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The polarisation of two-photon excited fluorescence in rotating molecules

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We report a general theory of the two-photon excited fluorescence (TPEF) of rotating molecules under the condition of anisotropic depolarisation. The obtained expressions for the TPEF intensity are based upon the spherical tensor approach and valid for any symmetric, or asymmetric top molecule and for any photon polarisation. The expressions are written in terms of the molecular parameters $M_K(R, R', t)$ which have clear tensor notation and contain all molecular information that can be extracted from the TPEF experiments. Two important extreme cases are discussed. If the molecular rotation period is much larger than the excited state lifetime, the obtained expressions describe the TPEF in non-rotating molecules under the condition of isotropic relaxation. The time-independent part of these expressions is in agreement with the earlier results of McClain [J. Chem. Phys., **58**, 324 (1973)]. The relationship between McClain's molecular parameters $\hat{Q}_i$ and the parameters $M_K(R, R', 0)$ is presented and analysed. If the molecular rotation period is much smaller than the excited state lifetime, the expressions describe anisotropy of fluorescence from isolated ro-vibrational molecular states. As shown, under certain approximations the expression still can be written in terms of the M-parameters which are reduced due to molecular rotation by about a factor of $(2K+1)$. This result manifests that the fluorescence anisotropy is reduced, but not lost due to the molecular rotation.

Keywords: two-photon excited fluorescence (TPEF); molecules; polarisation

1. Introduction

Multi-photon excitation in molecules followed by analysis of the intensity and anisotropy of the produced fluorescence has now become a powerful tool for probing complex molecular structure and dynamics [1,2]. Recent advantages in the development of the femtosecond lasers have stimulated increasing interest to this research area, because they extend the potential of the multi-photon methods to investigate complex biologically-relevant molecules and provide the possibility of studying the molecular dynamics in the real time-domain [3,4].

The theoretical background for the two-photon excited fluorescence (TPEF) has been established by McClain [5,6], Callis [7], and Wan and Johnson [8,9] who discussed the properties of the two-photon absorption tensor in an ensemble of randomly oriented molecules. McClain [5,6] pointed out that linear combinations of the elements of the two-photon absorption tensor and the elements of the fluorescent tensor can be probed experimentally. He introduced two sets of parameters: the experimentally-controlled polarisation parameters $\hat{P}_i$ which depend on the polarisation of all three photons involved and the molecular parameters $\hat{Q}_i$ which contain all molecular information that can be extracted from experiment. Using the spherical tensor formalism Wan and Johnson [8,9] considered the dynamical case involving isotropic rotational diffusion of the fluorophores.

The theory of the TPEF can be often divided into two processes: (i) two-photon excitation (TPE) of a molecular sample resulting in the molecular excited state polarisation and (ii) time-dependent evolution of the polarised excited state. TPEF can be described by three isotropic molecular parameters which refer to the population of the molecular excited state and by a number of anisotropic parameters which refer to the polarisation of the molecular excited state. The isotropic parameters do not contribute to the fluorescence polarisation and can be determined by measuring the total TPE intensity with linearly and circularly polarised excitation light [10]. The anisotropic parameters can be determined by measuring the fluorescence anisotropy. These parameters are sensitive to the

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excited state depolarisation and therefore contain information about the intermolecular interactions with the environment [6–8].

Most of the theoretical and experimental studies in the field have been done in the condensed molecular phase (solution, polymers, membranes, etc.), see [7,8,11–16] and references therein, however a number of studies have been carried out in the gas phase [17–25]. The gas phase/molecular beam studies are of fundamental importance for understanding the TPEF dynamics of polyatomic molecules in the collision-free regime because they can be supported by high accuracy quantum mechanical *ab initio* calculations which in most cases are not available for the condensed matter studies.

Most of the theoretical studies on the multiphoton processes in rotating molecules in the gas phase which have been done until now were focused on the TPE of a molecule into a single ro-vibrational excited state [18,20,21]. The expressions for the intensities of TPEF from a single ro-vibrational state of a symmetric top molecule have been derived by Chen and Yeung [22], who however did not analyse the fluorescence polarisation values.

In this paper we report a general and compact theory of TPEF in the molecules excited by a short laser pulse under the condition of isotropic collision-induced depolarisation. The theory can be used in the gas and in the condensed phase. The obtained expressions are written in the spherical tensor form, they are valid for any symmetric, or asymmetric top molecule, any experimental geometry, and for any relation between the molecular rotation period and the excited state lifetime. The light polarisation-dependent part of the TPEF intensity is expressed as a tensor product of three photon polarisation matrices and allows one to take into consideration any type of the photon polarisation, including elliptical and partial polarisations.

Two important extreme cases of the obtained expression are discussed. If the molecules do not rotate by themselves in the excited state which may be a result of the interaction with the surrounding condensed phase molecules, or a result of the small excited state lifetime, summation over the rotation quantum numbers including all coherent terms can be performed. This summation leads to the expressions for the TPEF which are similar to the expressions for the non-rotating molecules reported elsewhere [6,8,13,26], however can describe arbitrary polarisation of each of the three photons involved in the photo-process. These expressions can be used either for the description of TPEF in the liquid phase environment under the condition of rotational diffusion, or in the gas phase under the condition of collision relaxation. The fluorescence intensity expression is written in terms of the $M_{K_e}(R, R', t)$-parameters which contain all information about TPE and following depolarisation dynamics. Three parameters with the rank $K_e = 0$ describe an isotropic part of the two-photon absorption tensor and the parameters with the ranks $K_e = 1$ and 2 describe the anisotropic part of the tensor and the fluorescence light polarisation. The relationship between the known McClain [5] molecular parameters $\hat{Q}_i$ and the parameters $M_{K_e}(R, R', 0)$ is tabulated and analysed.

If the molecules perform many periods of rotation during the excited state lifetime, the TPEF expression describes fluorescence from isolated ro-vibrational molecular states which is most appropriate for description of the gas phase environment, or liquid phase with very low viscosity. As shown in the paper, under certain approximations the expression can still be written in terms of the M-parameters. In the high-J approximation the zeroth rank parameters $M_0(R, R', t)$ remain the same as in the first extreme case, while the high-rank parameters are reduced by a factor of $(2K_e + 1)$. The obtained result shows that in this case the fluorescence anisotropy is reduced due to the molecular rotation, however it is not lost prior to emission as may be assumed from the first glance [15]. The physical reason for this effect is discussed in our paper.

The paper is organised as follows. Section 2 contains the derivation of the general expressions for the TREF intensity in an asymmetric top molecule in the spherical tensor formalism. In Section 3 these general expressions are simplified and analysed for the extreme case of the fluorescence in a non-rotating molecules, when the rotation period is much larger than the excited state lifetime. In Section 4 these expressions are simplified and analysed for the extreme case of fast-rotating molecules, when the rotation period is much smaller than the excited state lifetime. The discussion of the obtained results is given in Section 5.

2. Formalism

2.1. *Basic expressions*

We consider the general case of TPEF in an asymmetric top molecule which is excited from the ground state $|g\rangle$ via the two-colour, two-photon transition to the resonant state $|e\rangle$ and then undergoes the internal/relaxation conversion to the state $|\tilde{e}\rangle$ and the spontaneous decay to the final state $|f\rangle$ emitting the

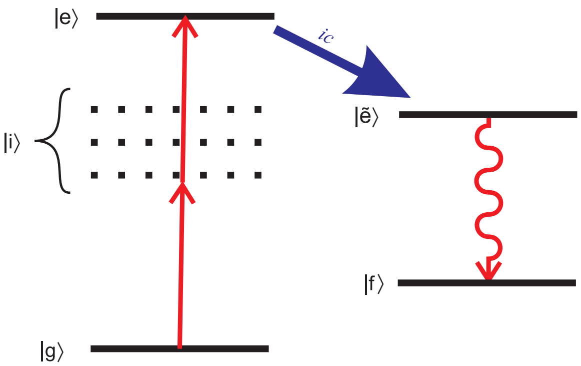

Figure 1. (Color online) Schematic diagram of the TPEF. The first step (two thin solid arrows) is a two-photon excitation of the molecule from the ground $|g\rangle$ state to the resonant state $|e\rangle$ via the non-resonant intermediate (virtual) states $|i\rangle$. The second step (a thick solid arrow marked *ic*), is the radiationless internal conversion $|e\rangle \to |\tilde{e}\rangle$. The third step (a wavy arrow) is a one-photon fluorescence transition from the relaxed state $|\tilde{e}\rangle$ to the final state $|f\rangle$.

fluorescence light as shown in Figure 1. The fluorescence intensity is given by the expression [27]:

$$I = C_{\mathrm{fl}} \sum_{f,\tilde{e},\tilde{e}'} \langle f|(\hat{\mathbf{d}}\cdot\mathbf{e}_{\mathrm{f}})|\tilde{e}'\rangle\langle f|(\hat{\mathbf{d}}\cdot\mathbf{e}_{\mathrm{f}})|\tilde{e}\rangle^{*}\rho_{\tilde{e}'\tilde{e}}, \tag{1}$$

where $\mathbf{e}_{\mathrm{f}}$ is the fluorescence polarisation vector, $\hat{\mathbf{d}}$ is the dipole moment operator, and $\rho_{\tilde{e}'\tilde{e}}$ is the density matrix of the state $|\tilde{e}\rangle$.

