

Interplay between the electric-dipole and nondipole-induced forward-backward asymmetries in the inner-shell photoionization of chiral molecules

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We investigate the laboratory-frame angular emission distribution of photoelectrons, ejected by circularly polarized light from chiral molecules, theoretically beyond the electric-dipole approximation. We demonstrate that the helicity-dependent forward-backward asymmetry, which is governed by the electric-dipole interaction and known as photoelectron circular dichroism (PECD), can be altered significantly by the helicity-independent asymmetry, which is induced by nondipole contributions. Our findings are exemplified by numerical calculations on the inner-shell photoionization of the bromine atom in the epibromohydrin molecule. The uncovered effect is expected to be omnipresent in the deep inner-shell ionization and needs to be taken into consideration in the interpretation of experiments on PECD in chiral molecules.

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Photoelectron circular dichroism (PECD) is a powerful tool for chiral recognition in the gas phase [1–3]. This chiroptical effect manifests as a helicity- and enantiosensitive forward-backward asymmetry in the photoelectron emission with respect to the direction of the propagation of the ionizing circularly polarized light. As was predicted theoretically many years ago [4], this asymmetry is induced by the electric-dipole contribution of the light-matter interaction. It survives an averaging over molecular orientations in space. First experiments on PECD utilized circularly polarized synchrotron radiation to investigate the one-photon ionization of outer molecular shells [5,6]. Later on, PECD was observed in the multiphoton ionization of outer shells of chiral molecules by circularly polarized laser pulses [7,8] in different intensity and frequency regimes [9,10]. PECD is observable for relatively low kinetic energies of the photoelectron, i.e., close to the ionization threshold.

In one-photon outer-shell ionization, two effects contribute to PECD [11]: a chiral charge distribution in the initial electronic state, on the one hand, and a sensitivity of the photoelectron to the chiral ionic potential, on the other. The inner-shell ionization of atomiclike electronic states offers an opportunity to suppress the former contribution and to inspect a possible chiral asymmetry of the electronic potential of the molecular ion. In addition, inner-shell ionization of molecules offers a possibility to selectively address a particular electron-emitting atom, located on a specific molecular site, and to

study thereby a sensitivity of the PECD to the ionic potential generated by different surroundings. It is thus not a surprise that many theoretical and experimental studies of PECD targeted inner-shell photoionization of chiral molecules [11–25].

Inner-shell photoionization, obviously, requires utilizing high-energy photons, where the spatial dependence of the radiation plane wave starts to play a noticeable role, and where higher-order Taylor expansion terms beyond the $e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} = 1$ contribute to the light-matter interaction [26–30]. Such nondipole contributions break the symmetry along the photon momentum vector $\mathbf{k}_\gamma$ and create a forward-backward asymmetry in the laboratory-frame photoelectron angular distributions (see, e.g., review articles [31,32] and references therein). For high photoelectron kinetic energies, one can straightforwardly prove that significantly more electrons are emitted along the light propagation direction [33–35], and the effect grows with the increase of the energy. Even for moderate kinetic energies, the nondipole-induced forward-backward asymmetry in the photoemission is positive [36]. However, for low photoelectron energies close to the ionization threshold, such asymmetry may also be sizable and can have different signs [37,38].

In the present letter, we investigate an intriguing interplay between the helicity-dependent, chiral and helicity-independent, nondipole-induced forward-backward asymmetries in the angular distributions of low-energy photoelectrons released by high-energy photons. In the electric-dipole approximation, the laboratory-frame photoelectron emission distribution from randomly oriented molecules ionized by the circularly polarized light of different helicities is expressed by the well-known expansion over Legendre polynomials [39]:

$$\frac{d\sigma_D^\pm}{d\Omega} = \frac{1}{4\pi} [B_0 \pm B_1 P_1(\cos \theta) + B_2 P_2(\cos \theta)]. \quad (1)$$

