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# Note: Derivation of two-photon circular dichroism—Addendum to "Two-photon circular dichroism" [J. Chem. Phys. 62, 1006 (1975)]

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## I. INTRODUCTION

Two-photon circular dichroism (TPCD), the differential absorption of two photons with different circular polarizations, has first been introduced as a theoretical concept by Tinoco in 1975.[1] Its first experimental realization has been published in 1995.[2] In 2005, the first computational treatment using response theory was presented by Jansík, Rizzo, and Ågren.[3] One year later, Rizzo and coworkers investigated the origin dependence of TPCD and could establish an origin-independent scheme for TPCD calculations which was based on the initial treatment by Tinoco.[4] Both the first experimental realization of TPCD and the origin independent computational treatment led to a large amount of applications which take place in the interplay between theory and experiment.[5–8] Therefore, the study of Tinoco in 1975 remains fundamental for the theoretical treatment of this molecular property.

The article of Tinoco presents the theory of two-photon circular dichroism in a very condensed form which makes it difficult to get into the details of the derivation. Facing these difficulties, I got in contact with Ignacio Tinoco and was kindly provided with copies of his original notes on two-photon circular dichroism. These notes were very helpful to understand the principles Tinoco has used. As Tinoco also allowed me to use these notes for publications as long as he is acknowledged properly, I decided to provide them to the public by this addendum which explains some of the derivation steps in the original article. Therefore, this addendum can be considered as supplementary material to Ref. 1. Finally, I will also explain a detail in the formulation of the "transition polarizabilities" in Ref. 1 and provide some error corrections.

## II. THEORY

In this section, I will present the derivation of some fundamental equations in Ref. 1. Mainly, the nomenclature from the original article will be used but if needed some additional indices and formattings will be introduced to make things clearer. In general, two-photon circular dichroism $\delta^{\mathrm{TPCD}}$ is defined as the differential two-photon absorption for left and right circularly polarized photons,

$$\delta^{\mathrm{TPCD}} = \delta_{\mathrm{L}}^{\mathrm{TPA}} - \delta_{\mathrm{R}}^{\mathrm{TPA}} = B\left[|\boldsymbol{\lambda} \cdot \mathbf{T}_{0f} \cdot \boldsymbol{\mu}|^2 - |\boldsymbol{\lambda}^* \cdot \mathbf{T}_{0f} \cdot \boldsymbol{\mu}^*|^2\right], \tag{1}$$

$$B = \left(\frac{e}{m}\right)^4 \left(\frac{1}{hc}\right)^2 \frac{g(\nu_\lambda + \nu_\mu)}{\nu_\lambda \nu_\mu}. \tag{2}$$

In this expression, $B$ is a constant factor consisting of the elemental charge $e$, the electron mass $m$, the Planck constant $h$, the speed of light $c$, the normalized line shape function $g$, and the frequencies $\nu_\lambda$ and $\nu_\mu$ corresponding to the photons $\lambda$ and $\mu$. The vectors $\boldsymbol{\lambda}$ and $\boldsymbol{\mu}$ are polarization vectors of the photons $\lambda$ and $\mu$. The asterisk denotes complex conjugation. A definition of the polarization vectors will be given later when they are evaluated. The central dot denotes a dot product between a polarization vector ($\boldsymbol{\lambda}$, $\boldsymbol{\mu}$, or its complex conjugates) and a perturbation vector ($\mathbf{p}$, $\mathbf{r}$, *vide infra*).

The tensor $\mathbf{T}_{0f}$ is the two-photon absorption probability tensor following the lines of Peticolas.[9] In the more recent literature, this tensor is often referred to as the "two-photon transition matrix element"[10] or the "two-photon transition moment."[11] The product $\boldsymbol{\lambda} \cdot \mathbf{T}_{0f} \cdot \boldsymbol{\mu}$ is defined as

$$\boldsymbol{\lambda} \cdot \mathbf{T}_{0f} \cdot \boldsymbol{\mu} = \sum_{i \neq 0} \Big[\frac{\boldsymbol{\lambda} \cdot (\mathbf{p}e^{\zeta_\lambda})_{0i} (\mathbf{p}e^{\zeta_\mu})_{if} \cdot \boldsymbol{\mu}}{\nu_{0i} - \nu_\lambda} + \frac{\boldsymbol{\lambda} \cdot (\mathbf{p}e^{\zeta_\lambda})_{if} (\mathbf{p}e^{\zeta_\mu})_{0i} \cdot \boldsymbol{\mu}}{\nu_{0i} - \nu_\mu}\Big], \tag{3}$$

where $\mathbf{p}$ is the momentum operator of the molecule.[1] The index 0 denotes the ground state, and $i$ and $f$ denote excited states with $f$ being the final state of the excitation and $i$ being an intermediate state. $\nu_{0i}$ denotes the excitation energy to state $i$ in atomic units and $\nu_\lambda$ is the frequency of photon $\lambda$. Note that for consistency with the original paper, we use frequencies and not circular frequencies as it is common in more recent publications. The exponent $\zeta_\lambda$ characterizes photon $\lambda$ according to

$$\zeta_\lambda = \frac{2\pi i \nu_\lambda \mathbf{k}_\lambda \cdot \mathbf{r}}{c}, \tag{4}$$

where $i$ is the imaginary unit, $\mathbf{k}_\lambda$ is a unit vector specifying the propagation direction of photon $\lambda$, $\mathbf{r}$ is the position operator of the molecule,[1] and $c$ is the speed of light.

