $x$ -axis.

Let us consider an elongated rod-shaped molecule with directions of absorption and emission transition moments,  $A$  and  $E$ , respectively, making an angle  $\beta$  and being rigidly linked with the LM. In addition, the LM is assumed to be in a rigid medium (e.g. a stretched PVA film). As shown in Fig. 1, the intensity ratio,  $I_{||}/I_{\perp}$ , occurring in (1) is time-independent (rotational motions are neglected) and expressed by

$$I_{||}/I_{\perp} = \langle \cos^2 \omega_2 \rangle. \quad (2)$$

The angles  $\omega_1$ ,  $\omega_2$ ,  $\beta$ , and  $\delta$  satisfy the relation

$$\cos \omega_2 = \cos \omega_1 \cos \beta + \sin \omega_1 \sin \beta \cos \delta. \quad (3)$$

By squaring (3) and averaging over an azimuthal angle  $\delta$  ( $\langle \cos \delta \rangle = 0$ ,  $\langle \cos^2 \delta \rangle = 1/2$ ), the following average value for the emission transition is obtained in the

case of a given direction of the absorption transition moment  $\omega_1$  [18]:

$$\langle \cos^2 \omega_2 \rangle = (\frac{3}{2} \cos^2 \omega_1 - \frac{1}{2}) (\cos^2 \beta - \frac{1}{3}) + \frac{1}{3}. \quad (4)$$

The angle  $\beta$  is constant for a given transition in the molecule.

By averaging (4) over all directions  $\omega_1$  one obtains

$$\langle \langle \cos^2 \omega_2 \rangle \rangle = (\frac{3}{2} \langle \cos^2 \omega_1 \rangle - \frac{1}{2}) (\cos^2 \beta - \frac{1}{3}) + \frac{1}{3} \quad (5)$$

which, upon substitution into (1) and taking account of (2), yields

$$r(\beta, \omega_1) = (\frac{3}{2} \langle \cos^2 \omega_1 \rangle - \frac{1}{2}) (\frac{3}{2} \cos^2 \beta - \frac{1}{2}), \quad (6)$$

where

$$\langle \cos \omega_1 \rangle = \frac{\int_0^{\pi/2} \cos^2 \omega_1 f(\omega_1) d\omega_1}{\int_0^{\pi/2} f(\omega_1) d\omega_1} \quad (7)$$

and  $f(\omega_1)$  is the distribution of directions in the excited state attained by absorption of polarized light. For molecules in the ground state, the following distribution function was found for oriented rods with respect to the stretching directions of the film (the  $z$ -axis) [19]:

$$f_g(\omega_1) = R s^2 \sin \omega_1 \{1 + R s^2 - 1\} \sin^2 \omega_1\}^{-3/2}, \quad (8)$$

where  $R s$  is the stretch ratio.

Assume generally that  $n$  simultaneously interacting photons are absorbed by the LM, and that the  $n$ -th photon interacts only with the collection of LM's that were preselected by the first, second and up to the  $(n-1)$ th photon. The orientation distribution for rod-shaped molecules excited with polarized light  $E$  (Fig. 1) is in this case given by

$$f(\omega_1) = f_g(\omega_1) \cos^{2n} \omega_1. \quad (9)$$

By substituting the function (9) with (8) into (7), expression (6) for the emission anisotropy is transformed into

$$r(\beta, R s) = (\frac{3}{2} F_n(R s) - \frac{1}{2}) (\frac{3}{2} \cos^2 \beta - \frac{1}{2}), \quad (10)$$

where for two-photon excitation ( $n = 2$ )

$$F_{n=2}(R s) = \frac{15a - 5a^2 - 2a^3 - 15\sqrt{a(1-a)} \arcsin \sqrt{a}}{4a(3a - a^2 - 3\sqrt{a(1-a)} \arcsin \sqrt{a})}, \quad (11)$$

and for three-photon excitation ( $n = 3$ )

$$F_{n=3}(R s) = \frac{105 - 35a^2 - 14a^3 - 8a^4 - 105\sqrt{a(1-a)} \arcsin \sqrt{a}}{6a(15a - 5a^2 - 2a^3 - 15\sqrt{a(1-a)} \arcsin \sqrt{a})}, \quad (12)$$

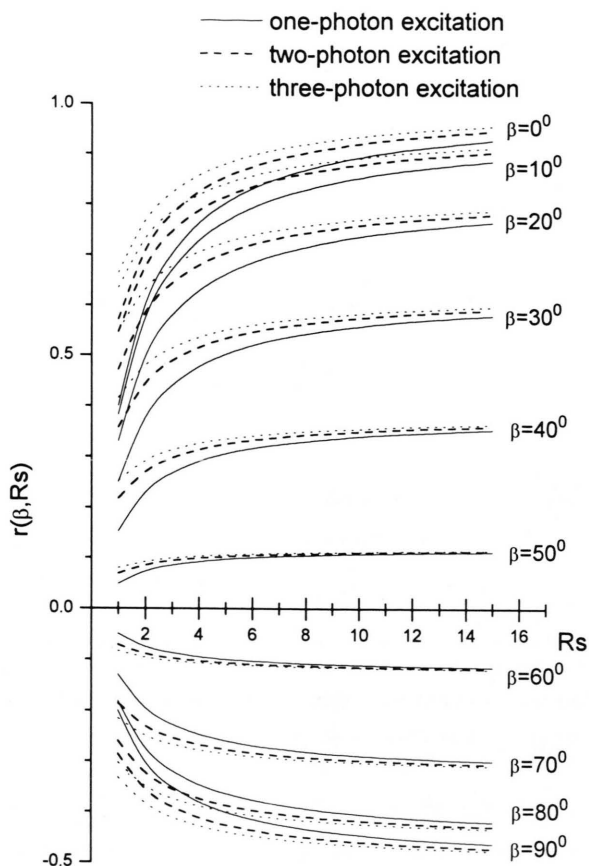


Fig. 2. Theoretical dependence of  $r(\beta, Rs)$  on stretch ratio  $Rs$ , for different values of  $\beta$  in case of one-, two- and three-photon excitation.

where

$$a = \frac{Rs^2 - 1}{Rs^2}. \quad (13)$$

For  $Rs = 1$  (isotropic solution), the fundamental anisotropy for one-, two- and three-photon excitation is  $2/5$ ,  $4/7$  and  $2/3$ , respectively.

For comparison, Fig. 2 shows the emission anisotropy  $r(\beta, Rs)$  for one-, two- and three-photon excitation and different angles  $\beta$ . As clearly seen, for two- and three-photon excitation the emission anisotropy  $r(\beta = \text{const}, Rs)$  at increasing  $Rs$  differs markedly from that at one-photon excitation, particularly for  $1 < Rs < 7$ . For  $Rs \rightarrow \infty$ , all curves corresponding to one-, two- and multi-photon excitation approach the same value of  $r(\beta, Rs \rightarrow \infty)$  for fixed  $\beta$ . For example,  $r = 1$  for  $\beta = 0^\circ$  and  $r = -1/2$  for  $\beta = 90^\circ$ .

### 3. Conclusion

As compared to one-photon excitation, two-photon excitation results in an enhanced photoselection. The quantum-mechanical selection principles for two-photon absorption differ from those for one-photon absorption [20]. Thus, two-photon absorption provides complementary information on transition dipole directions.

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