# Polarization-Angle-Scanning 2DIR Spectroscopy of Coupled Anharmonic Oscillators: A Polarization Null Angle Method

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Supporting Information

**ABSTRACT:** Two-dimensional (2D) optical spectroscopy based on stimulated photon echo geometry requires multiple ultrashort pulses of which spatiotemporal properties and optical phases can be precisely controlled. Also, it is possible to change the incident beam polarization directions defined in a laboratory frame. Here, we introduce the polarization-angle-scanning (PAS) 2D spectroscopy and show that the diagonal and cross-peak amplitudes in the 2D spectrum can be arbitrarily modulated by spatially controlling the beam polarization directions. For a coupled anharmonic oscillator system, we specifically



demonstrate that either diagonal or cross-peaks in the measured 2DIR spectra can be selectively eliminated and show that such polarization angles provide direct information on the relative angles between coupled transition dipoles and thereby on intricate details of molecular structures. We thus anticipate that the present PAS 2D optical spectroscopy can be a useful experimental method enabling us to probe structural evolutions of nonequilibrium state molecules by monitoring the time-dependent changes of the relative transition dipole directions.

# **1. INTRODUCTION**

Two-dimensional (2D) optical spectroscopy utilizing multiple ultrashort pulses in the infrared or UV-visible frequency ranges, which has been considered to be a vibrational or electronic analogue of pulsed 2D NMR, has been one of the most rapidly developing spectroscopic tools over the past decade. It has been proven to be quite useful for determining structures of complicated molecules including polypeptides and proteins as well as for investigating exciton dynamics in semiconductors and lightharvesting complexes in condensed phases. Similar to typical 2D NMR spectra, the diagonal peaks observed in the 2D optical spectra directly correspond to the absorption bands in the linear spectra. It is the cross-peaks appearing in the off-diagonal regions in a given 2D spectrum that manifest dynamic correlations and couplings between different vibrational or electronic degrees of freedom.<sup>1–7</sup> In addition, the time-dependent changes of crosspeak amplitudes and lineshapes provide information on stateto-state energy transfers,<sup>8,9</sup> quantum coherence evolutions,<sup>10,11</sup> chemical exchanges such as hydrogen-bond making and breaking,<sup>12–14</sup> solute–solvent complexation,<sup>15</sup> exciton corre-lation,<sup>16</sup> protein folding–unfolding processes,<sup>17,18</sup> or ultrafast solvation dynamics.<sup>19</sup>

Among a variety of 2D optical spectroscopic methods, the heterodyne-detected stimulated photon echo is one of the most popular techniques. In this case, the first and third pulse-matter interactions create quantum coherences and they are separated by an experimentally controllable waiting time (T). The phase

and amplitude of the resultant signal electric field generated by the third-order polarization are fully characterized by analyzing the spectral interferograms produced by the interference between the signal field and an additional reference (local oscillator) field. Consequently, four time-delayed laser pulses are generally required to perform a 2D photon echo measurement. In this case, there are a number of experimentally controllable variables of incident radiations, such as (i) center frequencies, (ii) pulse-to-pulse delay times, (iii) relative optical phases, (iv) propagation directions, and (v) polarization states, e. g., linearly, circularly, or elliptically polarized radiations. However, one of the most important spatial properties of the linearly polarized radiations is their linear polarization directions in the laboratory frame. In the present paper, we show that such spatial controls of beam polarization directions can provide rich information on structural details of multicomponent systems.<sup>20</sup>

It should, however, be mentioned that discrete controls of incident beam polarization directions have been experimentally achieved before.<sup>21,22</sup> As an example, the parallel and perpendicular polarization 2D spectra were used to measure the so-called cross-peak anisotropy, which is in turn related to the relative angle between the transition dipoles associated with the

Special Issue: Shaul Mukamel Festschrift

Received:	October 26, 2010
Revised:	November 24, 2010
Published:	December 28, 2010

cross-peak. Furthermore, it was shown that all the diagonal peaks can be eliminated by taking a proper difference between the parallel and perpendicular 2D spectra so that a great enhancement of frequency resolution could be achieved. Hochstrasser and co-workers further demonstrated that a single measurement with a properly adjusted beam polarization configuration is enough to achieve such a complete suppression of diagonal peaks in the 2D spectrum.<sup>23</sup>

However, there have been no experimental attempts to selectively eliminate particular cross-peaks by controlling the beam polarization directions. Recently, a theoretical description on the so-called polarization-angle-scanning (PAS) 2D spectros-copy, where one of the four polarization direction angles with respect to a reference axis in the laboratory frame is arbitrarily varied, has been briefly discussed.<sup>20</sup> It turns out that there should be a specific beam polarization configuration that makes a particular cross-peak disappear in the 2D spectrum.

Before we present and discuss experimental results, it should be mentioned that the PAS 2D spectroscopy can be considered as one of the null methods that have been used in a variety of linear and nonlinear optical spectroscopies for accurate measurements of ellipsometry, orientation angle of molecules on surfaces or at interfaces, Raman depolarization ratio etc.<sup>24-31</sup> In particular, the polarization null angle (PNA) method was used in second-harmonic-generation by Shen and co-workers.<sup>25</sup> Later, by Wang and co-workers it was applied to the sum-frequencygeneration measurements for accurate determination of orientational parameter of molecules at interfaces.<sup>29,30</sup> The polarization angles of the incident beams and SFG signal can be controlled (scanned) by using analyzers to find the null angle configuration, where the SFG signal vanishes. Then, a careful spectra fitting can provide much more accurate results on the molecular orientation than the polarization intensity ratio (PIR) method<sup>32</sup> does. Here, the latter approach relies on measurements of SFG spectra with only two polarization configurations. It is interesting to note that the present PAS 2D spectroscopy is conceptually analogous to the PNA-SFG, whereas the cross-peak anisotropy measurement in 2D spectroscopy is analogous to the PIR-SFG method. In the cross-peak anisotropy measurement in 2D photon echo spectroscopy, S<sub>ZZZZ</sub> and S<sub>ZYYZ</sub> components of 2D spectra are measured with just two different polarization configurations and the 2D anisotropy spectrum is obtained by calculating the ratio  $(S_{ZZZZ} - S_{ZYYZ})/(S_{ZZZZ} + 2S_{ZYYZ})$  at the cross-peak position. This amplitude ratio is directly related to the relative angle between coupled transition dipoles. Much like the PIR-SFG method,<sup>25</sup> the cross-peak anisotropy method in 2D spectroscopy, however, tends to be susceptible to laser intensity fluctuations and problems of signal calibration unless SZZZZ and SZYYZ components are measured at the same time. On the other hand, in the PAS 2D spectroscopy, a series of 2D spectra are obtained by varying the polarization angles of incident beams and are used to determine the relative angles of coupled transition dipoles. Therefore, PAS 2D spectroscopy could be more accurate than the cross-peak anisotropy measurement method.

