

## Optical chirality in Raman scattering

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(Received 2 December 2024; accepted 9 September 2025; published 2 October 2025)

Raman optical activity (ROA) offers a powerful tool for distinguishing chiral molecules. However, the inherent properties of light that unveil the “handedness” of molecules remain unclear in the realm of ROA. Here, we find two optical measures—the optical chirality tensor and the optical quadrupole tensor—that contribute to ROA excitations. Subsequently, we propose a theoretical framework to elucidate the relationship between the optical chirality quantities and their molecular counterparts in Raman scattering. This framework allows for more selective and tunable ROA excitations. As a demonstration, we identify linearly polarized standing waves as a good configuration for superchiral ROA excitations, where the optical chirality is locally enhanced. Our work provides insights into optical chirality and paves the way to precisely manipulate chiroptical responses.

DOI: [10.1103/b7bv-fpz9](https://doi.org/10.1103/b7bv-fpz9)

### I. INTRODUCTION

Chirality exists universally in nature. For example, the vast majority of biomolecules, including proteins, carbohydrates, and nucleic acids, are chiral [1–3]. Chiral matter features a well-known characteristic: It cannot be superimposed on its mirror image (enantiomer). The chirality of matter is usually hidden because enantiomers are identical in terms of most of their physical properties. However, the opposite enantiomers can respond differently in their interactions with other chiral entities, and such responses can be measured [4,5]. Light plays a crucial role in measuring the chiroptical responses since light can be chiral, with circularly polarized light (CPL) as the premier example [6,7]. Generally, chiroptical effects are manifested through the interplay of chiral materials with right- and left-handed CPL (RCP and LCP) by light absorption or scattering. Well-known chiroptical techniques include optical rotatory dispersion [8,9], circular dichroism (CD) absorption [10,11], and Raman optical activity (ROA) [12,13]. As a scattering spectroscopy, ROA enables peering into the vibrational states of molecules, providing rich information on their structures and functionalities [14,15]. In particular, ROA persists in aqueous solutions, and thus underpins a powerful technique to quantify molecular chirality in biology and chemistry [16,17].

As chiroptical methodologies progress, there is a growing interest in elucidating the specific properties of light that reveal the “handedness” of the molecules [18,19]. Conventionally, the spin angular momentum (SAM) was considered an indispensable factor for both CD and ROA [20–22].

However, in 2010, Cohen and coworkers found that the optical chirality pseudoscalar (OCP) rather than the SAM plays a decisive role in CD and a model of CD was established as a result [23,24]. This finding paves the way for manipulating chiral absorption responses via sculpted light fields, for instance, enhanced discrimination between enantiomers by superchiral light [25]. Compared to the CD absorption, optical activity scattering exhibits much more complexity due to its coupling with the observation direction. However, the well-established ROA theory obtains only the scattering intensity of light for several specific types of polarization states [26,27], without uncovering the underlying players in revealing the molecular chirality.

In this work, we propose a theoretical framework that elucidates the intrinsic optical quantities responsible for the ROA. This model correlates the Raman scattering intensities with four primary optical quantities: SAM, OCP, optical chirality tensor (OCT), and optical quadrupole tensor (OQT), which characterize the chirality of electromagnetic fields. Notably, the OCT and OQT are first identified as the key factors contributing to ROA excitations. Our model illustrates that each chiral parameter of a molecule has a corresponding counterpart in light. Consequently, we present four distinct ROA forms that can be selectively accessed by the chiral light fields carrying the respective optical quantities. In particular, our theory identifies the linearly polarized standing wave (LPSW), which is achiral in the conventional sense, as a good configuration for superchiral excitations, where optical chirality is locally enhanced. Our findings broaden the concepts of optical chirality, promising to unlock precision control in chiral light-matter interactions.

