

Enantiosensitivity of spin polarization in molecular photoionization

Anton N. Artemyev ¹, Daniel M. Haubenreißer ¹, Boris M. Lagutin ², and Philipp V. Demekhin ^{1,*}

¹*Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany*

²*Rostov State Transport University, Narodnogo Opolcheniya Square 2, 344038 Rostov-on-Don, Russia*



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Angular distributions of photoelectrons with a defined spin orientation, released by the absorption of a single circularly polarized photon from randomly oriented chiral molecules, are derived and analyzed within the electric-dipole approximation. The revealed symmetry properties of the distributions support previous findings that the total spin polarization of photoelectrons is independent of the enantiomer of a chiral molecule, whereas the angular distribution of the spin polarization is enantiosensitive. Numerical applications to the achiral HI and chiral 1-iodo-2-methylbutane molecules illustrate that these analytical results also hold for multiphoton ionization processes.

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I. INTRODUCTION

Spin polarization (SP [1]) in photoemission was first predicted and studied in the one-photon ionization [2–6] and has been reinvestigated recently in the multiphoton ionization regime. This relativistic effect is caused by a spin-orbit interaction and relies on a substantial energy splitting between the respective fine-structure components. Motivated by the theoretical results of Ref. [7], a number of experimental [8–10] and theoretical [8–17] studies revealed a sizable SP in multiphoton and strong-field tunnel ionization of the outer shells of atoms and molecules. Several theoretical approaches were employed in these works to investigate SP in different laser-field regimes, e.g., nonadiabatic tunneling [7], the strong-field approximation [11,12], and numerical solutions of the time-dependent Schrödinger equation (TDSE) [8,10,14–17]. Among them, the time-dependent single-center method (TDSC [18]) was developed and applied in our previous works to study SP in multiphoton above-threshold ionization of Xe [17], HI [16], and 1-iodo-2-methylbutane (IMB) [10] with circularly polarized laser pulses.

The IMB molecule is chiral, i.e., it exists in form of the $R(-)$ and $S(+)$ enantiomers, which are mirror images of each other. When randomly oriented chiral molecules in the gas phase are ionized by circularly polarized light, the corresponding photoelectron angular distributions exhibit a helicity- and enantiosensitive forward-backward asymmetry with respect to the light propagation direction, which is known as photoelectron circular dichroism (PECD [19–22]). In our previous work on IMB [10], SP in the total photoelectron spectrum was

found to be independent of the molecular enantiomer, both experimentally and theoretically. Nevertheless, our numerical calculations revealed that PECD can differ significantly for photoelectrons with different spin projections. Taking into account that PECD is a chiroptical effect, this numerical result suggests that the angular distribution of spin-polarized photoelectrons is, in turn, enantiosensitive. A similar conclusion is drawn in the very recent theoretical works [23,24], which analyzed spin-polarized photoelectron currents.

In the present work, we derive from first principles and analyze the angular distributions of spin-polarized photoelectrons emitted from randomly oriented chiral molecules in the simplest case of absorption of a single circularly polarized photon, which enables a transparent analysis (Sec. II). The symmetry properties of the angle-resolved SP with respect to the exchange of light helicity and molecular enantiomers are analyzed in Sec. III. Using our previous numerical results for the achiral HI [16] and chiral IMB [10] molecules, we further demonstrate that these symmetry properties persist in the multiphoton ionization regime. We conclude in Sec. IV with a brief summary. Atomic units are used throughout the paper.

II. PHOTOELECTRON ANGULAR DISTRIBUTIONS

We first derive the angular distribution of photoelectrons with defined spin projection $\mu = \pm \frac{1}{2}$ ionized by absorption of one circularly polarized photon with helicity $q = \pm 1$. These quantum numbers are defined in the laboratory frame (LF). For this purpose, we proceed along the steps reported in Ref. [25] for the case of spin polarization (see also the very recent work Ref. [26] for more details on spin-unresolved photoemission). An alternative approach that makes use of molecular symmetry can be found in Ref. [27]. In particular, the helicity of the incoming photon is transformed from the LF to the molecular frame (MF). This transformation is performed by the Wigner rotation matrices D for each orientation of the MF relative to the LF, which is defined by the Euler

