Two-dimensional electronic spectroscopy using optical pulse shaper : Origin of coherent oscillations in Zn-Naphthalycanine aggregate

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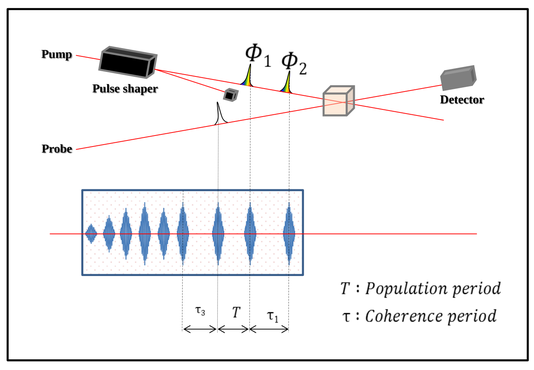
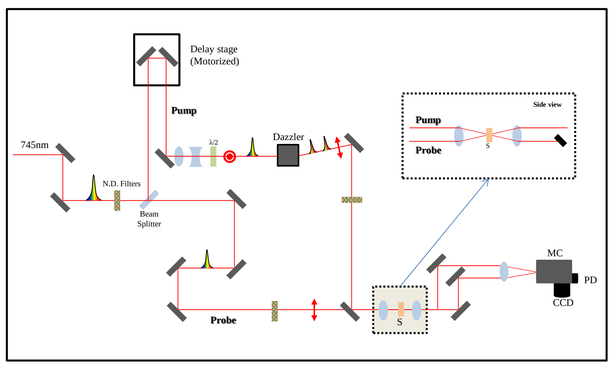
Introduction

2D electronic spectroscopy



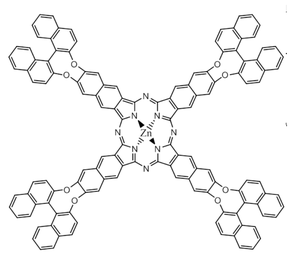
Simple scheme of 2D electronic spectroscopy system



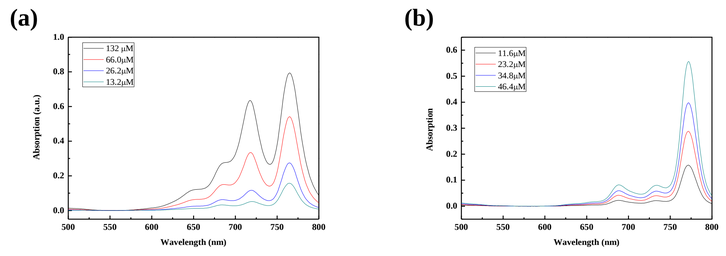
Experimental scheme of 2D electronic spectroscopy system

- Three femtosecond optical pulses interact with the sample to generate a third order nonlinear signal.
- The optical pulse shaper generates two replica pump pulses with high phase accuracy.

