**Observation of enhanced chiral asymmetries in the inner-shell photoionization of uniaxially oriented methyloxirane enantiomers**

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(Dated: February 2, 2022)

Most large molecules are chiral in their structure: they exist as two enantiomers, which are mirror images of each other. Whereas the rovibrionic sublevels of two enantiomers are almost identical, it turns out that the photoelectric effect is sensitive to the absolute configuration of the ionized enantiomer – an effect termed Photoelectron Circular Dichroism (PEC). Our comprehensive study demonstrates that the origin of PEC can be found in the molecular frame electron emission pattern connecting PEC to other fundamental photophysical effects as the circular dichroism in angular distributions (CDAD). Accordingly, orienting a chiral molecule in space enhances the PEC by a factor of about 10.

PACS numbers: 33.80.-b, 32.80.Hd, 33.55.+b, 81.05.Xj

Photoionization of unpolarized electronic states of an atom is insensitive to the light’s helicity: The count rate on an electron detector placed at any particular angle does not change when switching between photons of different circular polarization. In order to make the photoelectron count rate sensitive to the photon helicity, the measurement conditions need to establish a coordinate frame which is fixed in space to stereoscopically image nearest neighbour distances. The normalized difference of these emission patterns for the two helicities is known as the Circular Dichroism in Angular Distributions (CDAD) and since it is symmetric in the forward/backward directions, it depends only on the azimuthal angle $\phi$ around the light propagation [5]: 

$$CDAD = \frac{I_{\phi} - I_{-\phi}}{I_{\phi} + I_{-\phi}}$$

Here $I_{\phi+1}$ and $I_{\phi-1}$ correspond to the ionization cross section by left or right circularly polarized light (labeled by positive or negative helicity ±1). The asymmetry of the electron flux induced by circularly polarized photons in the up/down directions has been successfully utilized, e.g., in surface science to stereoscopically image nearest neighbour distances [6]. For molecules which are fixed in space, CDAD values up to 100% can be observed [5].

A forward/backward asymmetry in the photoemission – even within the electric-dipole approximation [7] – can arise due to scattering of the electron in the molecular potential whenever the structure of a fixed-in-space molecule breaks that symmetry. The change of this forward/backward asymmetry in the emission distribution that arises when switching the light’s helicity is termed Photoelectron Circular Dichroism (PEC). PEC occurs as the molecular structure acts as a gearbox, which translates the rotation of the electric field vector into a change of the forward (or backward) directed electron flux. A mechanical analogue for such machinery is a nut on a thread. The thread transforms the rotation of the nut into forward (or backward) directed motion.
from fixed in space R(+) methyloxirane (C\textsubscript{3}molecular level: our calculated electron emission patterns

Figures 1c and 1d show the corresponding effect on the

Polar and azimuthal angles \{\theta, \phi\} are indicated in panel (d).

Figures 1: (Color online) Three-dimensional molecular frame photoelectron angular distributions. Top: for the C 1s-electrons emitted from CO for left (a) and right (b) circularly polarized light (taken from Ref. 5). Bottom: theoretical distributions computed here for the O 1s-ionization of R(+) methyloxirane by left (c) and right (d) circularly-polarized light. The molecules are oriented as depicted in the insets. Polar and azimuthal angles \{\theta, \phi\} are indicated in panel (d).