The summation indices $\tilde{e}$, $\tilde{e}'$ and f in Equation (1) are the sets of quantum numbers describing electronic, vibrational, and rotational degrees of freedom of the excited and the final states of the molecule. If the fluorescence occurs directly from the resonant state $|e\rangle$, the indices $\tilde{e}, \tilde{e}'$ in Equation (1) should be replaced by e, e', see Figure 1.

Assuming the validity of the relationship $\tau_{\mathrm{ex}} \ll \tau_{\mathrm{ic}} \ll \tau_{\mathrm{r}}$, where τ_{ex} is the duration of the excitation laser pulse, τ_{ic} is the internal conversion and vibration relaxation time, and τ_{r} is the rotation relaxation time, the equation of motion for the excited state density matrices $\rho_{e'e}$, $\rho_{\tilde{e}'\tilde{e}}$ [27,28] can be written in the form of three expressions each valid for a certain time interval:

$$\frac{\mathrm{d}\rho_{e'e}}{\mathrm{d}t} = \delta(t)F_{e'e} \quad \text{for } t \le \tau_{\mathrm{ex}}, \tag{2}$$

$$\frac{\mathrm{d}\rho_{\tilde{e}'\tilde{e}}}{\mathrm{d}t} = \left(\frac{\mathrm{d}\rho_{\tilde{e}'\tilde{e}}}{\mathrm{d}t}\right)_{\mathrm{ic}} \quad \text{for } \tau_{\mathrm{ic}} \ge t > \tau_{\mathrm{ex}}, \tag{3}$$

$$\frac{\mathrm{d}\rho_{\tilde{e}'\tilde{e}}}{\mathrm{d}t} = -\mathrm{i}\Delta\omega_{\tilde{e}'\tilde{e}}\rho_{\tilde{e}'\tilde{e}} - \frac{1}{T}\rho_{\tilde{e}'\tilde{e}} - \left(\frac{\mathrm{d}\rho_{\tilde{e}'\tilde{e}}}{\mathrm{d}t}\right)_{\mathrm{relax}} \quad \text{for } \tau_{\mathrm{r}} \ge t > \tau_{\mathrm{ic}}, \tag{4}$$

where the δ-function $\delta(t)$ in Equation (2) represents the short laser pulse at time $t = 0$.

The term on the right-hand side in Equation (3) describes the internal conversion and vibration relaxation from the resonant state $|e\rangle$ to the relaxed state $|\tilde{e}\rangle$.

The first term on the right-hand part in Equation (4) describes the rotational evolution of the electronic state $|\tilde{e}\rangle$, where $\Delta\omega_{\tilde{e}'\tilde{e}}$ is the energy splitting between different rotation states $|\tilde{e}\rangle$ and $|\tilde{e}'\rangle$. The second term term in Equation (4) describes the spontaneous decay due to radiation transitions to the ground state $|f\rangle$. The last term in Equation (4) describes the rotation relaxation which in the Markov approximation [27] can be presented in the form:

$$\left(\frac{\mathrm{d}\rho_{\tilde{e}'\tilde{e}}}{\mathrm{d}t}\right)_{\mathrm{relax}} = \sum_{\tilde{e}'',\tilde{e}'''} \Gamma_{\tilde{e}',\tilde{e}}^{\tilde{e}'',\tilde{e}'''}\, \rho_{\tilde{e}''\tilde{e}'''}, \tag{5}$$

where $\Gamma_{\tilde{e}',\tilde{e}}^{\tilde{e}'',\tilde{e}'''}$ is the rotation relaxation matrix. This term is responsible for the rotational diffusion under the condition of the high viscosity environment, or for the collision relaxation under the condition of the gas phase environment.

The term $F_{e'e}$ in Equation (2) is the excitation matrix which is given by the second order perturbation theory expression [28,29]:

$$\begin{aligned} F_{e'e} = F_0 \sum_{gg'ii'} &\left[\frac{\langle e'|(\hat{\mathbf{d}}\cdot\mathbf{e}_2)|i'\rangle\langle i'|(\hat{\mathbf{d}}\cdot\mathbf{e}_1)|g'\rangle}{E_{i'} - E_{g'} - \hbar\omega_1} \right. \\ &\left. + \frac{\langle e'|(\hat{\mathbf{d}}\cdot\mathbf{e}_1)|i'\rangle\langle i'|(\hat{\mathbf{d}}\cdot\mathbf{e}_2)|g'\rangle}{E_{i'} - E_{g'} - \hbar\omega_2}\right] \\ &\times \left[\frac{\langle e|(\hat{\mathbf{d}}\cdot\mathbf{e}_2)|i\rangle\langle i|(\hat{\mathbf{d}}\cdot\mathbf{e}_1)|g\rangle}{E_i - E_g - \hbar\omega_1} \right. \\ &\left. + \frac{\langle e|(\hat{\mathbf{d}}\cdot\mathbf{e}_1)|i\rangle\langle i|(\hat{\mathbf{d}}\cdot\mathbf{e}_2)|g\rangle}{E_i - E_g - \hbar\omega_2}\right]^{*} \rho_{g'g}, \end{aligned} \tag{6}$$

where $\mathbf{e}_j$ with $j = 1, 2$ are the polarisation vectors of the first and the second absorbed photons in Figure 1, ω_j are the corresponding photon frequencies, and $\rho_{g'g}$ is the density matrix of the ground molecular state.

The summation indices g, g' and i, i' in Equation (6) are the sets of all quantum numbers describing the ground $|g\rangle$ and intermediate (virtual) $|i\rangle$ states, respectively. We neglect the imaginary parts ($\mathrm{i}\Gamma_i$) in the denominators in Equation (6) assuming that all $|g\rangle \to |i\rangle$ transitions are non-resonant [28]. Therefore, all denominators in Equation (6) are real.

Under condition of validity of the Born–Oppenheimer approximation, the total ground state wave function can be written as a product of the electronic $|n_g\rangle$, vibration $|v_g\rangle$, and rotation $|J_g M_g \tau_g\rangle$ wave functions:

$$|g\rangle = |n_g\rangle\,|v_g\rangle\,|J_g M_g \tau_g\rangle, \tag{7}$$

where J_g is a total angular momentum, M_g is the projection of J_g onto the laboratory axes, and v_g is a set of all vibration quantum numbers.

The value τ_g in Equation (7) is a rotation quantum number [30]. In general, there are $(2J_g+1)$ states labelled each by a certain τ_g-value for a given angular momentum J_g. For a symmetric top molecule the quantum number τ_g in Equation (7) is replaced by Ω_g, the projection of the total angular momentum J_g onto the molecular z-axis, while for an asymmetric top molecule the quantum number τ_g is related to the frequently used spectroscopic quantum numbers K_1 and K_{-1}: $\tau_g = K_1 - K_{-1}$ [30]. Further we will assume for simplicity that the electronic and vibrational wave functions in Equation (7) do not depend on the angular momentum J_g. Similar expressions stand for the wave functions of the intermediate $|i\rangle$, excited $|e\rangle$, $|\tilde{e}$, and final $|f\rangle$ states.

The rotation wave function of an asymmetric top molecule can always be expanded over the eigenfunctions of the symmetric top molecule [20,28,31]:

$$|JM\tau\rangle = \sum_{\Omega} A^J_{\tau\Omega}\,|JM\Omega\rangle, \tag{8}$$

where $|JM\Omega\rangle$ are the normalised Wigner D-functions [32]

$$|JM\Omega\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} D^{J^*}_{M\Omega}(\phi,\theta,\gamma) \tag{9}$$

and $A^J_{\tau\Omega}$ are expansion coefficients. The Eulerian angles (ϕ,θ,γ) in Equation (9) specify the molecular body frame xys.

The expansion coefficients $A^J_{\tau\Omega}$ in Equation (8) obey the orthogonality relation:

$$\sum_{\tau} A^J_{\tau\Omega'} A^{J^*}_{\tau\Omega} = \delta_{\Omega,\Omega'}. \tag{10}$$

2.2. *General expression for the TPEF intensity*

The expression for the TPEF intensity in an asymmetric top molecule can be obtained by combining Equations (1), (2), (4), and (6). This expression contains the molecular rotation wave functions and can be used for description of TPEF in either rotating, or non-rotating molecules. The coefficients $A^J_{\tau\Omega}$ in Equation (8) depend on the ratios of three principal momenta of inertia and can be readily calculated for any molecule. However, under certain approximations transformation and calculation of the TREF intensity for an arbitrary molecule can be performed in general, irrespectively of the details of the molecular structure.

