Mode-Selective Optical Kerr Effect Spectroscopy

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INTRODUCTION

- Two pump pulses controlled : polarization , intensity , timming

- Same polarization : intramolecular vibrations enhanced or suppressed without the reorientation diffusion contribution to the signal significantly

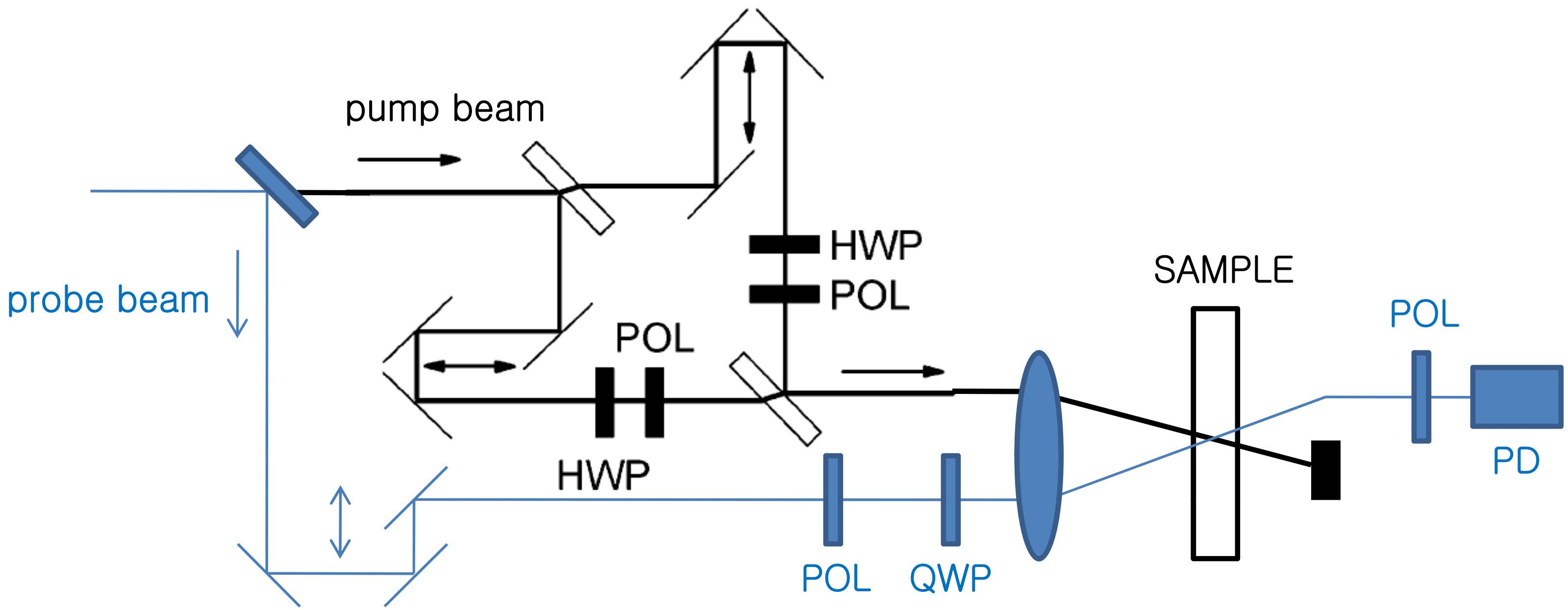
- Polarization perpendicular : possible to suppress the reorientation diffusion component of the signal

- Two intramolecular vibrational modes : possible to enhance one while completely suppressing the other

Set-up

- 60fs, 800nm, 76MHz, 500mW
- polarization -> pump : vertical , probe : 45°
- schematic of the optics for creation of dual pump pulses

