Unscrambling Structured Chirality with Structured Light at the Nanoscale Using Photoinduced Force

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Supporting Information

ABSTRACT: We show that the gradient force generated by the near field of a chiral nanoparticle carries information about its chirality. On the basis of this physical phenomenon we propose a new microscopy technique that enables the prediction of spatial features of chirality of nanoscale samples by exploiting the photoinduced optical force exerted on an achiral tip in the vicinity of the test specimen. The tip–sample interactive system is illuminated by structured light to probe both the transverse and longitudinal (with respect to the beam propagation direction) components of the sample’s magnetoelectric polarizability as the manifestation of its sense of handedness, i.e., chirality. We specifically prove that although circularly polarized waves are adequate to detect the transverse polarizability components of the sample, they are unable to probe the longitudinal component. To overcome this inadequacy and probe the longitudinal chirality, we propose a judiciously engineered combination of radially and azimuthally polarized beams as optical vortices possessing pure longitudinal electric and magnetic field components along their vortex axis, respectively. The proposed technique may benefit branches of science such as stereochemistry, biomedicine, physical and material science, and pharmaceutics.

KEYWORDS: chirality, optical forces, photoinduced force microscopy, azimuthally polarized beam, structured light, nanophotonics

Structure determination of chiral specimens is of great interest since the fundamental building blocks of life, i.e., proteins and nucleic acids, are built of chiral amino acids and chiral sugar. Indeed, the optical activity of chiral structures is a key parameter in molecular identification techniques to recognize the type of molecule or to determine its structure thanks to the discriminatory behavior of chiral molecules in interaction with the incident light possessing a distinct sense of polarization. For instance, for a protein, determining the structure refers to resolving its four levels of complexity, i.e., primary, secondary, tertiary, and quaternary, which defines not only the sequence of amino acids but also reveals the three-dimensional arrangement of atoms in that protein. This information is of supreme importance in modifying and utilizing proteins for new purposes such as creating protein-based antibody drug conjugates for cancer treatment or modifying the proteins in bread. To determine the structure of chiral samples such as protein, noninvasive spectroscopic techniques based on optical rotation (OR), circular dichroism (CD), and Raman optical activity (ROA) have been proposed and vastly studied. In these methods, owing to the optical activity of chiral structures, the difference between the absorbed left-hand and right-hand circularly polarized (CP) light is measured, and not only the chirality but also some important information about the structure of a chiral sample is obtained. Specifically using CD, one can approximate the secondary structure of a protein. However, the main limitations of this method are as follows: (i) it is unable to provide high-resolution structural details and (ii) it demands a considerable amount of material for detection. These limitations mainly originate from the fact that CD measures the average far-field radiation, which misses the essential information carried only in the near field; thus, this dearth calls for possible potent near-field measurement techniques that are more promising for providing nanoscale details.

The capability of atomic force microscopy (AFM), which was originally introduced to derive the morphological properties of a specimen, has been recently expanded to measure optical properties of the specimen by exciting the tip–sample interactive system with an incident light beam in the so-called photoinduced force microscopy (PiFM). (By interactive system, we are pointing out the fact that in PiFM both the tip and sample are polarized by an external electromagnetic field and the exerted force on the tip is due to the interaction between the polarized tip and the sample.) In PiFM the tip–sample system is illuminated by an electromagnetic field, and the force exerted on the tip in the vicinity of the sample is measured and used to perform linear and nonlinear spectroscopy to obtain optical characteristics of the sample at the nanoscale. Unlike conventional spectroscopy techniques, PiFM utilizes the near-field data from the interaction between the tip–sample interactive system and light and, hence, is not limited by diffraction and has a high

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signal-to-noise ratio (SNR).

Recently, PiFM has been utilized to report the chirality and enantiomer type of a chiral sample theoretically, with an achiral tip, and experimentally, with a spiral tip. (Enantiomer refers to each of a pair of chiral samples that are mirror images of each other.)

In this theoretical study, by taking advantage of the PiFM concept, we propose a new technique to determine the longitudinal and transverse chirality components of specimens with high resolution. Unlike CD, this method has high spatial resolution on the sub-100 nm scale. In particular, we calculate the exerted force on the tip in the vicinity of a test sample to identify the different components of the sample handedness, which are identified through the magnetoelectric polarizability (or equivalently chirality parameter). Specifically, we prove that proper excitations for detection of transverse (with respect to the propagation direction) components of sample chirality in our proposed method are CP waves since they possess field components transverse to the direction of propagation. Despite this capability, we unravel the failure of CP waves in detecting the longitudinal (i.e., along the propagation direction) component of sample chirality. We particularly prove that a light beam with longitudinal electric or (and) magnetic field component(s) would be an appropriate candidate for the detection of the longitudinal chirality component. In this context, optical vortices with a longitudinal electric or magnetic field component along the vortex axis serve as suitable practical excitations. With the goal of detection of the longitudinal component of chirality and in order to optimize the interaction between the chiral sample and the excitation, we propose a combination of an azimuthally and a radially polarized beam (APB and RPB) with an appropriate phase difference as the illumination. As we prove, our proposed technique for the excitation and probing of the longitudinal chirality component provides a fundamental advantage in experiments where we are limited to illumination from one side, which is common and applied in most PiFM cases.

The paper is structured as follows: First, we demonstrate the operation principle of our proposed method by applying the dipolar approximation technique. Then we use CP excitations to detect the transverse components of the sample handedness (or equivalently magnetoelectric polarizability) and show how they fail in probing the longitudinal chirality component. Next, we bring up the idea of superposition of an APB and an RPB as a suitable excitation scenario for detecting the longitudinal component of the sample handedness that was unrecognizable under CP excitation. Lastly, we conclude the paper with some remarks.

