Connection between chiroptical signal enhancements and weak values

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It is shown that there is a direct connection between the enhancement effects of chiroptical spectroscopic signals using perpendicular-polarization detection method and the amplifications of various weak effects, known as weak-value measurements, in quantum optics. In addition, the acceptable range of chiroptical weak values is discussed.

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I. INTRODUCTION

The notion of measurement is at the core of quantum mechanics: a measurement of an observable collapses the system being measured into an eigenstate of the corresponding Hermitian operator and such measurement yields the corresponding eigenvalue. Thus it has been believed that, if the initial state of system is a linear combination of eigenstates, i.e., superposition state, nondestructive measurement that is weak enough to leave the state vector unchanged, is not possible. However, in 1988 Aharonov, Albert, and Vaidman (AAV) theoretically proposed a new concept of weak measurement as opposed to the conventional measurement that is often referred to as "strong" or "projective" measurement [1].

The idea behind weak measurement is to consider the case that the interaction strength between the measuring device "meter" and the system is sufficiently weak enough to leave the system negligibly disturbed [2–4]. Assume the Hamiltonian of the standard measurement can be written as $\hat{H} = -\alpha x \hat{A}$, where x is a canonical variable of the meter and α is either a unity or a normalized time-dependent function compactly centered at the time of measurement. Considering an ensemble of particles, e.g., photons in optical measurement, with a *preselected* initial state $|\psi_i\rangle$ and a *postselected* final state $|\psi_f\rangle$ with $|g(x)\rangle$ the initial state of the measuring device, one can obtain, taking the Taylor expansion reexponentiation of the exponential function of measurement operator,

$$\begin{aligned}\langle\psi_f|\Psi\rangle &= \langle\psi_f|e^{-i\int \hat{H}(t)dt}|g(x)\rangle|\psi_i\rangle\\ &\cong \langle\psi_f|1 - i\int \hat{H}(t)dt|g(x)\rangle|\psi_i\rangle\\ &= \langle\psi_f|\psi_i\rangle(1 - ixA_w)|g(x)\rangle\\ &\cong \langle\psi_f|\psi_i\rangle e^{-ixA_w}|g(x)\rangle, \end{aligned} \tag{1}$$

where the weak value of the system operator $\hat{A}$ is defined as (1),

$$A_w \equiv \frac{\langle\psi_f|\hat{A}|\psi_i\rangle}{\langle\psi_f|\psi_i\rangle}. \tag{2}$$

Here, a central assumption for successful weak-value measurements is that the initial spread or root-mean-square dispersion (Δ_p) of the conjugate momentum (p) of x is significantly larger than A_w. Then, it was suggested that the weak value can be arbitrarily large, far outside the range of eigenvalues of $\hat{A}$, if one can make the overlap $\langle\psi_f|\psi_i\rangle$ between the pre- and postselected states very small [1,2]. The postselection probability is then defined as

$$P_{\rm ps} = |\langle\psi_f|\psi_i\rangle|^2. \tag{3}$$

Aside from the fundamental physics interest in weak values, they have been found to be quite useful in amplifying weak effects or weak signals with sacrificing most of the data, e.g., transmitted photons passing through optical measurement device, in the postselection process, i.e., decrease in $P_{\rm ps}$, for enhanced detections.

In 1991, Ritchie *et al.* [5] carried out an experiment that has been believed to be an optical analog of the spin-1/2 experiment which was originally proposed by AAV [1] and Duck *et al.* [6]. Using a Gaussian-mode laser beam and also a pair of optical polarizers replacing the preselection and postselection Stern-Gerlach magnets in the AAV thought experiment, they were able to detect amplified weak effect that is the birefringent material-induced separation of the two orthogonal linear-polarization states of light. More recently, Hosten and Kwiat [7] were able to detect a polarization-state-dependent beam deflection of 1 Å, and Ben Dixon *et al.* [8] reported the use of a Sagnac ring interferometric weak measurement of very small (approximately hundreds of femtoradians) transverse deflection of an optical beam. Later, Brunner and Simon [9] showed that a weak measurement of small longitudinal phase shift is also experimentally feasible. In addition, a phase-and-amplitude measurement of photon wave function was performed by Lundeen *et al.* [10].

In chiroptical spectroscopy [11–14] that has been used to determine absolute configuration of chiral molecules, there have been quite extensive efforts to make enhanced detections of weak optical activity signals from chiral molecules in isotropic media using self- and active-heterodyne detection schemes [15–21]. One of the most successful approaches is known as ellipsometric detection with quasinull polarization geometry. Kliger and co-workers [15] in 1985 experimentally demonstrated that a significant enhancement of chiroptical signal is achievable by controlling the ellipticity angle of incident elliptically polarized lights (EPLs) and using two optical polarizers whose optic axes are orthogonal to each other. More recently, we showed that the modified Mach-Zehnder interferometric detection of extremely weak vibrational optical activity signal from chiral molecules in solutions becomes possible when two orthogonal polarizers placed before and

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after a chiral solution sample are properly used [17,19,20]. Here, it must be emphasized that the key element in these chiroptical signal enhancements are a pair of perpendicular polarizers and in fact they are the common elements used in the seemingly unrelated weak measurements [5,7,9,10] mentioned above. Nevertheless, it has not been realized that the two research fields, chiroptical spectroscopy in molecular physics and weak measurements in ultrasensitive metrology and quantum optics, are closely related to each other in many respects. Among different approaches to the amplification of weak chiroptical signals [20], we shall specifically consider, as a simple but representative example, the ellipsometric detection method pioneered by Kliger [15,22], though the same principle applies to other amplification schemes used in chiroptical spectroscopy.