HWP=half-wave plate, POL=polarizer



✓ Generally Optical Kerr Effect   in isotropic medium

$$\delta\chi(\omega') = \Delta\chi_{xx} - \Delta\chi_{yy} = (\chi_{1111} - \chi_{1221})|E_0(\omega)|^2 = 2\chi_{1212}|E_0(\omega)|^2$$

$$\chi_{1111} = \chi_{1212} + \chi_{1221} + \chi_{1122}$$

$$\chi_{1111} = 3\chi_{1212} = 3\chi_{1221} = 3\chi_{1212}$$

$$\chi_{1111} - \chi_{1221} = \chi_{1212} + \chi_{1122} = 2\chi_{1212}$$

✓ pump vertical / probe polarized 45° : $R^{(3)}_{xyxy}(\tau)$

pump holizontal / probe polarized 45° : $-R^{(3)}_{xyxy}(\tau)$

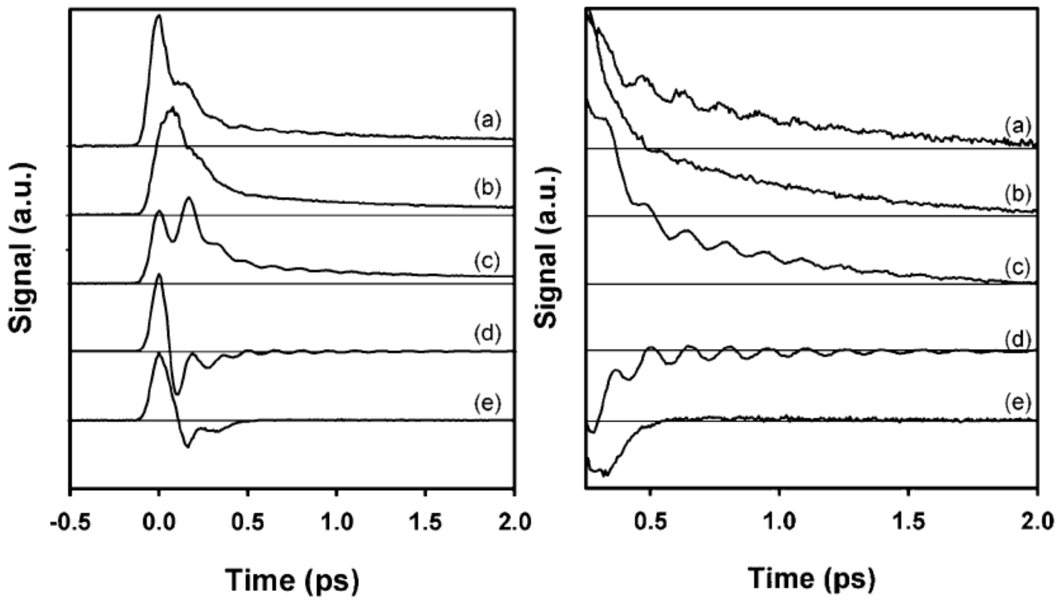
✓ ①pump vertical ②pump verticall / probe polarized 45° : $R^{(3)}_{xyxy}(\tau) + \alpha R^{(3)}_{xyxy}(\tau - t_p)$

①pump vertical ②pump horizonral / probe polarized 45° : $R^{(3)}_{xyxy}(\tau) - \alpha R^{(3)}_{xyxy}(\tau - t_p)$

α : constant,depand on two pump pulses intensities

t_p : pump pulses separeted time

▪ OKE decays for room-temperature propionitile Ⅰ)



(a) a single pump pulse

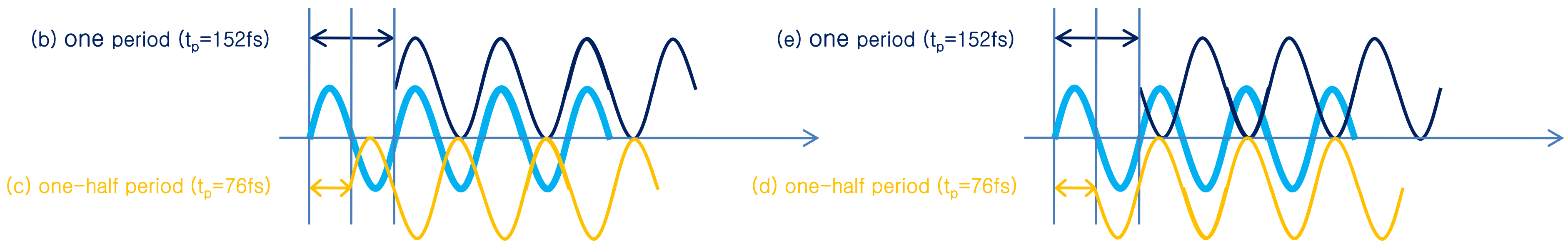
(b) parallel-polarized pump pulses separated by one-half period (76fs) of the intramolecular vibration (α)