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### A. The derivation of the two-photon absorption tensor beyond the dipole approximation

The exponential $e^{\zeta_\lambda}$ is expanded according to

$$e^{\zeta_\lambda} = 1 + \zeta_\lambda + \cdots. \tag{5}$$

For ordinary two-photon absorption, only the first element of this expansion is taken into account while for TPCD, this expansion is interrupted after the linear term. Inserting Eq. (5) into Eq. (3) and keeping only the terms which are at maximum linear in either $\zeta_\lambda$ and $\zeta_\mu$, we obtain

$$\begin{aligned}\boldsymbol{\lambda}\cdot\mathbf{T}_{0f}\cdot\boldsymbol{\mu} = \sum_{i\neq 0}\Bigg(&\frac{\boldsymbol{\lambda}\cdot\mathbf{p}_{0i}\mathbf{p}_{if}\cdot\boldsymbol{\mu}+\frac{2\pi i}{c}\Big(\boldsymbol{\lambda}\cdot(\mathbf{pr})_{0i}\cdot\mathbf{k}_\lambda\nu_\lambda\mathbf{p}_{if}\cdot\boldsymbol{\mu}+\boldsymbol{\mu}\cdot(\mathbf{pr})_{if}\cdot\mathbf{k}_\mu\nu_\mu\mathbf{p}_{0i}\cdot\boldsymbol{\lambda}\Big)}{\nu_{0i}-\nu_\lambda}\\ &+\frac{\boldsymbol{\mu}\cdot\mathbf{p}_{0i}\mathbf{p}_{if}\cdot\boldsymbol{\lambda}+\frac{2\pi i}{c}\Big(\boldsymbol{\mu}\cdot(\mathbf{pr})_{0i}\cdot\mathbf{k}_\mu\nu_\mu\mathbf{p}_{if}\cdot\boldsymbol{\lambda}+\boldsymbol{\lambda}\cdot(\mathbf{pr})_{if}\cdot\mathbf{k}_\lambda\nu_\lambda\mathbf{p}_{0i}\cdot\boldsymbol{\mu}\Big)}{\nu_{0i}-\nu_\mu}\Bigg),\end{aligned} \tag{6}$$

and for the complex conjugate,

$$\begin{aligned}\boldsymbol{\lambda}^*\cdot\mathbf{T}^*_{0f}\cdot\boldsymbol{\mu}^* = \sum_{j\neq 0}\Bigg(&\frac{\boldsymbol{\lambda}^*\cdot\mathbf{p}_{0j}\mathbf{p}_{jf}\cdot\boldsymbol{\mu}^*-\frac{2\pi i}{c}\Big(\boldsymbol{\lambda}^*\cdot(\mathbf{pr})_{0j}\cdot\mathbf{k}_\lambda\nu_\lambda\mathbf{p}_{jf}\cdot\boldsymbol{\mu}^*+\boldsymbol{\mu}^*\cdot(\mathbf{pr})_{jf}\cdot\mathbf{k}_\mu\nu_\mu\mathbf{p}_{0j}\cdot\boldsymbol{\lambda}^*\Big)}{\nu_{0j}-\nu_\lambda}\\ &+\frac{\boldsymbol{\mu}^*\cdot\mathbf{p}_{0j}\mathbf{p}_{jf}\cdot\boldsymbol{\lambda}^*-\frac{2\pi i}{c}\Big(\boldsymbol{\mu}^*\cdot(\mathbf{pr})_{0j}\cdot\mathbf{k}_\mu\nu_\mu\mathbf{p}_{jf}\cdot\boldsymbol{\lambda}^*+\boldsymbol{\lambda}^*\cdot(\mathbf{pr})_{jf}\cdot\mathbf{k}_\lambda\nu_\lambda\mathbf{p}_{0j}\cdot\boldsymbol{\mu}^*\Big)}{\nu_{0j}-\nu_\mu}\Bigg).\end{aligned} \tag{7}$$

Note that in contrast to Eq. (1), the complex conjugate here is also formed for the transition tensor and not only for the polarization vectors. Eqs. (6) and (7) are intermediate factors used to form the product in Eq. (8). In Eq. (1), a difference between two of these squares is formed with different polarization vectors. We have formed a summation of the terms linear in $\zeta_k$ where every different type of $\mathbf{p}$ ($\mathbf{p}_{0i}$, $\mathbf{p}_{if}$, etc.) is linear in $\zeta$ in one term. This resembles an alternative derivation scheme for TPCD presented by Meath and Power in their 1987 study where electric dipole operators are replaced in turn by magnetic dipole and electric quadrupole operators.[12] The approach Tinoco has used, however, is more flexible and introduces the magnetic dipole and electric quadrupole operators at a later stage. Ignoring all terms higher than linear in $\zeta$, we can write the product of the two expressions in Eqs. (6) and (7) according to

