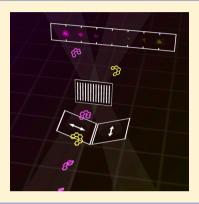
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Diffraction Gratings for Chiral Molecules and Their Applications

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ABSTRACT: We suggest the use of certain readily producible types of light to exert a force that points in opposite directions for the enantiomers of a chiral molecule and propose multiple devices based upon this novel manifestation of optical activity: in particular, our discriminatory chiral diffraction grating; a device that could be employed, for example, to measure the enantiomeric excess of a sample of chiral molecules simply and to high precision. Our work is relevant for many types of molecules and our proposed devices may be realizable using currently existing technology.



■ INTRODUCTION

The word chiral was introduced by Kelvin¹ to refer to any geometrical figure or group of points that cannot be brought into coincidence with its mirror image, thus possessing a sense of handedness. Chirality pervades the natural world: it may be found at both large and small scales and even in the laws of physics themselves.^{2,3} Many molecules are chiral owing to the arrangement in space and the nature of their constituent atoms. 2-5 The mirror-image forms, or enantiomers, of a chiral molecule are observed to behave identically in many circumstances but differently in others, 2-5 and the fact is wellestablished, in particular, that molecular chirality is crucial to biological function.^{2,6} This is reflected by the existence of chiral molecules, the enantiomers of which interact differently with living things:² one enantiomer of carvone is found in spearmint leaves, whereas the opposite enantiomer is found in caraway seeds, thus being associated with different aromas; one enantiomer of methamphetamine is used as a decongestant, whereas the opposite enantiomer is recognized as being a harmful narcotic; one enantiomer of mecoprop functions as a herbicide, whereas the opposite enantiomer is ineffective in this context. The ability to characterize, discriminate between, and resolve the enantiomers of a chiral molecule is desirable in both academic and industrial contexts and yet remains elusive in many cases. Thus, the development of means with which to probe and utilize molecular chirality constitutes a vibrant field of modern research.^{2,7,8}

We have recently suggested the use of certain readily producible types of light to exert a force that points in opposite directions for the enantiomers of a chiral molecule. This novel manifestation of optical activity forms the basis of several proposals for devices that might assist in the probing and utilization of molecular chirality.9 In the present article, we summarize this work and extend it, in particular through the introduction of our discriminatory chiral diffraction grating; a

device that could be employed, for example, to measure the enantiomeric excess of a sample of chiral molecules simply and to high precision. Our discriminatory optical force differs crucially from others that have been proposed 10-13 in that it exists independent of any critical assumptions regarding the energy-level structure of the molecule. Our work is, therefore, relevant for many types of molecule and our proposed devices may be realizable using currently existing technology.

In what follows, we imagine ourselves to be in an inertial frame of reference with time t and a right-handed Cartesian coordinate system x, y, z. We adopt S.I. units, with ε_0 and μ_0 the electric and magnetic constants, $c = 1/(\varepsilon_0 \mu_0)^{1/2}$ the speed of light, and \hbar the reduced Planck constant.

DISCRIMINATORY OPTICAL FORCE

We consider a neutral, chiral molecule that is translating slowly while rotating and perhaps vibrating somewhat⁴ in the presence of (otherwise) freely propagating monochromatic light. 14 Taking the molecule to be very much smaller than the wavelength $2\pi c/\omega$, we quantify its internal response to the light in a multipolar description based upon polarizabilities. This entails expanding the coupling of the molecule to the light in a series, successive terms of which account for the variation of the light across the spatial extent of the molecule with increasing accuracy. $^{3-5}$ We assume that the angular frequency ω and strength of the light are such that we may work in a linear regime neglecting absorption³ and, in particular, molecular alignment: we imagine the molecule to be tumbling freely. In reality, the molecule might be a constituent of a molecular beam and the light might originate from a near-infrared laser.