In particular, for an off-resonant two-photon transition contribution from the molecular rotation to the energy differences in the denominators in Equation (6) is much smaller than the contribution from all other terms. Therefore, the denominators practically do not depend on the rotational quantum numbers J_i, τ_i, M_i, J_i', τ_i', M_i', which allows for performing the summation over all these quantum numbers in the transition dipole moment matrix elements in the numerators in Equation (6) without noticeable loss of accuracy. This summation can be carried out irrespectively of the values of the coefficients $A^J_{\tau\Omega}$ in Equation (8) using the closure relation:

$$\sum_{J_i,M_i,\tau_i} |J_i, M_i, \tau_i\rangle\langle J_i, M_i, \tau_i| = 1 = \sum_{J_i,M_i,\Omega_i} |J_i, M_i, \Omega_i\rangle\langle J_i, M_i, \Omega_i|, \tag{11}$$

which allows one to replace the summation in Equation (6) over the complete set of the *asymmetric top* rotational wave functions in Equation (8) by the summation over the complete set of the *symmetric top* rotational wave functions in Equation (9).

The expressions for the TPEF intensity in Equations (1) and (6) depend on the polarisation of three photons: $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_\mathbf{f}$. These expressions can be greatly simplified by transferring from the reducible representation of the molecular density matrix $\rho_{J'M'\tau'JM\tau}$ to the irreducible state multipole representation $\rho_{KQ}(J\tau\, J'\tau')$ using the formula [27,30,33]:

$$\rho_{KQ}(J\tau J'\tau') = \sum_{M,M'} (-1)^{J-M}(2K+1)^{1/2} \times \begin{pmatrix} J & J' & K \\ M & -M' & -Q \end{pmatrix} \rho_{J'M'\tau'JM\tau}, \tag{12}$$

where the term in parenthesis is a $3j$-symbol [32] and the indices K and Q denote the state multipole rank and its projection, respectively.

The inverse transformation is given by:

$$\rho_{J'M'\tau'JM\tau} = \sum_{KQ} (-1)^{J-M}(2K+1)^{1/2} \times \begin{pmatrix} J & J' & K \\ M & -M' & -Q \end{pmatrix} \rho_{KQ}(J\tau J'\tau'). \tag{13}$$

The state multipole moment in Equation (12) is a *covariant* component of the irreducible tensor with rank K and projection Q. The complex conjugate components are given by $[\rho_{KQ}(J\tau J'\tau')]^* = (-1)^{J'-J+Q}\rho_{K-Q}(J'\tau' J\tau)$. The rank $K=0$ state multipole moment refers to the overall population of the rotational states, three first rank components $K=1$, $Q=0, \pm 1$ refer to the molecular angular momentum orientation, and five second rank components $K=2$, $Q=0, \pm 1, \pm 2$ refer to the alignment [27].

The transformation (12) is very convenient because it allows for separation of the light polarisation-dependent terms from the terms which contain the transition dipole moment matrix elements and describe the multiphoton dynamics. Also, under the condition of isotropic depolarisation the collision relaxation matrix in Equation (5) in the state multipole representation is diagonal over the ranks K, K' and does not depend on the laboratory frame projections Q, Q' [27,34], which greatly simplifies the following analysis.

Note that the indices referring to the electronic and vibrational quantum numbers are dropped in Equation (12) for brevity. However, in general the collision relaxation matrix does depend on these indices.

After transformation of the expression for the fluorescence intensity in Equation (1) to the state multipole representation, it can be presented in the form [25,27]:

$$I = C_{\mathrm{fl}} \sum_{f\tilde{e}\tilde{e}'K_e} \left(\boldsymbol{\rho}_{K_e} \cdot \mathbf{E}^{\mathrm{fl}}_{K_e}\right)(-1)^{J'_e+J_f+K_e} \begin{Bmatrix} J_e & J'_e & K_e \\ 1 & 1 & J_f \end{Bmatrix} \times \langle n_f J_f \| \hat{d} \| \tilde{n}'_e J'_e \rangle \langle n_f J_f \| \hat{d} \| \tilde{n}_e J_e \rangle^*, \tag{14}$$

where the term in the curly brackets is a 6*j*-symbol [32], $\langle n_f J_f \| \hat{d} \| \tilde{n}_e J_e \rangle$ is the reduced dipole moment matrix element, and n_f and $\tilde{n}_e$ are all others but J and M quantum numbers labelling the final and excited electronic states, respectively.

The explicit form of the reduced matrix element for an asymmetric top molecule is given by:

$$\langle n_f J_f \| \hat{d} \| \tilde{n}_e J_e \rangle = \sum_{\Omega_f, \Omega_e} A^{J_f^*}_{\tau_f \Omega_f} A^{J_e}_{\tau_e \Omega_e} (2J_e + 1)^{1/2} \times \sum_q C^{J_f \Omega_f}_{J_e \Omega_e\, 1q} \langle n_f | \hat{d}_q | \tilde{n}_e \rangle, \tag{15}$$

where $\hat{d}_q$ with $q=0, \pm 1$ are spherical components of the molecular dipole moment [30], and $C^{J_f\Omega_f}_{J_e\Omega_e\, 1q}$ is a Clebsch–Gordan coefficient[32].

If the electronic molecular functions $|\tilde{n}_e\rangle$ and $|n_f\rangle$ in Equation (15) are non-degenerate, the spherical components of the one-photon fluorescence tensor

$$\mathbf{F}_1 = \langle n_f | \hat{\mathbf{d}} | \tilde{n}_e \rangle \tag{16}$$

obey the symmetry relation $(F_{1q})^* = (-1)^q F_{1-q}$. However, if the electronic states are degenerate, the tensor F_1 may have a complex value.

The term in the parenthesis in Equation (14) is a scalar product [32] of the state multipole moment $\rho_{KQ}(J\tau J'\tau')$ and the fluorescence light polarisation matrix $E^{\mathrm{fl}}_{K_eQ_e}(\mathbf{e})$:

$$\left(\boldsymbol{\rho}_{K_e} \cdot \mathbf{E}^{\mathrm{fl}}_{K_e}\right) = \sum_{Q_e} (-1)^{Q_e} \rho_{K_eQ_e} E^{\mathrm{fl}}_{K_e-Q_e}. \tag{17}$$

The matrix $E^{\mathrm{fl}}_{K_eQ_e}(\mathbf{e})$ is defined as [30]:

$$E_{KQ}(\mathbf{e}) = [\boldsymbol{e} \otimes \boldsymbol{e}^*]_{KQ} = \sum_{qq'} (-1)^{q'} C^{KQ}_{1q1-q'} e_q \left(e_{q'}\right)^*, \tag{18}$$

where e_q is a spherical component of the light polarisation vector $\mathbf{e}$.

The values of the matrices $E^K_Q = [E_{KQ}(\mathbf{e})]^*$ for different particular light polarisations are tabulated by Kummel and co-workers [24]. Convenient expressions for the polarisation matrices $\Phi^K_Q(\mathbf{e}) = (-1)^Q \times (2K+1)^{-1/2} E_{KQ}(\mathbf{e})$ and $\Phi_{KQ}(\mathbf{e}) = (-1)^{K+1} E_{KQ}(\mathbf{e})$ as a function of the direction of the polarisation vector $\mathbf{e}$ can be found in [29] and [35], respectively. Note that the definition of the light polarisation matrix in Equation (18) differs from that used by Fitz [13].

We further assume, that the molecular ground state $|g\rangle$ is isotropic. In this case, the ground state multipole moment in Equation (6) is equal to: $\rho_{K_gQ_g}(J_g\tau_g J'_g\tau'_g) = (2J_g+1)^{-1/2}\delta_{K_g,0}\delta_{Q_g,0}\delta_{J_gJ'_g}\delta_{\tau_g\tau'_g}$.