### II. THEORY

The purpose of Raman scattering theory is to derive expressions for various observables in the molecular scattering of polarized light, such as the scattering intensity, ellipticity,

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or Stokes parameters. Conventionally, explicit expressions are extracted by specifying the desired polarization state of the incident electromagnetic field and the direction of scattering [26–28]. In contrast, we turn to finding the physical quantities underlying the molecular scattering. For this purpose, we consider the fundamental symmetries of molecular parameters and define three optical tensors to characterize the electromagnetic fields ( $\mathbf{E}$  and  $\mathbf{B} = \nabla \times \mathbf{E}/i\omega$  are the complex electric and magnetic fields):

$$\begin{aligned} I_{ij} &\triangleq -cT_{ij} = \frac{c\varepsilon_0}{2} \text{Re}[\delta_{ij}\mathbf{E}^* \cdot \mathbf{E} - 2E_i^*E_j], \\ C_{ij} &\triangleq cN_{ij} = \frac{c\varepsilon_0}{2\omega} \text{Im}[\delta_{ij}\mathbf{E}^* \cdot \mathbf{B} - (E_i^*B_j + E_j^*B_i)], \\ Q_{i,jk} &\triangleq \frac{c\varepsilon_0}{2\omega^2} \text{Re}[E_i^*\partial_j E_k + E_i^*\partial_k E_j], \end{aligned} \quad (1)$$

where  $T_{ij}$  is the Maxwell stress tensor,  $N_{ij}$  is the  $ij$ -infrazilches tensor [29,30], and  $\delta_{ij}$  denotes the Kronecker delta.  $c = 1/\sqrt{\varepsilon_0\mu_0}$  represents the speed of light in vacuum ( $\varepsilon_0$  and  $\mu_0$  are, respectively, the absolute permeability and permittivity in vacuum).  $\omega$  is the angular frequency of light.  $I_{ij}$  has a dimension of the power density, whereas  $C_{ij}$  and  $Q_{i,jk}$  have the same dimension as the SAM density. We call the quantities  $I_{ij}$ ,  $C_{ij}$ , and  $Q_{i,jk}$  the intensity tensor, OCT, and OQT, respectively, with the following properties:

$$\begin{aligned} I_{ij} &= I_{ji}, \quad C_{ij} = C_{ji}, \quad Q_{i,jk} = Q_{i,kj}, \\ I &= \delta_{ij}I_{ij} = \frac{c\varepsilon_0}{2} \text{Re}[\mathbf{E}^* \cdot \mathbf{E}], \\ C &= \delta_{ij}C_{ij} = -\frac{c\varepsilon_0}{2\omega^2} \text{Re}[\mathbf{E}^* \cdot (\nabla \times \mathbf{E})], \end{aligned} \quad (2)$$

where  $I$  is the intensity of the light field and  $C$  is the OCP that is defined slightly different in dimension from that in the previous study [23,30]. Note that the English subscripts of the tensor refer to the Cartesian indices in the laboratory-fixed frame, and the Greek subscripts in subsequent text denote the Cartesian indices in the molecule-fixed frame. For repeated subscripts, the Einstein rule for summation over the Cartesian indices is implied. Note that the isotropic average of OQT,  $\varepsilon_{ikl}Q_{k,lj}$ , can be proven a conserved quantity (see the Supplemental Material [31]), where  $\varepsilon_{\beta\gamma\alpha}$  is the *third-rank* isotropic tensor.

These optical quantities are used to derive the general expression of the scattered light field, which is considered to be the radiation field generated by the oscillating electric and magnetic multipole moments induced by a molecule. In terms of the electric dipole-electric dipole molecular polarizability tensor  $\tilde{\alpha}_{\alpha\beta}$ , the electric dipole-electric quadrupole optical activity tensor  $\tilde{A}_{\alpha,\beta\gamma}$ , and the electric dipole-magnetic dipole optical activity tensor  $\tilde{G}_{\alpha\beta}$ , the oscillating induced moments are the real parts of the following complex expressions [12,26]:

$$\begin{aligned} \tilde{\mu}_\alpha &= \tilde{\alpha}_{\alpha\beta}E_\beta + \frac{1}{3}\tilde{A}_{\alpha,\beta\gamma}E_{\beta\gamma} + \tilde{G}_{\alpha\beta}B_\beta + \cdots, \\ \tilde{\Theta}_\alpha &= \tilde{A}_{\gamma,\alpha\beta}^*E_\gamma + \cdots, \quad \tilde{m}_\alpha = \tilde{G}_{\beta\alpha}^*E_\beta + \cdots, \end{aligned} \quad (3)$$

where  $E_{\beta\gamma} = \partial_\beta E_\gamma$  is the electric field gradient at the molecule.  $\tilde{\mu}_\alpha$ ,  $\tilde{\Theta}_\alpha$ , and  $\tilde{m}_\alpha$  are the induced complex electric dipole, electric quadrupole, and magnetic dipole of the molecule, respectively. In the absence of static external fields,

