A geometric approach to decoding molecular structure and dynamics from photoionization of isotropic samples - Electronic Supplementary Information

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A Real spherical harmonics

The real spherical harmonics (with tilde) are defined in terms of the complex spherical harmonics (without tilde) according to

$$\tilde{Y}_l^m = \begin{cases} \sqrt{2}\,(-1)^m \,\mathrm{Im}\left\{Y_l^{|m|}\right\}, & m<0, \\ Y_l^0 & m=0, \\ \sqrt{2}\,(-1)^m \,\mathrm{Re}\left\{Y_l^{|m|}\right\}, & m>0, \end{cases} \tag{A.1}$$

and satisfy the orthonormality relation

$$\int \mathrm{d}\Omega\, \tilde{Y}_l^m \tilde{Y}_\lambda^\mu = \delta_{l,\lambda}\delta_{m,\mu}. \tag{A.2}$$

For an arbitrary function W, the relation between the coefficients of the real and the complex spherical harmonics can be derived from

$$W = \sum_{l,m} b_{l,m} Y_l^m = \sum_{l,m} \tilde{b}_{l,m} \tilde{Y}_l^m \tag{A.3}$$

and yields

$$\tilde{b}_{l,m} = \begin{cases} -(-1)^m \sqrt{2}\mathrm{Im}\left\{b_{l,|m|}\right\}, & m<0, \\ b_{l,m}, & m=0, \\ (-1)^m \sqrt{2}\mathrm{Re}\left\{b_{l,m}\right\}, & m>0. \end{cases} \tag{A.4}$$

B Derivation of the $\tilde{b}_{l,m}$ coefficients in one-photon-ionization

According to Eqs. (5) and (11), and following Ref. [1] for the orientation averaging, we obtain

$$\begin{aligned} b_{0,0}^{(1)} &= \left|A^{(1)}\right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \, Y_0^0(\hat{k}^{\mathrm{L}}) \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right), \\ &= \frac{\left|A^{(1)}\right|^2}{\sqrt{4\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right), \\ &= \frac{\left|A^{(1)}\right|^2}{3\sqrt{4\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \left|\vec{D}^{\mathrm{M}}\right|^2 \left|\vec{F}^{\mathrm{L}}\right|^2. \end{aligned} \tag{B.1}$$

$$\begin{aligned} b_{1,0}^{(1)} &= \left|A^{(1)}\right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \, Y_1^0(\hat{k}^{\mathrm{L}}) \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right), \\ &= \left|A^{(1)}\right|^2 \sqrt{\frac{3}{4\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right) \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right), \\ &= \left|A^{(1)}\right|^2 \frac{1}{6} \sqrt{\frac{3}{4\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \left[\hat{k}^{\mathrm{M}} \cdot \left(\vec{D}^{\mathrm{M}*} \times \vec{D}^{\mathrm{M}}\right)\right] \left[\hat{z}^{\mathrm{L}} \cdot \left(\vec{F}^{\mathrm{L}*} \times \vec{F}^{\mathrm{L}}\right)\right]. \end{aligned} \tag{B.2}$$

$$\begin{aligned} b_{2,0}^{(1)} &= \left|A^{(1)}\right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \, Y_2^0(\hat{k}^{\mathrm{L}}) \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right), \\ &= \left|A^{(1)}\right|^2 \frac{1}{4} \sqrt{\frac{5}{\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left[3\left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right)^2 - 1\right] \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) \\ &= \left|A^{(1)}\right|^2 \frac{3}{4} \sqrt{\frac{5}{\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right)^2 \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) - \sqrt{\frac{5}{4}} b_{0,0}^{(1)}, \end{aligned} \tag{B.3}$$