In this paper, we briefly present a theoretical framework of the polarization-angle-scanning (PAS) 2D spectroscopy and then show that the PAS 2DIR spectroscopy is a potentially useful experimental method for determining the relative angles between coupled transition dipoles. We demonstrate its experimental feasibility by carrying out the experiments for a simple coupled anharmonic-oscillator system, which is [dicarbonylacetylacetonato]rhodium(I) (Rh(CO)<sub>2</sub>C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>: RDC) in chloroform.



**Figure 1.** Polarization-angle-scanning (PAS) 2DIR spectroscopy. In the upper panel, a schematic representation of the polarization angle scanning technique is shown, where the wire grid polarizers are used to control the polarization directions (angles  $\varphi_1 - \varphi_3$ ) of the three incident beams ( $\mathbf{k}_1 - \mathbf{k}_3$ ). The delay times between the first and second pulses and between the second and third pulses are  $\tau$  and *T*, respectively. In the lower panel, the PAS 2DIR spectrometer is schematically drawn. See the text for more detail.

#### 2. EXPERIMENTAL METHODS

In Figure 1, a schematic representation of the polarizationangle-scanning technique and the entire PAS 2DIR experimental setup is depicted (see Supporting Information for experimental details). Mid-IR pulses ( $\sim 60$  fs) centered at  $\sim 2070$  cm<sup>-1</sup> were used for the PAS 2DIR experiments. The three mid-IR pulses were focused onto the sample and their relative time-delays were controlled.<sup>33,34</sup> The signal emitted from the sample in a new phase-matched direction was heterodyne-detected by combining a local oscillator (LO) pulse. 2DIR signals were collected by scanning the  $\tau$ -axis at a fixed T and were frequency-resolved through the spectrometer with the HgCdTe (MCT) array detector to record the temporal interferograms as a function of  $\tau$  at the emission frequencies  $(\omega_t)$ .<sup>33,34</sup> Numerical Fourier transformation of the temporal interferograms along the  $\tau$ -axis yielded the spectrum of the excitation frequency axis ( $\omega_{\tau}$ ). 2DIR spectrum at a given T is displayed with the excitation  $(\omega_{\tau})$  and emission  $(\omega_t)$  frequencies.

To carry out the PAS 2DIR experiments, a pair of half-wave plate and wire grid polarizers were inserted in the three incident beam and the LO beam paths. They were used to independently control the polarization directions of all the four beams. Each polarizer was calibrated with respect to a reference polarizer to enhance the angle resolution. The polarization directions specified by  $\varphi_1$ ,  $\varphi_2$ , and  $\varphi_3$  angles of the three incident beams were measured again right before the sample cell to further minimize the depolarization due to beam reflections by mirrors. In addition, an analyzer polarizer was additionally placed right after the sample cell to control the LO polarization directions angle  $\varphi_s$  of the detected signal field. In this paper, the polarization directions of the beam 1 ( $\mathbf{k}_1$ ) and the signal field were fixed to be parallel to the *Z*-axis, i.e.,  $\varphi_1 = \varphi_s = 0^\circ$ . The pairs of half-wave plate and wire grid polarizer placed in the beams 2 and 3 ( $\mathbf{k}_2$  and  $\mathbf{k}_3$ ) were

mounted on computer-controlled motorized rotational stages. The BaF<sub>2</sub> wire grid polarizer used in our PAS 2DIR experiment has an extinction ratio of ~200:1 and thus the polarization angle of each individual beam is precisely controlled within  $\pm 1^{\circ}$  accuracy.

[Dicarbonylacetylacetonato]rhodium(I) (Rh(CO)<sub>2</sub>C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>, RDC) and chloroform (CHCl<sub>3</sub>) were purchased from Sigma-Aldrich and used without further purification. RDC (3.0 mM) in CHCl<sub>3</sub> solution was prepared by directly dissolving the compounds in CHCl<sub>3</sub>. The sample solution was housed in a Harrick cell with two CaF<sub>2</sub> windows (2 mm thick) and a 250  $\mu$ m thick Teflon spacer. The FTIR spectrum of the sample solution was meausured and the absorbances of the carbonyl stretch modes in the sample solutions were about 0.2. All experiments here were conducted at 22 °C.

## **3. THEORETICAL DETAILS**

In 2D optical spectroscopy, the multiple interactions of the electric fields with the molecular system can be theoretically analyzed in terms of the nonlinear response function of the system. Particularly, the macroscopic third-order polarization can be written as

$$\mathbf{P}^{(3)}(\mathbf{r},t) \propto \operatorname{Tr}[\mu\rho^{(3)}(t)] \\
= \int_{0}^{\infty} dt_{3} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{1} \mathbf{R}^{(3)}(t_{3},t_{2},t_{1}) \\
\times \mathbf{E}(\mathbf{r},t-t_{3})\mathbf{E}(\mathbf{r},t-t_{3}-t_{2})\mathbf{E}(\mathbf{r},t-t_{3}-t_{2}-t_{1}) \quad (1)$$

Here, the nonlinear response function  $\mathbf{R}^{(3)}(t_3, t_2, t_1)$  given by

$$\mathbf{R}^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \theta(t_3) \ \theta(t_2) \ \theta(t_1)$$
$$\times \langle \mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1), [\mu(t_1), [\mu(0), \rho_{eq}]]] \rangle \quad (2)$$

where  $\mu(t) = \exp(iH_0t/\hbar)\mu \exp(-iH_0t/\hbar)$  is the dipole operator in the interaction picture and the angular bracket in eq 2 denotes the trace of a matrix. The Heaviside step function  $\theta(t)$  in eq 2 imposes the causality condition.