the molecular property tensors for a molecule in the transparent region ( $\omega$  is far from the absorption frequency) satisfy the conditions [26,32]

$$\begin{aligned} \tilde{\alpha}_{\alpha\beta} &= \alpha_{\alpha\beta} = \alpha_{\beta\alpha}, \quad \tilde{A}_{\alpha,\beta\gamma} = A_{\alpha,\beta\gamma} = A_{\alpha,\gamma\beta}, \\ \tilde{G}_{\alpha\beta} &= -iG'_{\alpha\beta}, \end{aligned} \quad (4)$$

where  $\alpha_{\alpha\beta}$ ,  $A_{\alpha,\beta\gamma}$  and  $G'_{\alpha\beta}$  are real and  $i$  is the imaginary unit. In this situation, the scattered electric field radiated by multiple time-dependent moments can be detected at a distance  $R$  ( $R \gg \lambda$ ,  $\lambda$  is the wavelength of the light) from the molecular origin, as the real part of [26,33]

$$\begin{aligned} E_\alpha^s &= \frac{\omega^2\mu_0}{4\pi R} e^{i\omega(R/c-t)} \left[ (\tilde{\mu}_\alpha - n_\alpha n_\beta \tilde{\mu}_\beta) - \frac{1}{c} \varepsilon_{\alpha\beta\gamma} n_\beta \tilde{m}_\gamma \right. \\ &\quad \left. - \frac{i\omega}{3c} (n_\beta \tilde{\Theta}_{\alpha\beta} - n_\alpha n_\beta n_\gamma \tilde{\Theta}_{\beta\gamma}) + \cdots \right], \end{aligned} \quad (5)$$

where  $\mathbf{n}$  denotes the propagation vector in the direction of the detected wave. Then, the Raman scattering intensity from a specifically oriented molecule can be obtained as  $I^s = c\varepsilon_0 E_\alpha^s E_\alpha^s/2$ , where each term involves the scattering geometry, incident field, and molecular property tensors (see Eqs. (S2) and (S3) in the Supplemental Material [31]).

For the Raman scattering from isotropic collections of molecules, measurements of Raman observables require an average over all molecular orientations to the laboratory coordinate system. We adopt a method for the isotropic averages of general molecular tensor components (see the Supplemental Material [31] for details). As such, all the terms in Eq. (5) can be calculated for the randomly oriented molecules in a unified way. Even so, the calculation is still too complex until optical tensors are introduced. In this manner, the expression can be given in terms of key physical quantities instead of the explicit form of the electromagnetic field. Considering that ROA-related signals are orders of magnitude weaker than spontaneous Raman scattering, the Raman scattering intensity is divided into two parts: the first-order and second-order Raman scattering intensity (FORI  $I_1^s$  and SORI  $I_2^s$ ). With the optical tensors given by Eq. (1), the final expressions can be reduced to

$$I_1^s = \frac{1}{2}K[\alpha_{\alpha\beta}\alpha_{\beta\alpha}(13I + n_in_jI_{ij}) + \alpha_{\alpha\alpha}\alpha_{\beta\beta}(-I + 3n_in_jI_{ij})], \quad (6)$$

$$\begin{aligned} I_2^s &= \omega K \left[ \frac{\omega}{3} \varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma,\delta\beta} (6n_i S_i + 2\varepsilon_{ikl} n_i n_j Q_{k,lj}) \right. \\ &\quad + \alpha_{\alpha\beta} G'_{\alpha\beta} (10n_i S_i + 13C + n_i n_j C_{ij}) \\ &\quad \left. + \alpha_{\alpha\alpha} G'_{\beta\beta} (-10n_i S_i - C + 3n_i n_j C_{ij}) \right], \end{aligned} \quad (7)$$

where  $S_i$  is the SAM, defined as  $\mathbf{S} = \varepsilon_0 \text{Im}[\mathbf{E}^* \times \mathbf{E}]/2\omega$ , and the constant  $K$  is given by  $K = (\omega^2\mu_0/4\pi R)^2/30$ . Considering  $\mathbf{n} \cdot \mathbf{n} = 1$ , the scalars  $I$  and  $C$  can be expressed as tensor products  $I = n_i n_i I_{jj}$  and  $C = n_i n_i C_{jj}$ . Detailed derivation of the expressions is presented in the Supplemental Material [31]. Our theoretical derivation relies on the universal electromagnetic scattering theory and a general method for averaging over molecular orientations. Thus, it also applies to other types of molecular scattering, such as Rayleigh scattering.