Combining Equations (6), (11)–(13), (14) and performing a summation over the quantum numbers M_g, M_i, M_e, J_i, Ω_i, the two-photon excitation matrix in Equation (6) after some angular momentum algebra transformations can be written in the form:

$$F_{K_eQ_e}(e, e') = F_0 \sum_{J_g\tau_g} \sum_{K_1K_2} \sum_{RR'} \left[\mathbf{E}^{(1)}_{K_1} \otimes \mathbf{E}^{(2)}_{K_2}\right]_{K_eQ_e} (-1)^{J_g+J_e+R} \times \frac{[(2K_1+1)(2K_2+1)(2R+1)(2R'+1)]^{1/2}}{(2J_g+1)} \times \begin{Bmatrix} K_1 & K_2 & K_e \\ 1 & 1 & R' \\ 1 & 1 & R \end{Bmatrix} \begin{Bmatrix} J_e & J'_e & K_e \\ R' & R & J_g \end{Bmatrix} \times S_{R'}(J_g, e') S_R(J_g, e)^* \mathcal{N}_{J_g\tau_g}, \tag{19}$$

where $\mathcal{N}_{J_g\tau g}$ is the initial state rotational distribution function, the terms in the curly brackets are 9*j*- and 6*j*-symbols [32], $e \equiv J_e, \tau_e, n_e$, and $\mathbf{E}^{(1)}_{K_1}$, $\mathbf{E}^{(2)}_{K_2}$ are the first and second photon polarisation matrices, and the term in the first line in the squared brackets is a direct tensor product:

$$\left[\mathbf{E}^{(1)}_{K_1} \otimes \mathbf{E}^{(2)}_{K_2}\right]_{K_eQ_e} = \sum_{Q_1Q_2} C^{K_eQ_e}_{K_1Q_1K_2Q_2} E^{(1)}_{K_1Q_1} E^{(2)}_{K_2Q_2}. \tag{20}$$

The scalar function $S_R(J_g, e)$ in Equation (19) is defined as:

$$S_R(J_g, e) = (2J_g + 1)^{1/2} \sum_{\Omega_e \Omega_g} \left(A^{J_e}_{\tau_e \Omega_e} \right)^* A^{J_g}_{\tau_g \Omega_g} C^{J_e \Omega_e}_{J_g \Omega_g R\gamma} S_{R\gamma}, \tag{21}$$

where

$$S_{R\gamma} = \sum_{q_1 q_2 n_i} C^{R\gamma}_{1q_1\, 1q_2} \langle n_e | \hat{d}_{q_2} | n_i \rangle \langle n_i | \hat{d}_{q_1} | n_g \rangle \times \left(\frac{1}{E_i - E_g - \hbar\omega_1} + \frac{(-1)^R}{E_i - E_g - \hbar\omega_2} \right) \tag{22}$$

is the spherical component of the two-photon absorption tensor $\mathbf{S}_R$ with the rank $R = 0, 1, 2$.

The two terms in parentheses in the second line in Equation (22) refer to the exchange of the first and the second absorbed photons. If these two photons are the same, then $\hbar\omega_1 = \hbar\omega_2$ and all components of the $R = 1$ tensor $\mathbf{S}_R$ are equal to zero.

Dependence of the two-photon excitation matrix in Equation (19) on the light polarisation is expressed by the state multipole rank K_e and its laboratory frame projection Q_e, while the dependence on the molecular transition symmetry in Equation (22) is expressed by the molecular frame quantum numbers γ, n_e and γ', n'_e.

In the case the state $|n_e\rangle$ is degenerate, $n_e \neq n'_e$, and the corresponding electronic wave functions can be complex [5,36]. However, if the state $|n_e\rangle$ is non-degenerate, $n_e = n'_e$ and the corresponding electronic wave functions are real.

Note that the spherical components $\hat{d}_q$ of dipole moment in Equation (22) are in general complex, therefore the tensor components $S_{R\gamma}$ are also complex. If the molecular electronic wave functions of the states n_g, n_i, n_e are non-degenerate, the spherical components $S_{R\gamma}$ in Equation (22) transform under rotation as a spherical tensor with the rank R and projection γ and obey the symmetry relation $(S_{R\gamma})^* = (-1)^{R-\gamma} S_{R-\gamma}$.

The spherical tensor $S_{R\gamma}$ in Equation (22) is equivalent to the complex conjugated molecular parameter M^R_γ introduced by Metz *et al.* [20] in their theory of two-photon spectroscopy in molecules.

The time-dependent rotational relaxation in the excited state $|e\rangle$ which is described by the relaxation matrix Γ in Equation (5) can in general be very complicated. As shown by Favro [37], Chuang and Eisenthal [38], and by Wan and Johnson [9] in their analysis of the relaxation anisotropy of rotational diffusion, an arbitrary asymmetric top molecule can have up to five exponential decays of the excited state alignment ($K_e = 2$). In the case when the classical diffusion equation for rotational motion is valid, the exponential decay factors can be explicitly expressed in terms of the diffusion operator matrix elements.

In the next two sections we will consider two important extreme cases of 'slow' and 'fast' rotation of the molecules.

3. TPEF intensity in non-rotating molecules

In this section the general expressions in Equations (2)–(4), (14), (19) will be used for considering the extreme case of non-rotating molecules, $1/T \gg \Delta\omega_{e,e'}$. In this limit, the term $\Delta\omega_{e,e'}$ in Equation (4) can be neglected and summation in Equation (14) over all rotational quantum numbers *including all coherent terms*: J_e, J'_e, τ_e, τ'_e can be performed. The physical meaning of the summation procedure is clear, because splitting between the rotational structure energy levels of a non-rotating molecule is much smaller than the excited state decay rate $1/T$. Note, that due to the selection rules for the dipole radiative transitions, all possible J_e, J'_e values range within the interval J_e, $J'_e = |J_g - 2| \cdots J_g + 2$. The expression for the TPEF intensity obtained after the summation is appropriate for treatment of the case of a homogeneous liquid environment under the condition of rotational diffusion. This case will be assumed later in this section.

Summation over the rotational quantum numbers J_e, τ_e can be performed in the same way as the summation over the quantum numbers J_i, τ_i by replacing the sum over the asymmetric top wave functions with the sum over the symmetric top wave functions using the closure relation in Equation (11).

We assume that the fluorescence light is detected without any spectral resolution. Then, Equations (14) and (15) can be further simplified by performing the summation over the quantum numbers J_f, τ_f, Ω_f using the orthogonality relation (10) and the sum rule for the Clebsch–Gordan coefficients and 6*j*-symbols in Equation 8.7.5.(31) from [32].

The time-dependent evolution of the excited state $|e\rangle$ due to the anisotropic relaxation has been taken into consideration by presenting the molecular axis angular distribution in terms of the excited state multipoles $\rho_{K_e Q_e} \sim F_{K_e Q_e}$ in Equation (19), expanding this angular distribution over the asymmetric top eigenfunctions [9,37,38], and substituting the time-dependent expansion coefficients into Equation (14). Then, performing the summation over the indices J_e, τ_e, J'_e, τ'_e, the expression for the TPEF intensity of a non-rotating molecule can be presented in the following compact tensor form (for calculation details see Appendix 1):

$$I = -\frac{C_{\mathrm{fl}}F_0}{3^{1/2}}\mathrm{e}^{-t/T}\sum_{K_1,K_2}\sum_{R,R'}\sum_{K_e}\left(\left[\mathbf{E}^{(1)}_{K_1}\otimes\mathbf{E}^{(2)}_{K_2}\right]_{K_e}\cdot\mathbf{E}^{\mathrm{fl}}_{K_e}\right) \times\frac{[(2K_1+1)(2K_2+1)(2R+1)(2R'+1)]^{1/2}}{2K_e+1} \times\begin{Bmatrix} K_1 & K_2 & K_e\\ 1 & 1 & R'\\ 1 & 1 & R\end{Bmatrix}M_{K_e}(R,R',t), \tag{23}$$

where $M_{K_e}(R,R',t)$ are time-dependent molecular parameters which contain all information, that can be extracted from the TPEF experiment. The exponential pre-factor in Equation (23) describes the spontaneous decay of the excited state population.

The tensor product in the first line in Equation (23) is calculated according to

$$\left(\left[\mathbf{E}^{(1)}_{K_1}\otimes\mathbf{E}^{(2)}_{K_2}\right]_{K_e}\cdot\mathbf{E}^{\mathrm{fl}}_{K_e}\right) = \sum_{Q_e,Q_1,Q_2}(-1)^{K_1-K_2}(2K_e+1)^{1/2} \times\begin{pmatrix} K_1 & K_2 & K_e\\ Q_1 & Q_2 & -Q_e\end{pmatrix}E_{K_1Q_1}E_{K_2Q_2}E_{K_e-Q_e} \tag{24}$$

and describes the dependence of the fluorescence intensity on the polarisation of the three photons involved.

The molecular parameters are scalar values which depend on the indices K_e, R, R'. If the molecular internal conversion is not important, the fluorescence occurs directly from the resonant state $|e\rangle$ (see Figure 1) and the molecular parameters are given by:

$$M_{K_e}(R,R',t) = -3^{1/2}\sum_{n_e,n'_e}\sum_{q_e,q'_e}\left[\mathbf{F}^*_1\otimes\mathbf{F}'_1\right]_{K_eq_e}\mathcal{D}^{K_e}_{q_eq'_e}(t) \times[\mathbf{S}'^*{}_{R'}\otimes\mathbf{S}_R]^*_{K_eq'_e}, \tag{25}$$

where the tensor product is calculated according to

$$\left[\mathbf{F}^*_1\otimes\mathbf{F}'_1\right]_{K_eq_e}\mathcal{D}^{K_e}_{q_eq'_e}(t)\,[\mathbf{S}'{}_{R'}\otimes\mathbf{S}_R]^*_{K_eq_{e'}} = \sum_{q_3,q'_3}\sum_{\gamma,\gamma'}(-1)^{R+q_3-\gamma'}(2K_e+1) \times\begin{pmatrix} 1 & 1 & K_e\\ -q_3 & q'_3 & -q_e\end{pmatrix}\begin{pmatrix} R' & R & K_e\\ -\gamma' & \gamma & -q'_e\end{pmatrix} \times F^*_{1q_3}F'_{1q'_3}S^*_{R\gamma}S'{}_{R'\gamma'}\mathcal{D}^{K_e}_{q_eq'_e}(t), \tag{26}$$

and the tensors $\mathbf{F}_1$ and $\mathbf{S}_R$ are given in Equations (16) and (22). The prime (′) at the functions $F'_{1q'_3}$ and $S'{}_{R'\gamma'}$ in Equations (25), (26) indicates the primed resonance state n'_e in Equations (19), (22).

