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

$$
\tilde{Y}_m^l = \begin{cases} 
\sqrt{2} (-1)^m \text{Im} \{Y_{|m|}^l\}, & m < 0, \\
Y_0^0, & m = 0, \\
\sqrt{2} (-1)^m \text{Re} \{Y_{|m|}^l\}, & m > 0,
\end{cases}
$$

(A.1)

and satisfy the orthonormality relation

$$
\int d\Omega \tilde{Y}_m^l \tilde{Y}_\lambda^\mu = \delta_{l,\lambda} \delta_{m,\mu}.
$$

(A.2)

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

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

(A.3)

and yields

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

(A.4)
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

$$b^{(1)}_{0,0} = |A^{(1)}|^2 \int d\Omega_k^M \int d\varrho \ Y^0_0(\hat{k}_L) \left( \vec{B}^{L*} \cdot \vec{F}^L \right) \left( \vec{B}^L \cdot \vec{F}^L \right),$$

$$= \frac{|A^{(1)}|^2}{\sqrt{4\pi}} \int d\Omega_k^M \int d\varrho \ \left( \vec{B}^{L*} \cdot \vec{F}^L \right) \left( \vec{B}^L \cdot \vec{F}^L \right),$$

$$= \frac{|A^{(1)}|^2}{3\sqrt{4\pi}} \int d\Omega_k^M \left| \vec{D}_M \right|^2 \left| \vec{F}_L \right|^2. \quad (B.1)$$

$$b^{(1)}_{1,0} = |A^{(1)}|^2 \int d\Omega_k^M \int d\varrho \ Y^0_1(\hat{k}_L) \left( \vec{B}^{L*} \cdot \vec{F}^L \right) \left( \vec{B}^L \cdot \vec{F}^L \right),$$

$$= \frac{|A^{(1)}|^2}{\sqrt{4\pi}} \int d\Omega_k^M \int d\varrho \ \left( \hat{k}_L \cdot \hat{z}_L \right) \left( \vec{B}^{L*} \cdot \vec{F}^L \right) \left( \vec{B}^L \cdot \vec{F}^L \right),$$

$$= \frac{|A^{(1)}|^2}{6} \frac{3}{4\pi} \int d\Omega_k^M \left[ \vec{k}_M \cdot \left( \vec{D}_M \times \vec{D}_M \right) \right] \left[ \hat{z}_L \cdot \left( \vec{F}_L \times \vec{F}_L \right) \right]. \quad (B.2)$$

$$b^{(1)}_{2,0} = |A^{(1)}|^2 \int d\Omega_k^M \int d\varrho \ Y^0_2(\hat{k}_L) \left( \vec{B}^{L*} \cdot \vec{F}^L \right) \left( \vec{B}^L \cdot \vec{F}^L \right),$$

$$= \frac{|A^{(1)}|^2}{\sqrt{4\pi}} \int d\Omega_k^M \int d\varrho \ \left[ 3 \left( \hat{k}_L \cdot \hat{z}_L \right)^2 - 1 \right] \left( \vec{B}^{L*} \cdot \vec{F}^L \right) \left( \vec{B}^L \cdot \vec{F}^L \right),$$

$$= \frac{|A^{(1)}|^2}{3\sqrt{4\pi}} \int d\Omega_k^M \int d\varrho \ \left( \hat{k}_L \cdot \hat{z}_L \right)^2 \left( \vec{B}^{L*} \cdot \vec{F}^L \right) \left( \vec{B}^L \cdot \vec{F}^L \right) - \sqrt{\frac{5}{4}} b^{(1)}_{0,0}. \quad (B.3)$$

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

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

where

$$\vec{g}^{(4)} = \begin{bmatrix} (\hat{k}_M \cdot \vec{k}_M)(\vec{D}_M) \cdot \vec{D}_M \cr (\hat{k}_M \cdot \vec{D}_M)(\vec{k}_M) \cdot \vec{D}_M \cr (\vec{k}_M \cdot \vec{D}_M)(\vec{k}_M) \cdot \vec{D}_M \end{bmatrix} = \begin{bmatrix} |\vec{D}_M|^2 \cr |\vec{k}_M \cdot \vec{D}_M|^2 \cr |\vec{k}_M \cdot \vec{D}_M|^2 \end{bmatrix} \quad (B.5)$$