TABLE I. Physical quantities and their parity-time symmetries of molecular properties and their light counterparts.

| Molecular properties                                                            | Optogeometrical quantities   |                                        | Space inversion | Time reversal |
|---------------------------------------------------------------------------------|------------------------------|----------------------------------------|-----------------|---------------|
| $\alpha_{\alpha\beta}$                                                          | $in_i E_j$                   |                                        | +               | +             |
| $G'_{\alpha\beta}$                                                              | $\varepsilon_{kij} E_k$      | $n_i B_j$                              | -               | +             |
| $A_{\alpha, \beta\delta}$                                                       | $n_i n_j E_k$                | $in_i \partial_j E_k$                  | -               | +             |
| Raman invariants                                                                | Optical conserved quantities |                                        | Space inversion | Time reversal |
| $\alpha_{\alpha\beta} \alpha_{\alpha\beta}$                                     | $n_i n_j I_{ij}$             |                                        | +               | +             |
| $\alpha_{\alpha\beta} G'_{\alpha\beta}$                                         | $n_i S_i$                    | $n_i n_j C_{ij}$                       | -               | +             |
| $\varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma, \delta\beta}$ | $n_i S_i$                    | $\varepsilon_{ikl} n_i n_j Q_{k, l j}$ | -               | +             |

In ROA, the molecular chirality is interpreted as three Raman invariants:  $\alpha_{\alpha\alpha} G'_{\alpha\beta}$ ,  $\alpha_{\alpha\beta} G'_{\alpha\beta}$ , and  $\omega \varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma, \delta\beta} / 3$ . Here, we focus on discussing the optical chirality in ROA. For this purpose, we rewrite the SORI as

$$I_2 \propto I_{\omega \varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma, \delta\beta} / 3} \frac{\omega}{3} \varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma, \delta\beta} + I_{\alpha_{\alpha\beta} G'_{\alpha\beta}} \alpha_{\alpha\beta} G'_{\alpha\beta} + I_{\alpha_{\alpha\alpha} G'_{\alpha\beta}} \alpha_{\alpha\alpha} G'_{\alpha\beta}, \quad (8)$$

where  $I_{\alpha_{\alpha\beta} G'_{\alpha\beta}}$ ,  $I_{\alpha_{\alpha\alpha} G'_{\alpha\beta}}$ , and  $I_{\omega \varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma, \delta\beta} / 3}$  are the optical coefficients of the three Raman invariants. Our focus is to study the influence of optical chirality on ROA excitations. Consequently, we use the optical coefficients to evaluate the ROA signals, irrespective of specific molecular parameters.

### III. OPTICAL CHIRALITY IN ROA

Our theory reveals the relationship between the molecular parameters and their light counterparts, the optogeometrical quantities (Appendix A), as listed in Table I. The molecular observables  $\alpha_{\alpha\alpha} \alpha_{\alpha\beta}$  and  $\alpha_{\alpha\beta} \alpha_{\alpha\beta}$  in the FORI correspond to the optogeometrical quantities  $n_i n_i I_{ij}$  and  $n_i n_j I_{ij}$ , where  $\alpha_{\alpha\beta}$  and  $I_{ij}$  feature identical parity-time symmetry. The light counterparts of  $\alpha_{\alpha\alpha} G'_{\alpha\beta}$  and  $\alpha_{\alpha\beta} G'_{\alpha\beta}$  are  $n_i n_i C_{ij}$  and  $n_i n_j C_{ij}$ . Unlike the polarizability tensor  $\alpha_{\alpha\beta}$ , which has only an electric field counterpart, the optical activity tensor  $G'_{\alpha\beta}$  includes electric and magnetic parts. Thus, the observables  $\alpha_{\alpha\alpha} G'_{\alpha\beta}$  or  $\alpha_{\alpha\beta} G'_{\alpha\beta}$  correspond to the optical quantities  $S_i$  and  $C_{ij}$ .  $S_i$  is a time-odd, parity-even vector, but its symmetry reverses once coupled with  $n_i$ . Thus, the optogeometrical quantity  $n_i S_i$  has the same symmetry as  $C_{ij}$ , which is time-even and parity-odd (chiral). By contrast,  $\varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma, \delta\beta}$  is connected with the optical chirality quantities  $n_i S_i$  and  $\varepsilon_{ikl} n_i n_j Q_{k, l j}$ . It follows that each Raman observable corresponds to the specific optical conserved quantities.