Our calculations shown in Figs. 1c and 1d demonstrate that PECD occurring for certain molecular orientations is strongly enhanced and in principle could reach 100%. In order to verify this prediction experimentally, one would need to fix the orientation of the examined molecule in space. The present work makes a first step towards this goal by studying uniaxially oriented methyloxirane molecules upon O(1s)-photoionization (h\omega = 550 eV) using the COLTRIMS-technique 26 with a specially designed high-resolution (3d focusing for electrons and ions) spectrometer without any meshes in order to increase the overall particle detection efficiency. The peak of observed photoelectrons was centered at a kinetic energy of about 11.5 eV. Before the nuclei start to rearrange in response to the creation of the O(1s)-hole, an ultrafast Auger decay takes place, which is finally followed by a Coulomb fragmentation of the doubly-charged ion. Even though fragments with the mass over charge ratio m/z equal to 14, 15, 25, 26, 27, 28, 29, 30, 31, and 42 have been observed in the Photoion-Photoion Coincidence (PIPIOICO) spectra, the present analysis was performed only for two types of molecular breakup with the following fragment combinations: \textit{C}_{3}\textit{H}_{5}^{+}(m/z 26) - \textit{COH}^{+}(m/z 29) and \textit{CH}_{3}^{+}(m/z 15) - \textit{C}_{2}\textit{H}_{2}O^{+}(m/z 42). For such a rather large molecule it is not straightforward to relate the measured asymptotic momenta of the ionic fragments to a given molecular axis. Therefore, the molecular orientation at the instant of the photoionization was an optimization parameter in the present electronic structure and dynamics calculations, which were carried out by the Single Center method and code 27, 28. Details on the experimental approach and the theory can be found in the Supplemental Materials document 29.

Fig. 2 compares the measured and computed PECD for randomly oriented molecules (a) and for the two cases where the fragmentation axis of the molecules was fixed-in-space (b and c). The PECD measured for the randomly oriented molecules (note that Fig. 2 comprises
FIG. 2: (Color online) PECD as a function of the photoelectron emission angle $\theta$, with respect to the photon propagation, measured and computed in the present work for the O 1s-photoionization of the two enantiomers of methyloxirane: (a) for randomly oriented molecules and $p$($26$\,amu) $-$ $p$($29$\,amu) fragmentation channel, (b) and (c) for the fragmentation axis being fixed at an angle $\beta = 90^\circ$ with respect to the light propagation direction and for the two different fragmentation channels $p$($26$\,amu) $-$ $p$($29$\,amu) and $p$($15$\,amu) $-$ $p$($42$\,amu).

only data for the $p$($26$\,amu) $-$ $p$($29$\,amu) channel) shows maximum values between 3\% and 4\%, whereas the PECD obtained after fixing the fragmentation axes in space parallel to the polarization plane (the angle between the fragmentation axis and the light propagation axis was between $85$ and $95^\circ$) shows much higher asymmetries (Figs. 2b and 2c). In particular, applying such a restriction to the fragmentation channel $p$($26$\,amu) $-$ $p$($29$\,amu) gives experimental asymmetry values up to 12\%, whereas theoretical curves lead to the maximum asymmetry of 10\%. Similar enhancement is observed for the fragmentation channel $p$($15$\,amu) $-$ $p$($42$\,amu). We also note that the generally expected change of sign of PECD with respect to the interchange of the enantiomers (R(+) and S(–) denote the two different enantiomers) is clearly observed for both randomly oriented and fixed-in-space molecules.

A more detailed view on the PECD is given in Figs. 3 and 4. These figures depict PECDs obtained for the two fragmentation channels as functions of the photoelectron emission angle $\theta$ and of the molecular orientation angle $\beta$ (angle between the fragmentation axis and the light propagation axis). One can see, as well, that the sign of the PECD changes when the enantiomers are swapped (cf. Figs. 3a with 3b and Figs. 4a with 4b). This latter finding confirms that the observed asymmetry has a chiral origin. Moreover, the measured two-dimensional PECDs confirm the following analytically derived symmetry property: $\text{PECD}(\pi - \theta; \pi - \beta) = -\text{PECD}(\theta; \beta)$. Since we observe different signs of PECD upon switching between the forward ($\theta = 0^\circ$) and the backward ($\theta = 180^\circ$) photoemission directions, the symmetry rule results in similar signs for the molecular axis oriented along the light propagation ($\beta = 0^\circ$, forward) and in the reversed direction ($\beta = 180^\circ$, backward). For a given enantiomer, the PECD reverses its sign when the molecular orientation changes from being parallel to the light propagation axis ($\beta = 0^\circ/180^\circ$) to the case when it is orthogonal to the
FIG. 4: (Color online) The same as in Fig. 3 but for the p(15 amu)−p(42 amu) fragmentation channel.

light propagation (β = 90°). Therefore, integration over all orientations results in a considerably smaller effect.