*Contact author: demekhin@physik.uni-kassel.de

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angles [28]. Thereafter, the electric-dipole transition matrix elements, $d_{\ell k' m' \mu'}$, for the emission of partial photoelectron continuum waves with angular momentum quantum numbers ℓ, m' [29] and spin projection $\mu' = \pm \frac{1}{2}$ upon absorption of a photon with helicity k' are computed (here, all quantum numbers are defined in the MF). Finally, the spatial and spin parts of the emitted partial waves are transformed back by inverse rotation matrices from the MF to the LF, where photoelectrons are observed. The corresponding total transition amplitude reads [25,26]

$$A_{\vec{k}}^{\pm 1, \pm \frac{1}{2}} = \sum_{ds} \sum_{\ell m k' m' \mu'} (-i)^\ell \times \mathcal{D}_{k' \pm 1}^1 \mathcal{D}_{m' m}^{\ell*} \mathcal{D}_{\mu' \pm \frac{1}{2}}^{\frac{1}{2}*} d_{\ell k' m' \mu'} Y_{\ell m}(\hat{k}). \quad (1)$$

In this equation, $\vec{k}$ is the photoelectron momentum vector with emission angles $\hat{k} = \{\theta, \varphi\}$ defined in the LF, $\mu = \pm \frac{1}{2}$ is its spin projection onto the laboratory z axis (i.e., the light

propagation direction), and the first summation runs over doubly degenerate states of the initial electron orbital and the final photoelectron state. Note that the matrix elements $d_{\ell k' m' \mu'}$ incorporate all necessary normalization coefficients and scattering phase shifts of the partial waves.

Taking the squared absolute value of the total amplitude (1), we obtain the spin-state- and emission-angle-resolved photoionization probability, which can be analytically simplified and averaged over all molecular orientation angles. The relations required for these transformations are documented in the Appendix (see also Refs. [25,26] for detailed step-by-step simplifications). As expected, the probability can be expanded in terms of Legendre polynomials,

$$I^{\pm 1, \pm \frac{1}{2}}(\theta) = \frac{1}{4\pi} \sum_L b_L^{\pm 1, \pm \frac{1}{2}} P_L(\theta), \quad (2)$$

where the helicity- and spin-state-specific expansion coefficients are given by

$$b_L^{\pm 1, \pm \frac{1}{2}} = \sum_{ds} \sum_{\ell_1 m'_1 k'_1 \mu'_1} \sum_{\ell_2 m'_2 k'_2 \mu'_2} (i)^{\ell_1 + \ell_2} (-1)^{\ell_2 + m'_1 + k'_2 \mp 1 + \mu'_1 \mp \frac{1}{2} + L} \sum_{JS} \sqrt{(2\ell_1 + 1)(2\ell_2 + 1)} \times \begin{pmatrix} 1 & 1 & J \\ k'_1 & -k'_2 & m'_2 + \mu'_2 - m'_1 - \mu'_1 \end{pmatrix} \begin{pmatrix} 1 & 1 & J \\ \pm 1 & \mp 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\mu'_1 & \mu'_2 & -\mu'_2 + \mu'_1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ \mp \frac{1}{2} & \pm \frac{1}{2} & 0 \end{pmatrix} \times \begin{pmatrix} \ell_1 & \ell_2 & L \\ -m'_1 & m'_2 & -m'_2 + m'_1 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} S & L & J \\ \mu'_2 - \mu'_1 & m'_2 - m'_1 & m'_1 + \mu'_1 - m'_2 - \mu'_2 \end{pmatrix} \times \begin{pmatrix} S & L & J \\ 0 & 0 & 0 \end{pmatrix} (2S + 1)(2L + 1)(2J + 1) d_{\ell_1 k'_1 m'_1 \mu'_1} d_{\ell_2 k'_2 m'_2 \mu'_2}^*. \quad (3)$$

This equation is consistent with the results of Ref. [30].

We begin the present analysis by considering the entire factor in Eq. (3) that depends on the spin state of the photoelectron, $\mu = \pm \frac{1}{2}$:

$$(-1)^{\mp \frac{1}{2}} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ \mp \frac{1}{2} & \pm \frac{1}{2} & 0 \end{pmatrix}. \quad (4)$$

From the $3j$ symbol [the fourth $3j$ symbol in Eq. (3)], it follows that only two values of the index $S = 0$ and 1 are allowed. In the case of $S = 0$, this $3j$ symbol is odd. Consequently, the factor (4), and thus the corresponding contribution to the photoionization probability, is independent of the spin projection $\mu = \pm \frac{1}{2}$. In contrast, for $S = 1$, this $3j$ symbol is even, and the corresponding contribution to the probability has opposite signs for opposite spin projections $\mu = \pm \frac{1}{2}$. This fact will be taken into account in the subsequent analysis of the symmetry properties of the expansion coefficients $b_L^{\pm 1, \pm \frac{1}{2}}$ (3).