II. RESULTS AND DISCUSSION

We now use the weak-value formalism to describe the enhancement effects of chiroptical signals when two orthogonal linear polarizers are used to select the initial polarization state of incident light and the final polarization state of the transmitted light after interacting with chiral molecules in isotropic media.

A. Chiroptical weak value

Using an appropriate phase shifter, one can convert a linearly polarized light (LPL) into EPL with controllable ellipticity angle θ [Fig. 1(a)]. Then, the electric fields (Jones vectors) of the normalized left (+) and right (−) EPLs can be expressed as linear combinations of two orthogonal polarization states, i.e.,

$$|\psi_i^{\pm}\rangle = \cos\theta|V\rangle \pm i\sin\theta|H\rangle, \tag{4}$$

where $|V\rangle$ and $|H\rangle$ denote the vertical and horizontal polarization states that are considered to be the optical analogs of the spin-1/2 systems. Consider the case that the EPL, which corresponds to the initial (preselected) state, interacts with chiral molecules dissolved in an isotropic medium. Then, using either the Jones matrix formalism [23] or linear-response function theory [16,24], one can show that the transmitted light affected by the medium containing chiral molecules is given as

$$|\Psi^{\pm}\rangle = e^{-i\hat{A}_c L}|\psi_i^{\pm}\rangle, \tag{5}$$

where the operator $\hat{A}_c$ representing the weak chiroptical effects on the propagating light is given as

$$\hat{A}_c = \left(\rho - \frac{i\kappa}{2}\right)\hat{I} - \left(\frac{\delta}{2} - \frac{i\eta}{4}\right)\hat{\sigma}_y. \tag{6}$$

Here, $\hat{I}$ and $\hat{\sigma}_y$ are the 2×2 identity matrix and the y-component vector of the Pauli matrices, respectively. L is the thickness of the solution sample and κ, ρ, η, and δ are the absorption coefficient [$=\ln(10)\varepsilon c$], dispersion [$=\ln(10)2\pi n/\lambda$], circular dichroism (CD) [$=\ln(10)(\varepsilon_L - \varepsilon_R)c$], and circular birefringence [$=\ln(10)2\pi(n_L - n_R)/\lambda$], respectively, where ε, n, λ, and c are, respectively, the decadic molar extinction coefficient, refractive index, wavelength, and speed of light. Typically, the ratios η/κ and δ/ρ are on the order of $|m/(\mu c)| \sim 10^{-3}$–10^{-2} [13,25], where m and μ represent the transition magnetic and electric dipoles of a chiral molecule. Equation (6) indicates that the two polarization (spin) states are weakly coupled to each other by the chiral molecules and the real and imaginary parts of the coupling constant are associated with circular birefringence and circular dichroism (CD), respectively [13,14]. Here, it should be noted that, due to the circular polarization-dependent loss of photons, i.e., circular dichroism, the operator $e^{-i\hat{A}_c L}$ in Eq. (5) is no longer unitary. Nevertheless, the weak-value formalism is still applicable as demonstrated in this paper.

In the ellipsometric chiroptical spectroscopy, an optical polarizer whose axis is perpendicular to the major axis of the initially prepared (preselected) EPL is placed after the solution sample so that the independent postselection is to project the transmitted light onto the y axis, i.e.,

$$|\psi_f\rangle = |H\rangle. \tag{7}$$

Now, since the linear chiroptical effects are indeed extremely weak, from Eq. (5) we find that, using the linearization-and-reexponentiation approximation of Eq. (1) instead of the Jones N-matrix technique [23,26],

$$\begin{aligned}\langle\psi_f|\Psi^{\pm}\rangle &= \langle\psi_f|e^{-i\hat{A}_c L}|\psi_i^{\pm}\rangle \cong \langle\psi_f|1 - i\hat{A}_c L|\psi_i^{\pm}\rangle \\ &= \langle\psi_f|\psi_i^{\pm}\rangle(1 - iA_{c,w}^{\pm}L) \cong \langle\psi_f|\psi_i^{\pm}\rangle e^{-iA_{c,w}^{\pm}L},\end{aligned} \tag{8}$$

where the chiroptical weak value $A_{c,w}^{\pm}$ is given as

$$A_{c,w}^{\pm} \equiv \frac{\langle\psi_f|\hat{A}_c|\psi_i^{\pm}\rangle}{\langle\psi_f|\psi_i^{\pm}\rangle} = \left(\rho \mp \frac{\delta}{2}\cot\theta\right) - i\left(\frac{\kappa}{2} \mp \frac{\eta}{4}\cot\theta\right). \tag{9}$$

Note that the weak value in Eq. (9) is a complex number since it represents both the circular dichroic (imaginary part of the chiral susceptibility) and circular birefringent (real part of the chiral susceptibility) responses of chiral molecules.