To describe the orientational contribution to the nonlinear response function, it is generally assumed that the coupling between the vibronic and rotational degrees of freedom is negligible.<sup>35</sup> Within this approximation, the molecular Hamiltonian can be partitioned as  $H_{\rm mol} = H_{\rm vib} + H_{\rm rot}$  and then the transition dipole moment is given by

$$\mu = \mu \hat{\mu} \tag{3}$$

where  $\mu$  is the vibronic part and  $\hat{\mu}$  is the unit vector defining the orientation of the transition dipole moment of a given chromophore in the laboratory frame. As shown in ref 35, the contribution from each Liouville space pathway to the nonlinear response function can then be factorized into a product of rotational and vibrational terms,

$$\mathbf{R}_{\alpha}(t_3, t_2, t_1) = Y_{\alpha}(t_3, t_2, t_1) R_{\alpha}(t_3, t_2, t_1)$$
(4)

The fourth-rank tensor  $Y_{\alpha}(t_3,t_2,t_1)$  represents the orientational contribution to the nonlinear response function, which is treated classical mechanically.

The reorientational motion of molecules in solution has been successfully described as a random walk over small angular orientations so that the Fokker–Planck equation for the conditional probability density in the rotational phase space (orientation and angular velocity) was found to be useful. Since the initial distribution of angular velocities is given by the Maxwell–Boltzmann expression, after taking the ensemble average over the angular velocities, it is possible to recast the rotational nonlinear response function,  $^{35-38}$   $Y_{\alpha}(t_3,t_2,t_1)$  in the following form

$$Y_{\alpha}(t_{3},t_{2},t_{1}) = \int d\nu_{3} \int d\nu_{2} \int d\nu_{1} \int d\nu_{0} \,\hat{\mu}_{3}(\nu_{3})$$
$$\times W(\nu_{3},t_{3}|\nu_{2}) \,\hat{\mu}_{2}(\nu_{2}) \,W(\nu_{2},t_{2}|\nu_{1})$$
$$\otimes \hat{\mu}_{1}(\nu_{1}) \,W(\nu_{1},t_{1}|\nu_{0}) \,\hat{\mu}_{0}(\nu_{0}) \,P_{0}(\nu_{0})$$
(5)

where the molecular orientation is specified by the Euler angles  $v \equiv (\phi, \theta, \chi)$  and the conditional probability function in an angular configurational space is denoted as  $W(v_{j+1},t_{j+1}|v_j)$ . The initial probability distribution of the molecular orientations is denoted as  $P_0(v_0)$ , which is  $1/8\pi^2$  for an isotropic system containing randomly oriented molecules, i.e., solutions.

In the case of the general 2D optical spectroscopy, a given Liouville space pathway contribution to the total nonlinear response function involves four different dipolar transitions, i.e.,

$$\hat{\mu}_{3} = \hat{\mu}_{d}$$
  $\hat{\mu}_{2} = \hat{\mu}_{c}$   $\hat{\mu}_{1} = \hat{\mu}_{b}$   $\hat{\mu}_{0} = \hat{\mu}_{a}$  (6)

Hereafter,  $Y_{ijkl}^{dcba}(t_3,t_2,t_1)$  will specifically denote the [i,j,k,l]'th element of the orientational part of the nonlinear response function tensor, where the indices i, j, k, and l represent the Cartesian coordinates. Therefore, the [i,j,k,l]'th tensor element of the corresponding nonlinear response function component can be written as a product form,  $Y_{ijkl}^{dcba}(t_3,t_2,t_1) \mathbb{R}^{dcba}(t_3,t_2,t_1)$ . Its vibrational part  $\mathbb{R}^{dcba}(t_3,t_2,t_1)$  was extensively studied before and various tensor elements of  $\mathbf{Y}_{\alpha}(t_3,t_2,t_1)$  were thoroughly discussed by Golonzka and Tokmakoff.<sup>37</sup>

In the 2D experiments, the incident electric field is composed of three pulses temporally separated by  $\tau$  and T and the signal field emitted in the direction  $\mathbf{k}_{\rm S} = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$  is measured. The incident field is generally expressed as

$$\mathbf{E}(\mathbf{r},t) = \mathbf{e}_{1}E_{1}(t+\tau+T) \exp(\mathbf{i}\mathbf{k}_{1}\cdot\mathbf{r}-\mathbf{i}\omega_{1}t)$$
  
+  $\mathbf{e}_{2}E_{2}(t+T) \exp(\mathbf{i}\mathbf{k}_{2}\cdot\mathbf{r}-\mathbf{i}\omega_{2}t)$   
+  $\mathbf{e}_{3}E_{3}(t) \exp(\mathbf{i}\mathbf{k}_{3}\cdot\mathbf{r}-\mathbf{i}\omega_{3}t) + (\mathbf{cc})$  (7)

where the unit vectors of linearly polarized beams are denoted as  $\mathbf{e}_j$  for j = 1, 2, 3. The resulting polarization under the rotating wave approximation is given as

$$\mathbf{P}(\mathbf{r},t) = e^{i\mathbf{k}_{S}\cdot\mathbf{r}-i\omega t} \int_{0}^{\infty} dt_{1} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{3} \mathbf{R}^{(3)}(t_{1},t_{2},t_{3}) \mathbf{e}_{3} \mathbf{e}_{2} \mathbf{e}_{1}^{*}$$

$$\times E_{3}(t-t_{3}) E_{2}(t+T-t_{3}-t_{2})$$

$$\times E_{1}^{*}(t+T+\tau-t_{3}-t_{2}-t_{1}) \exp(i\omega t_{3}-i\omega t_{1}) \qquad (8)$$

where  $\mathbf{R}^{(3)}(t_1,t_2,t_3)$  is the third-order response function.<sup>20</sup> The photon echo polarization in eq 8 produces the signal electric field, i.e.,  $\mathbf{E}_{sig}(t) \propto i\mathbf{P}(t)$ . This signal depends on three time variables  $\tau$ , T, and t. The 2D photon echo spectrum is obtained by performing the 2D Fourier-Laplace transformation of  $\mathbf{E}_{PE}(t, T, \tau)$  with respect to  $\tau$  and t as

$$E_{\text{sig}}(\omega_t, T, \omega_\tau)$$
  
=  $\int_0^\infty dt \int_0^\infty d\tau \ \mathbf{E}_{\text{sig}}(t, T, \tau) \exp(\mathrm{i}\omega_t t + \mathrm{i}\omega_\tau \tau)$  (9)

