Hard X-ray helical dichroism of disordered molecular media

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Chirality is a structural property of molecules lacking mirror symmetry that has strong implications in diverse fields, ranging from life sciences to materials science. Chirality-sensitive spectroscopic methods, such as circular dichroism, exhibit weak signal contributions on an achiral background. Helical dichroism, which is based on the orbital angular momentum (OAM) of light, offers a new approach to probe molecular chirality, but it has never been demonstrated on disordered samples. Furthermore, in the optical domain the challenge lies in the need to transfer the OAM of the photon to an electron that is localized on an ångström-size orbital. Here we overcome this challenge using hard X-rays with spiral Fresnel zone plates, which can induce an OAM. We present the helical dichroism spectra of a disordered powder sample of enantiopure salts of the molecular complex of \([\text{Fe}(4,4'-\text{diMebpy})_3]^2-\) at the iron K edge (7.1 keV) with OAM-carrying beams. The asymmetry ratios for the helical dichroism spectra are within one to five percent for OAM beams with topological charges of one and three. These results open a new window into the studies of molecular chirality and its interaction with the OAM of light.

Chiral molecules exist in two mirror-image non-superimposable configurations that are called enantiomers. Although chemically identical, the two enantiomers can have dramatically different chemical reactions and biological functions. Therefore, the asymmetric synthesis and the detection of a single type of enantiomer of chiral compounds are topics of crucial importance, due to their numerous applications, ranging from life sciences to materials sciences.

The two most commonly used methods for distinguishing enantiomers are optical rotatory dispersion (ORD) and circular dichroism (CD). ORD is the rotation of the plane of linear polarization of visible-ultraviolet light induced by propagation through a chiral medium, whereas CD denotes the difference in absorption of left- and right-handed circularly polarized light in chiral molecular systems. Since CD and ORD vanishes in achiral media, it is a unique probe of molecular chirality. Both ORD and CD are based on interactions of the investigated chiral molecules with the spin angular momentum (SAM) of light. The SAM of light can take a value of \(+1\) or \(-1\), which correspond to the left and right circular polarization states, respectively. These techniques rely on magnetic dipole interactions, a higher order term in the multipolar expansion of the interaction Hamiltonian of light with matter. As a consequence, CD signals correspond to typically \(-0.1\%\) of the total linear absorption.

In addition to a SAM, photons can possess an unbound OAM, which corresponds to the spatial phase distribution of the wavefront. In contrast to CD, transferring the OAM of a photon beam to an electron in an atom or molecule is extremely challenging and hard to detect. The main reason for this lies in the need to transfer the phase of an electromagnetic wave, which can easily extend over several hundreds of nanometres, to an electron that is typically localized in an ångström-size orbital. In addition, the centre of the investigated molecule or atom is never perfectly aligned with the centre of the phase vortex and it has been shown that the relative position of the material system with respect to the OAM centre is of crucial importance for the amplitudes of the transitions. Despite these difficulties, progress has been made in the observation of momentum transfer from an OAM beam to bound electrons, and recently to photoelectrons that were ionized from Rydberg states by an OAM-carrying infrared beam. A scheme using OAM beams to trap and discriminate optically chiral molecules has also been proposed.

Helical dichroism (HD) is the differential absorption between two linearly polarized OAM beams with left and right helicities. Similar to the case of the electronic wavefunction, a non-zero OAM field is obtained when the expectation value of the OAM operator \(L = r \times p\) is non-zero, where \(r\) and \(p\) are the position and momentum operators. In particular, fields that are eigenvectors of this operator with a non-zero eigenvalue carry an OAM (or topological charge) of an integer value \(L\). These fields display a phase twist along the axis of propagation of \(e^{i\varphi}\) where \(\varphi\) is the angle in cylindrical coordinates. The SAM and OAM of vortex beams have long been discussed using either classical or quantum approaches. However, although various theoretical studies have demonstrated their high potential to discriminate chiral objects, the properties of vortex beams interacting with molecules have scarcely been used in spectroscopic applications so far.