For the remaining integral over orientations in $b_{2,0}^{(1)}$ we have

$$\int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right)^2 \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) = \vec{g}^{(4)} \cdot M^{(4)} \vec{f}^{(4)} \tag{B.4}$$

where

$$\vec{g}^{(4)} = \begin{bmatrix} (\hat{k}^{\mathrm{M}} \cdot \vec{k}^{\mathrm{M}})(\vec{D}^{\mathrm{M}*} \cdot \vec{D}^{\mathrm{M}}) \\ (\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}*})(\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}) \\ (\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}})(\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}*}) \end{bmatrix} = \begin{bmatrix} |\vec{D}^{\mathrm{M}}|^2 \\ |\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}|^2 \\ |\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}|^2 \end{bmatrix} \tag{B.5}$$

$$M^{(4)} = \frac{1}{30} \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \tag{B.6}$$

$$\vec{f}^{(4)} = \begin{bmatrix} \left(\hat{z}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right)\left(\vec{F}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}}\right) \\ (\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}*})(\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}) \\ (\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}})(\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}*}) \end{bmatrix} = \begin{bmatrix} |\vec{F}^{\mathrm{L}}|^2 \\ |\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}|^2 \\ |\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}|^2 \end{bmatrix} \tag{B.7}$$

Replacing Eqs. (B.5), (B.6), (B.7) in Eq. (B.4) we get

$$\begin{aligned} &\int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right)^2 \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right)\left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) \\ &\qquad = \frac{1}{15}\left\{\left[2\left|\vec{D}^{\mathrm{M}}\right|^2 - \left|\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}\right|^2\right]\left|\vec{F}^{\mathrm{L}}\right|^2 - \left[\left|\vec{D}^{\mathrm{M}}\right|^2 - 3\left|\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}\right|^2\right]\left|\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right|^2\right\}, \end{aligned} \tag{B.8}$$

and replacing Eq. (B.8) in Eq. (B.3) we arrive to the rather symmetric result

$$b_{2,0}^{(1)} = \frac{\left|A^{(1)}\right|^2}{12\sqrt{5\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \left(3\left|\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}\right|^2 - \left|\vec{D}^{\mathrm{M}}\right|^2\right)\left(3\left|\hat{z}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right|^2 - \left|\vec{F}^{\mathrm{L}}\right|^2\right) \tag{B.9}$$

Similarly, by replacing $\hat{z}^{\mathrm{L}}$ by either $\hat{x}^{\mathrm{L}}$ or $\hat{y}^{\mathrm{L}}$ in Eq. (B.8) we obtain

$$\begin{aligned} \tilde{b}_{2,2}^{(1)} &= \left|A^{(1)}\right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho\, \tilde{Y}_2^2(\hat{k}^{\mathrm{L}}) \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right)\left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right), \\ &= \left|A^{(1)}\right|^2 \frac{1}{4}\sqrt{\frac{15}{\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left[\left(\hat{k}^{\mathrm{L}} \cdot \hat{x}^{\mathrm{L}}\right)^2 - \left(\hat{k}^{\mathrm{L}} \cdot \hat{y}^{\mathrm{L}}\right)^2\right]\left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right)\left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) \\ &= \left|A^{(1)}\right|^2 \frac{1}{4\sqrt{15\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \left[3\left|\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}\right|^2 - \left|\vec{D}^{\mathrm{M}}\right|^2\right]\left[\left|\hat{x}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right|^2 - \left|\hat{y}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right|^2\right]. \end{aligned} \tag{B.10}$$

Finally,

$$\begin{aligned} \tilde{b}_{2,-2}^{(1)}(k) &= \left|A^{(1)}\right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho\, \tilde{Y}_2^{-2}(\hat{k}^{\mathrm{L}}) \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right)\left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right), \\ &= \left|A^{(1)}\right|^2 \frac{1}{2}\sqrt{\frac{15}{\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{x}^{\mathrm{L}}\right)\left(\hat{k}^{\mathrm{L}} \cdot \hat{y}^{\mathrm{L}}\right)\left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right)\left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) \\ &= \left|A^{(1)}\right|^2 \frac{1}{2}\sqrt{\frac{15}{\pi}} \int \mathrm{d}\Omega_k^{\mathrm{M}} \frac{1}{30}\left[3|\hat{k}^{\mathrm{M}} \cdot \vec{D}^{\mathrm{M}}|^2 - |\vec{D}^{\mathrm{M}}|^2\right]\left[(\hat{x}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}*})(\hat{y}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}) + \mathrm{c.c.}\right] \\ &= 0 \end{aligned} \tag{B.11}$$

where the last equality follows from assuming that the field is either elliptically polarized in the xy plane or linearly polarized along z.