$$\begin{aligned}|\boldsymbol{\lambda}\cdot\mathbf{T}_{0f}\cdot\boldsymbol{\mu}|^2 &= (\boldsymbol{\lambda}\cdot\mathbf{T}_{0f}\cdot\boldsymbol{\mu})(\boldsymbol{\lambda}^*\cdot\mathbf{T}^*_{0f}\cdot\boldsymbol{\mu}^*)\\ &= \mathbf{p}_{0i}\mathbf{p}_{if}\mathbf{p}_{0j}\mathbf{p}_{jf} : \boldsymbol{\mu}^*\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda}f_{\lambda\lambda}+\mathbf{p}_{0i}\mathbf{p}_{if}\mathbf{p}_{0j}\mathbf{p}_{jf} : \boldsymbol{\lambda}^*\boldsymbol{\mu}^*\boldsymbol{\mu}\boldsymbol{\lambda}f_{\lambda\mu}\\ &\quad+\mathbf{p}_{0i}\mathbf{p}_{if}\mathbf{p}_{0j}\mathbf{p}_{jf} : \boldsymbol{\mu}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\mu}f_{\mu\lambda}+\mathbf{p}_{0i}\mathbf{p}_{if}\mathbf{p}_{0j}\mathbf{p}_{jf} : \boldsymbol{\lambda}^*\boldsymbol{\mu}^*\boldsymbol{\lambda}\boldsymbol{\mu}f_{\mu\mu}\\ &\quad+\frac{2\pi i}{c}\Big[\Big(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf} : \boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\lambda-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j} : \boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\mu\\ &\quad+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if} : \boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\mu}^*\boldsymbol{\lambda}^*\cdot\nu_\lambda+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i} : \boldsymbol{\lambda}\mathbf{k}_\mu\boldsymbol{\mu}\boldsymbol{\mu}^*\boldsymbol{\lambda}^*\cdot\nu_\mu\Big)f_{\lambda\lambda}\\ &\quad+\Big(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf} : \boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\mu-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j} : \boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\lambda\\ &\quad+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if} : \boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\mu}^*\cdot\nu_\lambda+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i} : \boldsymbol{\lambda}\mathbf{k}_\mu\boldsymbol{\mu}\boldsymbol{\lambda}^*\boldsymbol{\mu}^*\cdot\nu_\mu\Big)f_{\lambda\mu}\\ &\quad+\Big(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf} : \boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\lambda-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j} : \boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\mu\\ &\quad+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if} : \boldsymbol{\lambda}\mathbf{k}_\mu\boldsymbol{\mu}\boldsymbol{\mu}^*\boldsymbol{\lambda}^*\cdot\nu_\mu+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i} : \boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\mu}^*\boldsymbol{\lambda}^*\nu_\lambda\cdot\Big)f_{\mu\lambda}\\ &\quad+\Big(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf} : \boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\mu-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j} : \boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\lambda\\ &\quad+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if} : \boldsymbol{\lambda}\mathbf{k}_\mu\boldsymbol{\mu}\boldsymbol{\lambda}^*\boldsymbol{\mu}^*\cdot\nu_\mu+\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i} : \boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\mu}^*\cdot\nu_\lambda\Big)f_{\mu\mu}\Big],\end{aligned} \tag{8}$$

$$f_{\lambda\lambda} = \frac{1}{(\nu_{0i}-\nu_\lambda)(\nu_{0j}-\nu_\lambda)}, \tag{9}$$

$$f_{\lambda\mu} = \frac{1}{(\nu_{0i} - \nu_\lambda)(\nu_{0j} - \nu_\mu)}, \tag{10}$$

$$f_{\mu\lambda} = \frac{1}{(\nu_{0i} - \nu_\mu)(\nu_{0j} - \nu_\lambda)}, \tag{11}$$

$$f_{\mu\mu} = \frac{1}{(\nu_{0i} - \nu_\mu)(\nu_{0j} - \nu_\mu)}, \tag{12}$$

where summation is over repeated indices and where the notation,

$$\begin{aligned}&\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf} : \boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda}\\ &\quad = (\mathbf{p}_{0i}\cdot\boldsymbol{\lambda})(\mathbf{p}_{if}\cdot\boldsymbol{\mu})(\mathbf{p}_{0j}\cdot\boldsymbol{\lambda}^*)(\mathbf{r}_{0j}\cdot\mathbf{k}_\lambda)(\mathbf{p}_{jf}\cdot\boldsymbol{\mu}^*),\end{aligned} \tag{13}$$

has been introduced. Note that this notation corresponds to the notation with the colon used in Ref. 1 which has not been explained there. The two tensors $\mathbf{T}_{0f}$ and $\mathbf{T}^*_{0f}$ which are multiplied in Eq. (8) are based on different intermediate state summations. Namely, the summation over states in the left-hand tensor is over $i$ while in the right-hand tensor, it is over $j$. The indices $i$ and $j$ illustrate that there are two different summations over the same manifold of intermediate states. This is also shown by the four different types of denominators $f_{\lambda\lambda}$, $f_{\lambda\mu}$, $f_{\mu\lambda}$, and $f_{\mu\mu}$. We further note that Eq. (8) has imaginary and real contributions. The real part, which is obtained only from contributions $e^\zeta \approx 1$ corresponds to a treatment in the dipole approximation and describes "normal" two-photon absorption. The imaginary parts however go beyond the dipole approximation. These terms are relevant for the treatment of two-photon circular dichroism. In the following, we will therefore only consider the imaginary parts and we will ignore the real parts. First, we rewrite Eq. (8) such that we gather terms which depend on the same polarization vectors,

$$\begin{aligned}\mathrm{Im}|\boldsymbol{\lambda}\cdot\mathbf{T}_{0f}\cdot\boldsymbol{\mu}|^2 = \frac{2\pi i}{c}\Big(&(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\mu}) : \boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\lambda\\
&+(\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\lambda\lambda} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\lambda}) : \boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\mu}^*\boldsymbol{\lambda}^*\cdot\nu_\lambda\\
&+(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\mu}) : \boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\mu\\
&+(\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\lambda\lambda} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\lambda}) : \boldsymbol{\lambda}\mathbf{k}_\mu\boldsymbol{\mu}\boldsymbol{\mu}^*\boldsymbol{\lambda}^*\cdot\nu_\mu\\
&+(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\mu\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\mu\mu}) : \boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\lambda\\
&+(\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\mu}) : \boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\mu}^*\cdot\nu_\lambda\\
&+(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\mu\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\mu\mu}) : \boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\mu\\
&+(\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\mu}) : \boldsymbol{\lambda}\mathbf{k}_\mu\boldsymbol{\mu}\boldsymbol{\lambda}^*\boldsymbol{\mu}^*\cdot\nu_\mu\Big).\end{aligned} \tag{14}$$

Eq. (14) is now used to derive two-photon circular dichroism as a difference for different circularly polarized photons.