In the present paper, we specifically assume that the Zcomponent of the signal field is measured, which can be achieved by using a linear polarizer to control the LO polarization direction, as discussed in section 2. To reduce the number of experimentally controlled polarization direction angles, we limit our consideration to the case that one of the three incident beam polarization directions, e.g.,  $\mathbf{e}_1$ , is parallel to the Z-axis. Thus, the unit vectors of the linearly polarized beams are given as

$$\mathbf{e}_{1} = \hat{Z} \qquad \mathbf{e}_{2} = \hat{Y} \sin \varphi_{2} + \hat{Z} \cos \varphi_{2}$$
$$\mathbf{e}_{3} = \hat{Y} \sin \varphi_{3} + \hat{Z} \cos \varphi_{3}$$
$$\mathbf{e}_{s} = \hat{Z} \qquad (10)$$

The 2D spectrum measured by using this polarization configuration thus becomes a function of  $\varphi_2$  and  $\varphi_3$  as

$$\tilde{E}_{\text{sig}} = \tilde{E}_{\text{sig}}(\omega_{\tau}, T, \omega_t; \varphi_2, \varphi_3)$$
(11)

In the PAS 2D spectroscopy, one can obtain a series of 2D spectra by varying  $\varphi_2$  and  $\varphi_3$  at a fixed waiting time *T*.

**Diagonal Peaks in the PAS 2D Spectrum.** We first consider the polarization-angle dependency of all the diagonal peaks in the PAS 2D spectrum. The orientational contribution to the diagonal peak amplitude is determined by  $Y_{Z\varphi_2\varphi_3Z}(\tau,T,t)$  in the impulsive limit. Then, using the unit vectors given in eq 10, we find that the orientational part associated with the *m*th diagonal peak is given as

$$Y_{Z\varphi_{3}\varphi_{2}Z}^{mmmm}(\tau,T,t) = Y_{ZZZZ}^{mmmm}(\tau,T,t) \cos \varphi_{2} \cos \varphi_{3}$$

$$+ Y_{ZYYZ}^{mmmmm}(\tau,T,t) \sin \varphi_{2} \sin \varphi_{3}$$

$$+ Y_{ZZYZ}^{mmmmm}(\tau,T,t) \sin \varphi_{2} \cos \varphi_{3}$$

$$+ Y_{ZYZZ}^{mmmmm}(\tau,T,t) \cos \varphi_{2} \sin \varphi_{3} \qquad (12)$$

Here, the transition dipole moments involved in the ground-state bleach (GB) and stimulated emission (SE) contributions to the diagonal peak are all identical to  $\mu_m$ . The excited-state absorption contribution to the diagonal peak involves the transition dipole between the first excited state and the overtone state. In general, due to the anharmonicity and non-Condon effects, the transition dipole direction between the first excited state and the overtone state can be different from that of the fundamental transition. However, we shall only consider the polarization-angle dependencies of the GB+SE diagonal and cross-peaks in this work for the sake of simplicity. In eq 12, the third and fourth terms vanish within the electric dipole approximation, unless the electric field-electric quadrupole and magnetic field-magnetic dipole interactions are taken into consideration.<sup>20</sup> Thus, eq 12 is simplified as

$$Y_{Z\varphi_{3}\varphi_{2}Z}^{mmnm}(\tau,T,t) = Y_{ZZZZ}^{mmnmm}(\tau,T,t) \cos \varphi_{2} \cos \varphi_{3} + Y_{ZYYZ}^{mmmmm}(\tau,T,t) \sin \varphi_{2} \sin \varphi_{3}$$
(13)

Here, the  $\tau$ -, *T*-, and *t*-dependent *ZZZZ* and *ZYYZ* tensor elements of  $\mathbf{Y}^{mmmm}(\tau, T, t)$  were already obtained and presented in ref 37 so that we have

$$Y_{Z\phi_{3}\phi_{2}Z}^{mmmm}(\tau,T,t) = c_{1}(\tau) c_{1}(t) y_{Z\phi_{3}\phi_{2}Z}^{mmmm}(T)$$
(14)

where the waiting time *T*-dependent part is given as

$$y_{Z\phi_{3}\phi_{2}Z}^{mmmm}(T) = \frac{1}{9} \left( 1 + \frac{4}{5}c_{2}(T) \right) \cos \varphi_{2} \cos \varphi_{3} + \frac{1}{15}c_{2}(T) \sin \varphi_{2} \sin \varphi_{3}$$
(15)

For a spherical rotor,  $c_l(t) = \exp[-l(l+1)D_{or}t \text{ and } D_{or}t \text{ is the orientational diffusion coefficient. The expressions for <math>c_l(t)$  for l = 1, 2 are obtained by using the small angle diffusion equation, but one can use the more general expressions for these by solving the Fokker–Planck equation. Here, we shall not pursue this here, because detailed derivations of the rotational relaxation functions are not of main interest in the present work. From eq 15, one can find that the  $\tau$  and t dependencies of  $Y_{Z(\rho;\varphi;\tau)}^{mmmm}(\tau,T,t)$  are determined by  $c_1(\tau) c_1(t)$ . Therefore, the 2D spectrum is additionally broadened by the rotational relaxations of the chromophores during  $\tau$  and t periods.