The term $\mathcal{D}^{K_e}_{q_eq'_e}(t)$ in Equations (25), (26) is the matrix element of the exponent of the rotational diffusion tensor in the molecular principal axis system:

$$\mathcal{D}^{K_e}_{q_eq'_e}(t) = \sum_n d^{K_e}_{q_en}\,e^{-E_{K_en}t}\,d^{K_e\,*}_{q'_en}, \tag{27}$$

where $d^{K_e}_{q_en}$ are the coefficients of expansion of the eigenfunctions of the rotational diffusion operator over the Wigner D-functions, E_{K_en} are the operator eigenvalues, and the index n is equal to $n = 1\ldots(2K_e+1)$ and labels different eigenvalues with the same K_e-value. The diffusion tensor matrix $\mathcal{D}^{K_e}_{q_eq'_e}(t)$ for $K_e\neq 0$ is in general not diagonal and for $K_e = 0$ this martix is equal to unity: $\mathcal{D}^0_{00}(t) = 1$.

Note that unlike Chuang and Eisenthal [38], and Wan and Johnson [9] who defined the rotational diffusion matrix with respect to the diffusion tensor principal axes, in Equation (27) this matrix is defined with respect to the molecular principal axes. According to the detailed analysis of Hantress [39], in an arbitrary asymmetric top molecule the diffusion tensor principal axes in general do not coincide with the molecular principal axes due to intermolecular interactions. However, for molecules such as spherical-, linear-, and symmetric top rotors, or asymmetric-top rotors with two perpendicular planes of symmetry, the rotational diffusion tensor principal axes system is determined by the symmetry of the molecule [39].

In general, the parameters $M_{K_e}(R,R',t)$ can have complex values, however in the case of the non-resonant TPEF all of them are real.

Equation (25) assumes that the fluorescence occurs from the same electronic and vibrational energy levels $n_e = \tilde{n}_e$ and $n'_e = \tilde{n}'_e$ which are excited by the two-photon transition, see Equations (14), (22). In this case, the coherent excitation between the electronic and vibrational energy states n_e and n'_e may be important and the TPEF should be treated as an essentially three-photon process [6].

If the molecular internal conversion occurs much faster than the molecular excited state radiation lifetime, which is typical for large molecules and clusters, the molecular parameters are given by:

$$M_{K_e}(R,R',t) = -3^{1/2}\sum_{n_e,\tilde{n}_e}\sum_{q_e,q'_e}\left[\mathbf{F}^*_1\otimes\mathbf{F}_1\right]_{K_eq_e}\mathcal{D}^{K_e}_{q_eq'_e}(t) \times[\mathbf{S}'^*{}_{R'}\otimes\mathbf{S}_R]^*_{K_eq'_e}, \tag{28}$$

where now the states $|e\rangle$ and $|\tilde{e}\rangle$ in Equations (14), (22) differ from each other: the state $|e\rangle$ is the *initial resonance state*, while the state $|\tilde{e}\rangle$ is a *relaxed* state, as shown in Figure 1. Both states $|e\rangle$ and $|\tilde{e}\rangle$ contain no electronic and vibrational coherence, $n_e = n'_e$, $\tilde{n}_e = \tilde{n}'_e$, because it is unlikely that the off-diagonal density matrix elements can be conserved during the internal conversion.

In this case, the TPEF should be treated as a superposition of two-photon absorption and one-photon fluorescence processes.

Equation (23) is written in terms of the spherical tensor operators and describes the TPEF fluorescence intensity in an arbitrary non-rotating molecules. Equation (23) is general and can be used for complete description of the TPEF intensity in any asymmetric top molecule as a function of the polarisation of each of the three photons: $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e_f}$.

The time-independent part of Equation (23) at $t = 0$ is equivalent to the general TPEF intensity expression given by McClain [6] in terms of Cartesian tensors. As will be shown later in Equations (31–36), the McClain's molecular parameters $\hat{Q}_i$ can be presented as linear combinations of the M-parameters. The time-dependent part of Equation (23) is similar to the expressions given earlier by Chuang and Eisenthal [38], and Wan and Johnson [9]. The parameters in Equation (25) are proportional to the parameters suggested earlier by Gaisenok [26]. Equation (23) generalises the TPEF expression reported by Gaisenok to the case of arbitrary polarisation of all three photons involved.

4. TPEF intensity in fast rotating molecules

In this section the general expressions (2–4), (14), (19) will be used in the extreme case of fast rotating molecules, $1/T \ll \Delta\omega_{e,e'}$. In this limit the molecule undergoes many periods of rotation during its lifetime and the term with $1/T$ in Equation (4) can be dropped for all off-diagonal state multipole matrix elements with the indices $\tilde{e} \neq \tilde{e}'$ referring to the non-degenerate energy states. Therefore, the $\tilde{e} \neq \tilde{e}'$ state multipole matrix elements in Equations (14) and (19) referring to the non-degenerate energy states are cancelled out due to fast rotation and only the diagonal $\tilde{e} = \tilde{e}'$ matrix elements are preserved. In the case of excitation with a short laser pulse (wide spectral line) summation over $\tilde{e} = \tilde{e}'$ in Equations (14) and (19) should be performed in general.

We first consider the molecules which are close to the symmetric top where $|\Omega_e|$ (the modulus of the projection of J_e onto the molecular axis) still can be considered as a good quantum number. The energy levels are clustered in doublets [40] due to the splitting of twofold-degenerate levels of the true symmetric top with a given value of $|\Omega|$ into the substates E_{τ_1} and E_{τ_2}. For a majority of the rotation levels the superfine energy splitting between the substates in the thermally accessible range of J-values ($J = 0$–100) is much smaller than the fine energy splitting between the energy states with different $|\Omega_e|$, see discussion in [40]. In this case, summation over the quantum numbers τ_e at fixed J_e, $|\Omega_e|$ values still can be performed *including* the coherent terms $\tau_e \neq \tau_e'$ making use of the orthogonality relation for the $A^J_{\tau,\Omega}$ coefficients in Equation (10), while the summation over the quantum numbers J_e and $|\Omega_e|$ can be performed in the high-J limit *excluding* the coherent terms with $J_e \neq J_e'$, $|\Omega_e| \neq |\Omega_e'|$ (see Appendix 2).

As shown in Appendix 2, this approach results in the same expression for the TPEF intensity as in Equation (23), where the molecular parameters $M^{\mathrm{rot}}_{K_e}(R, R', t)$ are given by the expression:

$$M^{\mathrm{rot}}_{K_e}(R, R', t) = -\frac{3^{1/2}}{2K_e + 1} \sum_{n_e, n_e'} \left[\mathbf{F}_1^* \otimes \mathbf{F}_1'\right]_{K_e 0} \mathcal{D}^{K_e}_{00}(t) \times [\mathbf{S}'^{*}{}_{+R'} \otimes \mathbf{S}_R]^*_{K_e q_e}. \tag{29}$$

In the case if Equation (29) describes TPEF in the gas phase environment under the condition of collision relaxation of the molecular angular momentum J_e, the rotational diffusion matrix element $\mathcal{D}^{K_e}_{00}(t)$ in Equation (29) should be replaced by the collision relaxation factor $e^{-\gamma_{K_e} t}$, where γ_{K_e} is the relaxation rate.

Equation (29) is written for the case when the molecular internal conversion is not important. The difference between the molecular parameter of fast rotating molecules in Equation (29) and that of non-rotating molecules in Equation (25) is that the former is reduced by a factor of $(2K_e + 1)$ and contains only the $q_e = q_e{}' = 0$ terms.

Therefore, the anisotropy of the two-photon absorption tensor described by the zeroth-rank ($K_e = 0$) molecular parameters is the same for rotating and for non-rotating molecules, while the anisotropy (polarisation) of the molecular fluorescence described by the molecular parameters of the rank $K_e = 1$ and $K_e = 2$ decreases due to the molecular rotation compared to the case of the non-rotating molecules by a factor of $(2K_e + 1)$, however this does not vanish prior to the fluorescence.