**OBJECTIVE AND OPERATIONAL PRINCIPLE**

Figure 1 depicts the PiFM setup that is utilized throughout this paper for both the transverse and longitudinal chirality investigations. As it is shown, the interactive system composed of a nanoscale chiral sample and the microscope tip is illuminated by incident focused light propagating along the positive z-direction (referred to here as the longitudinal direction) from the bottom side through an objective lens. The incident beam induces electric and perhaps magnetic polarization currents on both the sample and tip-apex, which consequently provide secondary scattered electromagnetic waves. In the PiFM technique, the sample and tip-apex are supposed to be close enough (compared to the operational wavelength) so that they interact through each other’s near-zone scattered fields. That is why a noticeable force is exerted on the tip-apex due to the transfer of momentum from the scattered photons. In this paper, we are specifically interested in the force exerted on the tip-apex in the longitudinal direction (z-direction in Figure 1) since it can be measured using a PiFM. Moreover, as discussed previously, unlike conventional chiroptical techniques such as CD for detecting chirality, PiFM is capable of detecting chirality at the nanoscale since it exploits the information carried in the near field scattered by the sample. It is important to mention that the nanoscale sample does not need to be in a solution, but it can be tethered to the tip or on the substrate, for which the orientation of the sample can be controlled.

We assume both tip-apex and sample to be small compared to the wavelength of incident light so that their main interaction feature is modeled via the dipoles’ near-field scattering. In our theoretical analysis and for the proof of concept, we approximate the tip-apex and sample as two nanospheres and model the tip-apex by equivalent electric and magnetic dipoles, as already done in refs 23, 27, 28, and 36 and the chiral sample by its bianisotropic polarizability and use the dipole approximation to investigate their interaction (see Figure 1(b)). Note that this dipolar approximation has successfully been exploited to model photoinduced force microscopy in refs 23, 27, 28, and 36 to extract optical properties of samples. Here, we model the sample with its photoinduced electric and magnetic dipole moments \( \mathbf{p} \) and \( \mathbf{m} \), respectively, given by

\[
\begin{align*}
\mathbf{p} &= [E^0(r_s) \mathbf{g}^e_s, E^0(r_s) \mathbf{g}^m_s, H^0(r_s) \mathbf{h}^e_s] \\
\mathbf{m} &= [E^0(r_s) \mathbf{g}^e_s, E^0(r_s) \mathbf{g}^m_s, H^0(r_s) \mathbf{h}^e_s]
\end{align*}
\]

where subscript “s” represents the “sample” and \( E^0 \) and \( H^0 \) are respectively the local electric and magnetic field vectors acting on the sample at position \( r_s \). Moreover, \( \mathbf{g}^e_s, \mathbf{g}^m_s, \mathbf{g}^e_r, \) and \( \mathbf{g}^m_r \) are second-rank tensors describing the electric, magnetic, magnetoelectric, and electromagnetic polarizabilities of the sample, respectively. The last two tensors are describing...
bianisotropy (including chirality) of the sample particle; that is, they represent the electric (magnetic) response of the particle to the magnetic (electric) excitation.\textsuperscript{7,36,40} Note that here the magnetic dipole moment is defined as $\mathbf{m} = \mu_0 \int_V \mathbf{r} \times J^e/2$, with $J$ and $\mathbf{r}$ being the volumetric current density and the position vector in volume $V$, respectively, and $\mu_0$ is the vacuum permeability. This definition (that includes $\mu_0$) provides the same units for the electromagnetic and magnetoelectric polarizabilities $\alpha_{em}^m$ and $\alpha_{em}^e$ and is chosen following ref \textsuperscript{28}. See chapter I of refs \textsuperscript{37, 41, and 42} for a detailed discussion about bianisotropic particles and also a summary in the Supporting Information. To summarize, a chiral particle must possess two specific properties in terms of the induced moment and the incident field: (a) it should be bi-isotropic (or bianisotropic), i.e., the electric (magnetic) dipole response must be induced by the incident magnetic (electric) field, and (b) the induced electric and magnetic dipole moments $p$ and $m$ must be parallel. For chiral particles the magnetoelectric and electromagnetic polarizability tensors reduce to a single one since $\alpha_{em}^m = - (\alpha_{em}^e)^T$ (which is true for any reciprocal particle; see Supporting Information) where $T$ is the tensor transpose, and in particular they are diagonal. The magnetoelectric polarizability tensor of a particle in Cartesian coordinates is represented by the matrix

$$
\alpha_{em}^m = \begin{bmatrix}
\alpha_{xx}^m & \alpha_{xy}^m & \alpha_{xz}^m \\
\alpha_{yx}^m & \alpha_{yy}^m & \alpha_{yz}^m \\
\alpha_{zx}^m & \alpha_{zy}^m & \alpha_{zz}^m
\end{bmatrix}
$$

(2)

In this paper, we investigate reciprocal chiral particles; that is, magnetoelectric polarizability is diagonal, having only $\alpha_{xx}^m$, $\alpha_{yy}^m$, or $\alpha_{zz}^m$ as nonvanishing components. Since the propagation direction of the incident field in our setup is along the $z$-axis, in the following we refer to the first two polarizability components $\alpha_{xx}^m$ and $\alpha_{yy}^m$ as the transverse components and the last component $\alpha_{zz}^m$ as the longitudinal one.