Furthermore, our model clarifies that the chirality of light is defined by SAM, OCP, OCT, and OQT. Each quantity characterizes a specific behavior of the electromagnetic field. Figure 1 presents their respective contributions to ROA via a three-dimensional (3D) scattering sphere. Specifically, SAM features time-varying rotating electric and magnetic vectors, and it connects to all the molecular activity tensors. The SORI excited by SAM is positive when scattered light propagates in the same direction as the SAM and negative in the opposite direction [Fig. 1(a)]. In contrast, OCP and OCT originate from the geometry configuration between the dynamic magnetic vector ( $\partial \mathbf{B} / \partial t$ ) and the electric vector. OCP appears except for the perpendicular case. Even so, OCT still exists. They excite

ROA in different forms. The polarity of SORI excited by OCP is independent of the scattering direction but relies on its sign [Fig. 1(b)]. The SORI for OCT exhibits a direction-related feature, as shown in Fig. 1(c). The optical quantity OQT is a *third-rank* tensor describing the chirality originating from the gradient of the electric field. For example, if the magnetic field vector lies along the  $x$  axis and  $\partial_x E_x$  is nonzero, such a field has no OCT but OQT. Its contribution to the ROA is shown in Fig. 1(d), showing a different direction-dependent form from other distributions.

A light field can be characterized by four chiral quantities. Therefore, we can selectively tune these optical coefficients for specific ROA excitations. We focus on identifying the specific fields that process different characteristics for distinct ROA excitations. A primary illustration is the classic experimental scheme where the RCP and LCP act as the excitation sources. The SAM of CPL is generally considered the key factor for ROA excitations [34,35]. However, we find that the CPL possesses all the four chiral quantities, as shown in Fig. 2(a). The ROA excited by CPL is evaluated via the optical coefficients in Eq. (8). Figure 2(b) shows their 3D distributions for the LCP, where the red and blue regions

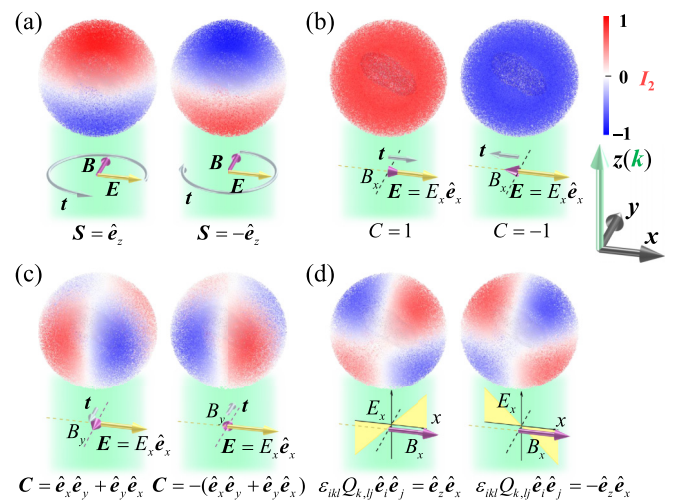


FIG. 1. Concept of optical chirality in Raman scattering and various ROA excitations. Four physical quantities, (a) SAM, (b) OCP, (c) OCT, and (d) OQT, are involved in ROA. Each quantity is described by the expression below and characterized by the oscillating electric and magnetic vectors. The scattering sphere presents the distribution of the ROA signal varying with the scattering direction.