The growing experimental interest in HD is triggered by the capability to produce OAM beams in a versatile fashion. Dichroic effects have been demonstrated on chiral molecules adsorbed on ordered arrays of plasmonic metallic nanoparticles. However, the

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interpretation of the signal is complicated by the details of the molecule–nanoparticle interaction. More recently, a giant HD from a single chiral microstructure was reported, reaching 20% in the visible range\(^1\). However, so far, and regardless of the spectral range, there has been no experimental demonstration of HD on randomly oriented enantiopure samples, let alone molecules.

In a previous theoretical study, Ye et al.\(^12\) showed how HD is a sensitive probe of molecular chirality, which, just like CD, vanishes in randomly oriented achiral samples. In Supplementary Section 1, we review the fundamentals of HD showing how it engages with molecular chirality. The use of the OAM for HD spectroscopy implies some fundamental differences with CD. First, CD is well formulated in the magnetic dipole approximation giving rise to the rotational strength, while the electric quadrupole term vanishes upon rotational averaging. On the other hand, HD strongly relies on the spatial relation of the phase and the molecule. Thus, it cannot be adequately described in the dipolar approximation. The multipolar expansion can be used to accurately describe the electric field near the singularity\(^15\). Alternatively, a non-local formalism was developed based on the minimal coupling Hamiltonian that encompasses all multipoles\(^16\). In this description, the light–matter coupling is described through an overlap integral of the vector potential and the current density operator (see Supplementary Section 1). Second, CD is limited to the difference between left and right circular polarizations, for a SAM of light limited to \(\pm 1\) values. On the other hand, HD can be carried with all integer \(\pm L\) values, leading to a variation of signal amplitudes at different wavelengths. This can be understood as follows: transition current densities can be expanded in vector spherical harmonics\(^17,18\), which also carry a phase twist. The OAM fields with an \(L\) value matching the dominant term in this spherical expansion will yield the strongest signals. In other words, HD is not only a measure of chirality but it also reveals the degree of chirality by the dependence of the magnitude of the signal difference on the \(L\) value.

Given the serious limitations of probing the HD of disordered media in the optical domain, the hard X-ray domain offers two major advantages. First, the increased amplitude of the wavevector \(k\) has the consequence that higher multipoles can contribute to the measured signal. These higher multipoles interact with spatial derivatives of the exciting fields and are thus more sensitive to their spatial variation, that is, the phase vortex in the present case. Second, the short wavelengths of X-rays enable much smaller focal spots than in the optical domain, leading to a phase gradient in the illuminated area that is orders of magnitude higher. This enhanced phase gradient is favourable since, in actual experiments, the vortex and the chiral compound under investigation are not perfectly aligned: the higher the phase gradient experienced by the chiral material, the larger the anticipated interaction cross-section. By contrast, a spatially large vortex locally induces a smaller field gradient, which is expected to lead to a substantially lower HD signal.

In this work we report the study of a helicity-dependent spectroscopic signal from an OAM beam at the iron (Fe) K edge (7.1 keV, 1.7 Å). We investigate an enantiopure sample of the chiral metal–organic dicationic molecular complex \([\text{Fe(4,4'‐diMebpy)}_3]^{2+}\), that is, \(\text{Fe}^{II}(4,4’\text{'‐dimethyl‐2,2’‐bipyridine)}_3\) shown in Fig. 1, which has right-handed (Δ) and left-handed (Λ) configurations. To control the three-bladed propeller structure, association with a chiral anion is used so that the molecule can be stabilized in single-configuration Δ or Λ salts\(^19\). The chiral anion used is enantiopure TRISPHAT [tris(tetrachlorobenzendiolato)phosphate(V)] (diastereoselectivity > 96%), whose synthesis and stereocontrol are described in Supplementary Section 5.