As we discussed, the goal is to characterize the transverse and longitudinal magnetoelectric polarizabilities of a chiral nanoparticle by exploiting different structured light illumination scenarios and by exploring the exerted force on the tip in the vicinity of the chiral sample. To that end, we consider an achiral tip-apex and use the dipolar approximation to model its response to an arbitrary electromagnetic wave as

$$
\mathbf{p}_t = \alpha_{\text{c}}^t \mathbf{E}^{\text{loc}}(\mathbf{r}_t), \quad \mathbf{m}_t = \alpha_{\text{mm}}^m \mathbf{H}^{\text{loc}}(\mathbf{r}_t)
$$

(3)

Here, the local fields $\mathbf{E}^{\text{loc}}$ and $\mathbf{H}^{\text{loc}}$ (which include the contributions from both the incident field and the scattered near field from the sample) are calculated at the tip-apex position $\mathbf{r}_t$, where subscript “c” denotes the “tip”. Note that in our setup we employ an achiral tip-apex, i.e., $\alpha_{\text{c}}^t = \alpha_{\text{c}}^m = 0$. Accordingly, the local electric and magnetic fields at the tip position are described by

$$
\mathbf{E}^{\text{loc}}(\mathbf{r}_t) = \mathbf{E}^{\text{inc}}(\mathbf{r}_t) + \mathbf{G}^{\text{EE}}(\mathbf{r}_t, \mathbf{r}_t) \mathbf{p}_t + \mathbf{G}^{\text{EM}}(\mathbf{r}_t, \mathbf{r}_t) \mathbf{m}_t,
$$

$$
\mathbf{H}^{\text{loc}}(\mathbf{r}_t) = \mathbf{H}^{\text{inc}}(\mathbf{r}_t) + \mathbf{G}^{\text{ME}}(\mathbf{r}_t, \mathbf{r}_t) \mathbf{p}_t + \mathbf{G}^{\text{MM}}(\mathbf{r}_t, \mathbf{r}_t) \mathbf{m}_t.
$$

(4)

Here $\mathbf{G}^{\text{EE}}$ and $\mathbf{G}^{\text{ME}}$ are the dyadic Green’s functions that provide the electric and magnetic fields due to an electric dipole $\mathbf{p}_t$, whereas $\mathbf{G}^{\text{EM}}$ and $\mathbf{G}^{\text{MM}}$ are the dyadic Green’s functions that provide the electric and magnetic fields due to a magnetic dipole $\mathbf{m}_t$, respectively.\textsuperscript{38,43,44} The Green’s functions include all the near-field and radiative terms, used in the numerical simulations, although the analytic results are based on the quasi static approximation (see Supporting Information) that depends on the cubic distance between the tip and the sample.

The general expression of the time-averaged optical force exerted on the tip reads\textsuperscript{45–49}

$$
F = - \frac{1}{2} \text{Re} \left[ \left( \mathbf{V} \mathbf{E}^{\text{loc}}(\mathbf{r}_t) \right) \cdot \mathbf{p}_t + \left( \mathbf{V} \mathbf{H}^{\text{loc}}(\mathbf{r}_t) \right) \cdot \mathbf{m}_t \right] - \frac{e^4}{6\pi} \left[ (\mathbf{p} \times \mathbf{m}_t) \right],
$$

(5)

in which $e$ is the speed of light and $k$ is the ambient wavenumber, the asterisk represents complex conjugation, and $\mathbf{V}$ is the gradient operator whose $i$th component, when applied to a vector $\mathbf{A}$, is equal to $\partial \mathbf{A} / \partial x_i$ (here, $i, j = x, y, z$ in Cartesian coordinates and $\partial$ is partial derivative with respect to the $i$th spatial coordinate; see more details in the Supporting Information and in refs \textsuperscript{27 and 28}). Moreover, we assume that every field is monochromatic, the time dependence $\exp(-i\omega t)$ is assumed and suppressed, and the International System of Units (SI) is utilized throughout the paper.

In this paper we employ right- and left-handed CP Gaussian beams as excitation for probing the transverse component of the sample’s magnetoelectric polarizability. However, we prove that the CP illumination scenario is unable to identify the longitudinal component of the magnetoelectric polarizability. Consequently, for the detection of the longitudinal component of the magnetoelectric polarizability, we propose an alternative illumination scheme based on a combination of an APB and RPB with a proper phase difference. The reason is that such combination exclusively interacts with the electric and magnetic dipoles of the sample in the longitudinal direction, interacting with the sample’s longitudinal chirality, whereas CP waves that propagate along the longitudinal direction lack such characteristic. Note that the dipolar approximation validity range for various inclusions and within different wavelength ranges has been investigated in refs \textsuperscript{50 and 51}, and as shown in these studies, it successfully predicts the electromagnetic response (i.e., force and scattering) of small inclusions and acceptably provides a physical trend and insight for optically large inclusions within a specific wavelength range.

Moreover, it has been shown that knowing the electric and magnetic polarizability, it is sufficient to determine the longitudinal and transverse polarizability by six illuminations and measurements;\textsuperscript{52} however, it requires a more complicated experimental setup and special care about the phases of exciting beams compared to our proposal.