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Here, θ is the angle between the propagation direction of the ionizing radiation and the direction of the emission of the photoelectrons. The total photoionization cross section is given by $\sigma = B_0$, the anisotropy parameter by $\beta_2 = -2B_2/B_0$, and the dichroic parameter is defined as $\beta_1 = \pm B_1/B_0$. The latter describes the forward-backward asymmetry in the emission of photoelectrons, which is present only for chiral molecules [4]. This chiral asymmetry is enantiosensitive and helicity dependent, as explicitly indicated by the $(\pm)$ signs in front of the second term in Eq. (1). The respective forward-backward asymmetry (i.e., the PECD) is quantified via the dichroic parameter as $\text{FB} = 2\beta_1$.

In order to include nondipole contributions to the light-matter interaction, in the present work, we approximated the plane wave of the vector potential of the ionizing radiation by the first two terms of the Taylor expansion $e^{i\mathbf{k}_\gamma \cdot \mathbf{r}} = 1 + i\mathbf{k}_\gamma \cdot \mathbf{r}$ and considered only the first-order corrections beyond the electric-dipole approximation, given by the electric-dipole–electric-quadrupole and electric-dipole–magnetic-dipole interference terms. Following Refs. [18,39–41], we derived the laboratory-frame differential photoionization probability of randomly oriented molecules beyond the electric-dipole approximation. The results our derivation are consistent with the previous derivations for molecules from Refs. [42,43]. The present derivations yield that the total differential photoionization cross section is the sum of the cross sections calculated in the electric-dipole approximation (D) and that given by the interference of the electric-dipole with electric-quadrupole and magnetic-dipole terms (QM):

$$\frac{d\sigma_{\text{DQM}}^\pm}{d\Omega} = \frac{d\sigma_{\text{D}}^\pm}{d\Omega} + \frac{d\sigma_{\text{QM}}^\pm}{d\Omega}. \quad (2)$$

The individual nondipolar contribution in Eq. (2) is given by the following explicit expansion:

$$\begin{aligned} \frac{d\sigma_{\text{QM}}^\pm}{d\Omega} = \frac{1}{4\pi} [& \pm C_0 + C_1 P_1(\cos \theta) \\ & \pm C_2 P_2(\cos \theta) + C_3 P_3(\cos \theta)]. \end{aligned} \quad (3)$$

The first term, $\pm C_0$, in this expansion is provided solely by the electric-dipole–magnetic-dipole interference, and it changes its sign upon the exchange of the light helicity. This term describes the conventional circular dichroism in the total absorption (CD [44]). The last term, C_3 , is induced by the electric-dipole–electric-quadrupole interference, while both included interference effects contribute to the second and third expansion terms in Eq. (3). As one can see from this equation, the sign of even expansion terms depends explicitly on the light helicity, while the odd terms, which contribute to the forward-backward asymmetry, are helicity independent. Combining both contributions from Eqs. (1) and (3) in Eq. (2), we obtain the following probability for the ionization of a chiral molecule by circularly polarized light:

$$\begin{aligned} \frac{d\sigma_{\text{DQM}}^\pm}{d\Omega} = \frac{1}{4\pi} [& \{B_0 \pm C_0\} + \{\pm B_1 + C_1\} P_1(\cos \theta) \\ & + \{B_2 \pm C_2\} P_2(\cos \theta) + \{C_3\} P_3(\cos \theta)]. \end{aligned} \quad (4)$$

For such extended angular distributions, which include contributions from higher odd Legendre polynomials, the total

forward-backward asymmetry was quantified in Refs. [45,46]. In this particular case, it is given as $\text{FB} = 2\beta_1 - \beta_3/2$ with the following definition of the odd β parameters,

$$\beta_1 = \frac{\pm B_1 + C_1}{B_0 \pm C_0} \quad \text{and} \quad \beta_3 = \frac{C_3}{B_0 \pm C_0}. \quad (5)$$