C Range of values of $b_{1,0}$ in one-photon PECD

From Eq. (25) and the fact that $T_\pm \geq 0$ it follows that $1 \pm \sigma\beta_1^{(1)} + \beta_2^{(1)} \geq 0$, which in particular means that $1 - |\beta_1^{(1)}| + \beta_2^{(1)} \geq 0$ and yields Eq. (24).

D Derivation of the $b_{0,0}$, $b_{1,0}$, and $b_{3,0}$ coefficients in two-photon PECD

From Eq. (9) we have that

$$b_{0,0}^{(2)} = \frac{1}{\sqrt{4\pi}} \left|A^{(2)}\right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left|\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right|^2 \left|\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right|^2, \tag{D.1}$$

where we use the shorthand notation $\vec{D}^{\mathrm{L}} \equiv \vec{d}^{\mathrm{L}}_{\vec{k}^{\mathrm{M}},1}$, $\vec{d}^{\mathrm{L}} \equiv \vec{d}^{\mathrm{L}}_{1,0}$, and $\vec{F}^{\mathrm{L}} \equiv \vec{F}^{\mathrm{L}}_{\omega_L}$. The orientation averaging can be performed following Ref. [1],

$$\int \mathrm{d}\varrho \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right)^* \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) \left(\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right)^* \left(\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) = \vec{g}^{(4)} \cdot M^{(4)} \vec{f}^{(4)}, \tag{D.2}$$

where[1]

$$\vec{g}^{(4)} = \begin{bmatrix} |\vec{D}^{\mathrm{M}}|^2 d^2 \\ |\vec{D}^{\mathrm{M}} \cdot \vec{d}^{\mathrm{M}}|^2 \\ |\vec{D}^{\mathrm{M}} \cdot \vec{d}^{\mathrm{M}}|^2 \end{bmatrix}, \tag{D.3}$$

$$\vec{f}^{(4)} = \begin{bmatrix} |\vec{F}^{\mathrm{L}}|^4 \\ |(\vec{F}^{\mathrm{L}})^2|^2 \\ |\vec{F}^{\mathrm{L}}|^4 \end{bmatrix}, \tag{D.4}$$

$M^{(4)}$ is given by Eq. (B.6). Replacing Eqs. (B.6), (D.2)-(D.4) in Eq. (D.1) yields

$$\begin{aligned} b_{0,0}^{(2)} = \frac{1}{\sqrt{4\pi}} \left|A^{(2)}\right|^2 \frac{1}{30} \int \mathrm{d}\Omega_k^{\mathrm{M}} \Big\{ &\left[|\vec{D}^{\mathrm{M}} \cdot \vec{d}^{\mathrm{M}}|^2 + 3|\vec{D}^{\mathrm{M}}|^2 d^2\right] |\vec{F}^{\mathrm{L}}|^4. \\ &+ \left[3|\vec{D}^{\mathrm{M}} \cdot \vec{d}^{\mathrm{M}}|^2 - |\vec{D}^{\mathrm{M}}|^2 d^2\right] |(\vec{F}^{\mathrm{L}})^2|^2 \Big\} \end{aligned} \tag{D.5}$$

This expression is valid for arbitrary $\vec{d}^{\mathrm{M}}$ and arbitrary polarization. If we choose the molecular frame so that $\vec{d}^{\mathrm{M}} = d\hat{z}^{\mathrm{M}}$, we focus on the case of circular polarization $\vec{F}^{\mathrm{L}} = F\left(\hat{x}^{\mathrm{L}} + i\sigma\hat{y}^{\mathrm{L}}\right)/\sqrt{2}$, and use the definition (32), Eq. (D.5) reduces to Eq. (28).