B. Imaginary part of chiroptical weak value

As demonstrated by the Kliger group, us, and many others, in the conventional ellipsometric chiroptical spectroscopy, it is the intensity of the postselected electric field, which is the horizontally polarized (spin-down) component, that is measured:

$$I_{\pm} = |\langle\psi_f|\Psi^{\pm}\rangle|^2 \cong |\langle\psi_f|\psi_i^{\pm}\rangle|^2 e^{2L\,\mathrm{Im}[A_{c,w}^{\pm}]}. \tag{10}$$

Thus the imaginary part of the chiroptical weak value, $\mathrm{Im}[A_{c,w}^{\pm}] = -(\kappa/2) \pm (\eta/4)\cot\theta$, is relevant and corresponds to the observable in this case of intensity measurement scheme. The approximations used in Eqs. (8) and (10) are valid when the linear chiroptical effect is sufficiently weak so that all the higher-order nonlinear chiroptical effects are negligible. Furthermore, $|A_{c,w}^{\pm}|L < 1$ and $\mathrm{Im}[A_{c,w}^{\pm}] \leqslant 0$. The quantity $|\langle\psi_f|\psi_i^{\pm}\rangle|^2$ in Eq. (10), which was called the postselection probability P_{ps} in weak measurements, is just the intensity of the horizontal component of the preselected initial EPL, which will be denoted as I_0—note that $I_{0,+} = I_{0,-} = \sin^2\theta$. Thus Eq. (10) can be rewritten as $I_{\pm} \cong I_0 e^{2L\,\mathrm{Im}[A_{c,w}^{\pm}]}$ and the experimentally measured difference in absorbances, i.e., CD,