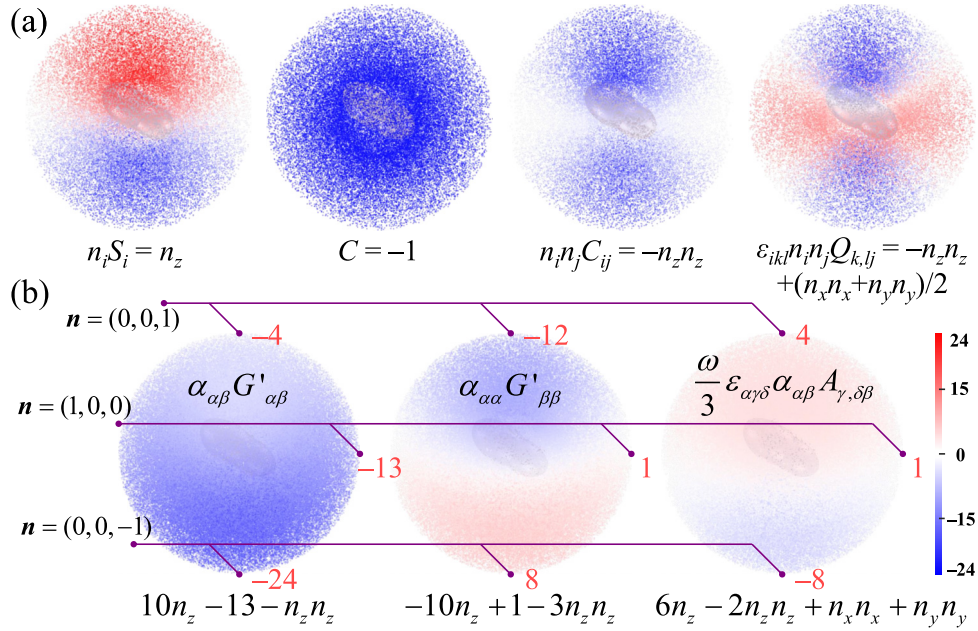


FIG. 2. Analysis of the chiral quantities of the LCP in ROA excitation. (a) Contributions of the four optical chiral quantities in LCP to the ROA intensity. From left to right: SAM, OCP, OCT, and OQT. (b) Optical coefficients of the three Raman invariants. Three specific scattering directions, i.e.,  $+z$  (0, 0, 1),  $-x$  (1, 0, 0), and  $-z$  (0, 0, -1), are labeled.

indicate positive and negative intensities. Furthermore, three specific directions, i.e.,  $+z$ ,  $+x$ , and  $-z$ , are highlighted with the coefficients labeled on the scattering sphere. As expected, these results are identical to those obtained in the established theory [12,26].

Apart from the CPL, we conceptualize three types of chiral light fields, taking into consideration the characteristics of the optical chirality quantities. They are the circularly polarized standing wave (CPSW) expressed as  $\mathbf{E} = \sqrt{2}E_0(\hat{\mathbf{e}}_x \cos kz - \hat{\mathbf{e}}_y \sin kz)$ , the LPSW with the form of  $\mathbf{E} = \hat{\mathbf{e}}_y E_0 \cos kz$ , and a superposed field with intensity gradient (SFIG) described by  $\mathbf{E} = E_0(\hat{\mathbf{e}}_x \cos px + \hat{\mathbf{e}}_y)e^{ikz}$  ( $p$  is a constant). The CPSW possesses OCP, OCT, and OQT, the LPSW includes OCT and OQT, and the SFIG only has the OQT. These fields produce distinct ROA excitations due to their unique optical chirality. Detailed calculations of the ROA excitations from these fields are presented in Note 5 of the Supplemental Material [31].

For further analysis, we depict the optical coefficients of ROA versus the elevation angle  $\theta$  for a fixed azimuthal angle  $\varphi = \pi/4$  and exciting position  $z = \pi/4k$ ,  $x = \pi/4p$  in Fig. 3. The ROA of the CPL is complicated because it involves four chiral quantities. In particular, the SAM vector causes asymmetric scattering along its direction [Fig. 3(a)]. In comparison, the ROA of CPSW shows a symmetric distribution where the OCP provides a bias to the scattering intensity [Fig. 3(b)]. Without the OCP, the bias becomes zero. In this case, the chiral response of such fields, e.g., the LPSW characterized by OCT and OQT, can only be observed at certain scattering angles, as illustrated in Fig. 3(c). Generally, an electromagnetic field with an OCT also has OQT, but not vice versa. For instance, the SFIG can only excite the Raman invariant  $\omega \varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma,\delta\beta}/3$  because its chirality is characterized by the

OQT alone [see Fig. 3(d)]. These cases are practical configurations for measuring such quantities in experiments (see more discussions in Appendix B). Moreover, we find the reported circular-vortex differential scattering (CVDS) [34,36] supports our model as well. In fact, the CVDS can be ascribed to the OQT arising from the phase gradient of the optical vortex (see details in Appendix C).