[1] In the absence of magnetic fields $\vec{d}^{\mathrm{M}}$ can be taken real.

Similarly, for the case of $b_{1,0}^{(2)}$ we get [see Eq. (9)]

$$b_{1,0}^{(2)} = \sqrt{\frac{3}{4\pi}} \left| A^{(2)} \right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}} \right) \left| \vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}} \right|^2 \left| \vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}} \right|^2 . \tag{D.6}$$

The integral over orientations ϱ reads as

$$\int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}} \right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}} \right)^* \left(\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}} \right)^* \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}} \right) \left(\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}} \right) = \vec{g}^{(5)} \cdot M^{(5)} \vec{f}^{(5)}, \tag{D.7}$$

where[2]

$$\vec{g}^{(5)} = \begin{pmatrix} \left[\hat{k} \cdot \left(\vec{D}^* \times \vec{d} \right) \right] \left(\vec{D} \cdot \vec{d} \right) \\ \left[\hat{k} \cdot \left(\vec{D}^* \times \vec{D} \right) \right] d^2 \\ \left[\hat{k} \cdot \left(\vec{D}^* \times \vec{d} \right) \right] \left(\vec{D} \cdot \vec{d} \right) \\ \left[\hat{k} \cdot \left(\vec{d} \times \vec{D} \right) \right] \left(\vec{D}^* \cdot \vec{d} \right) \\ 0 \\ \left[\hat{k} \cdot \left(\vec{D} \times \vec{d} \right) \right] \left(\vec{D}^* \cdot \vec{d} \right) \end{pmatrix}, \qquad \vec{f}^{(5)} = \left[\hat{z} \cdot \left(\vec{F}^* \times \vec{F} \right) \right] \left| \vec{F} \right|^2 \begin{pmatrix} 0 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \end{pmatrix}, \tag{D.8}$$

$$M^{(5)} = \frac{1}{30} \begin{pmatrix} 3 & -1 & -1 & 1 & 1 & 0 \\ -1 & 3 & -1 & -1 & 0 & 1 \\ -1 & -1 & 3 & 0 & -1 & -1 \\ 1 & -1 & 0 & 3 & -1 & 1 \\ 1 & 0 & -1 & -1 & 3 & -1 \\ 0 & 1 & -1 & 1 & -1 & 3 \end{pmatrix}. \tag{D.9}$$

Since $M^{(5)} \vec{f}^{(5)} = \vec{f}^{(5)}$, then

$$\begin{aligned} \vec{g}^{(5)} \cdot M^{(5)} \vec{f}^{(5)} = \frac{1}{30} & \left\{ \left[\hat{k} \cdot \left(\vec{D}^* \times \vec{D} \right) \right] d^2 + \left[\hat{k} \cdot \left(\vec{D}^* \times \vec{d} \right) \right] \left(\vec{D} \cdot \vec{d} \right) + \left[\hat{k} \cdot \left(\vec{d} \times \vec{D} \right) \right] \left(\vec{D}^* \cdot \vec{d} \right) \right\} \\ & \times \left\{ \left[\hat{z} \cdot \left(\vec{F}^* \times \vec{F} \right) \right] \left| \vec{F} \right|^2 \right\} \end{aligned} \tag{D.10}$$

With the help of some vector algebra the second and third terms can be rewritten as

$$\left[\hat{k} \cdot \left(\vec{D}^* \times \vec{d} \right) \right] \left(\vec{D} \cdot \vec{d} \right) - \left[\hat{k} \cdot \left(\vec{D} \times \vec{d} \right) \right] \left(\vec{D}^* \cdot \vec{d} \right) = d^2 \left[\hat{k} - \left(\hat{k} \cdot \hat{d} \right) \hat{d} \right] \cdot \left(\vec{D}^* \times \vec{D} \right). \tag{D.11}$$