In order to demonstrate the relative strength of the nondipolar contribution to the forward-backward asymmetry as compared to the PECD, we performed a systematic investigation of the inner-shell photoionization of different emitter atoms in different chiral molecules. We carried out the corresponding numerical calculations in the frozen-core Hartree-Fock approximation using the equilibrium internuclear geometry of the ground neutral electronic state and by employing the stationary single center method and code [47–49]. We have used this approach earlier to study the PECD in chiral molecules [17–25]. In our calculations, the single-center expansions of bound electronic states of the molecules were restricted to $\ell \leq 99$, and for the photoelectron in the continuum to partial waves with $\ell_\epsilon \leq 35$. As a very first step to ensure that the present numerical procedure properly describes the nondipolar contributions we studied the N 1s photoionization of randomly oriented N₂ molecules and reproduced the near-threshold nondipole effects predicted in Ref. [43] (see Fig. 5 there).

Thereafter, the O 1s photoionization of methyloxirane and *sec*-butyl trimethylsilylether molecules was studied for photoelectron energies below 15 eV. In all cases, we found the forward-backward asymmetry induced by the nondipole contributions to be below 0.1%, which can be neglected as compared to the respective PECD. As a next step, we examined the inner-shell photoionization of a heavier atom from the third row of the periodic table, namely of the *K*, *L*, and *M* shells of the Si atom in *sec*-butyl trimethylsilylether molecules. For the 1s and 2s shells of Si, we observed noticeable but still small contributions from nondipole effects to the forward-backward asymmetry. We found these to be below 1% for photoelectron energies below 15 eV. For the other shells, the computed effect was negligibly small. The nondipole-induced forward-backward asymmetry was comparable to that of the PECD effect only for the inner-shell photoionization of an even heavier atom from the fourth row of the periodic table, namely for the *K*, *L*, and *M* shells of the Br atom in the epibromohydrin molecule. Those results are discussed below in detail.

We start our discussion of the inner-shell photoionization of the Br atom in the epibromohydrin molecule with the PECD effect. The forward-backward asymmetries, computed for the photoionization of the *K*, *L*, and *M* shells of Br in *R*-epibromohydrin in the electric-dipole approximation for circularly polarized light with positive helicity, $2\beta_1$ (D+), are depicted in Fig. 1 as functions of the photoelectron energy. Note that the respective photon energies differ dramatically because of the very different ionization potentials of about 13.47 keV for the 1s, 1.78 keV for 2s, 1.60 and 1.55 keV for 2p_j, 257 eV for 3s, and 189 and 182 eV for 3p_j shells [50]. Note also that for the *np* shells the computed effect is averaged over the *np_x*, *np_y*, and *np_z* contributions, and it can be considered as a total average over the *np_{1/2}* and *np_{3/2}* subshells.

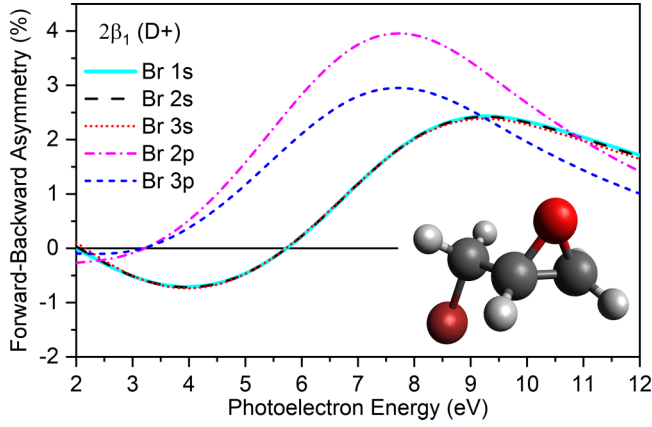


FIG. 1. Forward-backward asymmetries occurring in the photoionization of different shells of the Br atom in the *R*-epibromohydrin molecule (C_3H_5BrO , see inset), as computed in the electric-dipole approximation for circularly polarized light with a positive helicity [$2\beta_1$ (D+)]. Note that the PECD effects, resulting from our computations for the deep *ns* shells, are almost identical (within the line thickness), while those for the deep *np* shells are rather similar to each other.