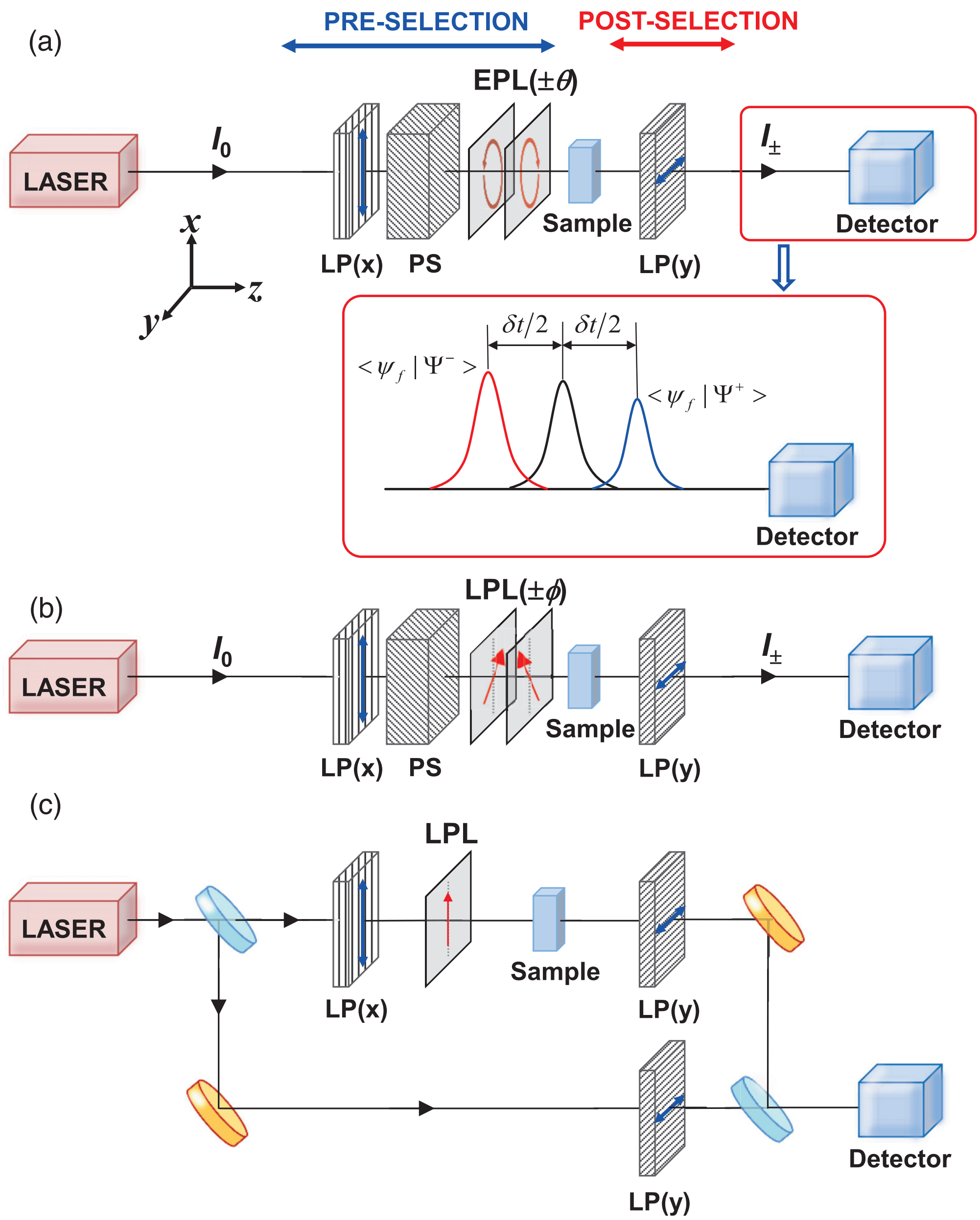

FIG. 1. (Color online) Schematic representation of the experimental setup for (a) quasinull ellipsometric detection of circular dichroism and (b) quasinull detection of optical rotatory dispersion. Here, LP and PS are linear polarizer and phase shifter, respectively. In both cases, the small y components of the incident EPLs (a) or LPLs (b) are used as an internal (self-) local oscillator that interferes with the chiroptical signal electric field in the y direction, which is generated by the major x-component electric field of the incident light [20]. In the inset of (a), the difference in arrival times of pulsed left and right EPL's at the detector is shown. Just for illustration purposes, it is assumed that $n_L < n_R$ and $\varepsilon_L > \varepsilon_R$. Therefore, the left(+)-EPL pulse $\langle\psi_f|\Psi^+\rangle$ arrives at the detector earlier by δt_w than the right(−)-EPL pulse $\langle\psi_f|\Psi^-\rangle$ does and the intensity of the left(+) EPL is smaller than that of the right(−) EPL. In the inset, the black Gaussian-shape pulse represents the temporal envelope of transmitted field through an isotropic achiral (racemic) medium. Instead of using the self-heterodyne detection schemes in (a) and (b), Mach-Zehnder interferometric detection method (c) can be used to selectively measure the y-polarized chiroptical signal field (see Ref. [17] for a detailed description).

is found to be

$$\Delta A \equiv \bar{A}_L - \bar{A}_R = \log_{10}\frac{I_+/I_0}{I_-/I_0}$$
$$= \frac{2}{\ln(10)}\{\mathrm{Im}[A^+_{c,w}] - \mathrm{Im}[A^-_{c,w}]\} = \frac{\eta L}{\ln(10)}\cot\theta, \quad (11)$$

where $\bar{A}_{L,R}$ are the absorbances measured by using left and right EPLs. Often, one can measure the dissymmetry factor defined as $g_{\mathrm{EPL}} = (I_+ - I_-)/\bar{I}$ with $\bar{I} = (I_+ + I_-)/2$ [13]. In the limiting case that $\eta L \cot\theta$ is small, the dissymmetry factor is given as $g_{\mathrm{EPL}} \simeq \eta L \cot\theta$.

These observables, ΔA and g_{EPL}, give information on the circular dichroism η ($\propto \varepsilon_L - \varepsilon_R$). Figure 1(b) depicts the experimental scheme for the quasinull enhanced measurement of optical rotatory dispersion (ORD) signal δ ($\propto n_L - n_R$) by using slightly rotated ($\pm\phi$) LPLs and by measuring the same absorption difference ΔA or dissymmetry factor g_{EPL}. In this case of the ORD measurement, the pre- and postselected states are $|\psi_i^{\pm}\rangle = \cos\phi|V\rangle \pm \sin\phi|H\rangle$ and $|\psi_f\rangle = |H\rangle$ [16,19]. Then, the corresponding weak values are found to be $A_{c,w}^{\pm} = -i\kappa/2 \mp (i\delta/2)\cot\phi + \rho \mp (\eta/4)\cot\phi$. Note that the attenuation of the incident (rotated) LPL is additionally dependent on circular birefringence $n_L - n_R$ and the dispersion change by circular dichroism $\varepsilon_L - \varepsilon_R$. The experimentally measured difference in absorbances and the dissymmetry factor are found to be, for a small rotation angle ϕ, $\Delta A = -(2\delta L \cot\phi)/\ln(10)$ and $g_{\mathrm{EPL}} \cong -2\delta L \cot\phi$. Such enhancements of weak chiroptical signals were experimentally demonstrated by using an independent (polarization-controlled) local oscillator in the Mach-Zehnder interferometry [Fig. 1(c)] [17]. However, the essential enhancement effect in the case of the ORD measurement using the scheme in Fig. 1(b) is identical to that in the ellipsometric detection of CD [Fig. 1(a)].