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During the course of their interactions the light and the molecule will, in general, exchange linear momentum, giving rise to an optical force that governs the center-of-mass motion of the molecule. 15,16 Well-established optical activity phenomena²⁻⁵ suggest to us the possibility that the enantiomers of the molecule will, in general, exchange linear momentum with light of chiral character at different rates thus experiencing different optical forces. This is indeed the case. In order to appreciate this difference, it is necessary to proceed beyond the approximations that are commonly employed in the calculation of the optical force 15,16 as it is not possible within the usual electric-dipole (single-point) approximation to appreciate any chiral character possessed by the light. Indeed, it is stated in Kelvin's definition that chirality is associated with groups of points. Accordingly, we take account of the electric-dipole coupling of the molecule to the light and, in addition, the magnetic-dipole and electric-quadrupole couplings, as is often done in calculations of optical activity.^{3,5} In this way we acknowledge that the light may vary across the spatial extent of the molecule and hence that the light may be of chiral character.^{3,5} Starting from the Lorentz force law,^{5,14} making use of the charge-free Maxwell equations for the electric field E and the magnetic flux density B comprising the light, 5,14 we find that the cycle-averaged, rotationally averaged optical force F may be expressed to leading order as

$$\mathbf{F} = a\nabla W + b\nabla H \tag{1}$$

where $a = [\alpha_{xx}(f_{\omega}) + \alpha_{yy}(f_{\omega}) + \alpha_{zz}(f_{\omega})]/3\varepsilon_0$ and b = $-(\mu_0)^{1/2}\omega[G'_{xx}(f_\omega)+G'_{yy}(f_\omega)]+G'_{zz}(f_\omega)]/3(\varepsilon_0)^{1/2}$ contain the only relevant molecular properties³ while W and H are the cycle-averaged forms of an electric energy density^{5,14} $\varepsilon_0 E \cdot E/2$ and a helicity density^{17–20} $(\varepsilon_0/\mu_0)^{1/2}(A \cdot B - C \cdot E)/2$. A and C are potentials 21,22 defined such that $E = -\nabla \times C/\varepsilon_0 \mu_0 = -\partial A/\partial t$ ∂t and $B = \nabla \times A = -\partial C/\partial t$ with ∇ the gradient operator. Whereas the energy $\int (\varepsilon_0 \mathbf{E} \cdot \mathbf{E} + (\mathbf{B} \cdot \mathbf{B}/\mu_0)) dV/2$ of any freely propagating light assumes a value equivalent to $\hbar\omega^{5,14}$ per circularly polarized plane-wave-mode photon of angular frequency ω , the helicity $\int (\varepsilon_0/\mu_0)^{1/2} (A \cdot B - C \cdot E) \ dV/2$ of the same assumes a value equivalent to $\hbar \sigma$, where $\sigma = \pm 1$ for left- or right-handed circular polarization in the optics convention. 14 Unlike W, H is thus intimately associated with the chirality of the light. The concept of helicity is familiar, perhaps, from particle physics, where $\hbar\sigma$ is recognized simply as being the value taken by the component of the photon's spin in the direction of propagation. 19 In spite of this intimate relationship, helicity is distinct from spin. Indeed, helicity is much to spin what energy is to linear momentum. 18-20

The first contribution to F, the dipole optical force $a\nabla W$, is attributable solely to the electric—dipole coupling of the molecule to the light 15,16 and does not discriminate between the enantiomers of the molecule. For either positive or negative values of a, the dipole optical force attracts the molecule toward those regions in the light where W is either maximized or minimized, a phenomenon that has been widely utilized to manipulate and control the center-of-mass motion of molecules 23–39 and atoms. 15,16 The second contribution to F, our discriminatory optical force $^9b\nabla H$, emerges as a result of having included the magnetic—dipole and electric—quadrupole couplings 3,5 of the molecule to the light. As b has equal magnitudes but opposite signs for the enantiomers of the molecule, $^{3-5}$ our discriminatory optical force is correspondingly of equal magnitude but points in opposite directions such that it attracts the enantiomer for which b = |b| toward those regions

in the light where H is maximized, while the opposite enantiomer, for which b = -|b|, is instead attracted toward those regions in the light where H is minimized. Notice that our discriminatory optical force necessarily vanishes for an *achiral* molecule, as b = 0.