$$M^{(4)} = \frac{1}{30} \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \quad (B.6)$$
Replacing Eqs. (B.5), (B.6), (B.7) in Eq. (B.4) we get

\[ \int d\varphi \left( \hat{k} \cdot \hat{z} \right)^2 \left( \vec{B}^{L*} \cdot \vec{F}^{L*} \right) \left( \vec{B}^L \cdot \vec{F}^L \right) = \frac{1}{15} \left\{ 2 \left| \vec{B}^M \right|^2 - \left| \vec{k} \cdot \vec{B}^M \right|^2 \left| \vec{F}^L \right|^2 - \left[ \left| \vec{B}^M \right|^2 - \left| \vec{k} \cdot \vec{B}^M \right|^2 \right] \left| \hat{z} \cdot \vec{F}^L \right|^2 \right\}, \tag{B.8} \]

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

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

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

\[ \tilde{b}_{2,2}^{(1)} = |A^{(1)}|^2 \int \frac{d\Omega_k^M}{4 \sqrt{15 \pi}} \int d\varphi \hat{Y}_2^{-1} \left( \hat{k} \cdot \hat{x} \right)^2 \left( \vec{B}^{L*} \cdot \vec{F}^{L*} \right) \left( \vec{B}^L \cdot \vec{F}^L \right), \]

\[ = |A^{(1)}|^2 \frac{1}{4} \sqrt{15 \pi} \int d\Omega_k^M \int d\varphi \left[ \left( \hat{k} \cdot \hat{x} \right)^2 - \left( \hat{k} \cdot \hat{y} \right)^2 \right] \left( \vec{B}^{L*} \cdot \vec{F}^{L*} \right) \left( \vec{B}^L \cdot \vec{F}^L \right), \]

\[ = |A^{(1)}|^2 \frac{1}{4} \sqrt{15 \pi} \int d\Omega_k^M \left[ 3 \left| \vec{k} \cdot \vec{B}^M \right|^2 - \left| \vec{B}^M \right|^2 \right] \left( \hat{z} \cdot \vec{F}^L \right)^2 - \left| \vec{F}^L \right|^2 \right]. \tag{B.10} \]

Finally,

\[ \tilde{b}_{2,-2}^{(1)} (k) = |A^{(1)}|^2 \int d\Omega_k^M \int d\varphi \hat{Y}_2^{-1} \left( \hat{k} \cdot \hat{y} \right)^2 \left( \vec{B}^{L*} \cdot \vec{F}^{L*} \right) \left( \vec{B}^L \cdot \vec{F}^L \right), \]

\[ = |A^{(1)}|^2 \frac{1}{4} \sqrt{15 \pi} \int d\Omega_k^M \int d\varphi \left( \hat{k} \cdot \hat{y} \right)^2 \left( \hat{k} \cdot \hat{y} \right) \left( \vec{B}^{L*} \cdot \vec{F}^{L*} \right) \left( \vec{B}^L \cdot \vec{F}^L \right), \]

\[ = |A^{(1)}|^2 \frac{1}{4} \sqrt{15 \pi} \int d\Omega_k^M \frac{1}{30} \left[ 3 \left| \vec{k} \cdot \vec{B}^M \right|^2 - \left| \vec{B}^M \right|^2 \right] \left( \hat{k} \cdot \vec{F}^{L*} \right) \left( \vec{F}^L \right) + c.c. \]

\[ = 0 \tag{B.11} \]

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

$$b_{0,0}^{(2)} = \frac{1}{\sqrt{4\pi}} \left| A_+^{(2)} \right|^2 \int d\Omega_{M} \int d\varphi \left| \vec{D}^L \cdot \vec{F}^L \right|^2 \left| \vec{d}^L \cdot \vec{F}^L \right|^2,$$

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

$$\int d\varphi \left( \vec{D}^L \cdot \vec{F}^L \right)^* \left( \vec{D}^L \cdot \vec{F}^L \right) \left( \vec{d}^L \cdot \vec{F}^L \right)^* \left( \vec{d}^L \cdot \vec{F}^L \right) = \vec{g}^{(4)} \cdot M^{(4)} \vec{f}^{(4)},$$

where

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

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

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

$$b_{0,0}^{(2)} = \frac{1}{\sqrt{4\pi}} \left| A_+^{(2)} \right|^2 \frac{1}{30} \int d\Omega_{M} \left\{ \left| \vec{D}^M \cdot \vec{d}^M \right|^2 + 3|\vec{D}^M|^2 d^2 \right\} |\vec{F}^L|^4.$$

$$+ \left[ 3|\vec{D}^M \cdot \vec{d}^M|^2 - |\vec{D}^M|^2 d^2 \right] \left| (\vec{F}^L)^2 \right|^2 \right\}$$