Replacing Eqs. (D.7)-(D.11) in Eq. (D.6) yields

[2] For the moment we omit the M superscript on $\vec{k}$, $\vec{D}$, $\vec{D}^*$, and $\vec{d}$; and the superscript L on $\hat{z}$, $\vec{F}$, and $\vec{F}^*$.

$$b_{1,0}^{(2)} = \sqrt{\frac{3}{4\pi}} \left|A^{(2)}\right|^2 \frac{d^2 \left|\vec{F}\right|^2}{30} \int \mathrm{d}\Omega_k^{\mathrm{M}} \left\{ \left[2\hat{k} - \left(\hat{k}\cdot\hat{d}\right)\hat{d}\right] \cdot \left(\vec{D}^* \times \vec{D}\right) \right\} \left\{ \left[\hat{z} \cdot \left(\vec{F}^* \times \vec{F}\right)\right] \right\}. \tag{D.12}$$

This expression is valid for arbitrary orientations of $\vec{d}^{\mathrm{M}}$ and arbitrary polarization. If we choose the molecular frame so that $\vec{d}^{\mathrm{M}} = d\hat{z}^{\mathrm{M}}$, focus on the case of circular polarization $\vec{F}^{\mathrm{L}} = F\left(\hat{x}^{\mathrm{L}} + i\sigma\hat{y}^{\mathrm{L}}\right)/\sqrt{2}$, and use definitions (33) and (35), Eq. (D.12) reduces to Eqs. (29) and (30)

Finally, for $b_{3,0}^{(2)}$ we get [see Eq. (9)]

$$\begin{aligned} b_{3,0}^{(2)} = {} & \frac{5}{4}\sqrt{\frac{7}{\pi}} \left|A^{(2)}\right|^2 \int \mathrm{d}\Omega_k^{\mathrm{M}} \int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right)^3 \left|\left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right)\right|^2 \left|\left(\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right)\right|^2 \\ & - \frac{3}{4}\sqrt{\frac{7}{\pi}}\sqrt{\frac{4\pi}{3}} b_{1,0}^{(2)} \end{aligned} \tag{D.13}$$

The orientation integral in the first term reads as

$$\int \mathrm{d}\varrho \left(\hat{k}^{\mathrm{L}} \cdot \hat{z}^{\mathrm{L}}\right)^3 \left(\vec{D}^{\mathrm{L}*} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}*}\right) \left(\vec{D}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) \left(\vec{d}^{\mathrm{L}} \cdot \vec{F}^{\mathrm{L}}\right) = \vec{g}^{(7)} \cdot M^{(7)} \vec{f}^{(7)} \tag{D.14}$$

From table III in Ref. [1] we see that $f_i^{(7)} = g_i^{(7)} = 0$ for $1 \le i \le 27$. For $28 \le i \le 36$ we get[3]

$$\vec{g}^{(7)} = \begin{bmatrix} \left[\hat{k}\cdot\left(\vec{D}^*\times\vec{d}\right)\right]\left(\hat{k}\cdot\hat{k}\right)\left(\vec{D}\cdot\vec{d}\right) \\ \left[\hat{k}\cdot\left(\vec{D}^*\times\vec{d}\right)\right]\left(\hat{k}\cdot\vec{d}\right)\left(\hat{k}\cdot\vec{D}\right) \\ \left[\hat{k}\cdot\left(\vec{D}^*\times\vec{D}\right)\right]\left(\hat{k}\cdot\hat{k}\right)\left(\vec{d}\cdot\vec{d}\right) \\ \left[\hat{k}\cdot\left(\vec{D}^*\times\vec{D}\right)\right]\left(\hat{k}\cdot\vec{d}\right)\left(\hat{k}\cdot\vec{d}\right) \\ \left[\hat{k}\cdot\left(\vec{D}^*\times\vec{d}\right)\right]\left(\hat{k}\cdot\hat{k}\right)\left(\vec{d}\cdot\vec{D}\right) \\ \left[\hat{k}\cdot\left(\vec{D}^*\times\vec{d}\right)\right]\left(\hat{k}\cdot\vec{D}\right)\left(\hat{k}\cdot\vec{d}\right) \\ \left[\hat{k}\cdot\left(\vec{d}\times\vec{D}\right)\right]\left(\hat{k}\cdot\hat{k}\right)\left(\vec{D}^*\cdot\vec{d}\right) \\ 0 \\ \left[\hat{k}\cdot\left(\vec{D}\times\vec{d}\right)\right]\left(\hat{k}\cdot\hat{k}\right)\left(\vec{D}^*\cdot\vec{d}\right) \end{bmatrix} \equiv \begin{bmatrix} g_1 \\ g_2 \\ g_3 \\ g_4 \\ g_1 \\ g_2 \\ -g_1^* \\ 0 \\ g_1^* \end{bmatrix} \tag{D.15}$$