We conducted the spectroscopic experiments using OAM beams of different topological charges at the cSAXS beamline of the Swiss Light Source (Paul Scherrer Institut, Villigen, Switzerland). The experimental setup is shown in Fig. 2. We used diffractive X-ray lenses, that is, spiral Fresnel zone plates (SZPs)\(^22\)–\(^24\), to generate the linearly polarized OAM-carrying beams. To this aim, we fabricated a set of SZPs with different topological charges in both helicities, including a conventional Fresnel ZP (FZP) without topological charge. The SZPs, made of gold, were prepared using the lithographic method described in detail in ref. \(^23\). They have a diameter of 120 μm, an outermost zone width of 60 nm and a height of 1.2 μm. The capabilities of these SZPs for generating OAM beams has been previously demonstrated\(^26\)–\(^29\). To confirm the quality of the vortexed wavefronts, we performed ptychographic scans of an available resolution test sample (Siemens star)\(^30\). Figure 3 shows the complex-valued illumination fields at the focal position, which were obtained together with the sample transmissivity in the ptychographic reconstruction and through propagation to the focus. They confirm the quality and geometric size of the phase vortex created by the SZPs. The \(L = +3\) vortex displays an elongated shape with two local minima, which indicates that it may not be perfect. Under non-optimal conditions, similar effects have been observed in the visible domain\(^31\). The molecular samples were placed at the focal position. The Fe K-edge X-ray absorption near-edge structure (XANES) spectra were then recorded for \(\omega = 7.10–7.15\text{keV}\) using the OAM-carrying beams. Several spectra were acquired for both positive and negative values of the OAM, and for both enantiomers. The XANES spectra were measured in total fluorescence yield (or TFY) detection mode using an Eiger 50k detector positioned at

Fig. 1 | Δ (right) and Λ (left) enantiomers of chiral \([\text{Fe(4,4’‐diMebpy)}_3]^{2+}\). This metal–organic complex is stabilized into a three-bladed propeller structure by association with a chiral anion. Colour code: Fe, orange; N, blue; C, dark grey; H, light grey. bpy, 2,2’-bipyridine.

Fig. 2 | Illustration of the experimental setup. The OAM-carrying beam is generated using an SZP. A central beam stop and an aperture ensure that only the first diffraction order of the zone plate reaches the sample, which is brought into the focus of the beam in solid form on a pin. Spectra are recorded using a TFY detector that is mounted on the side close to the sample.
90° from the incoming beam to minimize elastic scattering. More details of the experimental procedures are given in Supplementary Section 3.

Figure 4 shows the Fe K-edge XANES spectra of the Λ- and Δ-enantiomers for values of the OAM carried by the beams of ±1 and ±3, as indicated by the $L$ value. The spectra for $L = ±4$ were also recorded but were too noisy due to the limited data acquisition time and are therefore not presented here. The spectra exhibit an overall similar shape with a pre-edge feature at 7.115 keV, an edge feature at 7.125 keV and the main edge peak at 7.131 keV. These features are comparable with already measured and computed XANES spectra at 7.125 keV and the main edge peak at 7.131 keV. These features are attributed to a dipolar 1s → 4p transition. The 7.131 keV feature represents the onset of the multiple scattering region typical of the above-edge XANES. The XANES spectra have similar amplitudes ($\sim(1 \pm 0.2) \times 10^5$ counts). We note that a slight difference of the XANES amplitude, stemming from variations of the sample thickness, does not alter substantially the asymmetry ratio as the spectra are normalized. Error bars are calculated as type-A uncertainties (see Supplementary Section 6).

It is worth stressing the differences between the $+L$ and $−L$ spectra of the different enantiomers in Fig. 4. In particular, for the Δ enantiomer the $+L$ values yield slightly more intense spectra, whereas the reverse is observed for the Λ enantiomer. This indicates that the transition current density of the dense of the Δ enantiomer has an OAM component more important in $+L$ than $−L$, that is, its vector multipolar expansion coefficient with a momentum $+L$ is larger than that with a momentum $−L$. The preferred sign for each enantiomer could be related to their three-bladed structure that favours a given sign of the OAM in the multipolar expansion.