#### IV. SUPERCHIRAL ROA

Our theory identifies LPSWs as a good configuration for superchiral ROA excitations, where optical chirality is locally enhanced. The LPSW is considered achiral in the conventional sense, but  $x$ - and  $y$ -polarized LPSWs form a pair of enantiomers in our model because they possess OCT and OQT. The optimal direction to measure the chiroptical response of such enantiomers lies at the middle of the  $x$  and  $y$  axes. To quantify their dissymmetry in ROA excitations, the  $g$  factor is used to measure the difference between the scattering intensities:

$$g = \frac{I_+^s - I_-^s}{I_+^s + I_-^s} = \frac{I_2^s}{I_1^s} \propto \frac{I_{\alpha_{\alpha\beta} G'_{\alpha\beta}} + I_{\alpha_{\alpha\alpha} G'_{\beta\beta}} + I_{\varepsilon_{\alpha\gamma\delta} \alpha_{\alpha\beta} A_{\gamma,\delta\beta}}}{I_{\alpha_{\alpha\beta} \alpha_{\alpha\beta}} + I_{\alpha_{\alpha\alpha} \alpha_{\beta\beta}}}, \quad (9)$$

where  $I_+^s$  represents the intensity from the “positive” chiral light and  $I_-^s$  corresponds to the “negative” chiral light. The optical coefficients  $I_{\alpha_{\alpha\beta} G'_{\alpha\beta}}$  and  $I_{\alpha_{\alpha\alpha} G'_{\beta\beta}}$  are related to the FORI. Since the FORI remains unchanged and the SORI reverses for excitations with opposite chirality, the  $g$  factor equals the ratio of the SORI to the FORI. The actual value of the  $g$  factor

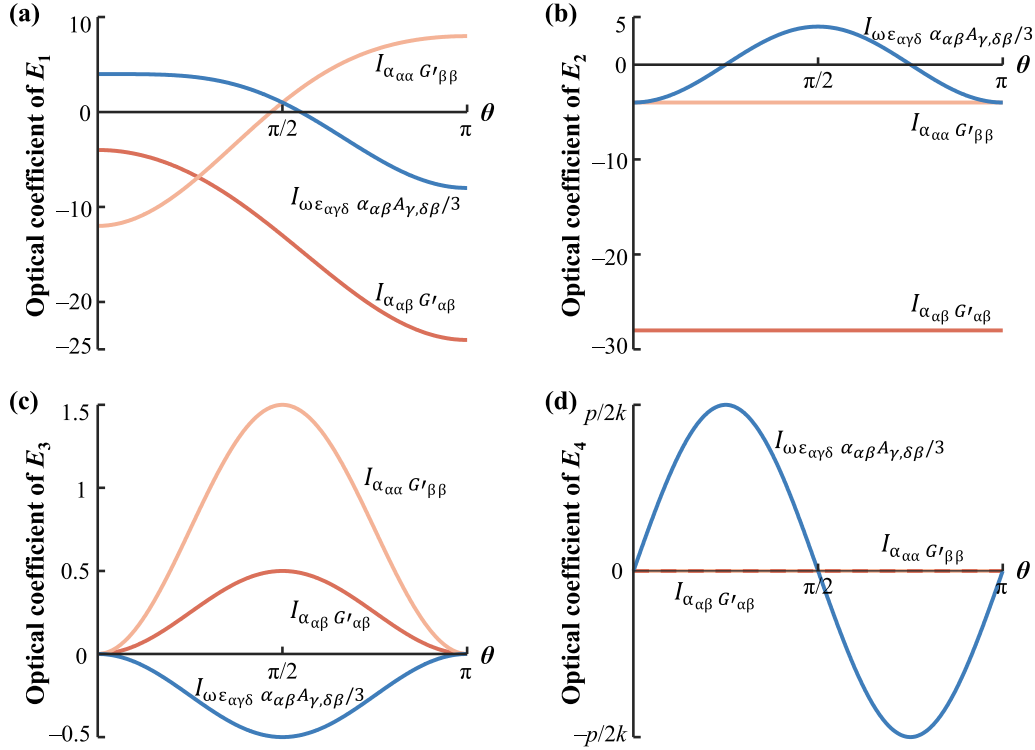


FIG. 3. ROA excitations by four types of chiral light fields: (a) LCP, (b) CPSW, (c) LPSW, and (d) SFIG. The scattering intensity is evaluated by the optical coefficients regardless of the specific molecular parameters.

is related to the specific molecular parameters. For general discussion, we evaluate it via the optical coefficients regardless of the molecular parameters. In this case, the dissymmetry factor of LPSWs is given by  $g = \tan(kz)/2$  (see Note 6 in the Supplemental Material [31]). When chiral molecules are excited near the nodes ( $kz \rightarrow \pi/2$ ), the  $g$  factor is dramatically amplified. It suggests that LPSW is more selective than CPL in preferentially exciting ROA in certain regions of space, such as the nodes of the standing wave.