(c) parallel-polarizerd , one period (152fs)

(d) perpendicularly-polarized , one-half period

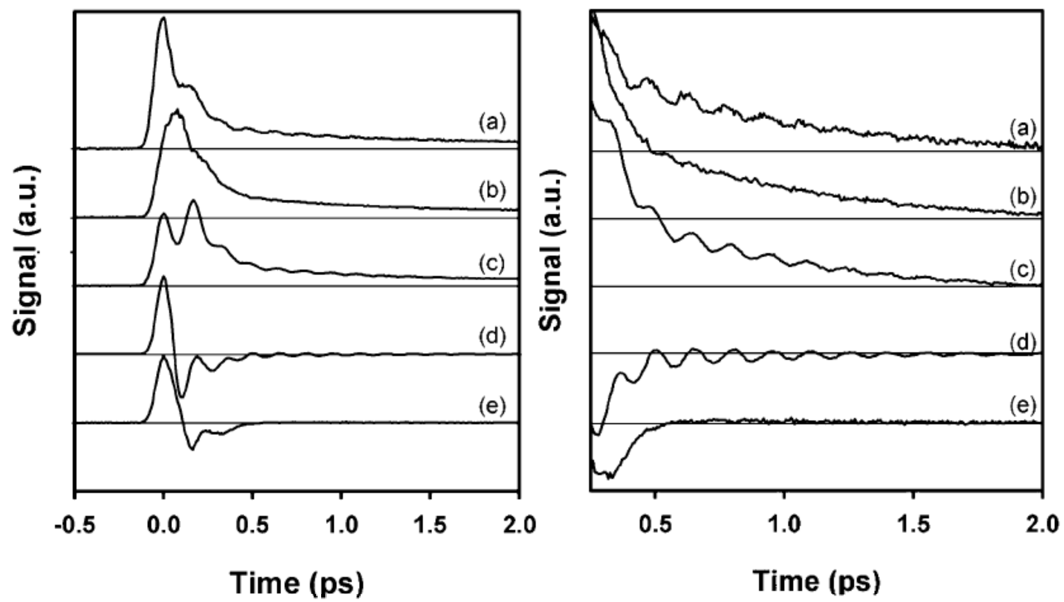
(e) perpendicularly-polarized , one period

※ intramolecular vibrational mode
: 220 cm^{-1} (corresponding 152 fs)



$$\sin(\omega\tau)\exp(-\frac{\tau}{\tau_d}) - \alpha \sin(\omega(\tau - t_p))\exp(-\frac{\tau}{\tau_d})$$

▪ OKE decays for room-temperature propionitile II)



✓ (b) , (c) same polarization : intramolecular vibrations enhanced or suppressed without the reorientation diffusion contribution to the signal significantly

intramolecular vibrational mode : $R^{(3)}_{xyxy}(\tau) \approx \sin(\omega\tau)\exp(-\frac{\tau}{\tau_d})$

ω : vibrational frequency
τ_d : dephasing time

diffusive reorientation : $\exp(-\frac{\tau}{\tau_r})$

τ_r : diffusive reorientational time

✓ (d) , (e) possible to suppress the reorientation diffusion component of the signal

(d) : strong intramolecular vibrational mode
(e) : only the intermolecular and electronic responses

✓ perpendicularly polarized pump pulses

$$R_{xyxy}^{(3)}(\tau)-\alpha R_{xyxy}^{(3)}(\tau-t_p)$$

$$=[\sin(\omega\tau)\exp(-\frac{\tau}{\tau_d})+\exp(-\frac{\tau}{\tau_r})]-\alpha[\sin(\omega(\tau-t_p))\exp(-\frac{(\tau-t_p)}{\tau_d})+\exp(-\frac{(\tau-t_p)}{\tau_r})]$$

$$=\sin(\omega\tau)\exp(-\frac{\tau}{\tau_d})-\alpha\sin(\omega(\tau-t_p))\exp(-\frac{(\tau-t_p)}{\tau_d})+\exp(-\frac{\tau}{\tau_r})-\alpha\exp(-\frac{(\tau-t_p)}{\tau_r})$$