### B. The derivation of TPCD

As we are only considering the imaginary parts of the polarization tensor, we can use the following relation between the different polarization tensors in Eq. (14):

$$\mathrm{Im}\boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda} = -\mathrm{Im}\boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\mu}^*\boldsymbol{\lambda}^* \tag{15}$$

and its analogs. With these relations, we can write the difference in Eq. (1) as

$$\begin{aligned}|\boldsymbol{\lambda}\cdot\mathbf{T}_{0f}\cdot\boldsymbol{\mu}|^2 - |\boldsymbol{\lambda}^*\cdot\mathbf{T}_{0f}\cdot\boldsymbol{\mu}^*|^2 = \frac{4\pi i}{c}\Big[&(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\mu}\\
&-\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\lambda\lambda} - \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\lambda}) : \mathrm{Im}\boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\lambda\\
&+(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\mu}\\
&-\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\lambda\lambda} - \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\lambda}) : \mathrm{Im}\boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\mu\\
&+(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\mu\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\mu\mu}\\
&-\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\lambda\mu} - \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\mu}) : \mathrm{Im}\boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\lambda\\
&+(-\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\mu\lambda} - \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\mu\mu}\\
&-\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\lambda\mu} - \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\mu}) : \mathrm{Im}\boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\lambda}\boldsymbol{\mu}\cdot\nu_\mu\Big].\end{aligned} \tag{16}$$

In the following we use that the two different intermediate states $i$ and $j$ are equivalent and we can exchange the summations such that the pairs $\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}$ and $\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}$ as well as $\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}$ and $\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}$ are equivalent. However in Eq. (16), they are multiplied by the denominators $f_{\lambda\lambda}$, $f_{\lambda\mu}$, $f_{\mu\lambda}$, and $f_{\mu\mu}$ (Eq. (9)). As a shift from $\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}$ to $\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}$ or from $\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}$ to $\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}$ refers to an exchange of the intermediate states $i$ and $j$ in the numerator, the shift also has to be carried out in the denominators and we therefore have to write, e.g.,

$$\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\mu} = \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\lambda}. \tag{17}$$

Note that shifts of the denominators only have to be carried out between $f_{\lambda\mu}$ and $f_{\mu\lambda}$. Though the denominators $f_{\lambda\lambda}$ and $f_{\mu\mu}$ also contain $\nu_i$ and $\nu_j$, both these energies are combined with either $\nu_\lambda$ or $\nu_\mu$ and therefore they are symmetric in the intermediate state energies. Furthermore, the imaginary parts of the polarization tensors are symmetric with respect to the exchange of contribution vector pairs according to

$$\mathrm{Im}\boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\mu}\boldsymbol{\lambda} = \mathrm{Im}\boldsymbol{\mu}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\mu}, \tag{18}$$

$$\mathrm{Im}\boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\mu}\boldsymbol{\lambda} = \mathrm{Im}\boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\lambda}\boldsymbol{\mu}. \tag{19}$$

Note that these relations only hold as long as there is no orientational average. These relations will become clear with the discussion of the polarization tensors in Subsection II C. Using these relations, we obtain from Eq. (16),

$$\begin{aligned}\delta_{\mathrm{L}}^{\mathrm{TPA}} - \delta_{\mathrm{R}}^{\mathrm{TPA}} = \frac{8\pi}{c}\cdot B\cdot\Big[\Big(&\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\lambda} + \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\lambda}\\ &+ \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\mu}\Big) : \mathrm{Im}\boldsymbol{\mu}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\mu}^*\boldsymbol{\lambda}^*\cdot\nu_\lambda + \Big(\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\lambda}\\ &+ \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\lambda} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\mu}\Big) : \mathrm{Im}\boldsymbol{\lambda}^*\mathbf{k}_\mu\boldsymbol{\mu}^*\boldsymbol{\mu}\boldsymbol{\lambda}\cdot\nu_\mu\Big].\end{aligned} \tag{20}$$

Note that compared to Eq. (16), all signs have been inverted in this expression as also the polarization tensors have been replaced by their complex conjugates (Eq. (15)). We now end up with a slightly modified version of Eq. (9) of Tinoco. The re-substitution of $\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}$ and $\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}$ yields exactly the same terms as in Ref. 1. For $\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}$ and $\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}$, the perturbation tensors $\mathbf{r}_{0i}$ and $\mathbf{r}_{if}$ are modified to $\mathbf{r}_{0j}$ and $\mathbf{r}_{jf}$, respectively, and treated as parts of the summation over $j$ and not of the summation over $i$. In $\mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}$, this also requires an exchange of the perturbation tensors $\mathbf{p}_{0i}$ and $\mathbf{p}_{ij}$.

Eq. (20) now describes two-photon circular dichroism of a molecule which is fixed in space, e.g., in a crystal. The description of an isotropic sample, e.g., a gas, a liquid, or a solution, requires rotational averaging which is carried out in the next part.

### C. Rotational averaging

The derivation of the isotropic two-photon circular dichroism cross section requires rotational averaging. The fundamental equations for rotational averaging of two-photon absorption have been presented by Monson and McClain in 1970.[13] There has been a lot of work on this topic after Ref. 1 was published, namely, by Andrews and Thirunamachandran[14] and Wagniére.[15] In the following, the expressions from Ref. 14 will be used to carry out the rotational averaging of Eq. (20).

In Ref. 14, rotational averaging of a general fifth-rank tensor is carried out according to

$$\begin{aligned}L = \frac{1}{30}\big(&\epsilon_{k_1k_2k_3}\delta_{k_4k_5}\epsilon_{\kappa_1\kappa_2\kappa_3}\delta_{\kappa_4\kappa_5} + \epsilon_{k_1k_2k_4}\delta_{k_3k_5}\epsilon_{\kappa_1\kappa_2\kappa_4}\delta_{\kappa_3\kappa_5} + \epsilon_{k_1k_2k_5}\delta_{k_3k_4}\epsilon_{\kappa_1\kappa_2\kappa_5}\delta_{\kappa_3\kappa_4} + \epsilon_{k_1k_3k_4}\delta_{k_2k_5}\epsilon_{\kappa_1\kappa_3\kappa_4}\delta_{\kappa_2\kappa_5}\\ &+ \epsilon_{k_1k_3k_5}\delta_{k_2k_4}\epsilon_{\kappa_1\kappa_3\kappa_5}\delta_{\kappa_2\kappa_4} + \epsilon_{k_1k_4k_5}\delta_{k_2k_3}\epsilon_{\kappa_1\kappa_4\kappa_5}\delta_{\kappa_2\kappa_3} + \epsilon_{k_2k_3k_4}\delta_{k_1k_5}\epsilon_{\kappa_2\kappa_3\kappa_4}\delta_{\kappa_1\kappa_5} + \epsilon_{k_2k_3k_5}\delta_{k_1k_4}\epsilon_{\kappa_2\kappa_3\kappa_5}\delta_{\kappa_1\kappa_4}\\ &+ \epsilon_{k_2k_4k_5}\delta_{k_1k_3}\epsilon_{\kappa_2\kappa_4\kappa_5}\delta_{\kappa_1\kappa_3} + \epsilon_{k_3k_4k_5}\delta_{k_1k_2}\epsilon_{\kappa_3\kappa_4\kappa_5}\delta_{\kappa_1\kappa_2}\big),\end{aligned} \tag{21}$$