## V. CONCLUSION

In summary, we have proposed a theoretical framework for ROA based on the relationship between optical chirality quantities and their molecular counterparts in Raman scattering. Within this framework, the chirality of light is characterized by four primary quantities, two of which, the OCT and OQT, are identified as contributing to the ROA excitation. We present four distinct ROA forms that can be selectively accessed by the chiral light fields carrying different optical chirality quantities. Furthermore, our theory reveals that the LPSW can be more selective than CPL in preferentially exciting ROA in certain regions of space due to the presence of OCT and OQT. These findings enhance our comprehension of optical chirality, which facilitates the manipulation of chiroptical responses. Additionally, our work provides theoretical guidance for exploring superchiral effects in response to excitations from structured light [37], with potential applications in spectroscopic imaging [38], absolute asymmetric synthesis [39], and ultrasensitive detection of chiral molecules [40].

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC) under Grants No. 12474318 (L.G.) and No. 124B2076 (Y.W.) and the Anhui Natural Science Foundation (Grant No. 2208085J24). L.G. acknowledges the support from the USTC Tang Scholarship.

## DATA AVAILABILITY

No data were created or analyzed in this study.

## APPENDIX A: PHYSICAL INTERPRETATION OF THE OPTOGEOMETRICAL QUANTITIES

Traditional theoretical results have shown that ROA responses exhibit distinct forms in different scattering directions. However, the underlying physics of such an effect is unclear. Our theory suggests that the optical measures and scattering geometry combine together in ROA, interpreted as the optogeometrical quantities, which act on the molecular scattering. Each optical measure characterizes a specific behavior of the electromagnetic field, but one can observe different features according to the choice of scattering geometry. Finally, the Raman scattering intensity measured in a certain direction depends on the observed features of the optical measure at that direction. Taking the SAM as an example, chiral properties arise from the rotating electric and magnetic vector fields as the time evolution. However, from the perspective of an observer, the rotation reverses if it is observed in the opposite direction; in particular, the rotation cannot be seen in the direction perpendicular to the SAM vec-

tor. As a result, the corresponding chiroptical effect disappears [Fig. 1(a)]. This observer effect in Raman scattering can be exploited for chiroptical measurements. For example, ROA responses can also be measured in two enantiomeric geometries instead of the traditional use of two chiral light fields for excitation.

## APPENDIX B: GUIDANCE ON THE EXPERIMENTAL VERIFICATION

Our theory does not impose any limitations on the chiral molecules. Thus, any chiral molecule can be used to verify the model, such as 1-phenylethanol,  $\alpha$ -pinene, and  $\beta$ -pinene [27]. In experiments, the actual values of the  $g$  factor are not only related to the excitation light field, but also rely on the specific molecular parameters, i.e., the values of the molecular Raman variants. Furthermore, it is noted that the  $g$  factor for the LPSW configuration can approach infinity theoretically at specific spatial locations, but its experimental value would not actually reach infinity due to certain constraints, such as

the size of molecular aggregates and optical diffraction of the exciting field.

## APPENDIX C: THEORETICAL EXPLANATION OF CIRCULAR-VORTEX DIFFERENTIAL SCATTERING

Our theoretical model can be applied to understand the physics behind forms of ROA that cannot be obtained within the conventional ROA theory, such as the recently reported ROA from twisted photons. In accordance with our model, the ROA that depends on the handedness of the incident twisted photons can be attributed to OQT, which arises from the phase gradient in the twisted light beam (or optical vortex). As defined in Eq. (1), the nonzero OQT exists if the incident field has a phase gradient distribution and circular polarization. That is why such a form of ROA is termed as the CVDS. Notably, since the value of OQT varies in response to the local phase gradient within the twisted light beam, the CVDS intensity is strongly dependent on the excitation position of the molecule. In addition, CVDS is solely manifested by the molecular tensor  $\varepsilon_{\alpha\gamma\delta}\alpha_{\alpha\beta}A_{\gamma,\delta\beta}$ , because this particular quantity serves as the molecular counterpart of OQT.

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