Interactions of twisted light with chiral molecules: An experimental investigation

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(Received 21 January 2005; published 11 May 2005)

We experimentally demonstrate that helical Laguerre-Gaussian light, which carries orbital angular momentum, is not specific in its interaction with chiral matter. Only circular polarization, associated with spin angular momentum, can engage with materials chirality.

Molecular chirality is a very important research topic in chemistry and materials science. In order to probe chirality, one generally uses characterization techniques that are based on the fact that chiral molecules exhibit optical activity effects, i.e., they interact differently with left- and right-hand circular polarized light. Well-known examples of optical activity effects are circular dichroism (CD) and optical rotation (OR). Circularly polarized light carries optical *spin* angular momentum, where the left and right forms designate the sign of the spin angular momentum and the circularity of the field vector. Therefore the interactions between circular polarized light and chiral matter are enantiomerically specific.

Recently, the properties of Laguerre-Gaussian light have been studied both from a fundamental point of view and for applications in optical engineering. Pioneering work by Allen *et al.* has demonstrated that Laguerre-Gaussian light propagates with vortical phase fronts and carries optical *orbital* angular momentum, instead of or in addition to spin angular momentum [1–3]. The sign of the orbital angular momentum indicates the handedness of the phase vortex in space, and therefore Laguerre-Gaussian light is often referred to as "twisted," "chiral," or "helical" light. Twisted light has been mostly investigated in its interactions with achiral matter and has led to new optical phenomena such as the optical spanner effect [4–9]. However, there has been great interest in the interactions of twisted light with chiral molecules, since it seems very natural to expect a chiro-optical response when Laguerre-Gaussian light is used to interrogate chiral materials. If so, this would lead to a new field of research with important applications in chemistry, physics, and biology.

Although several theoretical reports have predicted unique properties of Laguerre-Gaussian light, recent theoretical work suggests that orbital angular momentum exchange between light and the internal states of molecules through an electric-dipole mechanism does not occur. This already suggests that chiral interactions such as those seen with circularly polarized light are not expected for Laguerre-Gaussian light [10]. Recently, a theoretical analysis on chiro-optics has shown that the helicity of the optical vortex of Laguerre-Gaussian light cannot interact with the chirality of a molecular system through an optical process [11]. However, in spite of some theoretical work and a lot of contraversy in this field, no experimental verification has been reported [10,11]. In this study, we experimentally determine unambiguously whether or not chiral interaction exists between the optical orbital angular momentum and a chiral molecular system.

The simplest experimental method to use would be a measurement of a difference in optical response in a chiral material to two different enantiomeric Laguerre-Gaussian light modes. Since this difference, if any, may be very small, such a measurement has to be sufficiently precise. In conventional optics, the most reliable and preferred way for such accurate measurements would be a modulation method. For example, traditional CD measurements are performed by means of a polarization modulator to obtain high-frequency switching of light circularity (or spin angular momentum). However, high-frequency switching of optical orbital angular momentum between two enantiomeric Laguerre-Gaussian modes is in practice difficult to realize. To be able to obtain unambiguous results, we opted for a different approach, where we use circularly polarized Laguerre-Gaussian light and compare the observed circular-difference effects with those observed in classical Hermite-Gaussian light. In practice this will lead to CD measurements on chiral molecules in solution using laser light with and without optical orbital angular momentum.

Lagerre-Gaussian light, $LG_p^{\,l}$ (with p and l the radial and azimuthal indices of the LG mode), involves optical angular momentum flux given by [12]

$$M^{spin} = \frac{\sigma}{\omega} F,$$

$$M^{orbital} = \frac{l}{\omega} F, \tag{1}$$

where F is the energy flux of the light having electric field $E(\kappa)$ given by

$$F = \frac{\pi}{2\omega\mu_0} \int_0^k d\kappa |E(\kappa)|^2 \frac{2k^2 - \kappa^2}{\kappa\sqrt{k^2 - \kappa^2}}. \tag{2}$$