(D.5)

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

1In the absence of magnetic fields $\vec{d}^M$ can be taken real.
Similarly, for the case of $b^{(2)}_{1,0}$ we get [see Eq. (9)]

$$b^{(2)}_{1,0} = \sqrt{\frac{3}{4\pi}} |A^{(2)}|^2 \int d\Omega_k \int d\varrho \left( \hat{k} \cdot \hat{z} \right) \left| \vec{B}^{\perp} \cdot \vec{F}_L \right|^2 \left| \vec{q} \cdot \vec{F}_L \right|^2. \quad (D.6)$$

The integral over orientations $\varrho$ reads as

$$\int d\varrho \left( \hat{k} \cdot \hat{z} \right) \left( \vec{B}^{\perp} \cdot \vec{F}_L \right)^* \left( \vec{q} \cdot \vec{F}_L \right) \left( \hat{k} \cdot \hat{z} \right) = \vec{g}^{(5)} \cdot M^{(5)} \vec{f}^{(5)}, \quad (D.7)$$

where\(^2\)

$$\vec{g}^{(5)} = \left( \begin{array}{c} \hat{k} \cdot \left( \vec{B}^* \times \vec{d} \right) \left( \vec{B} \cdot \vec{d} \right) \\ \hat{k} \cdot \left( \vec{B}^* \times \vec{d} \right) \end{array} \right), \quad \vec{f}^{(5)} = \left( \begin{array}{c} 0 \\ 1 \\ 1 \\ 1 \\ 0 \end{array} \right), \quad (D.8)$$

$$M^{(5)} = \frac{1}{30} \left( \begin{array}{cccccc} 3 & -1 & -1 & 1 & 1 & 0 \\ -1 & 3 & -1 & -1 & 0 & 1 \\ -1 & -1 & 3 & 0 & -1 & -1 \\ 1 & -1 & 0 & 3 & -1 & 1 \\ 1 & 0 & -1 & -1 & 3 & -1 \\ 0 & 1 & -1 & 1 & -1 & 3 \end{array} \right). \quad (D.9)$$

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

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

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

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

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

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

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This expression is valid for arbitrary orientations of $\vec{d}$ and arbitrary polarization. If we choose the molecular frame so that $\vec{d} = \vec{d}^M$, focus on the case of circular polarization $\vec{F}^L = F (\hat{z}^L + i \sigma \hat{y}^L) / \sqrt{2}$, 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)]

$$b_{3,0}^{(2)} = \frac{5}{4} \sqrt{\frac{7}{\pi}} \left| A^{(2)} \right|^2 \int d\Omega^M \int d\varrho \left( \hat{k} \cdot \hat{z}^L \right) \left| \left( \hat{D}^L \cdot \vec{F}^L \right) \right|^2 \left| \left( \vec{d} \cdot \vec{F}^L \right) \right|^2 - \frac{3}{4} \sqrt{\frac{7}{\pi}} \sqrt{\frac{4\pi}{3}} b_{1,0}^{(2)}$$

(D.13)

The orientation integral in the first term reads as

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

(D.14)

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

$$g^{(7)} = \begin{bmatrix} \left[ k \cdot (\hat{D}^L \times \hat{d}) \right] \left[ \vec{k} \cdot \vec{k} \right] \left[ \hat{D} \cdot \vec{d} \right] \\ \left[ \hat{k} \cdot (\hat{D}^L \times \hat{d}) \right] \left[ \vec{k} \cdot \vec{d} \right] \left[ k \cdot \hat{D} \right] \\ \left[ \hat{k} \cdot (\hat{D}^L \times \hat{D}) \right] \left[ \vec{k} \cdot \vec{d} \right] \left[ k \cdot \hat{D} \right] \\ \left[ \hat{k} \cdot (\hat{D}^L \times \hat{D}) \right] \left[ \vec{k} \cdot \vec{d} \right] \left[ k \cdot \hat{D} \right] \\ \left[ \hat{k} \cdot (\hat{D}^L \times \hat{d}) \right] \left[ \vec{k} \cdot \vec{k} \right] \left[ \hat{D}^L \cdot \vec{d} \right] \\ \left[ \vec{k} \cdot (\hat{D} \times \vec{d}) \right] \left[ k \cdot k \right] \left[ \hat{D}^L \cdot \vec{d} \right] \\ \left[ \vec{k} \cdot (\hat{D} \times \vec{d}) \right] \left[ k \cdot k \right] \left[ \hat{D}^L \cdot \vec{d} \right] \end{bmatrix} \equiv \begin{bmatrix} g_1 \\ g_2 \\ g_3 \\ g_4 \\ g_5 \\ g_6 \\ g_7 \\ g_8 \end{bmatrix}$$