As one can see from Fig. 1, our calculations yield almost identical forward-backward asymmetries for the three *ns* shells considered for Br. This is a direct consequence of the above-mentioned fact, that the inner-shell PECD is governed solely by the final-state contribution. Indeed, in all three cases, being launched in a small volume localized around the nucleus of the Br atom, the photoelectron wave packets multiply scatter on the molecular scaffold and experience, thereby, very similar chiral potentials. Those ionic potentials differ only in the region of localization of the atomiclike *ns* shells, where the molecular chiral effects are negligible. Extended calculations showed that this similarity does not hold for the delocalized 4*s* shell of Br. Even for the 2*p* and 3*p* shells of the Br atom, the computed forward-backward asymmetries are similar to each other. A notable difference, however, originates from a contribution from the 3*p_z* orbital, which points from Br towards the molecule.

We now turn to the discussion of the nondipole-induced forward-backward asymmetry. We show the results of our calculations for the *K* and *L* shells of the Br atom of a *R*-epibromohydrin molecule in Fig. 2, and those for the *M* shell in Fig. 3. The individual contributions $2\beta_1$ (D $\pm$), induced by the electric-dipole term, i.e., the PECD effect from Fig. 1, are shown by dashed curves for both light helicities. As expected, the effects have opposite signs, i.e., the respective curves are just mirrored with respect to FB = 0. The individual contributions, induced by the nondipole effects, are shown by dotted curves. As follows from Eqs. (5), in the absence of the PECD when $B_1 = 0$, the respective odd expansion coefficients β_1 and β_3 are almost independent of the light helicity. In particular, the very weak $\pm C_0 \ll B_0$ contribution in the denominators of Eqs. (5) describes changes of the total photoionization cross section via the conventional CD effect and can be neglected. Thereby, the depicted $2\beta_1 - \beta_3/2$ (QM) asymmetry is helicity independent. As one can see from the figures, the computed nondipole-induced forward-backward asymmetry is compara-