$\sigma = 0, +1$, and -1 for linear, left- and right-handed circular polarized light, respectively, and where k and ω represent the wave number and frequency of the Laguerre-Gaussian light beam. As shown in Eq. (1), momentum indices σ and l contribute equally to total optical angular momentum flux,

$$M^{total} = M^{spin} + M^{orbital} = \frac{\sigma + l}{\omega} F. \tag{3}$$

Therefore, if optical orbital angular momentum can participate in chiral linear optics, its response would depend on total optical angular momentum flux shown in Eq. (3). Since
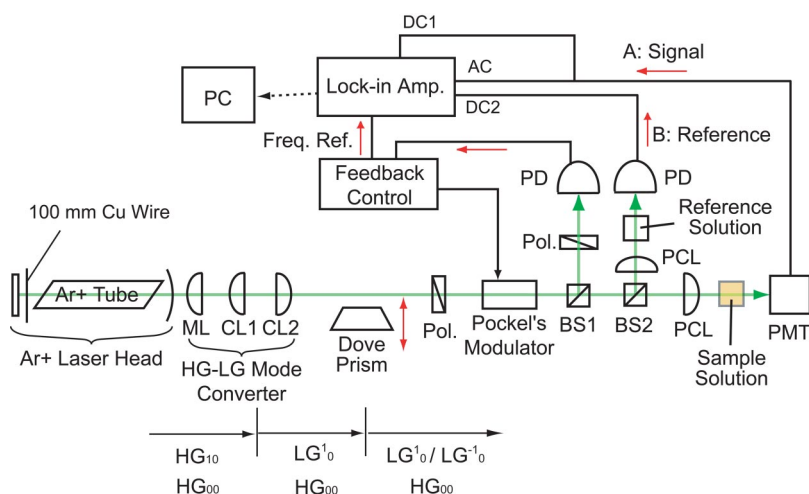
FIG. 1. Optical scheme for CD measurement using a Gaussian beam. ML: mode-matching lens; CL: cylindrical lenses; Pol.: polarizers; BS: beamsplitters; PD: photodiodes; PCL: plano-convex lens; and PMT: photomultiplier.

the contribution of l to total optical angular momentum described in Eq. (1) is comparable with that of σ, a chiral response due to optical orbital angular momentum exchange would be of similar magnitude as the classical CD response.

Usually, a CD response is recognized as a difference in absorbance for left- ($\sigma = +1$) and right- ($\sigma = -1$) handed circular polarized light without optical orbital angular momentum. In principle, this response is symmetric; for two enantiomers, the CD values are the same in magnitude but opposite in sign because M^{total} is symmetric about $\sigma = 0$ when $l = 0$. However, since M^{total} is no longer symmetric about $\sigma = 0$ when $l \neq 0$, Laguerre-Gaussian light would lead to a drastically different CD behavior.

The optical scheme for CD measurements with and without optical orbital angular momentum is shown in Fig. 1. Laguerre-Gaussian light modes were created from Hermite-Gaussian light modes by means of a Gaussian converter consisting of two cylindrical lenses ($f \sim 60$ mm) at a mutual distance of $\sqrt{2}f$. This Gaussian mode converter exchanges Hermite-Gaussian light mode HG_{mn} and Laguerre-Gaussian light mode LG_p^l under a general transformation rule; $l = m - n$ and $p = \min(m, n)$ [13,14]. The light source was an argon ion laser head generating 514.5 nm light, with a thin copper wire precisely positioned just in front of the high reflector of the laser resonator. By controlling the wire position, we could choose lasing Gaussian mode between HG_{00} and HG_{10} corresponding to HG_{00} ($= LG_0^0$: nonchiral) and LG_0^1 mode after the converter, respectively. A Dove prism was introduced to switch the helicity of Laguerre-Gaussian light.

For a sensitive detection of the CD signal, a Pockel's cell was used to modulate the polarization between left-hand and right-hand circular polarization. A feedback circuit was used for a precise modulation between both circular polarizations. The polarization-modulated light was strongly focused on the sample by a plano-convex lens ($f = 20$ mm) and the intensity of the transmitted light from the sample was detected by a photomultiplier tube (PMT). In our system, total optical angular momentum flux is switching between $M^{total} = (+1/\omega)F(\sigma = +1, l = 0)$ and $M^{total} = (-1/\omega)F(\sigma = +1, l = 0)$ for HG_{00}, and $M^{total} = (+2/\omega)F(\sigma = \pm 1, l = \pm 1)$ and $M^{total} = 0(\sigma = \mp 1, l = \mp 1)$ for LG_0^1 (double signs in same order; upper and lower, respectively, for left- and right-handed helicity of light) at a frequency of ~ 200 Hz. Hence, as mentioned above, if optical orbital angular momentum can interact with chiral matter, the CD response for HG_{00} and LG_0^1 would be different because of the difference in total angular momentum.