C. Real part of chiroptical weak value

In the conventional ellipsometric chiroptical spectroscopy measuring the difference intensity, $I_+ - I_-$, one cannot measure the difference in the arrival times of the chiroptical signal fields associated with left and right EPLs. In the inset of Fig. 1(a), the temporal envelopes of chiroptical signal fields for left and right EPLs are schematically drawn. Here, without loss of generality, it is assumed that the refractive index for left(+) EPL is smaller than that of right(−) EPL, i.e., $n_L < n_R$, so that the left(+) EPL arrives at the detector earlier by δt than the right(−) EPL. In the inset of Fig. 1(a), the black Gaussian-shape pulse corresponds to the temporal envelope of the transmitted light when the medium is racemic (50:50 mixture of left- and right-handed chiral molecules) and $n_L = n_R$. Here, we also assume that $\varepsilon_L > \varepsilon_R$, so that the intensity of the left(+) EPL is smaller than that of the right(−) EPL in this case. Of course, the relative magnitudes of the refractive indices and absorption coefficients for left- and right-handed EPLs are fully determined by the absolute configuration of a dissolved chiral molecule, i.e., molecular chirality. In the previous subsection, we presented a discussion on how to measure the imaginary part of the chiroptical weak value via intensity difference ($I_+ - I_-$) measurement scheme.

Here, one of the possible schemes for detecting the real part of the chiroptical weak value, which is related to the time delay of EPL caused by circular birefringent medium, is presented and discussed. If the weak value amplification scheme [Fig. 1(a)] is not used, the difference in the arrival times of the left- and right-handed EPLs is simply proportional to δ ($\propto n_L - n_R$). More specifically, in this case we have $\delta t_0 = (n_L - n_R)L/c$. However, when the experimental scheme with the quasinull polarization setup in Fig. 1(a) is used, the difference in the arrival times becomes

$$\delta t_w = \frac{(n_L - n_R)L}{c}\cot\theta = \frac{\lambda L}{2\pi c\,\ln(10)}\{\mathrm{Re}[A_{c,w}^{+}] - \mathrm{Re}[A_{c,w}^{-}]\} = \frac{\lambda L}{2\pi c\,\ln(10)}\delta\,\cot\theta. \tag{12}$$

The arrival time difference (δt_w) measured with the weak value amplification scheme differs from that (δt_0) without it by $\cot\theta$. Note that this arrival time difference corresponds to the shift of the pointer position.

To measure such arrival time difference δt_w, one can utilize an interferometric detection scheme. For instance, the modified Mach-Zehnder interferometry for measuring the real part of the chiroptical weak value is shown in Fig. 2. The pre- and postselection process is identical to the setup shown in Fig. 1(a). However, instead of measuring the field intensities, one can selectively measure the interference term between the $\tilde{E}_c^{\pm}$ ($=\langle\psi_f|\Psi^{\pm}\rangle$) and a local oscillator field $\tilde{E}_{\mathrm{LO}}$ whose polarization direction is set to be parallel to the y axis. In this case, the signal at the output of the spectrometer reads

$$S^{\pm}(\omega) = |\tilde{E}_{\mathrm{LO}}(\omega)|^2 + |\tilde{E}_c^{\pm}(\omega)|^2 + 2\,\mathrm{Re}\big[\tilde{E}_{\mathrm{LO}}^{*}(\omega)\tilde{E}_c^{0}(\omega)\exp(i\omega\tau_d^{\pm})\big], \tag{13}$$

where the time difference $\tau_d^{\pm}$ is that between the postselected field with preselected left(+)- or left(−)-EPL pulse and the reference local oscillator pulse and $\tilde{E}_c^{0}(\omega)$ is the spectrum of the chiroptical signal field. To remove the homodyne signals, which are the first two terms in the above equation, and to measure the heterodyned (interference) term only, a shutter in the reference arm (lower pathway in Fig. 2) and a chopper in the chiroptical signal arm (upper pathway) could be used. Once the heterodyne-detected spectral interferogram, which is the third term in Eq. (13), is measured, the standard Fourier transformation procedure [27,28] can be used to convert it to complex electric field as well as to characterize the relative delay times $\tau_d^{\pm}$ with respect to the local oscillator pulse. Note that the latter is possible by examining the interference fringe pattern of the measured spectral interferogram and that the absolute arrival times of chiroptical signals at detector are not measured but the relative time difference between them is accurately measured. This will in turn provide information on $\delta t_w(=\tau_d^{+} - \tau_d^{-})$ as well as the real part of the chiroptical weak value with Eq. (12), where the latter directly corresponds to the shift of the pointer position in the weak-value formalism.

D. Enhancement and limits of chiroptical weak value

To show the enhancement (amplification) effect found in the quasinull ellipsometry for chiroptical measurements, let us consider the limit of small ellipticity angle θ. In this case, the measured dichroic signal ($\bar{A}_L - \bar{A}_R$) or the dissymmetric factor g_{EPL} are both proportional to $\cot\theta \sim 1/\theta$. One or two orders of magnitude enhancement of CD signals has thus been experimentally demonstrated by making θ approach zero [18]. Here, it is the small (experimentally controllable) parameter θ that represents the measure of deviation from perfect orthogonality between the pre- and postselected states or approximately the square root of postselection probability P_{ps} ($=\sin^2\theta$). Now, it becomes clear from Eqs. (9) and (11) that, for the amplification of such a weak (chiroptical) effect, the price to pay is throwing away most of the transmitted photons in vertical polarization state, which may correspond to "creating impossible ensembles" [2]. In fact, exactly the same enhancement factors proportional to $\cot\theta$ ($\sim 1/\theta$ for small θ) with θ being a small variable, such as transverse deflection [see Eq. (5) in Ref. [8]], longitudinal phase shift