The form seen in eq 1 has been derived *specifically* for light that is (otherwise) freely propagating in accord with the charge-free Maxwell equations. ^{5,14} As written, it is not appropriate for light, the electric field of which possesses a nonvanishing irrotational component. ^{5,14} Such light may be found, for example, in the *near* field of a radiating structure. ¹⁴ We encourage the interested reader to consult our derivation of eq 1.9

Expressions for the optical force experienced by a small isotropic chiral dipole of unspecified constitution, as induced by monochromatic light, have recently been reported elsewhere. In these expressions, a contribution can be identified that coincides with our discriminatory optical force. This is natural, of course, as we have treated the molecule much like such a dipole.

■ ISOLATING THE DISCRIMINATORY OPTICAL FORCE

Given that the dimensionless ratio $\omega |a/b|$ is $\sim 10^3 - 10^5$ typically, 3,5 it may appear that our discriminatory optical force $b\nabla H$ is overshadowed by the dipole optical force $a\nabla W$. This is not necessarily the case, however: it is possible to conceive light for which the cycle-averaged electric energy density W is homogeneous ($\nabla W = 0$), while the cycle-averaged helicity density H is not ($\nabla H \neq 0$, in general). Such light gives rise to a cycle-averaged, rotationally averaged optical force $F = b\nabla H$ that is, in general, nonvanishing and is purely discriminatory; pointing in opposite directions for the enantiomers of the molecule.

Consider, for example, light comprised of two plane electromagnetic waves of equal angular frequency ω and equal electric-field amplitude E_0 , the wavevectors of which enclose a small angle 2θ and the polarizations of which are linear and orthogonal. The waves do not interfere with each other and W is homogeneous, equaling $\varepsilon_0 E_0^2/2$ at all points in space; the sum of the values $\varepsilon_0 E_0^2/4$ attributable to the waves individually. The waves do, however, exhibit nontrivial quasi-interference ε_0^{20} and ε_0^{20} and ε_0^{20} , with associated wavelength $\varepsilon_0 E_0^2/\omega$, in any given transverse plane; see Figure 1. Light possessing such 'helicity fringes' has been produced experimentally in other contexts.

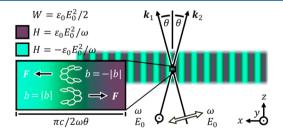


Figure 1. Light possessing helicity fringes can give rise to a cycle-averaged, rotationally averaged optical force $F=b\nabla H$ that is, in general, nonvanishing and is purely discriminatory; pointing in opposite directions for the enantiomers of a chiral molecule as illustrated for the enantiomers of hexahelicene.

NEWTONIAN MOLECULAR OPTICS

The field of Newtonian molecular optics is concerned with the manipulation of the center-of-mass motion of a molecule in a regime where this motion can be viewed in terms of Newtonian trajectories, ^{15,16} as we have assumed to be the case for the molecule so far. Following experiments that have harnessed the dipole optical force $a\nabla W$ in this regime, ^{23–34} we contemplate the novel possibilities offered instead by our discriminatory optical force $b\nabla H$.

We envisage deflecting the center-of-mass trajectory of the molecule either to the left or to the right, depending upon the chirality of the molecule, by passing it through a single helicity fringe as illustrated in Figure 2. In homage to a traditional

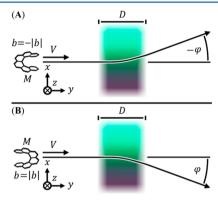


Figure 2. Our chiral Stern—Gerlach deflector: a single helicity fringe deflects the (Newtonian) center-of-mass trajectory of a chiral molecule in a discriminatory manner as illustrated for the left- (A) and right-handed (B) enantiomers of hexahelicene.