In the limiting case that the waiting time *T* is zero or that the rotational motion is sufficiently slow compared to the vibrational relaxation or other relevant chemical or physical processes, one can replace  $c_2(T)$  in eq 15 with a unity so that we have

$$Y_{Z\varphi_{3}\varphi_{2}Z}^{mmmm}(\tau, T = 0, t)$$
  
=  $\frac{1}{15}c_{1}(\tau) c_{1}(t) \{3 \cos \varphi_{2} \cos \varphi_{3} + \sin \varphi_{2} \sin \varphi_{3}\}$  (16)

Thus, the diagonal peak amplitude of the *m*th mode is given as

$$\tilde{E}_{\text{diag}}(\omega_{\tau},\omega_{t};\varphi_{2},\varphi_{3}) \approx \frac{1}{15} \mu_{m}^{4} \{3\cos\varphi_{2}\cos\varphi_{3} + \sin\varphi_{2}\sin\varphi_{3}\} \Gamma(\omega_{\tau},\omega_{t}) \quad (17)$$

Here,  $\mu_m$  is the vibrational transition dipole matrix element. The 2D line shape function is denoted as  $\Gamma(\omega_\tau, \omega_t)$  and its precise functional form is not important here in the present work. Although individual diagonal peak amplitudes are different from one another, they depend on the same factor that is determined by the two polarization direction angles,  $\varphi_2$  and  $\varphi_3$ . This suggests that all the diagonal peaks vanish every time when we have

$$3 \cos \varphi_2 \cos \varphi_3 + \sin \varphi_2 \sin \varphi_3 = 0$$
  
or equivalently 
$$\varphi_3 = \tan^{-1}(-3 \cot \varphi_2) \qquad (18)$$

**Cross-Peaks in the PAS 2D Spectrum.** We next consider the polarization-angle dependencies of cross-peak amplitudes. Here, let us specifically consider the cross-peak at  $\omega_{\tau} = \omega_m$  and  $\omega_t = \omega_m$ 

=

 $(m \neq n)$ . Without loss of generality, it is assumed that the direction of  $\hat{\mu}_m$  is parallel to the *z*-axis in a molecule-fixed frame, i. e.,  $\hat{\mu}_m = \hat{z}$ , and that  $\hat{\mu}_n$  is on the z-x plane in the molecule-fixed frame as

$$\hat{\mu}_n = \hat{z} \, \cos \theta_{n,m} + \hat{x} \sin \theta_{n,m} \tag{19}$$

where the angle between  $\hat{\mu}_m$  and  $\hat{\mu}_n$  is denoted as  $\theta_{n,m}$ .

The corresponding cross-peak spectra originating from the GB and SE contributions can then be written as

$$\tilde{E}_{cross}^{GB}(\omega_{\tau},T,\omega_{t};\varphi_{2},\varphi_{3}) \propto \mu_{n}^{2} \mu_{m}^{2} y_{Z\varphi_{3}\varphi_{2}Z}^{nnmm}(T) \Gamma_{cross}^{GB}(\omega_{\tau},T,\omega_{t})$$
(20)

$$\tilde{E}_{\text{cross}}^{\text{SE}}(\omega_{\tau}, T, \omega_{t}; \varphi_{2}, \varphi_{3}) \propto \mu_{n}^{2} \mu_{m}^{2} y_{Z\varphi_{3}\varphi_{2}Z}^{nmm}(T) \Gamma_{\text{cross}}^{\text{SE}}(\omega_{\tau}, T, \omega_{t})$$

$$(21)$$

Again, the *T*-dependent orientational parts in eqs 20 and 21 depend on the two polarization direction angles and they are found to be

$$y_{Z\varphi_{3}\varphi_{2}Z}^{mmnm}(T)$$

$$= \frac{1}{9} \left\{ 1 + \frac{4}{5} c_{2}(T) \left[ \cos^{2} \theta_{n,m} - \frac{1}{2} \sin^{2} \theta_{n,m} \right] \right\} \cos \varphi_{2} \cos \varphi_{3}$$

$$+ \frac{1}{15} c_{2}(T) \left[ \cos^{2} \theta_{n,m} - \frac{1}{2} \sin^{2} \theta_{n,m} \right] \sin \varphi_{2} \sin \varphi_{3} \quad (22)$$

$$\times y_{Z\varphi_{3}\varphi_{2}Z}^{mmnm}(T) = \frac{1}{9} \left\{ \cos^{2} \theta_{n,m} + \frac{1}{5} c_{2}(T) [4 \cos^{2} \theta_{n,m} + \frac{1}{5} c_{2}(T) [4 \cos^{2} \theta_{n,m} + \frac{1}{5} c_{2}(T) (4 \cos^{2} \theta_{n,m} + \frac{1}{$$

$$+ 3 \sin^{2} \theta_{n,m} \bigg] \bigg\} \cos \varphi_{2} \cos \varphi_{3}$$

$$+ \frac{1}{12} \bigg\{ \frac{1}{5} c_{2}(T) [4 \cos^{2} \theta_{n,m} + 3 \sin^{2} \theta_{n,m}]$$

$$- c_{1}(T) \sin^{2} \theta_{n,m} \bigg\} \sin \varphi_{2} \sin \varphi_{3} \qquad (23)$$

In the limiting case that the rotational relaxation is sufficiently slow compared to the other dynamic time scales or at T = 0, one can show that  $y_{Z\varphi_3\varphi_2Z}^{nnmm}(T=0) = y_{Z\varphi_3\varphi_2Z}^{nnmm}(T=0)$  regardless of the sequence of involved dipolar transitions, either  $m \rightarrow m \rightarrow n \rightarrow n$ or  $m \rightarrow n \rightarrow m \rightarrow n$ . Since the orientationally averaged transition strengths of the (m,n) cross-peak originating from the GB+SE contribution are the same in this limit, we have

$$\tilde{E}_{\text{cross}}^{\text{GB}}(\omega_{\tau},\omega_{t};\varphi_{2},\varphi_{3}) \propto \mu_{n}^{2} \mu_{m}^{2} y_{Z\varphi_{3}\varphi_{2}Z}^{nnmm} \Gamma_{\text{cross}}^{\text{GB}}(\omega_{\tau},T,\omega_{t})$$
(24)

$$\tilde{E}_{\text{cross}}^{\text{SE}}(\omega_{\tau},\omega_{t};\varphi_{2},\varphi_{3}) \simeq \mu_{n}^{2} \mu_{m}^{2} y_{Z\varphi_{3}\varphi_{2}Z}^{nnnm}(T) \Gamma_{\text{cross}}^{\text{SE}}(\omega_{\tau},T,\omega_{t})$$
(25)

where

$$y_{Z\varphi_{3}\varphi_{2}Z}^{nnmm} = \frac{1}{30} \{ \cos \varphi_{2} \cos \varphi_{3} (4 \cos^{2} \theta_{n,m} + 2) + \sin \varphi_{2} \sin \varphi_{2} (3 \cos^{2} \theta_{n,m} - 1) \}$$
(26)