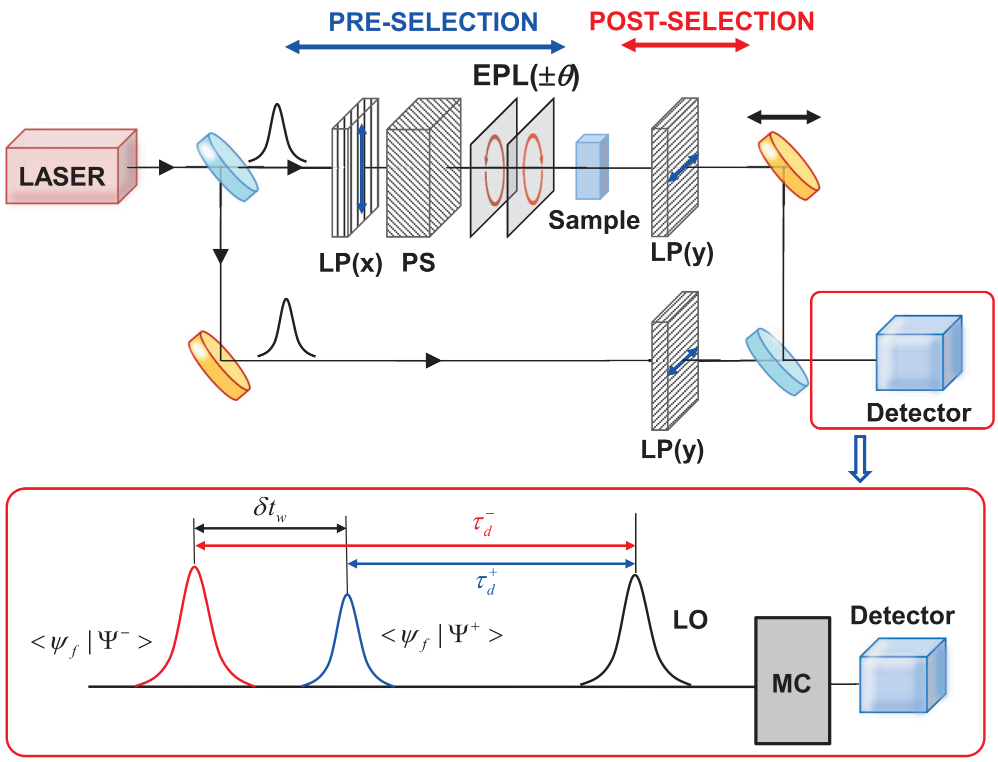

FIG. 2. (Color online) Experimental scheme for measuring the real part of the chiroptical weak value in Eq. (9). This is a modified Mach-Zehnder interferometer. The experimental setup on the signal (upper) pathway in the interferometer is identical to that for quasinull ellipsometry in Fig. 1(a). The local oscillator field propagates through the reference (lower) pathway in the interferometer and its y-polarized component is allowed to interfere with the weak-value-amplified chiroptical signal field at the detector. Then, comparing the fringe patterns of measured spectral interferograms for left and right EPL's, which are recorded by using MC (monochromator) and photon detector, one can estimate the difference in the arrival times, δt_w, of the two EPL's at the detector, which is related to the real part of the chiroptical weak value. Here, to adjust the relative delay time of the chiroptical signal field with respect to the local oscillator field, one of the mirrors (with an arrow on it) is movable. To achieve an enhanced detection sensitivity, finite time delay between the detected signal field and the local oscillator pulse is deliberately introduced. After measuring the two delay times, τ_d^+ and τ_d^-, the difference in the arrival times δt_w can be estimated with $\delta t_w = \tau_d^+ - \tau_d^-$.

[Eq. (7) in Ref. [9]], polarization angle [Eq. (5) in Ref. [10]], relative phase shift Δ [Eq. (3) in Ref. [7]], and so on, were found in various weak measurements. Thus it is believed that the direct connection between them is proven.

In the interferometric detection (Fig. 2) of the real part of the chiroptical weak value, the experimental observable is the difference in the arrival time, δt_w [Eq. (12)]. The enhancement factor in this case is again given as $\delta t_w/\delta t_0 = \cot\theta \sim 1/\theta$ for small θ.