Experimentally, we find an asymmetry of up to 15% for the p(26 amu)−p(29 amu) breakup and even higher asymmetries up to 30% in the case where (θ = 0°; β = 160°) for the fragmentation channel p(15 amu)−p(42 amu). The higher asymmetry observed at some molecular orientations for the latter fragmentation channel can be explained by the fact that it corresponds to a single bond breaking (loss of methyl group), whereas the former requires the breaking of two bounds. As a consequence, the analysis of the coincident data allows for a more accurate determination of the molecular orientation for the p(15 amu)−p(42 amu) breakup, whereas in the case of the p(26 amu)−p(29 amu) channel, an additional averaging over orientations can be present. The computed PECDs (Figs. 3c and 4c) show a good overall agreement with the experimental data: Both have similar signs of asymmetries, but the theoretical values are somewhat overestimated. For the fragmentation channel p(26 amu)−p(29 amu), the calculations show asymmetries up to 30%, whereas PECD of about 35% is computed for the fragmentation channel p(15 amu)−p(42 amu). Integration of the signals I±1 over all angles β gives the much smaller PECD observed for randomly oriented samples (Fig. 2a). Finally, the dichroic parameter b1 computed and measured for R(+) enantiomer is very small and equal to 1.35% and 1.56%±0.25%, respectively. These results support the intuitive prediction that selecting a particular 3D orientation, rather than averaging over all orientations, enables to remove any cancelation that occurs due to compensation of the PECD for different molecular orientations.

As PECD depends only on the angle θ with respect to the light propagation axis, we have so far averaged the electron distribution over the azimuthal angle φ in the polarization plane. By selecting molecular orientations to be perpendicular to the light propagation direction (β = 90°), the CDAD as a function of the azimuthal emission angle φ in the polarization plane can be extracted from the experimental coincident data. The measured CDADs are depicted in Fig. 5. Unlike PECD, which have different signs for the two enantiomers, the CDAD is enantiomer insensitive, having equal trends for R(+) and S(−) methyloxirane. Accordingly, the CDAD has to vanish for randomly oriented chiral molecules, similarly to the case of randomly oriented achiral molecules. Finally, the computed CDADs reproduce the trends of the experimental asymmetry, although the theory slightly overestimates its magnitude (Fig. 5). We notice that CDAD and PECD were obtained by two very different data treatments (see Sup-
plemental Materials [29] for details). This can be a reason for the larger disagreement between the theory and experiment for CDAD, since building a new coordinate system for the data analysis could result in larger uncertainties of the emission and orientation angles determination. The observed discrepancy therefore exceeds the purely statistical error bars shown in Fig. 7.

In conclusion, all previous studies of PECD in the gas phase were performed for randomly oriented chiral molecules. In those studies, PECD was discussed in terms of laboratory frame angular distribution and described as a forward/backward asymmetry in the photoelectron emission which survives after averaging over all molecular orientations. Our theoretical predictions illustrate that fixing three-dimensional orientation of a target in space may in principle result in a 100% effect, as it is known for CDAD. Using coincident detection technique we provide the first experimental proof for those expectations and demonstrate that chiral asymmetry for O(1s)-photoionization of methyloxiran can be significantly enhanced already by fixing one molecular fragmentation axis. Providing larger asymmetries makes PECD of oriented chiral molecules a more sensitive tool for the enantiomeric excess determination. The present analysis supports the transparent picture of the photoelectron scattering on the molecular potential being at the heart of the PECD. By interrelating the fundamental PECD and CDAD phenomena with the molecular frame photoelectron angular distribution we pave the way for a detailed understanding of the origin of this fundamental photo physical effect.

The work was supported by the State of Hesse Initiative for the Development of Scientific and Economic Excellence (LOEWE) within the focus-project Electron Dynamics of Chiral Systems (ELCH). Financial support by the Deutsche Forschungsgemeinschaft (DFG Project No. DE 2366/1–1) is gratefully acknowledged. We thank Thomas Baumert for suggesting to us the nut/thread analogy, which was originally discussed by Ivan Powis in Ref. [16]. We thank T. Daniel Crawford for providing us with the optimized geometry of methyloxiran.

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