### PROBING THE TRANSVERSE HANDEDNESS OF CHIRAL SAMPLES

As discussed, CP beams are used as excitation in our proposed PiFM setup. Specifically, we first send a right-hand CP (RCP) beam and then a left-hand CP (LCP) beam and calculate the $z$-directed exerted force on the tip-apex in the vicinity of the sample for each case. For an achiral sample, the calculated forces exerted on the tip-apex are equal for both excitation scenarios. However, owing to the optical activity of chiral materials and their rotational asymmetry, a chiral sample reacts differently under illuminations with opposite sense of handed-
ness (here RCP and LCP). This distinction is manifested in the exerted force on the tip-apex. To verify it, we consider an example when the test sample and the plasmonic tip-apex are illuminated with a CP Gaussian beam propagating along the z-direction with a 1 mW incident power at a wavelength of $\lambda = 400$ nm. We assume that the waist of the Gaussian beam is $w_0 = 0.73 \mu m$ (note that the actual waist of the beam is $2w_0$). Moreover, the sample is placed at the minimum waist z-plane of the beam (which hereafter we call beam waist) due to the higher strength of the field. For simplicity and in order to demonstrate the capability of our proposed method, we first assume that the sample is isotropic, i.e., $\alpha_s^m = \alpha_s^1$ and spherical. The chirality of the sample is denoted by the chirality parameter $\kappa$, which describes the degree of handedness of a material, and here we vary it from $-1$ to $1$. The tip-apex is also assumed to be isotropic and spherical, and both the sample and the tip-apex are considered to have equal radii $a_s = a_t = 50 \text{ nm}$ with a center-to-center distance of $d = 110 \text{ nm}$ (see Figure 2). Furthermore, without loss of generality and for the proof of concept, the relative permittivity of the sample is assumed to be $\varepsilon_s = 2.4$, whereas that of the plasmonic tip-apex is assumed to be $\varepsilon_t = -3.6 + i0.19$ (this is the relative permittivity of silver at the operational wavelength). In Figure 2, we have depicted the $z$-component of the exerted force on the plasmonic tip-apex versus chirality parameter of the sample for both RCP and LCP incident waves using eq 5. The results clearly exhibit the potential of our proposed method in the detection of sample chirality at the nanoscale. We demonstrate the differential force exerted on the plasmonic tip-apex for two CP plane wave illuminations with opposite handedness read,63

$$\Delta F_z \approx -\frac{3|E_0|^2}{4\pi \sqrt{\varepsilon_0 \mu_0} d^4} \Im\{\alpha_e \kappa (\alpha_e^* \kappa)^*\}$$  \hspace{1cm} (6)$$

in which $E_0$ is the vacuum permittivity and $d$ is the center-to-center distance between the sample and tip-apex. Note that in deriving this formula we assume CP plane waves with electric field magnitude $|E_0|$ on the beam axis since it simplifies our analytical calculations. Gaussian beams with a large beam waist can be reliably approximated by plane waves around their beam axis. Note that the optical force calculated in eq 6 modifies the vibration of the cantilever in the PiFM system and the cantilever dynamics is comprehensively studied in ref 21. First, eq 6 clearly demonstrates that the differential force depends linearly on the electric polarizability of the tip-apex; hence, the material, size, and shape of the tip-apex play crucial roles in determining the differential force. Specifically, in a previous study,57 the importance of the shape and material of the tip-apex has been further discussed.57 For example, as discussed previously,28 by choosing a plasmonic tip-apex, we get stronger electric dipolar response and hence observe more pronounced differential force on the tip-apex. More importantly, eq 6 illustrates that the differential force is also linearly related to the magnetoelectric polarizability of the sample, which in the quasi-static regime is approximated by,51,62

$$\alpha_e^m = 12i\alpha_s \sqrt{|E_0|d^3} \frac{\kappa}{(\varepsilon_s + 2)(\mu_s + 2) - \kappa^2}$$ \hspace{1cm} (7)$$

where the subscript  “s ” represents “sample”. After inserting eq 7 into eq 6 we observe that $\Delta F_z$ is linearly proportional to $\kappa$ since $(\varepsilon_s + 2)(\mu_s + 2)$ at the denominator is usually much larger than $\kappa^2$. Moreover, we observe that the sign of the differential force $\Delta F_z$ depends on the sign of the chirality parameter $\kappa$, which proves that our proposed method is capable of identifying the enantiomer type. Note that eq 7 is valid under the quasi static limit for the sphere polarizability.63

Equation 7 also implies that the degree of handedness of a sample could be quantified, i.e., “how chiral is a given object”, as studied in ref 64 by using our proposed method, if the electric polarizability of the tip is known by observing the sign and magnitude of eq 6. Furthermore, it is also worth noting that $\Delta F_z$ is inversely related to the quartic power of the probe–sample distance, under the quasi static approximation. It has been shown that using this method, with a beam power of 1 mW and minimum waist radius related to $w_0 = 353 \text{ nm}$, and a tip-apex with radius $a_t = 60 \text{ nm}$ and assuming a force of 0.1 pN as the instrument sensitivity,17-28 a sample with radius $a_s = 70 \text{ nm}$ and chirality of $\kappa = 0.04$ can be detected. It is worth mentioning that a chirality parameter on the order of $\kappa \approx 10^{-3}$, which corresponds to a specific rotation (defined as the optical rotation in degrees per decimeter divided by the
density of optically active material in grams per cubic centimeter) of $[\alpha]_D \approx 1000000$, is still a large value compared to chirality parameters of abundant chiral molecules in nature such as glucose (C$_6$H$_12$O$_6$) or testosterone (C$_{19}$H$_{28}$O$_2$), which is on the order of $10^{-56}$.68 (corresponding to specific rotation on the order of $[\alpha]_D \approx 100-200$). Indeed, only a few molecules and compounds such as helicene or norbornenone possess specific rotation angles on the order of $[\alpha]_D \approx 1000000$.68,70

However, we emphasize that our technique, in contrast to conventional chiroptical techniques, is capable of detecting nanosamples on the order of $\sim 50-100$ nm. The detection of chiral samples with a smaller chirality parameter requires some extra considerations, such as increasing the incident power, which may be possible in cryogenic conditions44 or in liquids45,46 or using nanotips with stronger electric polarizability, or even exploring nanotips able to express magnetic response.59 Note that the displacement of the tip–sample interactive system from the center of the beam could potentially affect the system.71 However, since we are not using tightly focused beams, as we have shown in ref 28, this problem would not significantly influence the proposed scheme based on differential force calculations.