Now, it is necessary to examine the possibility that "the weak value with a properly preselected state and an independently postselected state can be far outside the allowed range of eigenvalues of $\hat{A}$" [1]. In the present case, the basis set consists of two polarization (spin) states, $|V\rangle$ and $|H\rangle$. The chiroptical effect operator $\hat{A}_c$ whose eigenvectors are left- and right-circular polarization states, $(|V\rangle \pm i|H\rangle)/\sqrt{2}$, with eigenvalues of $(\rho \pm \delta/2) - i(\kappa/2 \pm \eta/4)$, is not Hermitian. The expectation values of $\hat{A}_c$ for the two basis states, which are complex and degenerate as $\langle V|\hat{A}_c|V\rangle = \langle H|\hat{A}_c|H\rangle = \rho - i\kappa/2$, are not necessarily quantum mechanical eigenvalues. Note that this degeneracy merely reflects the fact that the absorption and dispersion of linearly polarized lights are the same for the two linear polarization states. Although the observables, ΔA and g_{EPL}, or the real and imaginary parts of the chiroptical weak value [Eq. (9)] appear to diverge as θ approaches zero, since no photon can be spontaneously produced it is impossible to achieve amplification larger than $(\varepsilon_L + \varepsilon_R)/|\varepsilon_L - \varepsilon_R| \sim 10^2$–$10^3$. Furthermore, because of the magnetic susceptibility contribution to the amplitude and phase of transmitted field at a very small θ, there is another factor that limits such enhancement effect [25] after all. Nevertheless, since $\mathrm{Im}[A^{\pm}_{c,w}]$ can have a value in the range from $-\kappa$ to 0, the imaginary part of $A^{\pm}_{c,w}$ can indeed be outside the range set by the imaginary parts of the two eigenvalues of $\hat{A}_c$, that are $-(\kappa/2) \pm (\eta/4)$. Thus this confirms the statement above. Nevertheless, it is noted that the real and imaginary parts of the weak value in Eq. (9) are still within *legitimate* physically allowed range. In the case of the imaginary part measurement, we should have $\mathrm{Im}[A^{\pm}_{c,w}] \leqslant 0$, which implies that the corresponding enhancement factor should have an upper bound $\cot\theta \leqslant 2\kappa/|\eta| \sim |\mu c/m| \sim 10^2$–$10^3$—note that $\mathrm{Im}[A^{\pm}_{c,w}] > 0$ means that the field intensity grows as the path length of the chiral medium increases, which cannot be realized. When one carries out an interferometric detection of the time delay δt_w, since we should have $\mathrm{Re}[A^{\pm}_{c,w}] \geqslant 0$, $\cot\theta \leqslant 2\rho/|\delta| \sim |\mu c/m| \sim 10^2$–$10^3$. Otherwise, ($\mathrm{Re}[A^{\pm}_{c,w}] < 0$), the refractive index for EPLs becomes negative, which is not acceptable.

Before this subsection is closed, it should be mentioned that there exist theoretical works showing that there is no limitation of the weak-value enhancement under the similar condition. In particular, Susa *et al.* considered the case for an arbitrary coupling interaction strength with the observable $\hat{A}$ satisfying $\hat{A}^2 = 1$ [29–31]. They obtained the general results for the expectation values of the position and momentum of the probe and showed that they are bounded when the probe wave function is assumed to be Gaussian. However, it was further demonstrated that the maximum shift in the probe position can have no upper bound for a specific optimal probe wave function. In the present work, it was shown that, even within the linearization approximation, the real and imaginary parts of the chiroptical weak value are bounded due to the requirements that the transmitted light intensity cannot increase as the beam passes through a dissipative medium and that the chiral medium refractive indices for left and right EPLs cannot be negative. There seems to be a contradiction between the present work and the previous theoretical prediction. However, it is not possible to directly compare the present work with Susa *et al.*'s theory mainly because the chiroptical observable $\hat{A}_c$ considered in this paper is not unitary, i.e., $\hat{A}_c^2 \neq 1$, whereas they specifically assumed $\hat{A}^2 = 1$. Nonetheless, it will be interesting to examine a possibility of finding an optimal probe wave function (temporal envelope function other than Fourier-transform limited Gaussian pulse), which gives the maximum shift (time delay δt_w) in the near future.

E. Comparisons with previous works

Among quite a few experimental demonstrations of amplification effects that can be described in terms of weak-value formalism, the present work is directly related to Brunner and Simon's weak measurements of small longitudinal phase shifts induced by birefringent materials. In the present work, the thickness of solution sample containing chiral molecules is L so that the duration of the interaction, denoted as Δt, is given as $\Delta t = nL/c$. Then, the transmitted light [Eq. (5)] affected by the chiral molecule medium can be rewritten as

$$|\Psi^{\pm}\rangle = e^{-i\hat{A}_c'\Delta t}|\psi_i^{\pm}\rangle, \tag{14}$$

where $\hat{A}_c' = c\hat{A}_c/n$. The chiroptical interaction Hamiltonian in Eq. (14), $\hat{A}_c'\Delta t$, shows the time-energy conjugate, where the field-matter interaction time Δt is conjugated to the complex frequency operator $\hat{A}_c'$, of which real and imaginary parts describe dispersion and absorption, respectively. Considering the circular birefringence and circular dichroism, which are related to the real and imaginary parts of the corresponding chiral susceptibility, induced by chiral molecules as small physical effects instead of measurement processes, one can make a direct connection of the results in this paper with Brunner and Simon's theory on weak-value detection of small longitudinal phase shifts induced by linear birefringence.