[3] For the moment we omit the M superscript on $\vec{k}$, $\vec{D}$, $\vec{D}^*$, and $\vec{d}$; and the superscript L on $\hat{z}$, $\vec{F}$, and $\vec{F}^*$.

$$\vec{f}^{(7)} = \begin{bmatrix} 0 \\ 0 \\ \left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right](\hat{z}\cdot\hat{z})\left(\vec{F}^*\cdot\vec{F}\right) \\ \left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right]\left(\hat{z}\cdot\vec{F}\right)\left(\hat{z}\cdot\vec{F}^*\right) \\ \left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right](\hat{z}\cdot\hat{z})\left(\vec{F}^*\cdot\vec{F}\right) \\ \left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right]\left(\hat{z}\cdot\vec{F}\right)\left(\hat{z}\cdot\vec{F}^*\right) \\ \left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right](\hat{z}\cdot\hat{z})\left(\vec{F}^*\cdot\vec{F}\right) \\ \left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right](\hat{z}\cdot\hat{z})\left(\vec{F}^*\cdot\vec{F}\right) \\ 0 \end{bmatrix} = \left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right]\begin{bmatrix} 0 \\ 0 \\ \left|\vec{F}\right|^2 \\ \left|F_z\right|^2 \\ \left|\vec{F}\right|^2 \\ \left|F_z\right|^2 \\ \left|\vec{F}\right|^2 \\ \left|\vec{F}\right|^2 \\ 0 \end{bmatrix} \tag{D.16}$$

The relevant part of $M^{(7)}$ in Ref. [1] reads as

$$M^{(7)} = \frac{1}{420}\begin{bmatrix} 51 & -33 & -21 & 15 & -21 & 15 & 18 & 18 & 0 \\ -33 & 45 & 15 & -15 & 15 & -15 & -12 & -12 & 0 \\ -21 & 15 & 51 & -33 & -21 & 15 & -18 & 0 & 18 \\ 15 & -15 & -33 & 45 & 15 & -15 & 12 & 0 & -12 \\ -21 & 15 & -21 & 15 & 51 & -33 & 0 & -18 & -18 \\ 15 & -15 & 15 & -15 & -33 & 45 & 0 & 12 & 12 \\ 18 & -12 & -18 & 12 & 0 & 0 & 30 & -6 & 6 \\ 18 & -12 & 0 & 0 & -18 & 12 & -6 & 30 & -6 \\ 0 & 0 & 18 & -12 & -18 & 12 & 6 & -6 & 30 \end{bmatrix}, \tag{D.17}$$

therefore

$$\vec{g}^{(7)}\cdot M^{(7)}\vec{f}^{(7)} = \frac{1}{70}\left[(2i\mathrm{Im}\{g_1\}+2g_3-g_4)\,|F|^2 + (4i\mathrm{Im}\{g_1\}-3g_3+5g_4)\,|F_z|^2\right]\left[\hat{z}\cdot\left(\vec{F}^*\times\vec{F}\right)\right]. \tag{D.18}$$