The above result shows that the cross-peak amplitude is determined by not only the polarization direction angles  $\varphi_2$  and  $\varphi_3$ but also the corresponding transition dipole angle  $\theta_{n,m}$ . From



**Figure 2.** Molecular structure, the FTIR spectrum of the CO stretching modes, and the paralell polarization 2DIR spectrum of RDC in chloroform measured at T = 0 ps. The low- and high-frequency peaks are associated with the antisymmetric and symmetric CO stretching modes, respectively.

eq 26, one can find that the GB+SE (m,n) cross-peak at  $\omega_1 = \overline{\omega}_m$ and  $\omega_3 = \overline{\omega}_n$  vanishes when the following equality is satisfied,

$$\cos \varphi_2 \cos \varphi_3 (4\cos^2 \theta_{n,m} + 2) + \sin \varphi_2 \sin \varphi_3 (3\cos^2 \theta_{n,m} - 1)$$
  
= 0 or equivalently  
$$\cos^2 \theta_{n,m} = \frac{\tan \varphi_2 \tan \varphi_3 - 2}{4 + 3\tan \varphi_2 \tan \varphi_3}$$
(27)

Again, there exist infinite possible pairs of  $\varphi_2$  and  $\varphi_3$  angles that satisfy the above relationship for a given  $\theta_{n,m}$  value. This is an interesting relationship showing that the macroscopically controlled polarization directions of the incident beams in the laboratory frame are directly related to the relative angle between a given pair of coupled transition dipoles in a randomly oriented molecule. For any  $\theta_{n,m}$  the cos<sup>2</sup>  $\theta_{n,m}$  value is in the range from 0 to 1. Therefore, it is not necessary to scan the entire range of  $\varphi_2$  and  $\varphi_3$  angles, i.e.,

$$0 \le \frac{\tan \varphi_2 \tan \varphi_3 - 2}{4 + 3 \tan \varphi_2 \tan \varphi_3} \le 1$$
(28)

In the following section, we shall present the experimental results on the PAS 2DIR spectroscopy of RDC.

# 4. RESULTS AND DISCUSSION

The 2DIR spectroscopy of a pair of anharmonic oscillators coupled to each other is a good model system for detailed investigation as well as for experimentally verifying theoretical results. We shall therefore consider the case that the two oscillators have the same frequency  $\omega_0$  and are coupled to each other with coupling constant of *J*. Then, the resultant (highfrequency) symmetric and (low-frequency) antisymmetric normal modes are split in frequency domain and their frequency difference is given by 2*J*. Here, RDC is an ideal system (see Figure 2 for the molecular structure), where, due to the finite



**Figure 3.** Polarization-controlled 2DIR spectra (T = 0.2 ps). The polarization directions of the first pulse and the detected signal (local oscillator) field are parallel to the *Z*-axis in the laboratory frame. The two polarization direction angles  $\varphi_2$  and  $\varphi_3$  are varied to make all the diagonal peaks vanish. The  $\varphi_2$  and  $\varphi_3$  angles are shown in the legend and they are ( $+30^\circ$ ,  $-79.1^\circ$ ), ( $+45^\circ$ ,  $-71.6^\circ$ ), and ( $+60^\circ$ ,  $-60.0^\circ$ ). The parallel polarization (*ZZZZ*) 2DIR spectrum (see the upper left panel) is shown for comparison. Note that the *z*-axis scale of the parallel polarization 2DIR spectrum differs from those of the other three spectra. The diagonal peak amplitudes in these polarization-controlled 2DIR spectra are less than 5% of those in the parallel polarization 2DIR spectra.

coupling, the two carbonyl (CO) stretching vibrations form symmetric and antisymmetric normal modes. The Fourier-transform IR (FTIR) spectrum of the CO stretch modes of RDC yields the coupling constant *J*. Furthermore, the anharmonic frequency shifts of the overtone and combination states of the two CO stretch normal modes can be estimated by analyzing the 2DIR spectrum of the RDC as experimentally shown by Tokmakoff and co-workers.

Parallel Polarization 2DIR. Figure 2 displays the real part of the parallel polarization 2DIR spectrum RDC in CHCl<sub>3</sub> at the waiting time T = 0 for the sake of completeness—note that the four beam polarization directions are all parallel to the reference Z-axis in the laboratory frame. The positive (red contours) lowand high-frequency diagonal peaks (1 and 2) originate from the ground-state bleach (GB) and stimulated emission (SE) contributions from the antisymmetric and symmetric CO stretch normal modes, respectively. The excited-state absorption (EA) peaks (3 and 4) are slightly red-shifted from the diagonal by the vibrational anharmonic frequencies. Consequently, the diagonal peaks appear as a couplet consisting of an upper positive peak (1 and 2) and a lower negative peak (3 and 4). Similarly, the cross-peaks in the parallel polarization 2DIR spectrum also appear as a couplet. As shown by Tokmakoff and co-workers,<sup>39</sup> detailed 2D spectral analyses provide quantitative information on the anharmonicity-induced frequency shifts of the overtone states  $|2,0\rangle$  and  $|0,2\rangle$  as well as of the combination state  $|1,1\rangle$ . In addition, the solvation dynamics affecting the vibrational transition frequency-frequency correlation function can be

investigated by monitoring the waiting time-dependent line shape changes, e.g., nodal line slope, center line slope, aspect ratio of the diagonal line width to the antidiagonal line width, and so on.  $^{40-43}$ 