So far, we have shown the ability of our proposed technique to detect and characterize isotropic chiral particles, i.e., particles with $\alpha_{xx}^{em} = \alpha_{yz}^{em} = \alpha_{zz}^{em}$ at the nanoscale. However, as we have already discussed, it would be interesting to investigate the capability of our proposed excitation scenario (RCP/LCP waves) in distinguishing between the transverse and longitudinal components of the magnetoelectric polarizability. To that end, we note that the magnetoelectric polarizability tensor of the sample, in Cartesian coordinates, is represented by the matrix

$$\alpha_{xx}^{em} = \begin{bmatrix} \alpha_{xx}^{em} & 0 & 0 \\ 0 & \alpha_{yy}^{em} & 0 \\ 0 & 0 & \alpha_{zz}^{em} \end{bmatrix}$$

(8)

We assume here the exciting beam and the tip-apex have the same parameters as in the previous example related to Figure 2. We study two different cases with samples’ polarizabilities given by (1) $\alpha_{xx}^{em} = \alpha_{yz}^{em} \neq 0$ and $\alpha_{zz}^{em} = 0$ and (2) $\alpha_{xx}^{em} \neq 0$ and $\alpha_{yz}^{em} = \alpha_{zz}^{em} = 0$. In this work we do not distinguish between the two transverse polarizability components $\alpha_{xx}^{em}$ and $\alpha_{yz}^{em}$ but we only distinguish between the transverse (i.e., $\alpha_{xx}^{em}$ and $\alpha_{yz}^{em}$) and longitudinal ($\alpha_{zz}^{em}$) polarizability components of the sample.
improper choice for the characterization of the longitudinal magnetoelectric polarizability component.

Based on the above discussion, the problem of probing the longitudinal magnetoelectric polarizability component calls for utilizing alternative types of beam illuminations, which is the subject of the next section.

**PROBING THE LONGITUDINAL HANDEDNESS OF CHIRAL SAMPLES**

As was explained in the previous section, it is not feasible to detect the longitudinal component of the sample’s magnetoelectric polarizability since the CP exciting field lacks the longitudinal field components. It is worth mentioning here that one may use CP waves which are incident obliquely with respect to the transverse plane (here, the $x$–$y$ plane) and, hence, providing field components in the $z$-direction (i.e., longitudinal direction in our formalism). However, utilizing a single oblique illumination results in the simultaneous presence of both the transverse and longitudinal field components and makes it impossible to distinguish the transverse and longitudinal polarizability components. Furthermore, in the scenario of oblique illumination, in order to create a purely longitudinal field component, we require illuminating the tip–sample system from both sides, which requires a more complicated experimental setup and special care about the phases of exciting beams compared to our proposal.

Therefore, in order to exclusively determine the longitudinal component of the magnetoelectric polarizability, it is essential to utilize illuminating beams that exclusively possess longitudinal electric and/or magnetic field components without the transverse components. Moreover, for experimental convenience, it is desirable to use beams that excite the sample from the bottom side of the surface where the sample is located, as customary in several microscopy systems. As mentioned earlier, APB and RPB are suitable candidates for our purpose since they have either a purely longitudinal magnetic or electric field component along their vortex axes, respectively. Indeed, as we show next, we utilize structured light excitation made of a combination of these two beams, with proper phase difference, to retrieve the sample handedness. In other words, we use a superposition of an APB and an RPB with a specific phase difference $\psi$ (hereafter, we call it the phase parameter) with their electric and magnetic fields given by

$$E_{\text{APB}} = E_{\text{APB}}^w + E_{\text{RPB}}^w$$
$$H_{\text{APB}} = H_{\text{APB}}^w + H_{\text{RPB}}^w$$

(10)

in which $E_{\text{APB}}$, $H_{\text{APB}}$, $E_{\text{RPB}}$, and $H_{\text{RPB}}$ are the electric and magnetic fields of the APB and RPB, respectively. The electric and magnetic fields of an APB in cylindrical coordinates under paraxial approximation are given by

$$E_{\text{APB}} = E_{\text{APB}}^w e^{\rho} \frac{V}{2} e^{-((\rho/w)^2/2 - 2\tan^{-1}(z/w))z} e^{ikz}$$

(11)

$$H_{\text{APB}} = \frac{-1}{\eta_0} \frac{1}{E_{\text{APB}}} \left[ 1 + \frac{\rho^2 - 2w^2_0}{w^2} \right]$$

(12)

in which $V$ is the amplitude coefficient, $\eta_0 = \sqrt{\mu_0/\varepsilon_0}$ is the ambient wave impedance, and $z_R$ (Rayleigh range), $\zeta$, and $w$ are given by

$$w = w_0 \left[ 1 + \left( \frac{z}{z_R} \right)^2 \right]$$
$$\zeta = \left[ 1 - \frac{z}{z_R} \right]$$

(13)

in which $w_0$ is called the beam parameter and controls the spatial extent of the beam in the transverse plane, i.e., the beam waist ($w_0$ tends to be the same as the beam waist for nonsharply collimated beams). The power carried by an APB reads

$$P_{\text{APB}} = \frac{|V|^2}{2\eta_0} \left( 1 - \frac{1}{2(\pi w_0/\lambda)^2} \right)$$

(14)

It is worth mentioning that in order to obtain eqs 11 and 12, we first calculate the transverse electric field with paraxial approximation and subsequently obtain the magnetic field using Maxwell’s equation $\omega \mu_0 H = \nabla \times E$. For an RPB, the expressions of the electric and magnetic fields read (note that these fields are twice the APB fields)

$$H_{\text{RPB}} = -\frac{1}{\sqrt{\eta_0}} e^{-((\rho/w)^2/2 - 2\tan^{-1}(z/w))z} e^{ikz}$$