Stern-Gerlach deflector, we refer to our device as a chiral Stern-Gerlach deflector.9 Considering a fringe attributable to waves of angular frequency $\omega = 2 \times 10^{15} \text{ s}^{-1}$, electric-field amplitude $E_0 = 6 \times 10^8 \text{ m·kg·s}^{-3} \cdot \text{A}^{-1}$, and angular separation θ = 5×10^{-2} , together with a longitudinal light width of $D = 10^{-4}$ m and a molecular speed of $V = 10^2 \text{ m} \cdot \text{s}^{-1}$, we predict, using Newton's second law, an angular deflection of $\varphi = \pm 5 \times 10^{-4}$ for the enantiomers of hexahelicene; $^{45-47}$ a molecule of mass M = 5×10^{-25} kg for which we estimate (see the appendix) the discriminatory optical force parameter to be $b = \pm 2 \times 10^{-17}$ m³·s⁻¹, the plus and minus signs corresponding to hexahelicene's right- and left-handed forms. 3,48 Although small, we believe that such deflections are detectable, perhaps using the methods that have already been employed in analogous experiments centered upon the dipole optical force. That is, the ionization of deflected molecules using an intense laser beam and their subsequent detection using a microchannel plate detector in a suitable geometry. ^{23–28,32} The utilization of these methods in particular to map modifications of molecular trajectories attributable to the dipole optical force has been well-demonstrated.^{25,27}

Our chiral Stern—Gerlach deflector could be employed as a robust means of spatially separating the enantiomers of a chiral molecule for further applications. It is possible that this might find practical use in pharmaceutical research, for example, where efficient methods of chiral resolution may not be known for a newly synthesized chiral molecule, and yet, it is of vital importance to work with enantiopure samples a priori, as is exemplified by methamphetamine and other drugs. In addition, our chiral Stern—Gerlach deflector might be utilized to measure

the magnitude and sign of *b* supported by a molecule by examining the magnitude and direction of the associated deflection. It could even be used as a means of determining the enantiomeric purity of a sample of chiral molecules by passing some of them through the device and comparing the numbers deflected to the left and to the right.

The possibility of deflecting the center-of-mass trajectories of certain molecules in a discriminatory manner using light has been suggested elsewhere. The previously proposed schemes rely crucially, however, upon specific molecular energy-level structures and the manner in which they are addressed. In contrast, our chiral-Stern deflector simply utilizes the enantiomer-dependent sign of b together with readily producible light and has, therefore, a universal character that earlier proposals lack.

de BROGLIE MOLECULAR OPTICS

Ultimately, the center-of-mass motion of a molecule is governed by the laws of quantum mechanics and should most accurately be viewed in terms of de Broglie waves. 15,16 The manipulation of these waves comprises the field of de Broglie molecular optics, in which there exist possibilities that cannot be understood in terms of Newtonian trajectories. 15,16 Indeed, the picture presented in Newtonian molecular optics is but an approximation to the more fundamental one presented in de Broglie molecular optics, much as the picture presented in geometrical optics is but an approximation to the more fundamental one presented in the wave theory of light.⁴ The regime of de Broglie molecular optics permits the performance of remarkably high precision measurements. 15,16 Following experiments that have harnessed the dipole potential energy aW in this regime, $^{35-39}$ we now consider coherent quantummechanical evolution of the center-of-mass motion of our molecule and contemplate the novel possibilities offered by our discriminatory potential energy bH.