Since the EPL in Eq. (4) can be written as a sum of linearly polarized light and circularly polarized light with unequal weighting factors, i.e.,

$$|\psi_i^{\pm}\rangle = (\cos\theta - \sin\theta)|V\rangle + \sin\theta(|V\rangle \pm i|H\rangle), \tag{15}$$

the circular birefringence makes the arrival times of left(+)- and right(−)-circularly polarized light at the detector different from each other. This corresponds to the small longitudinal phase shift studied in Ref. [9], when they measured a purely imaginary weak value with the pre- and postselected polarization states corresponding to $|\psi_i\rangle = (|H\rangle + i|V\rangle)/\sqrt{2}$ and $|\psi_f\rangle = (ie^{i\varphi}|H\rangle + e^{-i\varphi}|V\rangle)/\sqrt{2}$ with small phase angle φ. Note that, in that case, the time of arrival of the pulse is the observable rather than average photon position measured experimentally before (see Refs. [5] and [8]). Despite the similarity between ours and Brunner and Simon's work, there are critical differences too. The material is a lossless (linear birefringent) medium, whereas ours is a lossy medium. When the pre- and postselected states are two nearly orthogonal linearly polarized lights, the corresponding weak value measured is purely real in their case. If the pre- and postselected states are two nearly orthogonal circularly polarized lights, the weak value is purely imaginary and it is measured by characterizing the frequency shift of the pointer spectrum. They proposed two different interferometric schemes for measuring the real and imaginary weak values in time and frequency domain, respectively. In our case, the chiroptical weak value in Eq. (9) intrinsically has both (dispersive) real and (absorptive) imaginary parts that are related to the real and imaginary parts of chiroptical susceptibility, because our chiroptical operator represents both the circular birefringent and dichroic properties of chiral medium, respectively.

Recently, Feizpour *et al.* [32] proposed a scheme for measuring Kerr nonlinearity using the weak-value-amplification method at the single-photon level. The nonlinear interaction investigated by them is related to the cross-Kerr effect, which couples a single-photon system to a classical probe field. They showed weak-value-amplification effects on the mean photon number at detector as well as on the average phase shift induced by a cross-phase modulation effect. In particular, they proposed an interferometric detection scheme for measuring the weak-value-amplified phase shift. The present work is similar to theirs. First, it was shown that there is an amplification effect on the normalized difference [$g_{\mathrm{EPL}} = (I_+ - I_-)/\bar{I}$] between the detected photon numbers at detector when the initially prepared states are left and right EPLs, which has been experimentally observed already. Second, the difference in the longitudinal phase shifts of left and right EPLs, which are induced by the circular birefringence of chiral medium, is shown to be measurable by using an interferometric scheme (Fig. 2), which has been referred to as the heterodyne detection method in chiroptical spectroscopy.

Brunner and Simon additionally pointed out an interesting connection between differential interference contrast (DIC) microscopy [33] and weak measurements (see Supplementary Material of Ref. [9]). The DIC microscopy was used to obtain a good visual contrast using the same quasinull polarization geometry shown in Fig. 1(a), which is also similar to crossed nicols. Note that light does not transmit in a crossed nicols state, but inserting an anisotropy between a polarizer and an analyzer changes the state of the polarized light, causing the light to pass through. In the DIC microscopy, the pre- and postselections are performed by 45° and 135° polarizers. The weak effect in this case is caused by a heterogeneous sample with varying refractive index or thickness, which makes the $|H\rangle$ and $|V\rangle$ fields travelling through different areas of the sample have slightly different phases. These small anisotropic effects are amplified by performing the weak measurement with very small postselection probability. The DIC technique is quite similar to the quasinull polarization detection of chiroptical weak value, but the latter is related to circular birefringence (difference in refractive indices for left- and right-handed fields) as well as circular dichroism (difference in absorptions for left- and right-handed fields) instead of linear birefringence.

III. SUMMARY AND A FEW CONCLUDING REMARKS

In summary, despite that there exist numerous reports on enhancement effects in a variety of optical phenomena, e.g., small transverse deflection [8], longitudinal phase shift [9], both phase and amplitude changes of photon wave function [10], spatial separation of optical beams induced by a birefringent material [5], and so on, the direct connection between the quasinull (perpendicular-polarization) chiroptical signal measurements and the weak-value measurements in quantum optics has been neither discussed nor clarified before. In this paper, a way of interpreting chiroptical signal enhancements in terms of weak values was presented and a few orders of magnitude amplification effects and their intrinsic upper limits were discussed. The chiroptical signal enhancement satisfies the basic requirements of weak measurements: (i) the pre- and postselected states are well defined and independently prepared, (ii) the measurement effect is sufficiently weak enough to leave the initial (superposition) state little disturbed, (iii) as the postselection probability is decreased, a significant enhancement in the observables is achievable, and (iv) the weak value can be far outside the range of eigenvalues of the chiroptical operator. It was also shown that both the real and imaginary parts of the chiroptical weak value are bounded. Aside from all the philosophy, we anticipate that the weak-value-amplification scheme for a possible enhancement of other weak effects in spectroscopy may well be of use in developing a variety of ultrasensitive spectroscopic tools for chemical and biological analyses.

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