Molecular Information



Molecular structure of ZnNPc

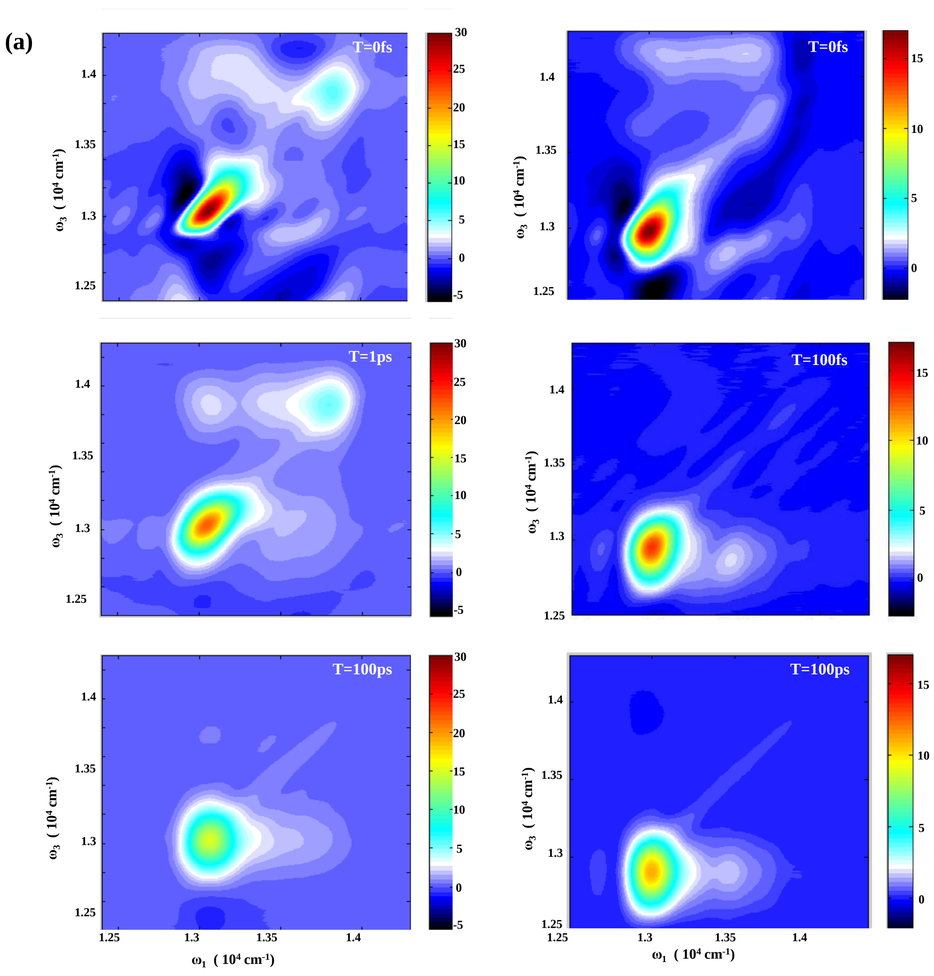


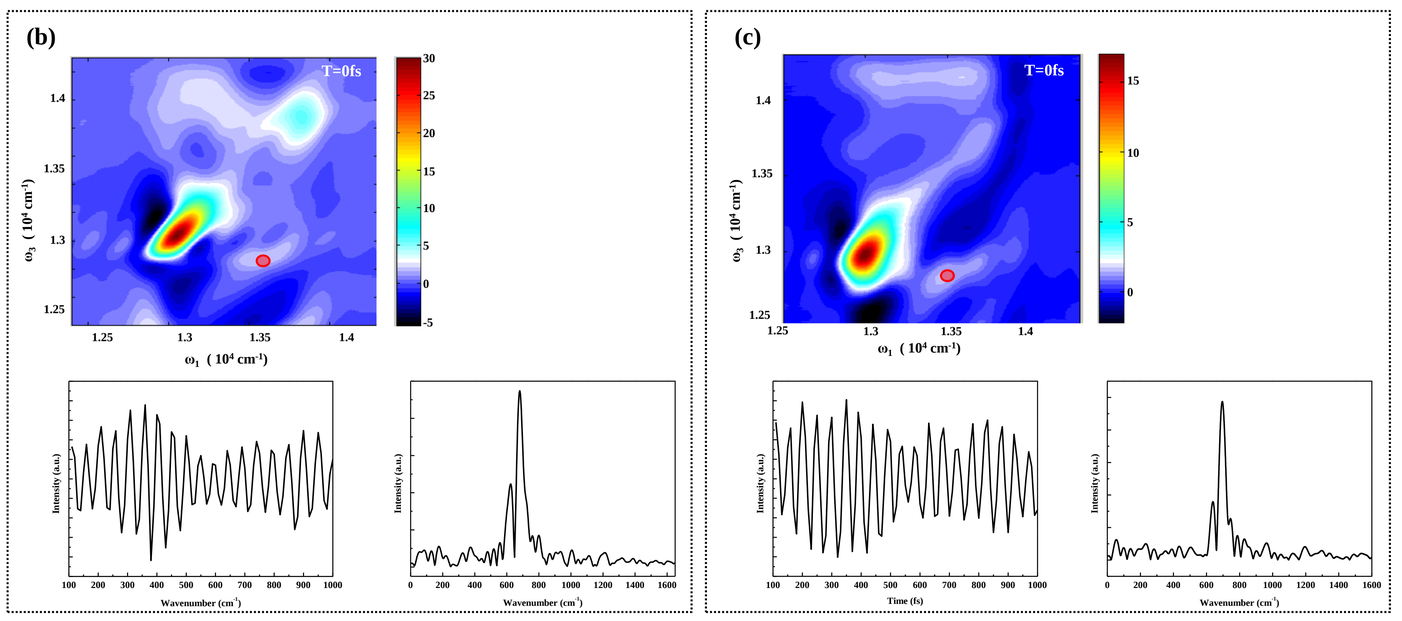
Absorption spectrum of ZnNPc dissolved (a) in THF and (b) in Benzonitrile.