We envisage diffracting the de Broglie waves associated with the center-of-mass motion of the molecule by passing them through a thin sheet of helicity fringes, as illustrated in Figure 3A. The sensitivity of the de Broglie waves to the helicity fringes, and thus the diffraction, is attributable to the molecule being *chiral* ($b \neq 0$). As illustrated in Figure 3B, the de Broglie waves associated with the center-of-mass motion of a similar achiral molecule are insensitive to the helicity fringes (as b = 0) and, therefore, no diffraction results. We refer to our device accordingly as a *chiral* diffraction grating. Using Schrödinger's equation, 49,50 we calculate the probabilities P_n associated with the diffraction orders $(n = 0, \pm 1, \pm 2,...)$ observable in the far field and find that they do not distinguish between the enantiomers of the molecule. The P_n are, however, remarkably sensitive to the degree of chirality of the molecule as embodied by the magnitude |b| of the discriminatory optical force parameter. Considering helicity fringes attributable to waves of angular frequency $\omega = 2 \times 10^{15} \text{ s}^{-1}$ and electric field amplitude $E_0 = 10^8$ m·kg·s⁻³·A⁻¹, together with a longitudinal light width of $D = 5 \times 10^{-5}$ m and a molecular speed of $V = 10^2$ $m \cdot s^{-1}$, we illustrate this sensitivity for hexahelicene by employing an analytical expression⁵¹ for b, allowing us, as seen in Figure 4A, to monitor the P_n as we decrease the magnitude $|\gamma|$ of the normalized pitch γ of the molecule from $|\gamma|$ = 1 to $|\gamma|$ = 0 in a hypothetical manner. These values correspond to the helical shapes $(\gamma = \pm 1)$ adopted by the enantiomers of hexahelicene in reality and to a completely flattened ($\gamma = 0$) version of the molecule, which is achiral. Thus,

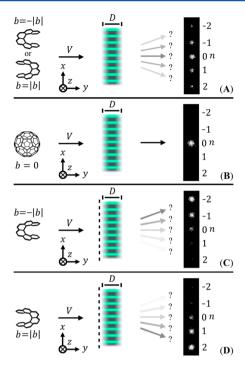


Figure 3. Our chiral diffraction grating: a thin sheet of helicity fringes, diffracts the de Broglie waves associated with the center-of-mass motion of a chiral molecule as illustrated for the enantiomers of hexahelicene (A). For an achiral molecule, such diffraction does not occur, as illustrated for buckminsterfullerene (B). Our discriminatory chiral diffraction grating: a composite of a thin mechanical transmission grating and a thin sheet of helicity fringes gives rise to diffraction patterns that discriminate *between* the enantiomers of a chiral molecule as illustrated for the left- (C) and right-handed (D) enantiomers of hexahelicene.

for $|\gamma| = 1$ we find the P_n expected of either enantiomer of hexahelicene in reality, whereas for $|\gamma| = 0$ no diffraction occurs and $P_0 = 1$. Between these limiting cases, the P_n vary drastically in response to small changes in $|\gamma|$. Evidently, our chiral

diffraction grating can be regarded as a rather sensitive molecular *chirality detector*: the very existence of diffraction indicates that $|b| \neq 0$ and hence that a molecule is chiral. Moreover, by examining the diffraction patterns it produces, our chiral diffraction grating could be employed to measure, to high precision, the *value* of |b| supported by a molecule. In practice, these diffraction patterns could be recorded using the same methods that have already been employed in molecular diffraction experiments centered upon the dipole optical force. That is, the ionization of diffracted molecules using an intense laser beam, translated across the diffraction pattern, and their subsequent detection using an electron multiplier.³⁵

We can combine the sensitivity of our chiral diffraction grating with the discriminatory character of our chiral Stern-Gerlach deflector simply by placing a thin mechanical transmission grating in front of the helicity fringes such that those regions for which $(\nabla H)_x > 0$ are obscured, as illustrated in Figure 3C,D. We find that the (modified) diffraction probabilities 52 P'_n now discriminate between the enantiomers of the molecule, being sensitive to both the magnitude and sign of b. We refer to our new device accordingly as a discriminatory chiral diffraction grating. The P'_n are plotted in Figure 4B for $\omega = 2 \times 10^{15} \text{ s}^{-1}$, D = 5×10^{-5} m, $V = 1 \times 10^{2}$ m·s⁻¹, and hexahelicene, with $b = \pm 2$ \times 10⁻¹⁷m³·s⁻¹. Evidently, the combination of a mechanical transmission grating with helicity fringes ensures that the P'_n are asymmetrical with respect to the line of zero angular deflection, with left-handed enantiomers being diffracted to the left and right-handed enantiomers being diffracted to the right.