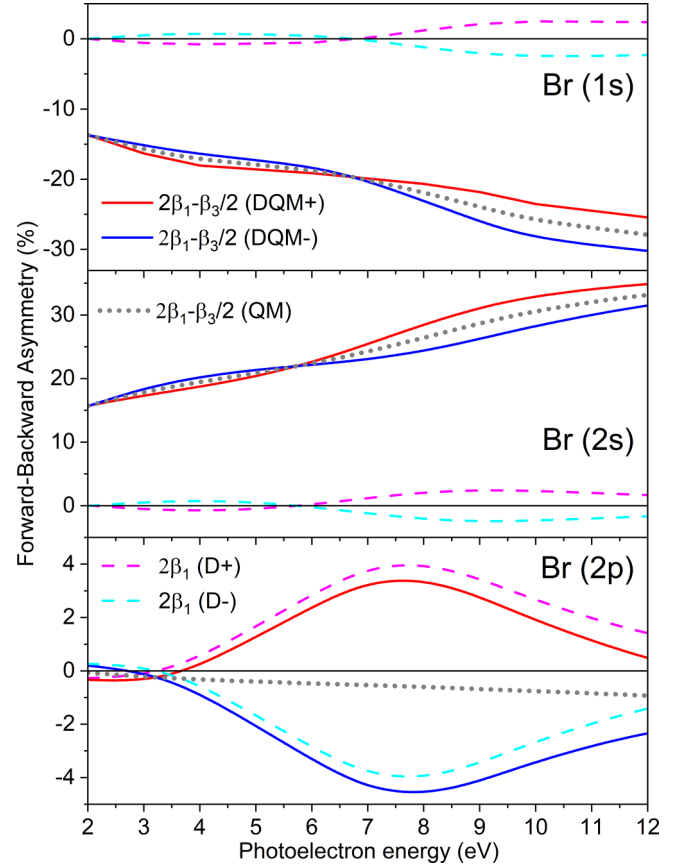


FIG. 2. Forward-backward asymmetries in the photoionization of 1*s*, 2*s*, and 2*p* shells of Br in the *R*-epibromohydrin molecule, as computed in different approximations (see legends). In addition to the individual helicity-dependent PECD effect, governed by the electric-dipole interaction with the circularly polarized light of different helicities [$2\beta_1$ (D $\pm$), dashed curves], the individual helicity-independent nondipole contribution [$2\beta_1 - \beta_3/2$ (QM), dotted curves], and the final results [$2\beta_1 - \beta_3/2$ (DQM $\pm$), solid curves] are shown.

ble to (for *np* shells) or even larger than (for *ns* shells) that from the PECD effect.

The combined forward-backward asymmetries $2\beta_1 - \beta_3/2$ (DQM $\pm$), as induced by the electric-dipole and the included nondipole contributions, are depicted in Figs. 2 and 3 for both light helicities by solid curves. As one can see, by interchanging the light helicity, this total asymmetry flips now with respect to the nondipole-induced contribution and not with respect to zero value. For the photoionization of *ns* shells of the Br atom, the effect of the nondipole contributions is enormous and even of different sign for 1*s* vs 2*s* and 3*s* shells. As the effect is particularly large in this case, even higher-order nondipole contributions to the light-matter interaction beyond the accounted for first-order magnetic-dipole and electric-quadrupole corrections (e.g., the second-order magnetic-dipole and electric-quadrupole corrections, or the first-order magnetic-quadrupole and electric-octupole [51]) might be observable as well. Moreover, for the considered deep shells, the core relaxation (a main electron-correlation effect here) and relativistic effects, which were neglected in the present calculation, may further influence both

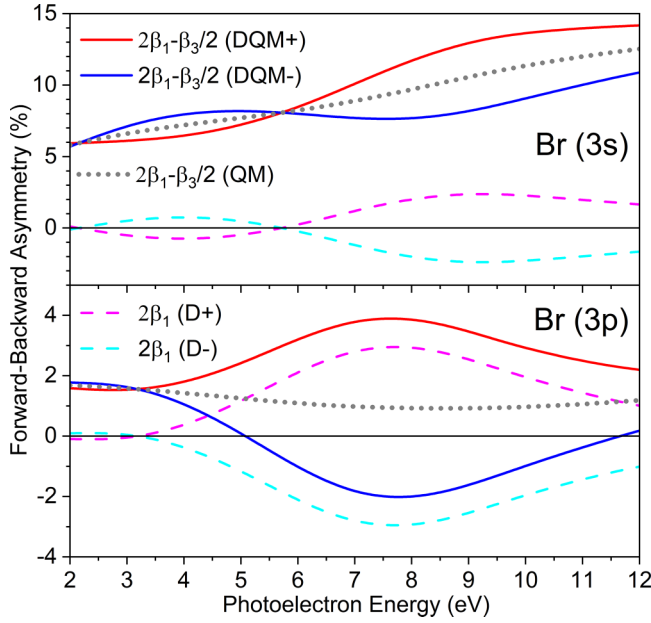


FIG. 3. The same as in Fig. 2 but for the 3s and 3p shells of Br. See the caption of Fig. 2 for details on the data representation.

asymmetries. Nevertheless, the qualitative effect predicted here is of a general nature and will persist. Since the created deep inner-shell hole relaxes by an ultrafast Auger-Meitner decay, postcollision interaction (PCI [52]) may significantly reduce the observed photoelectron energy. This needs to be considered when comparing the results presented here to a real experiment. In order to suppress PCI effects, one can consider higher photoelectron kinetic energies, but still within the significance interval of PECD. Alternatively, if the final ionic charge state is measured in coincidence with the photoelectron, cases of radiative decay which are not subject to PCI can be filtered out and inspected.