The samples were chloroform solutions (0.1 mmol/l) of the $(+)$ and $(-)$ optically pure enantiomers and the racemic mixture of a chiral helicene bisquinone derivative [15,16]. This molecule was chosen because it possesses a strong optical activity at 514.5 nm and is optically stable. Rectangular cuvettes of optical grade fused quartz were used as sample cells and were settled at the focus of the beam.

In Fig. 2 we show the UV-VIS and CD spectra of each solution, measured by commercial spectrometers (Perkin-Elmer Lamda 900 for UV-VIS and JASCO J-810 for CD). Every solution has significant absorption at 514.5 nm
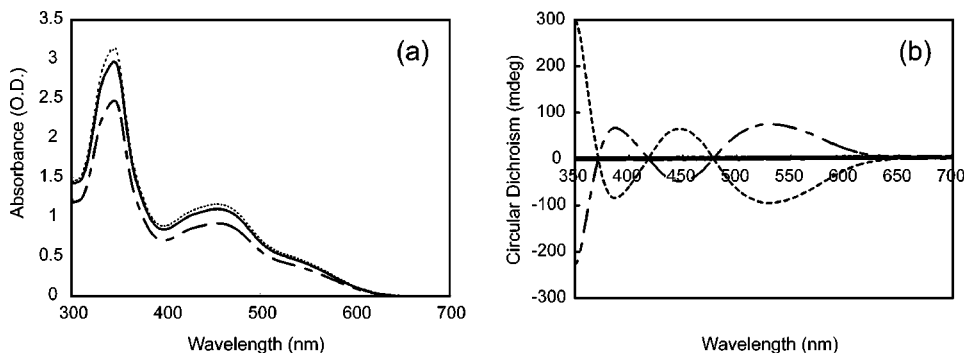

FIG. 2. (a) UV-VIS and (b) CD spectra for racemic mixture (solid line), $(+)$ (broken line), and $(-)$ (dashed line) enantiomers of helicene solutions.

TABLE I. Comparison of estimated CD values (ellipticities). (L) and (R) indicate helicity of optical vortex of Laguerre-Gaussian light (units: mdeg).

	(+) enantiomer			
	HG_{00}	LG_0^1 (L)	LG_0^1 (R)	CD spectrometer
Observed CD	68.8	69.5	69.1	69.0
Standard deviation S	1.5	1.2	1.7	
	(−) enantiomer			
	HG_{00}	LG_0^1 (L)	LG_0^1 (R)	CD spectrometer
Observed CD	−88.2	−87.9	−87.7	−87.2
Standard deviation S	1.4	1.3	1.6	

($\sim$0.5 absorbance), but only the enantiomerically pure samples show optical activity. The magnitude of the CD values (ellipticity θ) for (+) and (−) solutions is on the order of 60–90 mdeg.

The results of a set of laser measurements, using circular polarized HG_{00} and LG_0^1 light are listed in Table I. The observed intensity differences (or differences in extinction coefficient, $\Delta\varepsilon$) were converted into ellipticity by $\theta=3300\,\Delta\varepsilon$. We observe, within experimental error, identical CD values for both HG and LG lasermodes. Furthermore, these values agree well with those measured by a conventional CD spectrometer, which confirms the reliability of our system. Hence we must conclude that there is no interaction of optical orbital angular momentum with chiral molecules through a linear optical process. This is consistent with recent theoretical work published by Babiker *et al.* [10].

We experimentally demonstrated that the chirality of Laguerre-Gaussian light cannot associate with molecular chirality. Note, however, that this conclusion is only valid for linear optical processes and does not exclude chiral interactions for higher-order optical processes.

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