Our discriminatory chiral diffraction grating could be employed as a means of spatially separating the enantiomers of a chiral molecule for further applications. In this context we might regard it as a chiral beam splitter for de Broglie waves. In addition, it might be utilized to measure, to *high precision*, the magnitude and sign of *b* supported by a molecule by examining the form of the associated diffraction pattern. If |*b*|, in particular, is already known for a type of chiral molecule, our discriminatory chiral diffraction grating could be employed instead to measure simply and to *high precision*, the

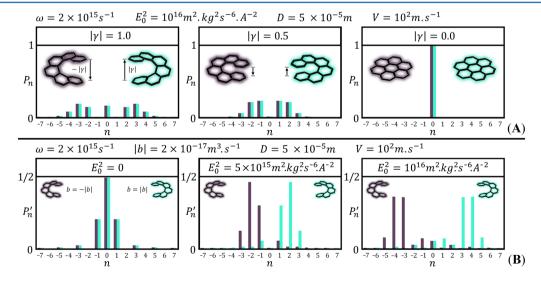


Figure 4. Probabilities P_n associated with our chiral diffraction grating are remarkably sensitive to the chiral geometry of a chiral molecule. This is seen in panel A, where we monitor the P_n while flattening the enantiomers of hexahelicene in a hypothetical manner. The probabilities P'_n associated with our discriminatory chiral diffraction grating enjoy similar sensitivity and, moreover, discriminate between the enantiomers of a chiral molecule. This is seen in panel B, where the P'_n are plotted for the enantiomers of hexahelicene at increasing values of the square electric-field amplitude E_0^2 . While producing these plots, we neglected van der Waals interactions between the mechanical grating and the molecule.

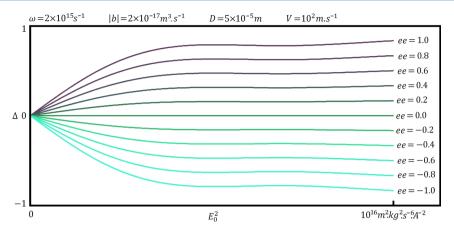


Figure 5. The enantiomeric excess $ee = (n_L - n_R)/(n_L + n_R)$ of a sample of chiral molecules could be measured, to high precision, by passing some of these molecules through our discriminatory chiral diffraction grating and measuring the fractional difference $\Delta = (N_L - N_R)/(N_L + N_R)$ exhibited by the resulting diffraction pattern.

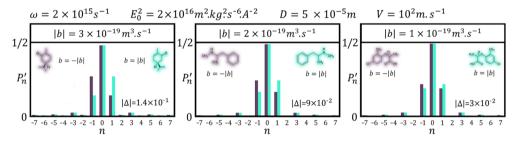


Figure 6. Probabilities P'_n associated with our discriminatory chiral diffraction grating and the magnitude $|\Delta|$ of the fractional difference, plotted for the enantiomers of carvone (left), methamphetamine (middle), and mecoprop (right).