The physical reason for this effect is very clear: the excited molecule angular momenta produced after light absorption are not randomly oriented in space. They are always aligned due to the anisotropy of the interaction between the pumping light and the molecules. For instance, if the transition dipole moment is directed along the molecular axis, the angular momenta are mostly aligned in the plane perpendicular to this axis. Therefore, fast rotation of each molecule about its angular momentum reduces, but not completely cancels the anisotropy in the molecular ensemble.

In the case when the molecular internal conversion is important, the expression for the molecular parameters can be readily obtained from Equations (26) and (28) by dividing Equation (28) by a factor of $(2K_e+1)$ and by preserving in the sum over q_e in Equation (26) only the $q_e=q_e'=0$ terms.

For the spherical top molecules the quantum numbers Ω are constants of motion and each rotational energy level with given J is $(2J+1)$ times degenerate with respect to the body-frame axis z. In this case, the expansion coefficients $A^J_{\tau\Omega}$ are equal to $A^J_{\tau\Omega}=\delta_{\tau,\Omega}$ and the summation in Equations (14) and (19) should be performed including all possible coherent $\Omega\neq\Omega'$ states. As shown in Appendix 2, the TPEF intensity in this case can still be written in the form in Equation (23) with the parameters $\tilde{M}^{\text{rot}}_{K_e}(R,R',t)$:

$$\tilde{M}^{\text{rot}}_{K_e}(R,R',t)=\frac{1}{2K_e+1}M_{K_e}(R,R',t), \qquad (30)$$

where the 'non-rotating' molecular parameters $M_{K_e}(R,R',t)$ are given in Equations (25) and (28).

5. Discussion

In the following we discuss the properties of the molecular parameters $M_{K_e}(R,R',0)=M_{K_e}(R,R')$ extrapolated to the excitation time $t\to 0$. As shown in Equations (25) and (28), the parameters $M_{K_e}(R,R')$, where $R,R'=0$, 1, 2 are written as a scalar product containing the tensor product of the two-photon absorption matrices $\mathbf{S}_R$ and the tensor product of the one-photon fluorescence matrices $\mathbf{F}_1$. Due to the symmetry properties of the vector coefficients in Equation (23), the parameter rank K_e is limited to the values $K_e=0$, 1, 2.

Three zeroth-rank parameters $M_0(0,0)$, $M_0(1,1)$, and $M_0(2,2)$ describe the anisotropy of the two-photon absorption tensor $\mathbf{S}_R$. These parameters are similar to the $\delta^{(0)}$, $\delta^{(1)}$, and $\delta^{(2)}$ parameters introduced earlier by Wan and Johnson [8], but not the same because they include also the square of the length of the one-photon fluorescence tensor $(\mathbf{F}_1\cdot\mathbf{F}_1^*)$ and the factor $(2R+1)^{-1}$.

The rank $K_e=1$ and $K_e=2$ molecular parameters describe the polarisation of TPEF fluorescence. The second-rank parameters $M_2(R,R')$ are proportional to the parameters $\delta^{(L,L')}$ introduced earlier by Wan and Johnson [8]. It is clear from the structure of the tensor product in Equation (24) that the rank $K_e=1$ parameters can be determined only using circularly/elliptically polarised fluorescence photons $\mathbf{e}_3$, while the rank $K_e=0$ and $K_e=2$ parameters can be determined using linearly polarised fluorescence photons.

Equation (23) provides a powerful tool for the experimentalist because it allows for determination from experiment a set of molecular parameters $M_{K_e}(R,R',t)$ which contain important information about the molecular structure and dynamics. As an example, we present in Table 1 the relationship between the TPEF intensity and the corresponding molecular parameters $M_{K_e}(R,R',t)$ for different polarisations of the pump and fluorescence photons for the

Table 1. The coefficients of expansion of the TPEF intensity over the molecular parameters $M_{K_e}(R,R',t)$ in Equation (23) for the parallel experimental geometry. The capital letters in the first column indicate the polarisation of the first, second, and the third photons (V is for vertical, H is for horizontal, R is for right-hand circular, L is for left-hand circular polarisation).

	$M_0(0,0,t)$	$M_0(1,1,t)$	$M_0(2,2,t)$	$M_2(1,1,t)$	$M_2(0,2,t)$	$M_2(1,2,t)$	$M_2(2,2,t)$
VVV	$\frac{1}{9}$	0	$\frac{2}{9(5^{1/2})}$	0	$\frac{4}{45}$	0	$\frac{4}{45(7^{1/2})}$
VVH	$\frac{1}{9}$	0	$\frac{2}{9(5^{1/2})}$	0	$-\frac{2}{45}$	0	$-\frac{2}{45(7^{1/2})}$
VHV	0	$\frac{1}{6(3^{1/2})}$	$\frac{1}{6(5^{1/2})}$	$-\frac{1}{30(3^{1/2})}$	0	$-\frac{1}{15}$	$\frac{1}{30(7^{1/2})}$
VHH	0	$\frac{1}{6(3^{1/2})}$	$\frac{1}{6(5^{1/2})}$	$-\frac{1}{30(3^{1/2})}$	0	$\frac{1}{15}$	$\frac{1}{30(7^{1/2})}$
RRV	0	0	$\frac{1}{3(5^{1/2})}$	0	0	0	$\frac{1}{15(7^{1/2})}$
RLV	$\frac{1}{9}$	$\frac{1}{6(3^{1/2})}$	$\frac{1}{18(5^{1/2})}$	$-\frac{1}{30(3^{1/2})}$	$\frac{1}{45}$	0	$-\frac{1}{90(7^{1/2})}$
RVV	$\frac{1}{18}$	$\frac{1}{12(3^{1/2})}$	$\frac{7}{36(5^{1/2})}$	$-\frac{1}{60(3^{1/2})}$	$\frac{2}{45}$	$\frac{1}{30}$	$\frac{11}{180(7^{1/2})}$
RVH	$\frac{1}{18}$	$\frac{1}{12(3^{1/2})}$	$\frac{7}{36(5^{1/2})}$	$-\frac{1}{60(3^{1/2})}$	$-\frac{1}{45}$	$-\frac{1}{30}$	$-\frac{1}{180(7^{1/2})}$

parallel experimental geometry where the fluorescence photons propagate in the same/opposite direction to the direction of propagation of the exciting photons. Time dependence $\exp(-t/T)$ which is the same for all expansion coefficients in Table 1, see Equation (23), is not shown. Note that the molecular parameters $M_{K_e}(R, R', t)$ in Table 1 have in general a complicated multi-exponential decay, see Equation (25).

As shown in Table 1, the particular values of the rank $K_e = 0$ and $K_e = 2$ molecular parameters at any time delay t can be determined from experiment by measuring the fluorescence light intensity which refers to different combinations of the linear and circular polarisation of the first, second, and the third (fluorescence) photons and by solving the corresponding set of algebraic equations.

In general, Equation (23) can be used also for describing an arbitrary elliptical, or partial polarisation of each of the three photons and any experimental geometry.

It is important to explore the relationship between the set of the parameters $M_{K_e}(R, R')$ in Equation (25) based on the spherical tensor representation and the widely used McClain's molecular parameters $\hat{Q}_i$ [5,6] based on the Cartesian tensor representation. As shown by McClain [5,6], the number of molecular parameters $\hat{Q}_i$ is equal to *eleven* in the general case of the *non-resonant* TPEF and is equal to *seven* in the case of the two-photon excited fluorescence. The same result can be readily obtained for the M-parameters in Equation (25).

Note that the parameters $M_{K_e}(R, R')$ obey the symmetry relation $M_{K_e}(R, R') = (-1)^{R+R'+K_e} M_{K_e}(R', R)$ and that the value of each rank R, R', K_e is limited to 0, 1, 2. If the electronic excited state $|e\rangle$ is degenerate, the corresponding molecular wave functions are complex and the Cartesian components of the tensors $\mathbf{F}_1$ and $\mathbf{S}_R$ in Equations (16), (22), and (23) are also complex. As can be shown from the analysis of Equation (25) all parameters of the first rank: $M_1(1,0)$, $M_1(1,1)$, $M_1(2,1)$, and $M_1(2,2)$ can be nonzero only if $n_e \neq n'_e$ coherent terms are involved in the TPEF. The total number of the parameters in this case is equal to *eleven*.

If no coherent terms contribute to the TPEF ($\tilde{n}_e = \tilde{n}'_e$ in Equation (28)), the tensor product $\sum_{\tilde{n}_e}\left[\mathbf{F}_1^* \otimes \mathbf{F}_1\right]_1$ is always equal to zero even if the electronic excited state $|\tilde{e}\rangle$ is degenerate. In this case all $M_1(R, R')$ parameters are equal to zero and the total number of the $M_0(R, R')$ and $M_2(R, R')$ parameters is equal to *seven*. The same result is true when the electronic state $|\tilde{e}\rangle$ is not degenerate, because the corresponding molecular wave function is real and n_e is always equal to n'_e.