(15)

$$H_{\text{RPB}}^w = \frac{1}{\omega_{\text{RPB}}} \left[ 1 + \frac{\rho^2 - 2w^2_0}{w^2} \right]$$

$$- \frac{1}{\sqrt{\eta_0}} e^{-((\rho/w)^2/2 - 2\tan^{-1}(z/w))z} e^{ikz}$$

(16)

and $I$ is the amplitude coefficient of the RPB. The power carried by an RPB reads

$$P_{\text{RPB}} = \frac{|I|^2}{2} \left( 1 - \frac{1}{2(\pi w_0/\lambda)^2} \right)$$

(17)

In order to obtain eqs 15 and 16, we calculate the transverse magnetic field with paraxial approximation and subsequently obtain the electric field using Maxwell’s equation $-\mu_0 \omega E = \nabla \times H$. On the axis of an ARPB, i.e., at $\rho = 0$, only the longitudinal field components are nonvanishing, and assuming the combined APB and RPB have the same beam parameter $w_0$ and same focal plane, the fields ratio is

$$\frac{H_{\text{ARPB}}}{E_{\text{ARPB}}} = \frac{H_{\text{APB}}^w}{E_{\text{APB}}} = \frac{V}{\eta_0 I}$$

(18)

in which $H_{\text{ARPB}}$ and $E_{\text{ARPB}}$ represent the $z$-component of the magnetic and electric field of the ARPB, respectively. The magnitude of different electric and magnetic field components of the ARPB has been demonstrated in the Supporting Information for various phase difference parameters $\psi$. Using the aforementioned combination of the beams with coincident vortex axes (the $z$-axis), assuming each of them (APB and RPB) has 1 mW power at $\lambda = 400$ nm, we place the tip-apex and chiral sample with parameters given in Figure 2 along the axis of the two beams, on which the transverse components of the electric and magnetic fields are vanishing whereas the longitudinal components are not. Specifically, we assume the
chiral sample to be on the focal plane of the beams due to high field intensity. Furthermore, we consider the beam parameter of both RPB and APB to be $w_0 = 0.7\lambda$. In order to detect the chirality, we change the phase-shift parameter $\psi$ in Eq 10 and calculate the exerted force on the tip-apex for two distinct cases: (a) a case with azimuthal chirality with $\alpha_{\phi\phi} = \alpha_{\phi\phi}^0 = \alpha_{\phi\phi}^{iso}$ ($\kappa = 0.75$) and $\alpha_{\phi\phi}^{zz} = 0$ and (b) a case with longitudinal chirality with $\alpha_{\phi\phi}^{zz} = \alpha_{\phi\phi}^{iso}$ ($\kappa = 0.75$) and $\alpha_{\phi\phi}^{zz} = \alpha_{\phi\phi}^{zz} = 0$, where $\alpha_{\phi\phi}^{em}$ ($\kappa = 0.75$) is the magnitude of magnetoelectric polarizability of the isotropic sphere of Fig. 2 with $\kappa = 0.75$. In Fig. 4(a) and (b), we have depicted the $z$-component of the force exerted on the tip-apex versus the phase parameter $\psi$ of the APB. In all the following figures results are obtained including the small (though negligible) force contribution due to the magnetic polarizability of the tip-apex as in Eq 5. We have also assumed that the APB has $F_z = [\eta \theta F_{z,APB} / F_{z,RPB}] = |V/\langle \eta J \rangle| = 1$. We recall that the field admittance normalized to the free space wave impedance $F_z = [\eta \theta F_{z,APB} / F_{z,RPB}]$ was defined previously in Refs 32, 33, and 59 to describe the magnetic to electric field ratio compared to that of a plane wave, since this is an important parameter when light interacts with magnetic dipoles [we discuss the field admittance parameter in more detail later in Eq 23]. As clearly observed, with this illumination, it is possible to distinguish between the sample’s transverse and longitudinal chirality handedness by investigating the exerted force on the tip-apex by varying the values of the phase parameter $\psi$. Note that the transverse component of the handedness cannot be probed by using this excitation since the exerted force on the tip-apex does not depend on the phase parameter; that is, the swing of the exerted force is zero (see Fig. 4(a)). Indeed, we propose to use the “swing” of the exerted force on the tip-apex defined as

$$\Delta F_z = \max(F_z^{ARPB}) - \min(F_z^{ARPB})$$

(19)

where $\max(F_z^{ARPB})$ and $\min(F_z^{ARPB})$ represent the maximum and the minimum of the exerted force on the tip-apex when varying the phase shift parameter $\psi$, observable in Fig. 4(b). These quantities are observed for two phase shift parameters that are 180 deg apart, i.e., $|\psi_{F,max} - \psi_{F,min}| = 180^\circ$ as shown in Fig. 4(b) (see Supporting Information). In summary we propose to use the swing in Eq 19 to calculate longitudinal chirality. We want to quantify the physical properties that determine the force on the tip-apex, in terms of electric and magnetoelectric polarizabilities of the tip-apex and sample, respectively. In the following we provide simple formulas for the $z$-component of the force obtained from Eq 5 by neglecting the tip-apex magnetic dipole moment, leading to $F_z^{ARPB} = \text{Re}\left(\partial E_z^{em}/\partial z\right)_{\psi=0} / 2$. The difference between the two optical forces for ARPB illuminations with two different phase parameters $\psi_1$ and $\psi_2$ reads (see Supporting Information)

$$F_z^{ARPB}_{\psi_1} - F_z^{ARPB}_{\psi_2} \approx -3F_z |E_0|^2 \int d^2 \phi \int d^2 \theta \left[ \text{Re}\left( e^{-i\psi_1 \alpha_{\phi\phi}^{zz}} \alpha_{\phi\phi}^{em} \right) - \text{Re}\left( e^{-i\psi_2 \alpha_{\phi\phi}^{zz}} \alpha_{\phi\phi}^{em} \right) \right]$$