We first consider the symmetry properties with respect to exchange of the light helicity from $q = +1$ to -1 , keeping the molecular enantiomer $\mathcal{E}$ fixed. In this case, only the second $3j$ symbol in Eq. (3) can influence the expansion coefficients, while the phase factor $(-1)^{\mp 1} = -1$ is independent of $q = \pm 1$. As follows from the last $3j$ symbol, for even values of L and $S = 1$, only odd values of J are allowed. As a result,

the second $3j$ symbol changes sign. This sign change can be compensated by exchanging the photoelectron spin projections owing to the factor (4). For the $S = 0$ contribution to even L , only even J are allowed, and the second $3j$ symbol retains its sign. Simultaneously, the factor (4) preserves its sign upon exchanging the spin projections. Combining the $S = 0$ and 1 contributions with the equivalent symmetry properties, we conclude that exchanging the light helicity preserves the sign of the even expansion coefficients but swaps the spin projections:

$$b_{\text{even}}^{\pm 1, \pm \frac{1}{2}}(\mathcal{E}) = b_{\text{even}}^{\mp 1, \mp \frac{1}{2}}(\mathcal{E}). \quad (5)$$

In contrast, for odd values of L , the last $3j$ symbol allows odd values of J for $S = 0$ and even of J for $S = 1$. This implies a sign change of the second $3j$ symbol for the $S = 0$ contribution, while the factor (4) remains unchanged upon swapping the spin projections. For the $S = 1$ contribution, the second $3j$ symbol does not change sign, whereas the factor (4) does. We thus conclude that exchanging the light helicity changes the sign of the odd expansion coefficients and simultaneously swaps the spin projections:

$$b_{\text{odd}}^{\pm 1, \pm \frac{1}{2}}(\mathcal{E}) = -b_{\text{odd}}^{\mp 1, \mp \frac{1}{2}}(\mathcal{E}). \quad (6)$$

We now fix the light helicity and exchange the molecular enantiomers $\mathcal{R} \leftrightarrow \mathcal{S}$. This is equivalent to a reflection of the molecular z' axis, which causes a sign change for all angular momentum projections m'_j and spin projections μ'_j in the MF [31]. For even values of L , the last $3j$ symbol allows S and J values of the same parity. As a consequence, two terms in Eq. (3) change sign simultaneously, namely the factor $(-1)^{\mu'_j}$ (since $\mu'_j = \pm \frac{1}{2}$) and either the third $3j$ symbol for $S = 0$ or the first $3j$ symbol for $S = 1$. Therefore, the total expansion coefficients with even L values do not depend on the molecular enantiomer:

$$b_{\text{even}}^{\pm 1, \pm \frac{1}{2}}(\mathcal{R}) = b_{\text{even}}^{\pm 1, \pm \frac{1}{2}}(\mathcal{S}). \quad (7)$$

In contrast, for odd values of L , only different parities of S and J are allowed. As a consequence, in addition to the factor $(-1)^{\mu'_j}$, either the first and the third $3j$ symbols simultaneously change sign for $S = 0$, or both retain their sign for $S = 1$. We thus conclude that exchanging the enantiomers changes the sign of all odd expansion coefficients:

$$b_{\text{odd}}^{\pm 1, \pm \frac{1}{2}}(\mathcal{R}) = -b_{\text{odd}}^{\pm 1, \pm \frac{1}{2}}(\mathcal{S}). \quad (8)$$

We note that, although the present analysis is performed to the case of one-photon ionization, the derived symmetry properties (5)–(8) of the expansion coefficients $b_L^{\pm 1, \pm \frac{1}{2}}$ also hold for multiphoton ionization, where higher-order expansion terms contribute to the expansion (2). In particular, in the case of n absorbed photons, amplitude (1) contains n rotation matrices $\mathcal{D}^1$, which transform the polarization of each absorbed photon into the MF. Employing Eq. (A1) step by step, all these matrices can be reduced to a single rotation matrix $\mathcal{D}^n$. Simultaneously, the second and the third rotation matrices, $\mathcal{D}^{\ell*}$ and $\mathcal{D}^{\frac{1}{2}*}$, in amplitude (1), which transform the projections of the photoelectron's angular momentum and spin into the LF, remain unchanged. Thereby, the corresponding multiphoton ionization amplitude takes the form of amplitude (1) containing only three rotation matrices, which can be handled and analyzed as discussed in Sec. II.