enantiomeric excess $ee = (n_L - n_R)/(n_L + n_R)$ of a sample, where $n_L + n_R = n$ is the total number of molecules, n_L of which are left-handed (b = -|b|) and n_R of which are right-handed (b= |b|). Passing $N = N_L + N_R$ molecules from this sample through our discriminatory chiral diffraction grating and counting the numbers N_L and N_R that appear to the left and right of the line of zero angular deflection in the resulting diffraction pattern would allow ee to be inferred from the fractional difference $\Delta = (N_L - N_R)/(N_L + N_R)$, the variation of which with ee and E_0^2 is illustrated in Figure 5 for ω = 2 \times 10^{15} s^{-1} , $V = 10^2 \text{m} \cdot \text{s}^{-1}$, $D = 5 \times 10^{-5} \text{ m}$, and hexahelicene, with $|b| = 2 \times 10^{-17} \text{ m}^3 \cdot \text{s}^{-1}$. A particularly appealing feature of Δ is that it can in principle be determined using detectors of low spatial resolution, as $N_{\rm L}$ and $N_{\rm R}$ are the only quantities that need to be measured. This is in line with recent molecular diffraction experiments centered upon the dipole potential energy, where simple measurements of total molecule flux, with no spatial resolution, have found favor. 36-39

ON THE GENERAL APPLICABILITY OF OUR DEVICES

Our devices, as introduced in the present article, constitute but a *first step* toward fully exploiting the potential offered by our discriminatory optical force. We have considered hexahelicene in our explicit calculations as the unusually large value of the discriminatory optical force parameter *b* supported by this molecule permits a clear demonstration of the principles involved. We emphasize here, however, the *general* nature of our discriminatory optical force and observe that our devices are also of relevance to chiral molecules that support smaller, more typical values of *b*. This is illustrated in Figure 6, where

the probabilities P'_n associated with our discriminatory chiral diffraction are plotted for the molecules discussed in the introduction, namely, carvone, methamphetamine, and mecoprop: the P'_n are still manifestly asymmetrical with respect to the line of zero angular deflection, and the fractional differences Δ remain rather large by optical activity standards, although the phenomenon is not as pronounced here as it is for hexahelicene, of course. A fundamental limitation on the measurement of Δ follows from the requirement that the total number of molecules N passed through our discriminatory chiral diffraction grating be sufficiently large so that $|\Delta| \gg 1$. For $N=1\times 10^4$ say, 35 molecules like bromochlorofluoromethane 53 ($|b|=9\times 10^{-21} \mathrm{m}^3 \cdot \mathrm{s}^{-1}$) would thus lie at the limit of sensitivity: we find that $|\Delta|=4\times 10^{-3}$ for the parameters listed in Figure 6.

There remains scope to significantly enhance and further optimize the functionality of our devices so as to see their domain of applicability *expanded*. We will return to this task in future publications.

DISCUSSION

We have demonstrated that, by employing readily producible light for which the cycle-averaged electric energy density W is homogeneous while the cycle-averaged helicity density H is not, we can produce an optical force that points in opposite directions for the enantiomers of a chiral molecule. We have indicated how this novel manifestation of optical activity can form the basis of several devices that may be used to spatially separate and/or characterize the enantiomers of a chiral molecule. Our devices might have important applications, for example, in pharmaceutical science, where the understanding, and control, of molecular chirality is vitally important.

APPENDIX

Our discriminatory optical force is intimately associated with the well-established phenomenon of optical rotation, a connection that we will elucidate in future publications. Consequently, the value taken by the discriminatory optical force parameter b at angular frequency ω can be estimated from the specific rotation $[\Delta\theta]$ measured at another transparent angular frequency ω_0 using the formula

$$b = \frac{\pi c \omega^2 M[\Delta \theta]}{6000 \omega_0^2 (n^2 + 2)} \frac{1 \text{m}^2 \cdot \text{kg}^{-1}}{1^\circ \cdot \text{cm}^3 \cdot \text{dm}^{-1} \cdot \text{g}^{-1}}$$
(2)

where c is the speed of light, M is the mass of the molecule, and n is the refractive index. In deriving this, we have made use of the Rosenfeld–Condon formula and an angular frequency scaling appropriate to optical rotatory dispersion in a transparent region.³

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Notes

The authors declare no competing financial interest.

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