(20)

Here, $\alpha_{\phi\phi}^{em}$ is the longitudinal component of the magnetoelectric polarizability of the chiral sample and $\alpha_{\phi\phi}^{em}$ is the electric polarizability of the tip-apex. In the calculation of the above equations we have neglected the field’s phase difference between the tip and sample due to their subwavelength distance. Moreover, we have simplified the electric and magnetic field expressions of the illuminating beam at the beam axis (i.e., at $\rho = 0$ since both the tip-apex and sample are placed on the axis of the beam) and have rewritten Eq 10 as

$$\Delta F_z = \max(F_z^{ARPB}) - \min(F_z^{ARPB})$$

(20)
Table 1: Summary of the suitable proposed illumination type to retrieve chirality of anisotropic chiral samples. In each case two measurements, Meas1 and Meas2, are necessary. An experiment with two CP beams is (not) able to determine the transverse (longitudinal) chirality. An experiment with two ARPB is (not) able to determine the longitudinal (transverse) chirality. ARPB+ and ARPB− represent the two ARPBs that lead to max(⟨P_{ARPB}⟩) and min(⟨P_{ARPB}⟩), respectively. The chirality in each direction is schematized by a helix, and the proper choice of excitation is highlighted with a shaded gray area. In all cases the tip-apex is modeled by an electric polarizable dipole and the choice of the excitation influences the direction of the induced dipole on the tip-apex, although the tip-apex is isotropic.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Summary of the suitable proposed illumination type to retrieve chirality of anisotropic chiral samples. In each case two measurements, Meas1 and Meas2, are necessary. An experiment with two CP beams is (not) able to determine the transverse (longitudinal) chirality. An experiment with two ARPB is (not) able to determine the longitudinal (transverse) chirality. ARPB+ and ARPB− represent the two ARPBs that lead to max(⟨P_{ARPB}⟩) and min(⟨P_{ARPB}⟩), respectively. The chirality in each direction is schematized by a helix, and the proper choice of excitation is highlighted with a shaded gray area. In all cases the tip-apex is modeled by an electric polarizable dipole and the choice of the excitation influences the direction of the induced dipole on the tip-apex, although the tip-apex is isotropic.

\[ E_{ARPB} = E_z = |E_0|e^{-2it\tan^{-1}(z/r)}e^{ik\rho}, \]

\[ H_{ARPB} = H_z = \left[ \frac{|E_0|}{\eta_0} \right]e^{-2it\tan^{-1}(z/r)}ik\rho e^{i\phi} \]  

(21)

where \( |E_0| = 4\pi l/(\sqrt{\pi} w^2\alpha_0\rho) \) is the amplitude of the electric field (directed along \( z \)) at the origin, i.e., at \( \rho = 0 \) and \( z = 0 \), where the sample is located. The swing of the exerted force on the tip-apex by varying the phase parameter \( \psi \) of the ARPB, neglecting the losses of the particles and assuming \( F_y = 1 \) (i.e., assuming that the powers of APB and RPB are equal; see eq 23), is given by the approximate formula (details in the Supporting Information)

\[ \Delta F_z \approx -\frac{3|E_0|^2}{2\pi \sqrt{\eta_0\rho_0}}\text{Re}(\alpha_{zz})\text{Im}(\alpha_{zz}^*) \]  

(22)

In the derivation of eq 22 we have neglected the field’s phase delay in the field interaction between the tip-apex and sample, due to their subwavelength distance; that is, we have used a quasi static Green’s function.\(^{28,77}\)

Equation 22, which is similar to the differential force formula for the CP illumination, demonstrates that the sample’s longitudinal magnetoelectric polarizability \( \alpha_{zz}^m \) is determined by exploiting a combination of two vortex beams (the ARPB) and a simple algorithm where the phase shift \( \psi \) between the composing APB and ARB is varied.

In Figure 5, we further demonstrate the ability of ARPB to detect the longitudinal chirality for two cases similar to those in Figure 3: (1) \( \alpha_{xx}^m = \alpha_{yy}^m \neq 0 \) and \( \alpha_{zz}^m = 0 \) and (2) \( \alpha_{xx}^m = \alpha_{yy}^m = 0 \). We depict the swing of the \( z \)-component of the exerted force on the tip-apex versus the nonzero component of the magnetoelectric polarizability, normalized to the magnetoelectric polarizability of the isotropic sample sphere studied in Figure 2 with \( \kappa = 0.75 \), i.e., \( \alpha_{zz}^{miso} (\kappa = 0.75) \). As one observes, this type of illumination is suitable for characterizing the longitudinal magnetoelectric polarizability \( \alpha_{zz}^m \) since \( \Delta F_z \neq 0 \) in Figure 5(c). It is noteworthy that the proposed ARPB field combinations with properly designed phases to be used for chirality detection are fields with well-defined helicities.\(^{78,79}\)

Figure 6 summarizes the main results of the current study in a concise table. It demonstrates different scenarios of illumination beams and test samples. In summary, for samples with longitudinal chirality components, the ARPB is a proper choice, whereas for samples with transverse chirality components, CP beams are suitable. The suitable proposed scenarios are highlighted by a gray color, where the differential force is nonzero and the sample’s chirality is retrievable from two distinct measurements.

In the previous discussion and results we have assumed that \( \eta_0 H_{ARPB}^2/F_y = V / (\eta_0 I) = 1 \), which means that both the APB and RPB carry the same power (assuming they have the same beam waist) and \( V \) and \( I \) have the same phase, since the phase difference between these two beams is represented by \( \psi \).