III. SPIN POLARIZATION

We now turn to the analysis of the symmetry properties of SP, which is defined (for each enantiomer and a given photoelectron kinetic energy) by the following normalized difference [7–9,25]:

$$\text{SP}^{\pm 1}(\theta) = \frac{I^{\pm 1, +\frac{1}{2}}(\theta) - I^{\pm 1, -\frac{1}{2}}(\theta)}{I^{\pm 1, +\frac{1}{2}}(\theta) + I^{\pm 1, -\frac{1}{2}}(\theta)}. \quad (9)$$

To obtain the SP in the total photoelectron spectrum, $\widetilde{\text{SP}}^{\pm 1}$, the emission probabilities $I^{\pm 1, \pm \frac{1}{2}}(\theta)$ (2), integrated over all photoemission angles θ , need to be substituted into Eq. (9). These total emission probabilities are equal to the expansion coefficient $b_0^{\pm 1, \pm \frac{1}{2}}$ (3), which has the known symmetry properties (5) and (7). When keeping the molecular enantiomer $\mathcal{E}$ fixed but exchanging the light helicity $+1 \leftrightarrow -1$, we obtain

$$\begin{aligned} \widetilde{\text{SP}}^{\pm 1}(\mathcal{E}) &= \frac{b_0^{\pm 1, +\frac{1}{2}}(\mathcal{E}) - b_0^{\pm 1, -\frac{1}{2}}(\mathcal{E})}{b_0^{\pm 1, +\frac{1}{2}}(\mathcal{E}) + b_0^{\pm 1, -\frac{1}{2}}(\mathcal{E})} \\ &= \frac{b_0^{\mp 1, -\frac{1}{2}}(\mathcal{E}) - b_0^{\mp 1, +\frac{1}{2}}(\mathcal{E})}{b_0^{\mp 1, -\frac{1}{2}}(\mathcal{E}) + b_0^{\mp 1, +\frac{1}{2}}(\mathcal{E})} = -\widetilde{\text{SP}}^{\mp 1}(\mathcal{E}). \end{aligned} \quad (10)$$

In contrast, keeping the light helicity q fixed but exchanging the molecular enantiomer $\mathcal{R} \leftrightarrow \mathcal{S}$ results in

$$\begin{aligned} \widetilde{\text{SP}}^{\pm 1}(\mathcal{R}) &= \frac{b_0^{\pm 1, +\frac{1}{2}}(\mathcal{R}) - b_0^{\pm 1, -\frac{1}{2}}(\mathcal{R})}{b_0^{\pm 1, +\frac{1}{2}}(\mathcal{R}) + b_0^{\pm 1, -\frac{1}{2}}(\mathcal{R})} \\ &= \frac{b_0^{\pm 1, +\frac{1}{2}}(\mathcal{S}) - b_0^{\pm 1, -\frac{1}{2}}(\mathcal{S})}{b_0^{\pm 1, +\frac{1}{2}}(\mathcal{S}) + b_0^{\pm 1, -\frac{1}{2}}(\mathcal{S})} = +\widetilde{\text{SP}}^{\pm 1}(\mathcal{S}). \end{aligned} \quad (11)$$

These two equations confirm that the total SP is helicity dependent but enantio independent.

In the case of angle-resolved SP (9), we need to use the full set of symmetry properties (5)–(8) of the expansion coefficients $b_L^{\pm 1, \pm \frac{1}{2}}$ and, in addition, the relation for Legendre polynomials: $P_L(\pi - \theta) = (-1)^L P_L(\theta)$. Considering separately the contributions from the expansion (2) with *even* and *odd* values of L , we straightforwardly obtain that, for a fixed enantiomer, it holds