If the absorbed photons on the two-photon transition $|g\rangle \to |e\rangle$ are the same, R, $R' \neq 1$, see Equation (22). In this case the number of independent parameters in Equation (25) is reduced to four in agreement with the previous results by McClain [5] and Callis [7].

The relationship between McClain's molecular parameters $\hat{Q}_i$ and the parameters $M_{K_e}(R, R')$ in Equation (25) can be obtained using Equation (23) of this paper and Equation (4) and Figure 1 in [6].

If the excited state $|n_e\rangle$ is non-degenerate, the relationship between the parameters $\hat{Q}_n$ and the parameters $M_{K_e}(R, R')$ is given by:

$$\hat{Q}_1 \equiv |\mathbf{F}|^2 \delta_G = M_0(0,0) + 3^{1/2} M_0(1,1) + 5^{1/2} M_0(2,2), \tag{31}$$

$$\hat{Q}_2 \equiv |\mathbf{F}|^2 \delta_F = 3 M_0(0,0), \tag{32}$$

$$\hat{Q}_3 \equiv |\mathbf{F}|^2 \delta_H = M_0(0,0) - 3^{1/2} M_0(1,1) + 5^{1/2} M_0(2,2), \tag{33}$$

$$\hat{Q}_{4,5} = \frac{1}{3} Q_1 + \frac{2}{3} M_2(0,2) - \frac{1}{2(3^{1/2})} M_1(1,1) \pm M_2(1,2) + \frac{7^{1/2}}{6} M_2(2,2), \tag{34}$$

$$\hat{Q}_6 = \frac{1}{3} Q_3 + \frac{2}{3} M_2(0,2) + \frac{1}{2(3^{1/2})} M_1(1,1) + \frac{7^{1/2}}{6} M_2(2,2), \tag{35}$$

$$\hat{Q}_7 = \frac{1}{3} Q_2 + M_2(0,2). \tag{36}$$

Note that the table of the parameters $\hat{P}_i$ in Figure 1 in [6] contains an error: the polarisation parameters $\hat{P}_4$ and $\hat{P}_5$ for the experimental cases 6 and 7 should be both equal to 1/2, not 1.

For completeness, we also present the relationship between the two-photon absorption molecular parameters δ_G, δ_F, δ_H introduced by Monson and McClain [10] and the scalar products of the irreducible two-photon tensors $\mathbf{S}_R$ in Equation (22):

$$\delta_G \equiv S_{\mu\nu} S^*_{\mu\nu} = (\mathbf{S}_0 \cdot \mathbf{S}_0) + (\mathbf{S}_1 \cdot \mathbf{S}_1) + (\mathbf{S}_2 \cdot \mathbf{S}_2), \tag{37}$$

$$\delta_H \equiv S_{\mu\nu} S^*_{\nu\mu} = (\mathbf{S}_0 \cdot \mathbf{S}_0) - (\mathbf{S}_1 \cdot \mathbf{S}_1) + (\mathbf{S}_2 \cdot \mathbf{S}_2), \tag{38}$$

$$\delta_F \equiv |\mathrm{Tr}\mathbf{S}|^2 = 3(\mathbf{S}_0 \cdot \mathbf{S}_0). \tag{39}$$

6. Conclusion

The paper presents general expressions for the two-colour TPEF intensity in an arbitrary asymmetric top molecule. The expressions take into account the molecular rotational structure and they are valid for any polarisation of each of the three photons involved. The expressions can be used for description of TPEF in rotating and non-rotating molecules. They also can be used for treating the problem of the TPEF depolarisation due to molecular rotation and interaction with other molecules in the gas and in the isotropic condensed phases. The theoretical treatment is based on the spherical tensor algebra which allowed for the derivation of the compact universal expressions. In the particular case of non-rotating molecules the obtained expressions are equivalent to the known expressions for the TPEF intensity reported earlier by other authors. In the case of fast rotating molecules, the fluorescence polarisation is reduced by about a factor of $(2K_e+1)$.

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Appendix 1. Derivation of Equation (23)

The probability that the molecule is oriented along the direction Ω at the time $t, f(\Omega, t)$, can be expressed in terms of density matrix of the molecular excited state $\rho J' M' \tau' J M \tau(t)$ as:

$$f(\Omega, t) = \sum_{J,J'} \sum_{M,M'} \sum_{\tau,\tau'} \rho_{J'M'\tau'JM\tau}(t) \Psi^{J*}_{M\tau}(\Omega) \Psi^{J'}_{M'\tau'}(\Omega), \tag{40}$$

where $\Psi^J_{M\tau}(\Omega) \equiv |JM\tau\rangle$ is the asymmetric top molecular rotational wave function and $\Omega \equiv (\phi, \theta, \gamma)$.

Transforming the molecular density matrix in Equation (40) to the state multipole representation in Equation (13), expanding the molecular wave functions $|JM\tau\rangle$ over the Wigner D-functions with respect to Equation (8), applying the Clebsch–Gordan series to the product of two Wigner D-functions [30], and performing the summation over the indices M and M', Equation (40) can be written in the form

$$f(\Omega, t) = \sum_{K,Q,q} \sum_{J,J'} \sum_{\tau,\tau'} \sum_{\Omega,\Omega'} \frac{[(2J+1)(2J'+1)]^{1/2}}{8\pi^2} (-1)^{J'-\Omega'} \times \rho_{KQ}(J\tau J'\tau', t)\, A^{J*}_{\tau\Omega} A^{J'}_{\tau'\Omega'} C^{Kq}_{J\Omega\, J'-\Omega'} D^K_{Qq}(\Omega), \tag{41}$$

which represents the expansion of the molecular axis distribution in terms of the Wigner D-functions $D^K_{Qq}(\Omega)$.

At the same time, in the classical rotational diffusion regime the temporal evolution of probability $f(\Omega, t)$ can be presented as [37]:

$$f(\Omega, t) = \sum_{K,Q,q} \sum_n d^K_{qn} f^K_{Qn}(t) D^K_{Qq}(\Omega), \tag{42}$$

where d^K_{qn} are the expansion coefficients of the diffusion operator eigenfunctions over the Wigner D-functions and the coefficients $f^K_{Qn}(t)$ depend on time as:

$$f^K_{Qn}(t) = f^K_{Qn}(0)\, \mathrm{e}^{-E_{Kn}t}, \tag{43}$$

where E_{Ln} are diffusion operator eigenvalues.

Comparing Equations (41) and (42) and using the orthogonality relationship for the expansion coefficients d^K_{qn}, one can obtain expression for the coefficients $f^K_{Qn}(t)$

$$f^K_{Qn}(t) = \sum_q d^{K*}_{qn} \sum_{J,J'} \sum_{\tau,\tau'} \sum_{\Omega,\Omega'} \frac{[(2J+1)(2J'+1)]^{1/2}}{8\pi^2} (-1)^{J'-\Omega'} \times \rho_{KQ}(J\tau J'\tau', t)\, A^{J*}_{\tau\Omega} A^{J'}_{\tau'\Omega'} C^{Kq}_{J\Omega\, J'-\Omega'}. \tag{44}$$

Combining Equations (2), (14), (15), (19), and (21) and excluding the excited state density matrix using Equation (44), one can obtain the expression for the time-dependent fluorescence intensity where the summation over all rotational indices: τ_f, τ_e, τ'_e, τ_g, J_e, J'_e, J_f, Ω_e, Ω'_e, Ω_f, and Ω_g should be performed.

The summation over the quantum numbers τ_f, τ_e, and τ'_e which involves only the coefficients $A^J_{\tau\Omega}$ can be performed using the orthogonality relation in Equation (10):

$$\sum_{\tau_f \tau_e \tau'_e} \left(A^{J_f}_{\tau_f\Omega'_f}\right)^* A^{J_f}_{\tau_f\Omega_f} \left(A^{J_e}_{\tau_e\Omega_e}\right)^* A^{J_e}_{\tau_e\tilde{\Omega}_e} A^{J'_e}_{\tau'_e\Omega'_e} \left(A^{J'_e}_{\tau'_e\tilde{\Omega}'_e}\right)^* \left(A^{J_g}_{\tau_g\Omega_g}\right)^* A^{J_g}_{\tau_g\Omega'_g} = \left(A^{J_g}_{\tau_g\Omega_g}\right)^* A^{J_g}_{\tau_g\Omega'_g} \delta_{\Omega_f\Omega'_f} \delta_{\Omega_e\tilde{\Omega}_e} \delta_{\Omega'_e\tilde{\Omega}'_e}. \tag{45}$$