Our final discussion before conclusion is about having different illumination powers of the APB and RPB, and then we justify the choice done beforehand, where \( F_y = 1 \), that leads to the best result. Therefore, we now assume that the parameter \( F_y \) differs from unity, where \( F_y^2 \) is the figure of merit that shows the ratio between the illumination power of the APB and RPB, previously defined as

\[ F_y^2 = \left| \frac{P_{APB}}{P_{RPB}} \right| = \frac{H_y}{E_z} \bigg|_{\rho=0} \bigg|_{z=0} = \frac{1}{\eta_0^2} \left| \frac{V}{I} \right| \]  

(23)

Note that \( F_y^2 \) represents the intensity of the longitudinal magnetic field over the intensity of the longitudinal electric field, at the focus of the beams (i.e., at the chiral sample location). This figure of merit is the squared magnitude of the normalized field admittance introduced in previous studies.\(^{32,33,59}\) We assume that the total power of the APB and RPB exciting beams is constant, and in particular \( P_{APB} + P_{RPB} = 2 \) mW (there is no cross power term since the polarization of the two beams is orthogonal). We also assume that the tip-apex and the sample have the same polarizability characteristics used in the example in Figure 4(a), i.e., \( \alpha_{xx}^m = \alpha_{yy}^{miso} (\kappa = 0.75) \) and \( \alpha_{zz}^m = \alpha_{yy}^m = 0 \). The color map in Figure 7(a) describes the exerted force on the tip-apex versus \( F_y^2 \) (in logarithmic scale) and phase difference \( \psi \) between the APB and RPB. One observes that as \( F_y^2 \) increases (increases the ratio between the
when we are limited to the illumination from the bottom side components at the nanoscale. Particularly, we have proved that distinguish between its transverse and longitudinal chirality to determine the enantiomer type of a chiral sample but also to We have shown an approach based on force detection not only scenarios result in chirality characterization at the nanoscale.

Figure 7. (a) Photoinduced optical force on the tip-apex varying the power distribution between the APB and the RPB and their phase difference $\psi$. The force increases with decreasing $F_2$. (b) Swing of the force versus $F_2$. In conclusion the maximum swing corresponds to the best possible scenario for longitudinal chirality detection, and it occurs when $F_2 = 1$, or equivalently when $|E_f|/|H_f| = \eta_0$

APB to RPB power, or alternatively the magnetic field increases with respect to the electric field), the exerted force on the tip-apex decreases, for all phase parameters $\psi$. The reason is that for both the tip-apex and sample, in general the electric responses are stronger than their magnetic counterparts; thus, a weaker electric field (larger $F_2$) leads to a weaker observed optical force on the tip-apex. However, it is important to note that for a reliable measurement the most important property is to observe the largest swing of the force, i.e., $\text{max}(\Delta F_z)$ (note that $\Delta F_z$ is defined in eq 19), which leads to higher resolution in detection of nanoscale chirality, and this feature may be more interesting than a large observable force. In other words, a stronger force does not necessarily lead to a larger swing force. In Figure 7(b) we have depicted $\Delta F_z$ versus $F_2$, and we observe that the maximum swing occurs when $F_2 = 1$, i.e., when, the illumination powers of the APB and RPB are equal or equivalently when $|E_f|/|H_f| = \eta_0$ or $|V_f|/|I_f| = \eta_0$. Indeed, it can be analytically proved (details in the Supporting Information) that, assuming a constant total power of APB and RPB (i.e., a constant power density), the maximum swing occurs when $F_2 = 1$.

With the above considerations, we conclude the discussion on introducing suitable high-resolution techniques to unscramble the chirality structure of a chiral sample. However, future work is necessary to distinguish between the two transverse components of the magnetoelectric polarizability tensor, i.e., $\alpha_{em}^{xx}$ and $\alpha_{em}^{yy}$. For that azimuthally anisotropic case, excitation types that possess either a pure electric or a pure magnetic field component in the transverse plane, i.e., the y-plane, would be useful following the scheme proposed in this paper.

**CONCLUSION**

On the basis of the concept of photoinduced optical force, we have presented how different structured-light excitation scenarios result in chirality characterization at the nanoscale. We have shown an approach based on force detection not only to determine the enantiomer type of a chiral sample but also to distinguish between its transverse and longitudinal chirality components at the nanoscale. Particularly, we have proved that when we are limited to the illumination from the bottom side of the tip–sample system (as shown in Figure 1), probing the transverse sample’s chirality requires transverse field components (with respect to the propagation direction) as in CP beams. Instead, probing longitudinal chirality is achievable by using a combination of longitudinal field components, obtained by performing two experiments, each one with a superposition of an APB and an RPB with proper phase shift $\psi$. There is an underlined difference between CP beams, whose light is chiral, and APBs and RPBs, whose light is not chiral. However, the combination of an APB and an RPB leads to chiral light; therefore we propose to use them together with a proper controlled phase shift $\psi$ and perform two experiments, with two different phase shifts. The difference between these two experiments, denoted as $\Delta F_z$, takes a maximum value when the APB and RPB exhibit the same power density at the chiral sample location. The quantification of the longitudinal and transverse components of the magnetoelectric polarizability helps to unscramble the structure of the chiral specimen. This work has the potential to advance studies of chirality of nanosamples and molecular concentrations, since chirality is a fundamental building block of nature.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.8b00765.

Detailed derivation of eq 22 as well as analytic discussion on the local fields at the tip-apex and sample locations under ARPB excitation, a summary of properties of bianisotropic particles, and the reason for the choice of $F_2 = 1$. (PDF)

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F.C. and H.K.W. conceived the ideas of this work; M.K., M.A., M.V., and F.C. developed the theoretical model for analysis, and M.R. and J.Z. revised the practical setup for the study. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