(D.15)

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

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

$$M^{(7)} = \begin{bmatrix}
15 & -21 & 15 & -21 & 15 & 18 & 18 & 0 \\
-21 & 15 & 51 & -33 & -21 & 15 & -18 & 0 \\
15 & -21 & 15 & -15 & 15 & -12 & 0 & -12 \\
-21 & 15 & -21 & 15 & -33 & -21 & 0 & 18 \\
15 & -15 & -33 & 45 & 15 & -15 & 12 & 0 \\
-21 & 15 & -21 & 15 & -33 & 45 & 0 & -18 \\
15 & -15 & 15 & -15 & -33 & 45 & 0 & 12 \\
18 & -12 & -18 & 12 & 0 & 0 & 30 & -6 \\
0 & 0 & 18 & -12 & -18 & 12 & 6 & -6 \\
0 & 0 & 18 & -12 & -18 & 12 & 6 & -6 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix},$$

(D.17)

therefore

$$\bar{g}^{(7)} \cdot M^{(7)} \vec{f}^{(7)} = 1/70 \left[ (2i \text{Im} \{g_1 \} + 2g_3 - g_4) \mid F \mid^2 + (4i \text{Im} \{g_1 \} - 3g_3 + 5g_4) \mid F_z \mid^2 \right] [\xi \cdot (\vec{F}^\ast \times \vec{F})].$$

(D.18)

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

$$b^{(2)}_{3.0} = 1/4 \sqrt{7/\pi} \left| A^{(2)} \right|^2 \frac{1}{70} \int d\Omega^M_{k} d^2 \left\{ \left[ \left( 1 - 5 \left( \hat{k} \cdot \hat{d} \right) \right) \hat{k} + 2 \left( \hat{k} \cdot \hat{d} \right) \hat{d} \right] \cdot \left( \vec{D}^\ast \times \vec{D} \right) \right\} \times \left\{ \zeta^L \cdot (\vec{F}^L \times \vec{F}^L) \right\} \left( \mid \vec{F}^L \mid^2 - 5 \mid F^L_z \mid^2 \right).$$

(D.19)

This expression is valid for arbitrary orientations of $\vec{d}^M$ and arbitrary polarization. If we choose the molecular frame so that $\vec{d}^M = d\hat{z}^M$, we focus on the case of circular polarization $\vec{F}^L = F (\hat{x}^L + i\sigma \hat{y}^L) / \sqrt{2}$, and we use definition (36), Eq. (D.19) reduces to Eq. (31).
Derivation of $b_{1,0}^{(2)}$

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

$$b_{1,0}^{(2)}(k) = |A^{(2)}|^2 d^2 |F| \int d\Omega_k M \int d\theta Y_1^0(|\hat{k}^L|) \cos^2 \beta |\vec{D}_L \cdot \vec{F}_L|$$

(E.1)

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

$$2b_{1,0}^{(2)} + b_{1,0}^{(2)}(k) = |A^{(2)}|^2 d^2 |F|^2 \int d\Omega_k M \int d\theta Y_1^0(|\hat{k}^L|) |\vec{D}_L \cdot \vec{F}_2^L|$$

$$= |A^{(2)}|^2 d^2 |F|^2 \frac{\sigma}{6} \sqrt{\frac{3}{4\pi}} \int d\Omega_k M |\hat{k}^L \cdot \vec{B}_M|^2$$

$$= \frac{C\sigma}{2\sqrt{3}} \delta_{0,0}$$

(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 $Y_0^0(\hat{k}) = \hat{k}/\sqrt{4\pi}$, Eq. (39) and the orthonormality of the spherical harmonics. Using Eq. (40) for $b_{1,0}^{(2)}$ yields Eq. (42).

References