Equations (D.12), (D.13), (D.14), and (D.18) yield

$$b^{(2)}_{3,0} = \frac{1}{4}\sqrt{\frac{7}{\pi}}\left|A^{(2)}\right|^2\frac{1}{70}\int \mathrm{d}\Omega^{\mathrm{M}}_k d^2\left\{\left[\left(1-5\left(\hat{k}\cdot\hat{d}\right)^2\right)\hat{k}+2\left(\hat{k}\cdot\hat{d}\right)\hat{d}\right]\cdot\left(\vec{D}^*\times\vec{D}\right)\right\}$$
$$\times\left\{\left[\hat{z}^{\mathrm{L}}\cdot\left(\vec{F}^{\mathrm{L}*}\times\vec{F}^{\mathrm{L}}\right)\right]\left(\left|\vec{F}^{\mathrm{L}}\right|^2-5\left|F^{\mathrm{L}}_z\right|^2\right)\right\} \tag{D.19}$$

This expression is valid for arbitrary orientations of $\vec{d}^{\mathrm{M}}$ and arbitrary polarization. If we choose the molecular frame so that $\vec{d}^{\mathrm{M}} = d\hat{z}^{\mathrm{M}}$, we focus on the case of circular polarization $\vec{F}^{\mathrm{L}} = F\left(\hat{x}^{\mathrm{L}}+i\sigma\hat{y}^{\mathrm{L}}\right)/\sqrt{2}$, and we use definition (36), Eq. (D.19) reduces to Eq. (31).

E Derivation of $b'^{(2)}_{1,0}$

Analogously to Eq. (27), the $b'^{(2)}_{1,0}$ coefficient corresponding to the process where the first photon is linearly polarized along $\hat{z}^{\rm L}$ and the second photon is circularly polarized in the $\hat{x}^{\rm L}\hat{y}^{\rm L}$ plane is given by

$$b'^{(2)}_{1,0}(k) = |A^{(2)}|^2 d^2 |F|^2 \int {\rm d}\Omega_k^{\rm M} \int {\rm d}\varrho \, Y_1^0(\hat{k}^{\rm L}) \cos^2\beta |\vec{D}^{\rm L} \cdot \vec{F}^{\rm L}|^2 \tag{E.1}$$

where we have added a prime in order to distinguish it from the $b^{(2)}_{1,0}$ coefficient in Eq. (29), and we have $\vec{F}_1^{\rm L} = F\hat{z}^{\rm L}$ and $\vec{F}_2^{\rm L} = F(\hat{x}^{\rm L} + i\sigma\hat{y}^{\rm L})/\sqrt{2}$. Using Eqs. (27) and (E.1) we obtain

$$\begin{aligned} 2b^{(2)}_{1,0} + b'^{(2)}_{1,0}(k) &= |A^{(2)}|^2 d^2 |F|^2 \int {\rm d}\Omega_k^{\rm M} \int {\rm d}\varrho \, Y_1^0(\hat{k}^{\rm L}) |\vec{D}^{\rm L} \cdot \vec{F}_2^{\rm L}|^2 \\ &= |A^{(2)}|^2 d^2 |F|^4 \frac{\sigma}{6} \sqrt{\frac{3}{4\pi}} \int {\rm d}\Omega_k^{\rm M} \, \hat{k}^{\rm M} \cdot \vec{B}^{\rm M} \\ &= \frac{C\sigma}{2\sqrt{3}} \mathcal{B}^Y_{0,0} \end{aligned} \tag{E.2}$$

where in the second line we solved the integral over orientations as in Eq. (B.2) and in the third line we used $\vec{Y}_{0,0}(\hat{k}) = \hat{k}/\sqrt{4\pi}$, Eq. (39) and the orthonormality of the spherical harmonics. Using Eq. (40) for $b^{(2)}_{1,0}$ yields Eq. (42).

References

[1] D. L. Andrews and T. Thirunamachandran. On three-dimensional rotational averages. *The Journal of Chemical Physics*, 67(11):5026–5033, December 1977.