where $k_i$ denotes laboratory-fixed coordinates which refer to the experimental setup (i.e., the polarization of the photons in this case) while $\kappa_i$ denotes molecule-fixed coordinates which refer to the transition tensor. $\epsilon_{ijk}$ is the Levi-Civita tensor and $\delta_{ij}$ is the Kronecker symbol. The strings with $\kappa$ and $k$ can be interpreted as operators working on the elements of the polarization tensor and the transition strength tensor, respectively.[16]

This expression implies that all contributions to the rotationally averaged transition cross section must have three different indices (three indices of the Levi-Civita tensor) and that one index must occur three times (once due to the index on the Levi-Civita tensor and twice due to the Kronecker delta).

The notation used by Andrews and Thirunamachandran refers to tensor components while in Ref. 1, a tensor notation is used,

$$\begin{aligned}\langle\mathbf{ABCDE}\cdot\mathbf{IJKKK}\rangle = \frac{1}{30}\Big[&(\mathbf{A}\cdot\mathbf{B}\times\mathbf{C})(\mathbf{D}\cdot\mathbf{E})\\ &+(\mathbf{A}\cdot\mathbf{B}\times\mathbf{D})(\mathbf{C}\cdot\mathbf{E})\\ &+(\mathbf{A}\cdot\mathbf{B}\times\mathbf{E})(\mathbf{C}\cdot\mathbf{D})\Big],\end{aligned} \tag{22}$$

where **ABCDE** refers to perturbation operators while **IJKKK** refers to basis vectors which form the polarization vectors. **I**,

**J**, and **K** denote right-handed orthogonal basis vectors which form the polarization vectors $\boldsymbol{\lambda}$, $\boldsymbol{\mu}$, $\boldsymbol{\lambda}^*$, and $\boldsymbol{\mu}^*$ (*vide infra*). The chevrons denote rotational averaging.

We immediately note that Eq. (22) contains the constraint that three different indices have to occur in contributing elements of the polarization tensors and that one of the indices has to occur three times.

An explicit rotational averaging now requires explicit knowledge of the polarization tensor. In the following, two photons with the same circular polarization propagating in the same direction will be assumed; however, other polarizations and propagation directions are possible. In this case, the polarization tensors in Eq. (16) can be simplified using

$$\boldsymbol{\mu} = \boldsymbol{\lambda} \qquad \boldsymbol{\mu}^* = \boldsymbol{\lambda}^* \qquad \mathbf{k}_\mu = \mathbf{k}_\lambda. \tag{23}$$

If we now define the polarization vector $\boldsymbol{\lambda}$ for a circularly left polarized photon,

$$\lambda = \frac{1}{\sqrt{2}}(\mathbf{I} - i\mathbf{J}), \tag{24}$$

where **I** and **J** are orthogonal unit vectors and the propagation direction vector $\mathbf{k}_\lambda$ as **K**, where **K** is a unit vector orthogonal to **I** and **J**, we can write the polarization tensor as

$$(\lambda^*\mathbf{k}_\lambda\lambda^*)(\lambda\lambda) = \tfrac{1}{4}[\mathbf{IKI} + i(\mathbf{JKI} + \mathbf{IKJ}) - \mathbf{JKJ}] \times [\mathbf{II} - i(\mathbf{JI} + \mathbf{IJ}) - \mathbf{JJ}]. \tag{25}$$

If we now leave out all terms that vanish in the rotational averaging for the reasons outlined above, we obtain

$$\langle(\lambda^*\mathbf{k}_\lambda\lambda^*)(\lambda\lambda)\rangle = \frac{1}{4}i\Big\langle -\mathbf{IKIJI} - \mathbf{IKIIJ} + \mathbf{JKIII} - \mathbf{JKIJJ} + \mathbf{IKJII} - \mathbf{IKJJJ} + \mathbf{JKJJI} + \mathbf{JKJIJ}\Big\rangle. \tag{26}$$

We are now able to do a cyclic exchange of **I**, **J**, and **K** according to $\mathbf{I} \to \mathbf{J} \to \mathbf{K} \to \mathbf{I}$. Using this procedure, we can apply Eq. (22) for every term of Eq. (26) and get

$$\langle(\lambda^*\mathbf{k}_\lambda\lambda^*)(\lambda\lambda)\rangle = \frac{1}{4}i\Big\langle -\mathbf{KJKIK} - \mathbf{KJKKI} + \mathbf{IJKKK} - \mathbf{KIJKK} + \mathbf{KJIKK} - \mathbf{JIKKK} + \mathbf{KIKKJ} + \mathbf{KIKJK}\Big\rangle. \tag{27}$$