Selective Elimination of Diagonal Peaks. The parallel polarization 2DIR spectroscopy utilizes four beams having polarization directions all parallel to each other. However, as discussed in section 3, the amplitudes and signs of the diagonal peaks and cross-peaks in the 2DIR spectrum depend on the polarization directions angles,  $\varphi_i$ 's. When  $\varphi_1 = \varphi_s = 0$  and when the polarization directions of the second and third incident beams specified by  $\varphi_2$  and  $\varphi_3$  angles are experimentally controlled, the 2DIR spectrum at T = 0 becomes dependent on  $\varphi_2$  and  $\varphi_3$ , as can be seen in eqs 17, 24, and 25. Particularly, all the diagonal peaks are expected to vanish when the two angles  $\varphi_2$  and  $\varphi_3$  satisfy the relationship in eq 18.

To experimentally verify this, we carried out a series of polarization-controlled 2DIR measurements at  $\varphi_2 = 30^\circ$ , 45°, and 60°, where the conjugate  $\varphi_3$  angles are  $-79.1^\circ$ ,  $-71.6^\circ$ , and  $-60.0^\circ$ , respectively. In Figure 3, the 2DIR spectra obtained with these beam polarization configurations are plotted and directly compared with the parallel polarization 2DIR spectrum  $S_{zzzz}$ . The diagonal peaks are indeed significantly smaller (<5%) than those in the  $S_{zzzz}$  spectrum as well as the two cross-peak couplets in these spectra. This verifies that the selective elimination of all the diagonal peaks is experimentally feasible by controlling any two polarization direction angles satisfying the theoretical relationship in eq 18.

Selective Elimination of Cross-Peaks. The reason that the  $\varphi_2$  and  $\varphi_3$  dependencies of all the diagonal peak amplitudes are the same can be understood by noting that each diagonal peak is determined by the orientational average of the fourth-rank tensor  $\mu_m \mu_m \mu_m \mu_m$ . Due to the randomness of the molecular orientations in solutions, the rotational average becomes independent of the molecule-fixed frame in this specific case. In contrast, the GB+SE cross-peak amplitude is determined by two coupled transition dipoles. We found that the cross-peak amplitude at  $\omega_{\tau} = \omega_m$  and  $\omega_t = \omega_n$  for  $m \neq n$  in a given 2D spectrum at T = 0vanishes when the two polarization direction angles  $\varphi_2$  and  $\varphi_3$ satisfy the equalities in eq 27. Due to the  $\theta_{n,m}$ -dependent factors in eq 27, each cross-peak amplitude depends on  $\varphi_2$  and  $\varphi_3$ differently. As a result, by scanning one of the two polarization direction angles with the other fixed, one can find the specific beam polarization configuration that can be used to selectively eliminate the m-n cross-peak at  $(\omega_{\tau} = \omega_m, \omega_t = \omega_n)$  in the measured PAS 2DIR spectrum. By denoting the corresponding beam polarization direction angles as  $\varphi_2^{(m,n)}$  and  $\varphi_3^{(m,n)}$ , the relative angle  $\theta_{n,m}$  of the two transition dipoles is found to be related to them as

$$\cos^{2} \theta_{n,m} = \frac{\tan \varphi_{2}^{(m,n)} \tan \varphi_{3}^{(m,n)} - 2}{4 + 3\tan \varphi_{2}^{(m,n)} \tan \varphi_{3}^{(m,n)}}$$
(27a)

Subsequently, the estimated  $\theta_{n,m}$  values obtained from the entire set of the PAS 2DIR spectra should be of use to determine the molecular structures, because the relative angles between the coupled transition dipoles are keenly dependent on the intricate details of the molecular structures.

In the present PAS 2DIR experiments, we further reduced the number of variables by fixing the  $\varphi_2$  angle to be 60° and varied the angle  $\varphi_3$  only. Since the value of  $\cos^2 \theta_{n,m}$  should be in the



**Figure 4.** Real parts of the PAS 2DIR spectra (T = 0 ps) of RDC in CHCl<sub>3</sub> for varying  $\varphi_3$  angle. The polarization directions of the first pulse and signal (local oscillator) field are parallel to the *Z*-axis, i.e.,  $\varphi_1 = \varphi_s = 0^\circ$ . For simplicity, the polarization angle  $\varphi_2$  of the second pulse is fixed to be 60° with respect to the *Z*-axis. As  $\varphi_3$  decreases, the cross-peak amplitude (at the upper left corner in each 2DIR spectrum) gets smaller and vanishes at around  $\varphi_3 = 50^\circ$ . As  $\varphi_3$  becomes smaller than 49°, the cross-peak amplitude with opposite sign increases again.

range from 0 to 1, the scanning range of the angle  $\varphi_3$  is from 49.1° to 120°. In our experiments, PAS 2DIR spectra were measured by varying  $\varphi_3$  from 80° to 40° with an interval of 2°. In Figure 4, the real parts of the PAS 2DIR spectra measured at several different  $\varphi_3$  values are plotted (the absolute magnitude PAS 2DIR spectra are also presented in Supporting Information).

As  $\varphi_3$  decreases from 80° to 40°, the amplitude of the crosspeak at ( $\omega_{\tau} = 2011 \text{ cm}^{-1}$ ,  $\omega_t = 2087 \text{ cm}^{-1}$ ) decreases drama-tically and approaches zero at about 50°—note that the same pattern is found for the lower-right cross-peak too. Then, as  $\varphi_3$ decreases further, the sign of the cross-peak changes and its absolute magnitude increases again. Meanwhile, the diagonal peak amplitudes slightly increase, as theoretically predicted here. From the entire set of PAS 2DIR spectra, the amplitudes of the cross-peak at  $\omega_{\tau} = 2011 \text{ cm}^{-1}$  and  $\omega_t = 2087 \text{ cm}^{-1}$  in the real parts of 2DIR spectra and in the absolute magnitude 2DIR spectra are plotted against  $\varphi_3$  in Figure 5a,b, respectively. The solid lines in Figure 5 are the values predicted from the theory in eqs 24-26. From the interpolated line connecting the measured cross-peak amplitudes in Figure 5a, we find that  $\varphi_2^{(m,n)}$ = 60° and  $\varphi_3^{(m,\hat{n})}$  = 49°. From the relationship in eq 27a, the relative angle between the two transition dipole vectors of the symmetric and antisymmetric CO stretching modes is indeed found to be close to 90° as expected. This clearly demonstrates