The HD signal, $S_{HD}$, is defined by the differential absorption of vortex beams carrying ±L OAM and, as for CD spectra, we normalize the signal by the average of the absorption of clockwise and counterclockwise helical beams to define the measured HD asymmetry as:

$$S_{HD} (L, \omega) = \frac{A_{+L}(\omega) - A_{-L}(\omega)}{\frac{1}{2} [\max A_{+L}(\omega) + \max A_{-L}(\omega)]}$$

where $A_{±L}(\omega)$ is the XANES spectrum. Unlike the asymmetry ratio commonly used in the optical regime, the maximum of the XANES spectrum is used for normalization. This tends to underestimate the HD in the observed spectral range, but it minimizes the uncertainty of dividing by an almost vanishing signal in the pre-edge region. The HD spectra resulting from Fig. 4 measured on enantiopure powders of the Δ- and Λ-enantiomers for $L = ±1$ and ±3 are displayed in Fig. 5, confirming that the HD signals exhibit opposite signs for opposite enantiomers, as demonstrated in the Supplementary Information.
The asymmetry ratio in HD ranges from 1% to 5%, which, considering the used normalization, is much higher than that commonly achieved in standard CD measurements in the optical domain, and also in the very few CD studies in the X-ray domain\textsuperscript{34–39}. This is a very promising result in view of the applications of HD for the characterization of molecular enantiomers.

The 1s\textrightarrow{}3d transition in the pre-edge region does not seem to provide a distinct feature, although the HD signal appears to set in around 7.140 eV, which is very close to the K- or L\textsubscript{1}-edge spectra that stem from states g and the core excited state c. The transition currents provide information on the current needed to move the charges from state g to state c. The phase twist of the field envelope is given by the \( \phi \) term, with \( \phi \) being the azimuthal angle in the plane transverse to the beam propagation. For a given molecule, \( j_{\phi}(r) \) is a vector field and the magnitude of each overlap integral, that is, the strength of the HD beam for a given OAM value, depends on its multipolar expansion. This multipolar expansion is expected to peak for a given L value and HD measurements repeated with various OAMs would provide a multipolar spectrum of the transition current density.

In the region above the absorption edge, the spatial shape of the electronic current operator varies slowly since the transition matrix elements concern a transition into the continuum. This explains the sign of the HD spectrum in that region. In addition, the strength of the HD signal decreases towards the end of our acquisition window, that is moving into the extended X-ray absorption fine structure (or EXAFS) region, in a similar fashion observed in X-ray natural CD (or XNCD) experiments\textsuperscript{34–39}. For XNCD, it was concluded that single scattering pathways that dominate the EXAFS region cannot lead to chiral sensitivity, because single scattering events involve only two atoms that always have inversion symmetry, independently of the nearby molecular potential. This reasoning is likely to hold for HD.

The transition matrix elements can also be used to understand the amplitude of the HD signal. It can be expected that it will be at a maximum for the best geometrical match between the electromagnetic field with a topological charge L and the current density matrix elements \( j_{\phi}(r) \). When \( j_{\phi}(r) \) is expanded into its multipolar components, the interaction is dominated by the multipoles with the same OAM as the incoming field. The measurement with one sign of L will cancel out the phase in the spherical integral in good approximation and lead to a high transition matrix element, whereas the measurement with the opposite L will add up the phases and result in a smaller overlap integral. In the current experiment we can observe that the HD signal is about three times smaller for measurements with \( L = \pm 3 \) than with \( L = \pm 1 \), indicating that the wavefront gradient of the topological charge \( L = \pm 1 \) fits the molecular geometry better than does \( L = \pm 3 \). In other words, the asymmetry ratio of HD as a function of L is a measure of the degree of chirality. More extensive measurements with a larger set of OAM values will enable us to obtain an accurate window into the spherical spatial variation of the transition under investigation.

As already mentioned, the difficulty in performing optical-domain HD is the reason why only two studies have successfully been carried out on fairly large plasmonic nanoparticle aggregates\textsuperscript{41} or a single microstructure\textsuperscript{42}. This also explains why most optical-domain experiments use much higher topological charges, typically between 10 and 50. By contrast, we demonstrate HD in a randomly oriented sample of molecular enantiomers. SZPs tuned for X-rays have the added advantage over spiral phase plates commonly used in the optical domain of being achromatic over an extended frequency range, enabling the scanning of spectra as presented here. The use of SZPs and a ptychography setup opens the way for making HD a standard technique at synchrotron facilities. Here we probed the iron atom, at the centre of a chiral three-bladed propeller geometry. It is interesting to consider what happens when atoms away from the stereogenic centre are interrogated. Simulations\textsuperscript{12,39} have suggested that the signal would decrease with increasing distance between the probed atom and the stereogenic centre.