Using Equation (45), the sum over the rest of the rotational quantum numbers can be written in the form:

$$\mathcal{S} = \sum_{J_g,\tau_g,\Omega_g,\Omega'_g} \sum_{J_f,\Omega_f} \sum_{J_e,\Omega_e} \sum_{J'_e,\Omega'_e} (-1)^{J_e+J'_e+J_f} [(2J_e+1)(2J'_e+1)]^{1/2} \times C^{J_f\Omega_f}_{J_e\Omega_e\, 1q_3} C^{J_f\Omega_f}_{J'_e\Omega'_e\, 1q'_3} C^{J_e\Omega_e}_{J_g\Omega_g\, R\gamma} C^{J'_e\Omega'_e}_{J_g\Omega'_g\, R'\gamma'} \begin{Bmatrix} J_e & J'_e & K_e \\ 1 & 1 & J_f \end{Bmatrix} \times \begin{Bmatrix} J_e & J'_e & K_e \\ R' & R & J_g \end{Bmatrix} \left(A^{J_g}_{\tau_g\Omega_g}\right)^* A^{J_g}_{\tau_g\Omega'_g} \mathcal{N}_{J_g\tau_g}, \tag{46}$$

where summation over the quantum numbers J_f, Ω_f and J_e, Ω_e can be performed by subsequent usage of the sum rule for the Clebsch–Gordan coefficients and 6*j*-symbols in Equation 8.7.5.(31) from the Varshalovich *et al.* monograph [32]. After the summation Equation (46) can be written as:

$$\mathcal{S} = \sum_{J_g\tau_g J'_e \Omega'_e \Omega_g \Omega'_g} \frac{(-1)^{1-R-J_g}}{[3(2R+1)]^{1/2}} C^{R\gamma}_{K_e q_e\, R'\gamma'} C^{1\,q'_3}_{1q_3\, K_e q_e} C^{J'_e\Omega'_e}_{J_g\Omega_g\, R'\gamma'} C^{J'_e\Omega'_e}_{J_g\Omega'_g\, R'\gamma'} \times \left(A^{J_g}_{\tau_g\Omega_g}\right)^* A^{J_g}_{\tau_g\Omega'_g} \mathcal{N}_{J_g\tau_g}, \tag{47}$$

where $q_e = \gamma - \gamma' = q'_3 - q_3$.

Summation over the indices J'_e, Ω'_e in Equation (47) is performed using the orthogonality relation of the Clebsch–Gordan coefficients. Also, having in mind that in heavy molecules the rotational levels τ_g which refer to a given total angular momentum J_g lie close to each other, it is possible to neglect the dependence of the population $\mathcal{N}_{J_g\tau_g} \simeq \mathcal{N}_{J_g}$ on τ_g and perform a summation over all quantum numbers τ_g using the orthogonality of the coefficients $A^{J_g}_{\tau_g\Omega_g}$ in Equation (10) which gives:

$$\mathcal{S} = \frac{(-1)^{1-R-J_g}}{[3(2R+1)]^{1/2}} C^{R\gamma}_{K_e q_e\, R'\gamma'} C^{1\,q'_3}_{1q_3\, K_e q_e} \sum_{J_g} \mathcal{N}_{J_g}. \tag{48}$$

Using Equation (48), one can obtain Equation (23), where the total population of the ground state $\mathcal{N} = \sum_{J_g} \mathcal{N}_{J_g}$ is set equal to unity. It is clear from Equations (23) and (48) that within the approximation used the fluorescence *intensity* is proportional to the total ground state population, however the fluorescence *anisotropy* does not depend on the ground state quantum numbers J_g and τ_g.

Appendix 2. Summation over the rotational quantum numbers excluding the (J, J') coherent terms

As discussed in Section 4, in case of fast rotating molecules summation in Equations (14), (15), (19), and (21) should be performed over the rotation quantum numbers including the coherence terms with $\tau_e \neq \tau'_e$, however excluding the coherence terms with $J_e \neq J'_e$.

The derivation below is relevant for spherical top molecules and for the molecules which are close to symmetric tops.

For the spherical top molecules the coefficients $A^J_{\tau\Omega}$, the quantum numbers Ω are constants of motion, and summation over them should be performed including all possible coherent terms with $\Omega_e \neq \Omega'_e$.

For the molecules which are close to symmetric tops, summation over the quantum numbers τ_e, τ'_e, τ_f is carried out using the orthogonality relations for the coefficients $A^{J_g}_{\tau\Omega}$ (10) resulting in Equation (45) where only non-negative values of Ω_e, Ω_g should be considered. For concreteness, we will consider below this case, however the derivation is valid also for the spherical top molecules.

After summation in Equation (46) over the quantum numbers J_f, Ω_f, it can be presented in the form:

$$\mathcal{S} = \sum_{J_e,\Omega_e,\Omega'_e,J_g,\Omega_g} (-1)^{1+J_e+K_e+J_g+R} C^{1q_3}_{K_eq_e\,1q'_3}\, C^{J_e\Omega'_e}_{K_eq_e\,J_e\Omega_e} \times \left(\frac{2J_e+1}{3}\right)^{1/2} \begin{Bmatrix} J_e & J_e & K_e \\ R' & R & J_g \end{Bmatrix} C^{J_e\Omega_e}_{J_g\Omega_g\,R\gamma}\, C^{J_e\Omega'_e}_{J_g\Omega_g\,R'\gamma'}\, \mathcal{N}_{J_g\Omega_g}, \tag{49}$$

where $J_e = J'_e$ and the index $q_e = q_3 - q'_3$ should be held to zero for symmetric top molecules in the high-J limit, $J_e \simeq J_g \gg 1$, $|\Omega_e| \gg 1$. For spherical top molecules all possible values of q_e should be taken into account. In the high-J limit, the Clebsch–Gordan coefficients and the 6*j*-symbol in Equation (49) can be presented in the form [32]:

$$C^{J_e\Omega'_e}_{K_e\delta\,J_e\Omega_e} \approx (-1)^{K_e}\,\delta_{\Omega'_e-\Omega_e,\delta}\, d^{K_e}_{q_e0}(\theta_e) \approx (-1)^{K_e}\,\delta_{\Omega'_e-\Omega_e,\delta}\, d^{K_e}_{q_e0}(\theta_g), \tag{50}$$

$$C^{J_e\Omega_e}_{J_g\Omega_g\,R\gamma} \approx \delta_{\Omega_e,\Omega_g+\gamma}\, d^{R}_{\gamma k}(\theta_g), \tag{51}$$

$$\begin{Bmatrix} J_e & J_e & K_e \\ R' & R & J_g \end{Bmatrix} \approx \frac{(-1)^{R+R'+2J_g}}{[2J_g(2K_e+1)]^{1/2}} C^{K_e0}_{R-k\,R'k}, \tag{52}$$

where $\cos\theta_g \approx \Omega_g/(J_g+1/2)$, $k = J_e - J_g$, and $d^{K_e}_{q_e0}(\theta_g)$ is the Wigner *d*-function.

Substituting Equations (50)–(52) into Equation (49), the summation over the indices k can be carried using Equation 4.6.2.(5) from [32]:

$$\begin{aligned} \mathcal{S} &= \sum_{k}\sum_{J_g,\Omega_g} \frac{(-1)^{1+R'+k}}{[3(2K_e+1)]^{1/2}}\, C^{1q_3}_{K_eq_e\,1q'_3}\, d^{K_e}_{q_e0}(\theta_g) \\ &\quad\times C^{K_e0}_{R-k\,R'k}\, d^{R}_{\gamma k}(\theta_g)\, d^{R'}_{\gamma' k}(\theta_g)\, \mathcal{N}_{J_g\Omega_g} \\ &= \sum_{k,k'}\sum_{J_g,\Omega_g} \frac{(-1)^{1+R'+\gamma}}{[3(2K_e+1)]^{1/2}}\, C^{1q_3}_{K_eq_e\,1q'_3}\, d^{K_e}_{\delta0}(\theta_g) \\ &\quad\times C^{K_e0}_{R-k\,R'k'}\, d^{R}_{-\gamma-k}(\theta_g)\, d^{R'}_{\gamma' k'}(\theta_g)\, \mathcal{N}_{J_g\Omega_g} \\ &= \sum_{J_g,\Omega_g} \frac{(-1)^{1+R'+\gamma}}{[3(2K_e+1)]^{1/2}}\, C^{1q_3}_{K_eq_e\,1q'_3}\, C^{K_eq_e}_{R-\gamma\,R'\gamma'} \left[d^{K_e}_{q_e0}(\theta_g)\right]^2 \mathcal{N}_{J_g\Omega_g}. \end{aligned} \tag{53}$$

Finally, using $\mathcal{N}_{J_g\Omega_g} \approx 2\mathcal{N}_{J_g}/(2J_g+1)$ and replacing the sum over Ω_g in Equation (53) by the integral over the angle θ_g:

$$\sum_{\Omega_g}\left[d^{K_e}_{\delta0}(\theta_g)\right]^2 \approx (J_g+1/2)\int_0^{\pi/2}\left[d^{K_e}_{q_e0}(\theta_g)\right]^2 \sin\theta_g\, d\theta_g = \frac{2J_g+1}{2(2K_e+1)}, \tag{54}$$

one can obtain Equations (30) and (29).