**Figure 5.** Amplitudes of the cross-peak at  $\omega_{\tau} = 2011 \text{ cm}^{-1}$  and  $\omega_t = 2087 \text{ cm}^{-1}$  (a) in the real parts of the 2DIR spectra of RDC (see Figure 4) and (b) in the absolute magnitude 2DIR spectra versus the polarization direction angle  $\varphi_3$  of the third pulse. Here, we have  $\varphi_1 = \varphi_s = 0^\circ$  and  $\varphi_2 = 60^\circ$ , and the cross-peak intensity is given in an arbitrary unit. The open circles are the experimental results and the error bars are obtained by averaging the results of three independent sets of PAS 2DIR experiments. The red line in this figure is the theoretical expression given in eqs 24 and 25.

that the PAS 2DIR spectroscopic technique is useful to estimate the relative angles between any pair of transition dipole vectors.

Here, a full control of beam polarization directions has been shown to be experimentally feasible and practically useful in this work. In particular, we showed that selective elimination of a cross-peak of interest is possible by properly adjusting the beam polarization configuration. This in turn allows us to extract information on the relative angles between coupled transition dipoles from the complete set of PAS 2DIR spectra. However, it should be mentioned that the same information can also be extracted by measuring the cross-peak anisotropy, which is obtained from  $(S_{ZZZZ} - S_{ZYYZ})/(\hat{S}_{ZZZZ} + 2S_{ZYYZ})^{22}$  In the simple case that the cross-peaks are spectrally well-resolved in the 2DIR spectra and that the measurements of the parallel and perpendicular 2DIR cross-peak amplitudes are quantitatively reliable, the present PAS 2DIR may not have notable advantage over the cross-peak anisotropy measurement method. However, as the number of cross-peaks increases and they are spectrally overlapped with the intense diagonal peaks, it becomes difficult to use the cross-peak anisotropy measurements to achieve the goal. Furthermore, if there exist multiple conformers in equilibrium, it is expected that the cross-peak amplitudes would not be monotonically dependent on  $\varphi_3$  angle (e.g., double minima for a two-species system) unlike the simple case of RDC shown in Figure 5b. Consequently, since the PAS 2D method takes advantage of additional dimensionality in 2D optical spectroscopy, it offers a new means to probe the structural motifs and conformational distributions of coupled multichromophore systems.

In the case of an isotropic system such as chromophores dissolved in solvents, there are four nonzero fourth-rank tensor elements needed to be considered, which are S<sub>ZZZZ</sub>, S<sub>ZZYY</sub>, S<sub>ZYYZ</sub>, and  $S_{ZYZY}$ . Only three of them are independent due to  $S_{ZZZZ}$  =  $S_{ZZYY} + S_{ZYYZ} + S_{ZYZY}$ . Therefore, any 2D spectrum with an arbitrary polarization configuration can be written as a linear combination of these three basis spectra. The PAS 2D spectrum with a specific polarization configuration discussed here can also be viewed as a linear combination of S<sub>ZZZZ</sub> and S<sub>ZYYZ</sub> because the polarization directions of the first incident beam and the detected signal electric field are set to be parallel to the Z-axis and those of the second and third incident beams are on the Y-Z plane. However, this does not invalidate the potential use of the PAS 2D method, which can be considered to be one of the null methods mentioned in the Introduction. Since the PAS 2D spectroscopy utilizes multiple spectra obtained by varying the polarization configurations, it should provide more accurate results.

### 5. SUMMARY

In this paper, we presented experimental results on the PAS 2DIR spectroscopy of RDC in chloroform, where the polarization directions of the incident beams are considered to be continuously variable parameters. This additional controllability factor in 2D optical spectroscopy has not been experimentally explored before. Although a simple coupled-anharmonic oscillator system, e.g., RDC, was used for the experimental demonstration, the PAS 2D spectroscopic method would be of potential use in studying coupled multichromophore systems in future. Let us consider the case that there are multiple cross-peaks in a given 2D spectrum. Since the relative angles between coupled transition dipoles vary for different pairs of modes or quantum states, each cross-peak associated with the ground-state bleach and stimulated emission contributions will disappear at different  $\varphi_3$  angles. The estimated  $\theta_{n,m}$  values will in turn be of use as an important set of constraints for further structure determination. After selecting one particular beam polarization configuration that makes a specific cross-peak vanish, one can follow subsequent changes in the cross-peak amplitude and sign as a function of *T*. This will provide us crucial information on structural changes of nonequilibrium state molecules as well as on population and/or coherence transfers by monitoring the time-dependent changes of the initially vanished cross-peaks. Despite that the present work focused on the application of the polarization-angle-scanning technique to extend the dimensionality of the heterodynedetected 2D photon echo spectroscopy, we anticipate that the same polarization null angle scheme discussed here can be applied to a variety of different coherent multidimensional spectroscopic methods,44-49 such as doubly vibrationally resonant IR-vis fourwave-mixing, wavepacket interferometry 2D electronic spectroscopy, 3DIR spectroscopy, double-quantum coherence 2D spectroscopy, and 2D nanoscopy, to enhance their spectroscopic sensitivities to molecular conformations and frequency resolutions.

# ASSOCIATED CONTENT

**Supporting Information.** Detailed theoretical descriptions on 2DIR spectroscopy of coupled anharmonic oscillators, experimental methods, and the entire set of the experimentally measured real part and absolute magnitude PAS 2DIR spectra (at zero waiting time) of RDC. This material is available free of charge via the Internet at http://pubs.acs.org.

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# ACKNOWLEDGMENT

This work was financially supported by NRF (20090078897), KBSI (T30401), and NRF (201000020209) grants to M.C.

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