$$\begin{aligned} \text{SP}^{\pm 1}(\mathcal{E}, \theta) &= \frac{\sum_{\text{even}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{E}) P_L(\theta) + \sum_{\text{odd}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{E}) P_L(\theta) - \sum_{\text{even}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{E}) P_L(\theta) - \sum_{\text{odd}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{E}) P_L(\theta)}{\sum_{\text{even}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{E}) P_L(\theta) + \sum_{\text{odd}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{E}) P_L(\theta) + \sum_{\text{even}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{E}) P_L(\theta) + \sum_{\text{odd}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{E}) P_L(\theta)} \\ &= \frac{\sum_{\text{even}} b_L^{\mp 1, -\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta) + \sum_{\text{odd}} b_L^{\mp 1, -\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta) - \sum_{\text{even}} b_L^{\mp 1, +\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta) - \sum_{\text{odd}} b_L^{\mp 1, +\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta)}{\sum_{\text{even}} b_L^{\mp 1, -\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta) + \sum_{\text{odd}} b_L^{\mp 1, -\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta) + \sum_{\text{even}} b_L^{\mp 1, +\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta) + \sum_{\text{odd}} b_L^{\mp 1, +\frac{1}{2}}(\mathcal{E}) P_L(\pi - \theta)} \\ &= -\text{SP}^{\mp 1}(\mathcal{E}, \pi - \theta). \end{aligned} \quad (12)$$

This equation suggests that, upon swapping the light helicity, the angular distribution of SP is reflected in the forward-backward direction (via $\theta \leftrightarrow \pi - \theta$) and, in addition, changes sign. In contrast, for a fixed helicity but different enantiomers,

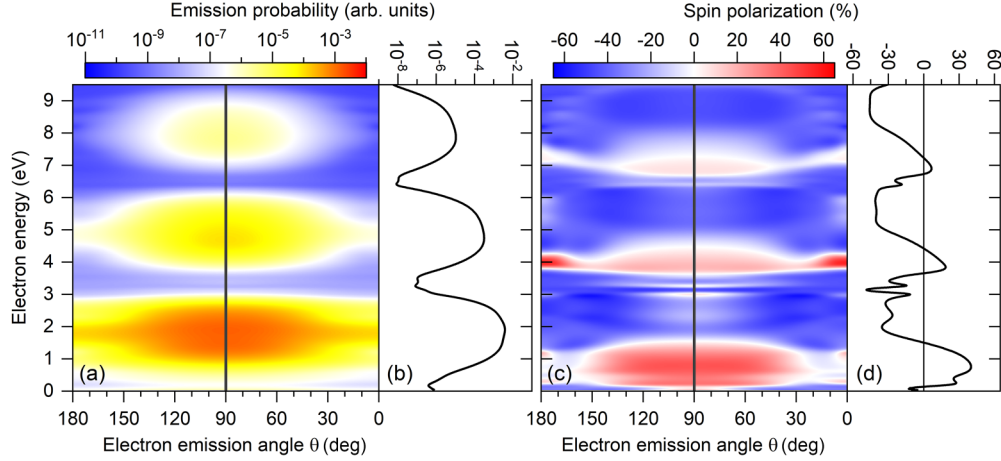


FIG. 1. (a) Emission probability and (c) spin polarization as functions of the photoelectron kinetic energy and emission angle, computed for randomly oriented HI molecules ionized by sine-squared circularly polarized laser pulses with a wavelength of 395 nm, 8 fs full width at half maximum (FWHM) duration, intensity of 5×10^{12} W/cm², and positive helicity ($q = +1$). (b) The corresponding total emission probability and (d) spin polarization as functions of the photoelectron kinetic energy.