- The normalized absorption spectra of ZnNPc dissolved in THF highly depend on the sample concentration.
- In benzonitrile, however, the normalized absorption spectra do not change significantly with concentration, indicating that the aggregation does not form.

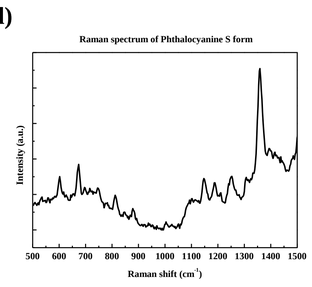
Experiments & Results

2D electronic spectroscopic results





(d)



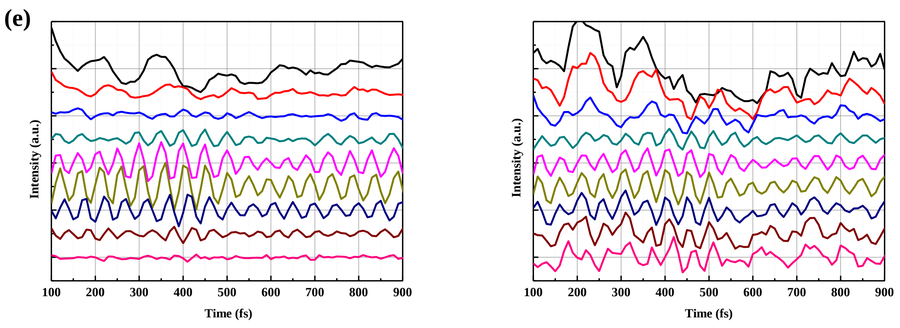
(b) Oscillation component at a specific peak position in aggregate (left) and the FFT result (right).

(c) Oscillation component at a specific peak position in monomer (left) and the FFT results (right).

(d) Raman spectrum of ZnNPc.

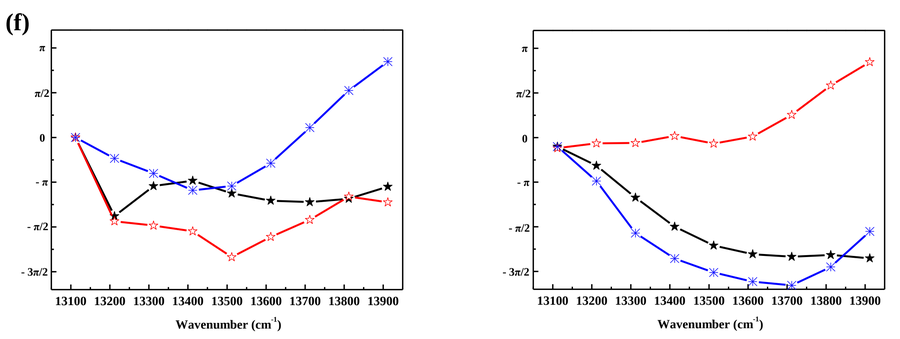
- Time-resolved 2D spectra of ZnNPc in THF (left) and benzonitrile (right) at T=0 fs, 1 ps and 100 ps.
- The lower diagonal peak is elongated diagonally due to inhomogeneous broadening at T=0 and that elongation rapidly disappears in 100 fs in monomer.
- In both diagonal and cross peaks of the 2D-ES spectra, oscillating signals which are correlated with the vibrational coherence are observed.
- A slow beating is observed due to the contribution of two oscillating components with different frequency (600, and 680 cm^{-1}), which is in good agreement with the vibrational frequency shown in the Raman spectrum of ZnNPc.

(e)



- The overlay of population oscillation at diagonal point from 13112 cm^{-1} (black) to 13912 cm^{-1} (pink) in monomer state (left) and aggregate (right).
- The phase at w_3=13112 cm^{-1} with w_1=13112 cm^{-1} to 13912 cm^{-1} (black) and w_1=13112 cm^{-1} with w_3=13112 cm^{-1} to 13912 cm^{-1} (red) and diagonal (blue) in monomer state (left) and aggregate (right).

(f)



- There is a 90° phase shift between the 2D peak oscillations that cannot be readily understood by considering conventional Feynman pathways.
- It was suggested that population-to-coherence transfer or vibronic coupling is responsible for such an in-quadrature phase shift between diagonal and cross peaks.

Summary & Perspective

1. We finally confirmed that the origin of slow beating signals at various peaks correlated with the phase relationship of two different modes through analysis of the 2D spectrum in monomer state.
2. This 2D approach will be extended to 2D chiroptical spectroscopy in combination with the heterodyne-detected chiroptical method with precise control of optical pulse sequence and polarization state.