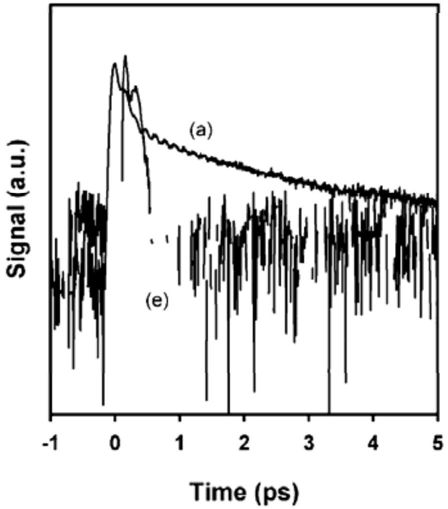
$$=\sin(\omega\tau)\exp(-\frac{\tau}{\tau_d})-\alpha\sin(\omega(\tau-t_p))\exp(-\frac{\tau}{\tau_d})-\alpha\sin(\omega(\tau-t_p))\exp(\frac{t_p}{\tau_d})+(1-\alpha)\exp(-\frac{\tau}{\tau_r})(1-\exp(\frac{t_p}{\tau_r}))$$

only intensity

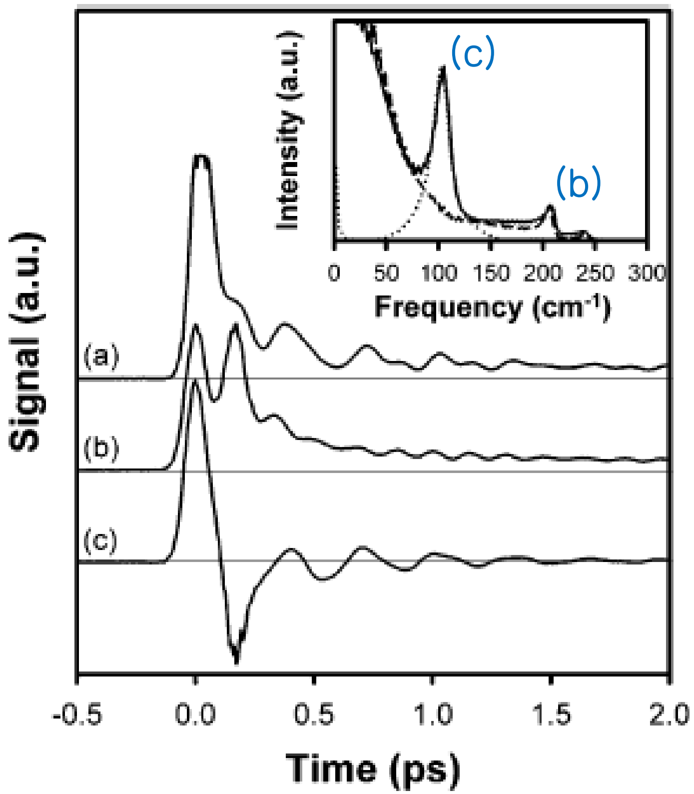
$$=\sin(\omega\tau)\exp(-\frac{\tau}{\tau_d})-\alpha\sin(\omega(\tau-t_p))\exp(-\frac{\tau}{\tau_d})$$

✓ constant α

diffusive mode completely absent (e)only inter– , electronin response



- OKE decays for room-temperature propionitile (S_2Cl_2)
  : more than one intramolecular vibration mode



(a) a single pump

(b) parallel-polarized , one period :

(c) perpendicularly-polarized , one period :
strong intramolecular vibrational mode

✓ Fourier transform :
$105cm^{-1}$ (318fs) , $206cm^{-1}$ (162fs)
two strong intramolucular vibration modes

✓ effecting contral over n contribution to the OKE signal will genernally require the use of the n pulses