it holds

$$\begin{aligned}
 & \text{SP}^{\pm 1}(\mathcal{R}, \theta) \\
 &= \frac{\sum_{\text{even}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{R}) P_L(\theta) + \sum_{\text{odd}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{R}) P_L(\theta) - \sum_{\text{even}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{R}) P_L(\theta) - \sum_{\text{odd}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{R}) P_L(\theta)}{\sum_{\text{even}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{R}) P_L(\theta) + \sum_{\text{odd}} b_L^{\pm 1, +\frac{1}{2}}(\mathcal{R}) P_L(\theta) + \sum_{\text{even}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{R}) P_L(\theta) + \sum_{\text{odd}} b_L^{\pm 1, -\frac{1}{2}}(\mathcal{R}) P_L(\theta)} \\
 &= \frac{\sum_{\text{even}} b_L^{\pm 1, +\frac{1}{2}}(S) P_L(\pi - \theta) + \sum_{\text{odd}} b_L^{\pm 1, +\frac{1}{2}}(S) P_L(\pi - \theta) - \sum_{\text{even}} b_L^{\pm 1, -\frac{1}{2}}(S) P_L(\pi - \theta) - \sum_{\text{odd}} b_L^{\pm 1, -\frac{1}{2}}(S) P_L(\pi - \theta)}{\sum_{\text{even}} b_L^{\pm 1, +\frac{1}{2}}(S) P_L(\pi - \theta) + \sum_{\text{odd}} b_L^{\pm 1, +\frac{1}{2}}(S) P_L(\pi - \theta) + \sum_{\text{even}} b_L^{\pm 1, -\frac{1}{2}}(S) P_L(\pi - \theta) + \sum_{\text{odd}} b_L^{\pm 1, -\frac{1}{2}}(S) P_L(\pi - \theta)} \\
 &= +\text{SP}^{\pm 1}(S, \pi - \theta).
 \end{aligned} \tag{13}$$

Thus, when exchanging the two enantiomers, the angular distribution of SP flips with respect to the forward-backward direction (via $\theta \leftrightarrow \pi - \theta$), enabling unambiguous identification of the enantiomer. Based on Eqs. (12) and (13), we conclude that the angle-resolved SP is a physical quantity that depends on helicity and enantiomer, making it a suitable observable for chiral recognition in the gas phase.

In our previous work on IMB [10], it was demonstrated experimentally and theoretically that the total SP is independent of the molecular enantiomer even in the multiphoton ionization regime. Below, by performing two numerical applications to real molecules, we demonstrate that the symmetry properties [Eqs. (12) and (13)] of the angle-resolved SP, derived for the one-photon ionization case, hold in the multiphoton ionization regime as well. The first example considers SP in the multiphoton ionization of the achiral HI molecule by 395 nm circularly polarized laser pulses, discussed in our previous theoretical work [16]. The calculations were performed using the TDSC method and code [17,18], while molecule-specific computational details were provided in Ref. [16]. Results of the calculations, relevant for the present study, are summarized in Fig. 1 (see also its caption for the pulse parameters used). The computed total photoelectron spectrum in Fig. 1(b) exhibits a sequence of photoionization and above-threshold ionization peaks. Each peak is composed of overlapping contributions from three outer-shell molecular

orbitals, which originate from the 5*p* electrons of the iodine atom (see Ref. [16] for detailed assignments). The corresponding angular distribution in Fig. 1(a) is forward-backward symmetric (with respect to the vertical black line at $\theta = 90^\circ$). This is expected for achiral molecules, where all odd terms in the expansion (2) vanish, $b_{\text{odd}}^{\pm 1, \pm \frac{1}{2}} = 0$. The total SP in Fig. 1(d) varies between +50% and −50% across the peaks.

Because $b_{\text{odd}}^{\pm 1, \pm \frac{1}{2}} = 0$, the computed angular distribution of SP in Fig. 1(c) is also forward-backward symmetric. Accordingly [see Eq. (12)], switching the light helicity simply changes the sign of the angular distribution of SP, i.e., inverts the red and blue colors in Fig. 1(c) (not shown here for brevity).

The second example considers multiphoton ionization of the chiral IMB molecule by 395 nm circularly polarized pulses, as studied in our previous work [10]. This reference provides molecule-specific details on the performed TDSC calculations. The present computational results are summarized in Figs. 2 and 3. Figure 2 depicts the total and angle-resolved photoelectron spectrum and the corresponding SP of photoelectrons, computed for the *R*(−) enantiomer and positive light helicity (see its caption for the pulse parameters used). The total photoelectron spectrum in Fig. 2(b) consists of overlapping contributions representing photoionization and above-threshold ionization from three outer-shell molecular orbitals of IMB, which are again mainly composed of 5*p*