Exploiting the Levi–Civita tensors in Eq. (21), we can formulate the following equalities:

$$\begin{aligned}
\langle \mathbf{ABCDE} \cdot \mathbf{IJKKK}\rangle &= -\langle \mathbf{ABCDE} \cdot \mathbf{JIKKK}\rangle \\
&= \frac{1}{30}\Big[(\mathbf{A}\cdot\mathbf{B}\times\mathbf{C})(\mathbf{D}\cdot\mathbf{E}) + (\mathbf{A}\cdot\mathbf{B}\times\mathbf{D})(\mathbf{C}\cdot\mathbf{E}) + (\mathbf{A}\cdot\mathbf{B}\times\mathbf{E})(\mathbf{C}\cdot\mathbf{D})\Big], && (28)\\
-\langle \mathbf{ABCDE} \cdot \mathbf{KIJKK}\rangle &= \langle \mathbf{ABCDE} \cdot \mathbf{KJIKK}\rangle \\
&= \frac{1}{30}\Big[(\mathbf{A}\cdot\mathbf{B}\times\mathbf{C})(\mathbf{D}\cdot\mathbf{E}) + (\mathbf{B}\cdot\mathbf{C}\times\mathbf{D})(\mathbf{A}\cdot\mathbf{E}) + (\mathbf{B}\cdot\mathbf{C}\times\mathbf{E})(\mathbf{A}\cdot\mathbf{D})\Big], && (29)\\
\langle \mathbf{ABCDE} \cdot \mathbf{KIKKJ}\rangle &= -\langle \mathbf{ABCDE} \cdot \mathbf{KJKKI}\rangle \\
&= \frac{1}{30}\Big[(\mathbf{A}\cdot\mathbf{B}\times\mathbf{E})(\mathbf{C}\cdot\mathbf{D}) - (\mathbf{B}\cdot\mathbf{C}\times\mathbf{E})(\mathbf{A}\cdot\mathbf{D}) - (\mathbf{B}\cdot\mathbf{D}\times\mathbf{E})(\mathbf{A}\cdot\mathbf{C})\Big], && (30)\\
\langle \mathbf{ABCDE} \cdot \mathbf{KIKJK}\rangle &= -\langle \mathbf{ABCDE} \cdot \mathbf{KJKIK}\rangle \\
&= \frac{1}{30}\Big[(\mathbf{A}\cdot\mathbf{B}\times\mathbf{D})(\mathbf{C}\cdot\mathbf{E}) - (\mathbf{B}\cdot\mathbf{C}\times\mathbf{D})(\mathbf{A}\cdot\mathbf{E}) + (\mathbf{B}\cdot\mathbf{D}\times\mathbf{E})(\mathbf{A}\cdot\mathbf{C})\Big]. && (31)
\end{aligned}$$

With these equations, we can simplify Eq. (27),

$$\langle(\lambda^*\mathbf{k}_\lambda\lambda^*)(\lambda\lambda)\rangle = \frac{1}{2}i\Big\langle \mathbf{KIKJK} + \mathbf{KIKKJ} + \mathbf{IJKKK} - \mathbf{KIJKK}\Big\rangle. \tag{32}$$

Using Eq. (32) and Eqs. (28)–(31), we can write

$$\begin{aligned}
&\langle \mathbf{ABCDE} \cdot (\mathbf{IJKKK} - \mathbf{KIJKK} + \mathbf{KIKKJ} + \mathbf{KIKJK})\rangle \\
&\quad = \frac{i}{30}\Big[(\mathbf{A}\cdot\mathbf{B}\times\mathbf{D})(\mathbf{C}\cdot\mathbf{E}) + (\mathbf{A}\cdot\mathbf{B}\times\mathbf{E})(\mathbf{C}\cdot\mathbf{D}) - (\mathbf{B}\cdot\mathbf{C}\times\mathbf{D})(\mathbf{A}\cdot\mathbf{E}) - (\mathbf{B}\cdot\mathbf{C}\times\mathbf{E})(\mathbf{A}\cdot\mathbf{D})\Big]. && (33)
\end{aligned}$$

The rotationally averaged TPCD will now be derived from Eq. (16) which is rewritten using our assumptions on the polarization tensors,

$$\begin{aligned}
\delta_{\mathrm{L}}^{\mathrm{TPA}} - \delta_{\mathrm{R}}^{\mathrm{TPA}} = \frac{4\pi i}{c}\cdot B\cdot \Big[&\Big(\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\lambda} + \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\lambda\lambda} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\lambda}\Big)\nu_\lambda \\
&+ \Big(\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\lambda\lambda} + \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\lambda\lambda} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\lambda}\Big)\nu_\mu \\
&+ \Big(\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\mu\lambda} + \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\mu\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\mu\mu}\Big)\nu_\lambda \\
&+ \Big(\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j}f_{\mu\lambda} + \mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\mu\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{if}\mathbf{p}_{0i}f_{\lambda\mu} + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\mu\mu}\Big)\nu_\mu\Big] : \lambda\mathbf{k}_\lambda\lambda^*\lambda^*. && (34)
\end{aligned}$$

This expression is further simplified using again the relation (see Subsection II B),

$$\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\lambda}\nu_\lambda + \mathbf{p}_{0j}\mathbf{p}_{jf}(\mathbf{pr})_{0i}\mathbf{p}_{if}f_{\lambda\lambda}\nu_\lambda = 2\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf}f_{\lambda\lambda}\nu_\lambda, \tag{35}$$

and its analogs to get

$$\begin{aligned}\delta_{\mathrm{L}}^{\mathrm{TPA}} - \delta_{\mathrm{R}}^{\mathrm{TPA}} = \frac{8\pi i}{c}\cdot B\cdot\Big[&(\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf})(f_{\lambda\lambda}\nu_\lambda + f_{\lambda\mu}\nu_\mu + f_{\mu\lambda}\nu_\lambda + f_{\mu\mu}\nu_\mu)\\ &+(\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j})(f_{\lambda\mu}\nu_\lambda + f_{\lambda\lambda}\nu_\mu + f_{\mu\mu}\nu_\lambda + f_{\lambda\mu}\nu_\mu)\Big] : \boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*.\end{aligned} \tag{36}$$