The present work also opens a new window into hard X-ray studies of molecular chirality. Such studies have previously only been achieved by recording the CD spectra of crystalline or oriented samples at the K edge of transition metals\textsuperscript{34–37}. The effect was attributed to the interference between allowed electric-dipole and electric quadrupole transition moments. The electric–magnetic dipole interaction of CD spectroscopy is even excluded for K- or L\textsubscript{1}-edge spectra that stem from s orbitals, so the only possible source of magnetic dipole intensity involves 1s–2p orbital mixing, due to their small energy separation in light atoms, and core–hole relaxation. Indeed, the only reported X-ray CD spectrum of a randomly oriented sample has concerned gas-phase methylxirane\textsuperscript{43} at the carbon K edge. The present work demonstrates the feasibility of hard X-ray chirality studies of randomly oriented samples. HD measurements can also be implemented in chiral solid materials with magnetic vortices\textsuperscript{44}. In this case, the signal will be given as the overlap between the magnetic vortex and the incoming beam phase vortex\textsuperscript{45}. Furthermore, time-resolved X-ray HD studies can now be envisioned\textsuperscript{46–48} and a recent deep-ultraviolet CD study of the excited-state chirality of the present compound has been achieved\textsuperscript{49}, which serves as an ideal basis.
In summary, the present work reports four achievements: the observation of HD in a disordered medium, the HD study of molecular systems, the demonstration of HD in the hard X-ray regime, and, for that matter, element-selective X-ray HD. These achievements promise exciting developments on the fundamentals of molecular chirality, which will undoubtedly pave the way to novel insights into molecular structure and dynamics.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41566-022-01022-x.

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Methods

Zone plate fabrication. For fabrication of the SZPs, a 2 × 2 mm and 250-nm-thick silicon nitride membrane was coated with a conductive metal layer and a 1.4-μm-thick poly(methyl methacrylate) film as a lithography resist. After exposure in a 100 kV electron lithography tool (Vistec EBPG 5000+) and development of the exposed parts in a mixture of isopropanol and water (7:3), a 1.2-μm-thick gold film was electrochemically deposited. In a subsequent step, the poly(methyl methacrylate) film was removed using acetone and the resulting structures where dried using supercritical CO2. With this method, we fabricated SZPs with a diameter of 120 μm, an outermost zone width of 60 nm and topological charges from \( L = -9 \) to \(+9\) (including conventional FZPs without topological charge).

Ptychography. Ptychography is a diffractive imaging technique that enables the simultaneous reconstruction of the amplitude and the phase of both the sample and the illuminating wave\(^{47,48}\). This technique is based on proportionality between the diffraction pattern in the far-field and a Fourier transform of the complex-valued transmissivity of the sample. In ptychography the sample is raster scanned using an area-by-area scan in a confined and coherent X-ray beam with a step size smaller than the illumination spot. This results in the same areas being partially illuminated in multiple scans. Since the probe at each point stays constant, this information can be used to retrieve the wavefront information\(^{26}\).

In the current experiment we used lithographically prepared star patterns (Siemens star) as a sample (see Supplementary Fig. 5). The general scheme of the setup is shown in Fig. 2. X-ray photons with an energy of 7.1 keV are selected using a fixed–exit double-crystal Si(111) monochromator. The defined illumination on the sample is produced using a central stop, an FZP and an order-sorting aperture. To record the scattered X-rays, we used a Pilatus 2M detector positioned 7.252 m from the sample in the forward direction. The sample was mounted on a piezo stage to enable accurate positioning with respect to the beam.

Data availability

Data needed to generate Figs. 3, 4 and 5 and associated scripts are available in the Supplementary Information.

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Author contributions

J.R.R., B.R., D. Karpov and M.C. conceived and organized the experiments. J.R.R., B.R., D. Karpov, C.B., G.F.M., D. Kinschel, O.C., C.S. and A.D. carried out the experiments. B.R. and C.D. designed and fabricated the spiral Fresnel zone plates. F.Z. and J.L. synthesized the chiral salts. M.O. characterized the samples and provided critical feedback. J.R.R., B.R. and M.C. interpreted the results and wrote the manuscript with contributions from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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