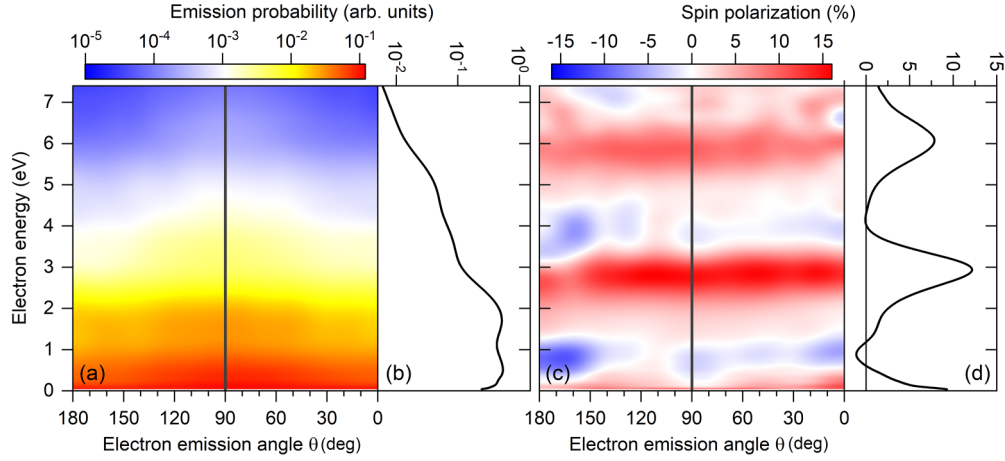


FIG. 2. Same as in Figs. 1(a)–1(d), but for the $R(-)$ enantiomer of the IMB molecule, ionized by sine-squared circularly polarized laser pulses with a wavelength of 395 nm, 4 fs FWHM duration, intensity of 10^{13} W/cm², and positive helicity ($q = +1$). See the caption of Fig. 1 for details on the data representation.

electrons of the iodine atom (see Ref. [10] for details). The computed total SP in Fig. 2(d) varies from about -1% to $+12\%$, which is in very good agreement with the experimental results of Ref. [10]. Because the molecule is chiral, its angular emission distribution in Fig. 2(a) is not forward-backward symmetric (i.e., not left-right symmetric with respect to the vertical black line at $\theta = 90^\circ$). This asymmetry arises from the odd terms $b_{\text{odd}}^{\pm 1, \pm \frac{1}{2}}(\mathcal{R}) \neq 0$ in the expansion (2), which are generally responsible for the PECD effect. Moreover, as seen in Fig. 2(c), the computed angular distribution of SP exhibits a sizable forward-backward asymmetry as well. This distribution is shown in Fig. 3(b) again, where it is compared with the corresponding distributions for the same enantiomer but opposite light helicity [Fig. 3(a)], and for the same helicity but the opposite enantiomer [Fig. 3(c)]. These computational results from Fig. 3 are consistent with the symmetry properties of SP derived in Eqs. (12) and (13). In particular, both distributions in Figs. 3(a) and 3(c) are mirrored with respect to the

vertical black line at $\theta = 90^\circ$, as compared to that in Fig. 3(b). For the helicity swap, the sign of the distribution is additionally inverted [i.e., the blue and red colors are exchanged in Fig. 3(a) as compared to Figs. 3(b) and 3(c)].

IV. SUMMARY

This work analyzes the angular emission distributions of spin-polarized photoelectrons upon ionization of randomly oriented molecules by circularly polarized light. The symmetry properties of the equations, derived for the case of one-photon ionization, confirm the well-known fact that both the total spin polarization and its angular distribution are dichroic observables [25,30]. In addition, they show that, while the total SP is independent of the enantiomer of a chiral molecule, its angular emission distribution is enantiosensitive. In this way, we establish the angular distribution of spin polarization as an additional observable for chiral recognition in the gas phase. Numerical applications to the multiphoton