Due to the notation with the colon (Eq. (13)) where the order of the polarization vectors and the perturbation vectors is inverted, the substitution of the uppercase perturbation vectors **A**, **B**, **C**, **D**, and **E** with the perturbation operators has to be performed backwards according to

$$\begin{aligned}\langle\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{0j}\mathbf{p}_{jf} : \boldsymbol{\lambda}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\lambda}\rangle &= \langle\mathbf{p}_{jf}\mathbf{r}_{0j}\mathbf{p}_{0j}\mathbf{p}_{if}\mathbf{p}_{0i}\cdot(\mathbf{IJKKK}+\mathbf{KIJKK}+\mathbf{KIKKJ}+\mathbf{KIKJK})\rangle\\ &= \frac{i}{30}\Big[(\mathbf{p}_{jf}\cdot\mathbf{r}_{0j}\times\mathbf{p}_{if})\mathbf{p}_{0j}\cdot\mathbf{p}_{0i} + (\mathbf{p}_{jf}\cdot\mathbf{r}_{0j}\times\mathbf{p}_{0i})\mathbf{p}_{0j}\cdot\mathbf{p}_{if}\\ &\quad -(\mathbf{r}_{0j}\cdot\mathbf{p}_{0j}\times\mathbf{p}_{if})\mathbf{p}_{jf}\cdot\mathbf{p}_{0i} - (\mathbf{r}_{0j}\cdot\mathbf{p}_{0j}\times\mathbf{p}_{0i})\mathbf{p}_{jf}\cdot\mathbf{p}_{if}\Big],\end{aligned} \tag{37}$$

$$\begin{aligned}\langle\mathbf{p}_{0i}\mathbf{p}_{if}(\mathbf{pr})_{jf}\mathbf{p}_{0j} : \boldsymbol{\lambda}^*\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}\boldsymbol{\lambda}\rangle &= \langle\mathbf{p}_{0j}\mathbf{r}_{jf}\mathbf{p}_{jf}\mathbf{p}_{if}\mathbf{p}_{0i}\cdot(\mathbf{IJKKK}+\mathbf{KIJKK}+\mathbf{KIKKJ}+\mathbf{KIKJK})\rangle\\ &= \frac{i}{30}\Big[(\mathbf{p}_{0j}\cdot\mathbf{r}_{jf}\times\mathbf{p}_{if})\mathbf{p}_{jf}\cdot\mathbf{p}_{0i} + (\mathbf{p}_{0j}\cdot\mathbf{r}_{jf}\times\mathbf{p}_{0i})\mathbf{p}_{jf}\cdot\mathbf{p}_{if}\\ &\quad -(\mathbf{r}_{jf}\cdot\mathbf{p}_{jf}\times\mathbf{p}_{if})\mathbf{p}_{0j}\cdot\mathbf{p}_{0i} - (\mathbf{r}_{jf}\cdot\mathbf{p}_{jf}\times\mathbf{p}_{0i})\mathbf{p}_{0j}\cdot\mathbf{p}_{if}\Big].\end{aligned} \tag{38}$$

These building blocks, which still have to be combined with the proper frequencies ($\nu_\lambda$, $\nu_\mu$) and denominators ($f_{\lambda\lambda}$, $f_{\lambda\mu}$, $f_{\mu\lambda}$, $f_{\mu\mu}$) can now be used to form the rotational average of Eq. (16),

$$\begin{aligned}\left\langle\delta_{\mathrm{L}}^{\mathrm{TPA}} - \delta_{\mathrm{R}}^{\mathrm{TPA}}\right\rangle = \frac{8\pi}{30c}\cdot B\cdot\Big[&\Big((\mathbf{p}_{jf}\cdot\mathbf{r}_{0j}\times\mathbf{p}_{if})\mathbf{p}_{0j}\cdot\mathbf{p}_{0i} + (\mathbf{p}_{jf}\cdot\mathbf{r}_{0j}\times\mathbf{p}_{0i})\mathbf{p}_{0j}\cdot\mathbf{p}_{if}\\ &-(\mathbf{r}_{0j}\cdot\mathbf{p}_{0j}\times\mathbf{p}_{if})\mathbf{p}_{jf}\cdot\mathbf{p}_{0i} - (\mathbf{r}_{0j}\cdot\mathbf{p}_{0j}\times\mathbf{p}_{0i})\mathbf{p}_{jf}\cdot\mathbf{p}_{if}\Big)(f_{\lambda\lambda}\nu_\lambda + f_{\lambda\mu}\nu_\mu + f_{\mu\lambda}\nu_\lambda + f_{\mu\mu}\nu_\mu)\\ &+\Big((\mathbf{p}_{0j}\cdot\mathbf{r}_{jf}\times\mathbf{p}_{if})\mathbf{p}_{jf}\cdot\mathbf{p}_{0i} + (\mathbf{p}_{0j}\cdot\mathbf{r}_{jf}\times\mathbf{p}_{0i})\mathbf{p}_{jf}\cdot\mathbf{p}_{if} - (\mathbf{r}_{jf}\cdot\mathbf{p}_{jf}\times\mathbf{p}_{if})\mathbf{p}_{0j}\cdot\mathbf{p}_{0i} - (\mathbf{r}_{jf}\cdot\mathbf{p}_{jf}\times\mathbf{p}_{0i})\mathbf{p}_{0j}\cdot\mathbf{p}_{if}\Big)\\ &\times(f_{\lambda\mu}\nu_\lambda + f_{\lambda\lambda}\nu_\mu + f_{\mu\mu}\nu_\lambda + f_{\lambda\mu}\nu_\mu)\Big].\end{aligned} \tag{39}$$