As a final point, we model in Fig. 4 how the nondipole-induced forward-backward asymmetry discussed above impacts a typical procedure of an extraction of the PECD from experimental data. In particular, it exemplifies how a nondipole contribution may impact the extraction of the PECD in an experiment leading to false measured results. In order to retrieve the β_L parameters, one usually fits the normalized difference between the photoelectron emission distributions, measured for a given photoelectron energy and two opposite light helicities $\frac{I^+ - I^-}{I^+ + I^-}$ [12,17,20,21,23,25]. Thereby, for instance, a possible angular dependence of the electron detection efficiency is negligible (i.e., it cancels in the numerator and denominator of this fraction). The electric-dipole contribution to the forward-backward asymmetry, i.e., the β_1 (D) parameter, survives in the numerator and cancels out in the denominator of the normalized difference. As a consequence, the normalized difference, computed in the electric-dipole approximation, is point symmetric, as is demonstrated in Fig. 4 by the solid curve using typical values of the β_1 (D) and β_2 (D) parameters. On the contrary, the nondipole contributions to the forward-backward asymmetry, i.e., the β_1 (QM) and β_3 (QM), cancel out in the numerator

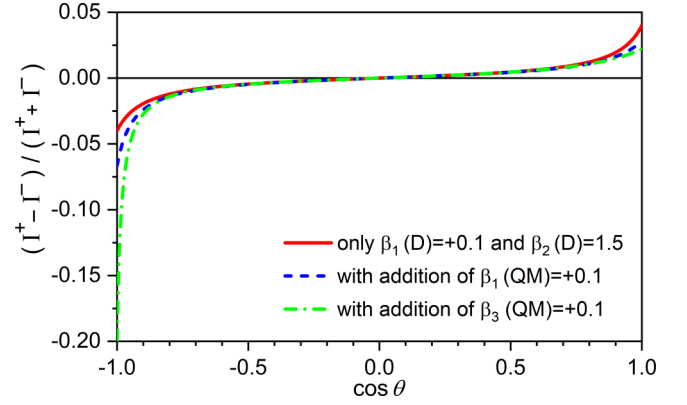


FIG. 4. Normalized difference of photoelectron emission distributions $(I^+ - I^-)/(I^+ + I^-)$, modeled for a given kinetic energy and two light helicities (indicated by the superscripts $\pm$) as a function of the photoelectron emission angle θ . Solid curve: electric-dipole approximation using the β_1 (D) = +0.1 and β_2 (D) = 1.5 parameters. Dashed curve: additionally including the nondipole contributions only via the β_1 (QM) = +0.1 parameter. Dashed-dotted curve: additionally including the nondipole-induced β_3 (QM) = +0.1 parameter.

but persist in the denominator of the normalized difference. Hence, the nondipole contributions break the point symmetry of the simulated normalized difference. As one can see from Fig. 4, incorporating the nondipole-induced β_1 (QM) in the simulations (dashed curve) and subsequently β_3 (QM) (dashed-dotted curve) parameters with their typical values and same sign (here positive) systematically reduces the normalized difference in the forward emission direction ($\cos \theta > 0$) and enlarges it in the backward ($\cos \theta < 0$).

In conclusion, we demonstrate theoretically that, for deep inner-shell photoionization of chiral molecules in the gas phase by circularly polarized radiation, the forward-backward asymmetry in photoemission, induced by the nondipole (retardation) effects, can have a larger magnitude as that caused by PECD. The latter is governed by the final-continuum state effect, while the former by the localization of the initial electronic state. Contrary to the PECD, the nondipolar asymmetry is helicity independent. As a consequence, switching between the light helicities results in a flip of the combined forward-backward asymmetry with respect to the nondipole contribution, and not with respect to zero. This effect is general and even substantial for deep inner shells of atoms from the fourth row of the periodic table, which are often present in chiral biomolecules (such as, e.g., an Fe atom). As a consequence, it needs to be taken into account in future experiments on the inner-shell PECD.

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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.

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