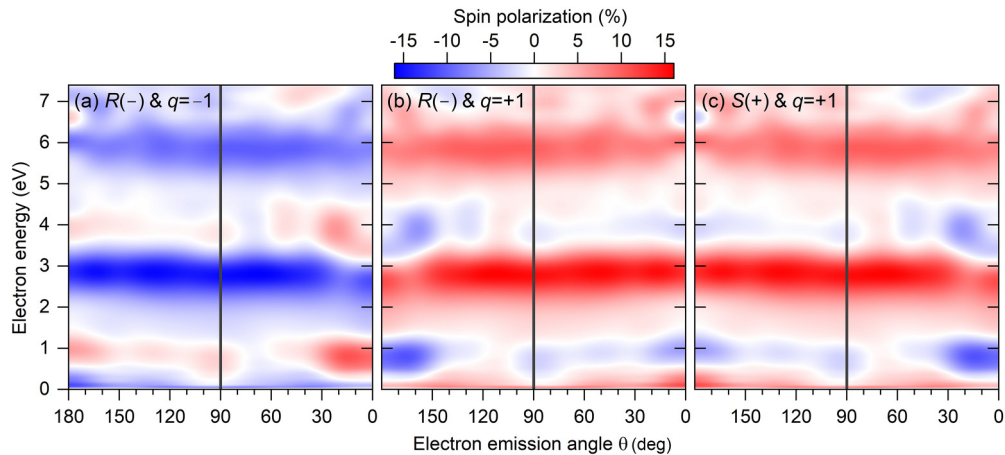


FIG. 3. Symmetry properties of the spin polarization, computed for two enantiomers of the IMB molecule, ionized by sine-squared circularly polarized laser pulses with a wavelength of 395 nm, 4 fs FWHM duration, intensity of 10^{13} W/cm², and different helicities. (a) $R(-)$ enantiomer and light with negative helicity, (b) $R(-)$ enantiomer and positive helicity [same as in Fig. 2(c)], and (c) $S(+)$ enantiomer and positive helicity.

ionization of HI and 1-iodo-2-methylbutane suggest that these conclusions also hold in the multiphoton ionization regime and illustrate how these observables are influenced by light helicity and molecular enantiomer.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX: USEFUL RELATIONS

The equations listed below are adapted to the present case from Ref. [28]. In particular, for the reduction of the product of two rotation matrices, we obtain

$$\mathcal{D}_{k'_1 \pm 1}^1 \mathcal{D}_{k'_2 \pm 1}^{1*} = (-1)^{k'_2 \mp 1} \sum_{Jj'} (-1)^{j'} (2J+1) \begin{pmatrix} 1 & 1 & J \\ k'_1 & -k'_2 & -j' \end{pmatrix} \begin{pmatrix} 1 & 1 & J \\ \pm 1 & \mp 1 & 0 \end{pmatrix} \mathcal{D}_{j'0}^J, \quad (\text{A1})$$

$$\mathcal{D}_{m'_1 m_1}^{\ell_1*} \mathcal{D}_{m'_2 m_2}^{\ell_2} = (-1)^{m'_1 - m_1} \sum_{Pp p'} (-1)^{p-p'} (2P+1) \begin{pmatrix} \ell_1 & \ell_2 & P \\ -m'_1 & m'_2 & -p' \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & P \\ -m_1 & m_2 & -p \end{pmatrix} \mathcal{D}_{p'p}^P, \quad (\text{A2})$$

$$\mathcal{D}_{\mu'_1 \pm \frac{1}{2}}^{\frac{1}{2}*} \mathcal{D}_{\mu'_2 \pm \frac{1}{2}}^{\frac{1}{2}} = (-1)^{\mu'_1 \mp \frac{1}{2}} \sum_{Ss'} (-1)^{s'} (2S+1) \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\mu'_1 & \mu'_2 & -s' \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ \mp \frac{1}{2} & \pm \frac{1}{2} & 0 \end{pmatrix} \mathcal{D}_{s'0}^S. \quad (\text{A3})$$

The reduction of the product of two spherical functions yields

$$Y_{\ell_1 m_1} Y_{\ell_2 m_2}^* = (-1)^{m_2} \sum_{LM} (-1)^M \sqrt{\frac{(2\ell_1+1)(2\ell_2+1)(2L+1)}{4\pi}} \begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & -m_2 & M \end{pmatrix} Y_{LM}^*. \quad (\text{A4})$$

Summation over the indices m_1 and m_2 yields:

$$\sum_{m_1 m_2} (-1)^{m_2 - m_1} \begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & -m_2 & M \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & P \\ -m_1 & m_2 & -p \end{pmatrix} = (-1)^{\ell_1 + \ell_2 + L} \frac{\delta_{LP} \delta_{Mp}}{2L+1}. \quad (\text{A5})$$

Finally, averaging the product of three rotation matrices over all molecular orientation angles gives:

$$\frac{1}{8\pi^2} \int d\Omega \mathcal{D}_{s'0}^S \mathcal{D}_{p'p}^P \mathcal{D}_{j'0}^J = \begin{pmatrix} S & P & J \\ s' & p' & j' \end{pmatrix} \begin{pmatrix} S & P & J \\ 0 & p & 0 \end{pmatrix}. \quad (\text{A6})$$

From the last two equations, it follows that $M = p = 0$.

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