If we now use the following relations for the cross product terms:

$$\mathbf{r}_{0j}\cdot\mathbf{p}_{0j}\times\mathbf{p}_{if} = \mathbf{p}_{if}\cdot\mathbf{r}_{0j}\times\mathbf{p}_{0j}\ \mathbf{p}_{if}\cdot\mathbf{p}_{0j}\times\mathbf{r}_{0j} = -\mathbf{p}_{if}\cdot\mathbf{r}_{0j}\times\mathbf{p}_{0j}, \tag{40}$$

we can rewrite the equation as

$$\begin{aligned}\left\langle\delta_{\mathrm{L}}^{\mathrm{TPA}} - \delta_{\mathrm{R}}^{\mathrm{TPA}}\right\rangle = \frac{8\pi}{30c}\cdot B\cdot\Big[&\Big(-\mathbf{p}_{0i}\cdot(\mathbf{pr})_{0j}\times\mathbf{p}_{jf}\cdot\mathbf{p}_{0i} - \mathbf{p}_{if}\cdot(\mathbf{pr})_{0j}\times\mathbf{p}_{jf}\cdot\mathbf{p}_{0i}\\ &+(\mathbf{p}_{if}\cdot\mathbf{p}_{0j}\times\mathbf{r}_{0j})\mathbf{p}_{jf}\cdot\mathbf{p}_{0i} + (\mathbf{p}_{0i}\cdot\mathbf{p}_{0j}\times\mathbf{r}_{0j})\mathbf{p}_{jf}\cdot\mathbf{p}_{if}\Big)(f_{\lambda\lambda}\nu_\lambda + f_{\lambda\mu}\nu_\mu + f_{\mu\lambda}\nu_\lambda + f_{\mu\mu}\nu_\mu)\\ &+\Big(-\mathbf{p}_{0i}\cdot(\mathbf{pr})_{jf}\times\mathbf{p}_{0j}\cdot\mathbf{p}_{if} - \mathbf{p}_{if}\cdot(\mathbf{pr})_{jf}\times\mathbf{p}_{0j}\cdot\mathbf{p}_{0i} + (\mathbf{p}_{if}\cdot\mathbf{p}_{jf}\times\mathbf{r}_{jf})\mathbf{p}_{0j}\cdot\mathbf{p}_{0i} + (\mathbf{p}_{0i}\cdot\mathbf{p}_{jf}\times\mathbf{r}_{jf})\mathbf{p}_{0j}\cdot\mathbf{p}_{if}\Big)\\ &\times(f_{\lambda\mu}\nu_\lambda + f_{\lambda\lambda}\nu_\mu + f_{\mu\mu}\nu_\lambda + f_{\lambda\mu}\nu_\mu)\Big],\end{aligned} \tag{41}$$

where (**pr**) denotes a tensor product. This is Eq. (11) in Ref. 1. The notation with the colon in Ref. 1 is the same as used here and yields, e.g.,

$$\mathbf{p}_{0i}\cdot(\mathbf{pr})_{0j}\times\mathbf{p}_{jf}\cdot\mathbf{p}_{if} = (\mathbf{pr})_{0j}\times\mathbf{p}_{jf} : \mathbf{p}_{0i}\mathbf{p}_{if}. \tag{42}$$

Depending on the experimental setup, other polarizations and propagation directions can be involved, e.g., antiparallel and perpendicular propagation as well as combinations of linear and circular polarization. Derivations for these combinations can be carried out in the same manner as outlined here. Results are shown in Ref. 1.

## III. DERIVATION OF TRANSITION POLARIZABILITIES

After deriving the fundamental expressions for TPCD, Tinoco reformulates them to "transition polarizabilities." In this transformation, the two identities,

$$(\mathbf{pr}+\mathbf{rp})_{0i} = \frac{2\pi i m}{e}\nu_{0i}\mathbf{Q}_{0i}, \tag{43}$$

$$(\mathbf{pr}-\mathbf{rp})_{0i} = \frac{2mc}{e}(\mathbf{I}\times\mathbf{m}_{0i}), \tag{44}$$

are used which in my opinion requires a short explanation. These identities are used to express the operator $(\mathbf{pr})_{0i}$ according to

$$(\mathbf{pr})_{0i} = \frac{m_e}{e}\frac{(\mathbf{pr}+\mathbf{rp})_{0i} - i(\mathbf{pr}-\mathbf{rp})_{0i}}{2}. \tag{45}$$

This enables the treatment of the non-Hermitian operator $(\mathbf{pr})_{0i}$ in terms of Hermitian operators. It is important to note that the operator $(\mathbf{p}\times\mathbf{r})_{0i}$ solely enters the magnetic dipole contributions to the transition polarizabilities but that the operator $(\mathbf{pr})_{0i}$ contributes to both the magnetic dipole and the electric quadrupole transition polarizabilities.

## IV. ERROR CORRECTIONS

For the sake of completeness, I will provide two minor error corrections in this section. Tinoco has acknowledged misprints in the original paper, namely, in Eq. (17) and in the non-numbered equation between Eqs. (16) and (17). The non-numbered equation is a tensor and therefore, the dot after $\mathbf{p}_{if}$ has to be removed. The correct equation then reads

$$\beta_{0f} = \sum_i \frac{\mathbf{p}_{0i}(\mathbf{p}\times\mathbf{r})_{if} + \mathbf{p}_{if}(\mathbf{p}\times\mathbf{r})_{0i}}{\nu_{0i}-\nu}. \tag{46}$$

In contrast to this, Eq. (17) in Ref. 1 is a scalar and therefore needs a dot after $\mathbf{p}_{if}$. It therefore reads

$$\beta_{0f} = \sum_i \frac{\mathbf{p}_{0i}\cdot(\mathbf{p}\times\mathbf{r})_{if} + \mathbf{p}_{if}\cdot(\mathbf{p}\times\mathbf{r})_{0i}}{\nu_{0i}-\nu}. \tag{47}$$

Furthermore, it has to be noted that it is difficult to distinguish between bold and normal symbols in the electronic form of Ref. 1 due to the digitalization. Bold symbols represent tensors while normal symbols represent scalars. In Eq. (14) of Ref. 1, the two last terms are scalars while the others are tensors which are contracted together. The first equation in Eq. (16) of Ref. 1 is a tensor, while the second one is a scalar. Eqs. (18) and (19) of Ref. 1 are both tensors.

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