Coherent dynamics in porphyrin dimers

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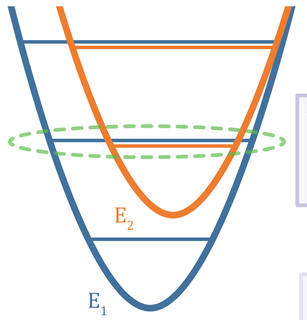
Electronic–vibrational coupling in porphyrins

Abstract A commonality among many highly efficient light harvesting protein complexes is that they exhibit strong and persistent coherent spectral signatures that coincide with the early steps of the energy transport process. Due in part to the inherent complexity and scale of protein systems, the source of these coherences remains unresolved, let alone their potential role in the light harvesting process. To overcome these challenges, we apply two-dimensional Fourier-transform spectroscopy to porphyrins and their dimers, which serve as model synthetic systems that are analogous to natural chlorophyll yet are more accessible to theoretical simulation. Combined with broadband visible excitation, this technique allows us to monitor the entire Q band region to reveal the coherent dynamics involved in the early stages of energy and charge transfer.

Non-adiabatic coupling

Central question:
How does vibrational resonance influence coupling between electronic states?



Near-degeneracy between vibrational and electronic transitions leads to strong non-adiabatic coupling.

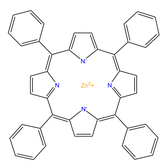
?

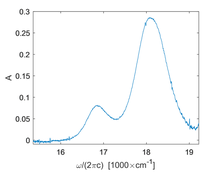
Fast and efficient energy and charge transfer.

Zinc porphyrins

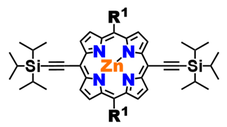
Monomers

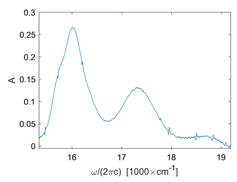
ZnTPP





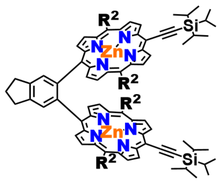
PZn(ETIPS)$_2$

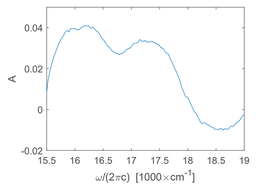




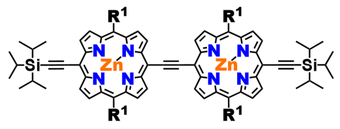
Dimers

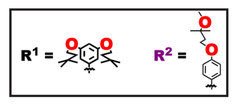
Cofacial PZn$_2$(ETIPS)$_2$





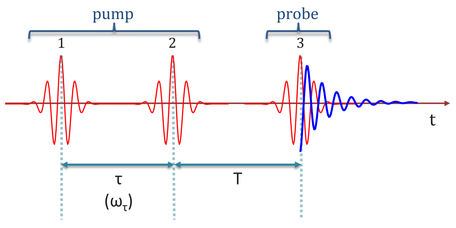
Linear PZn$_2$(ETIPS)$_2$



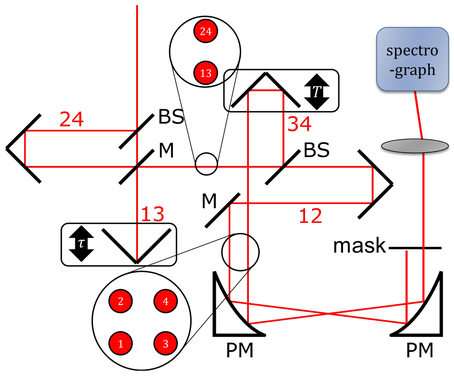


Broadband 2DFT and 3DFT spectroscopy

Optical apparatus

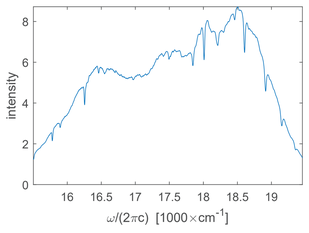


Partially common-path design yields passive phase stability. Rapid delay scanning increases acquisition speed and signal to noise.



Capabilities

- Extremely broadband:
  < 7 fs
- Large spectral volume:
  (5000 cm^{-1})^3
- Rapid acquisition:
  1 s/2DFT spectrum
  10 min/3DFT spectrum
- Passively phase stable on the timescale of hours.



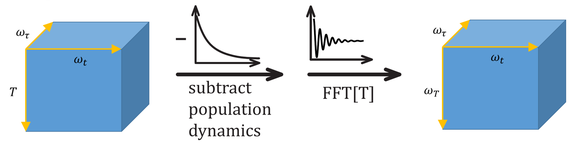
Data analysis

Global analysis

Dynamics in 2DFT spectra $S(\omega_\tau, T, \omega_t)$ are fit to a sum of complex exponentials with a common set of complex parameters s_i but independent amplitudes at each (ω_τ, ω_t) point.

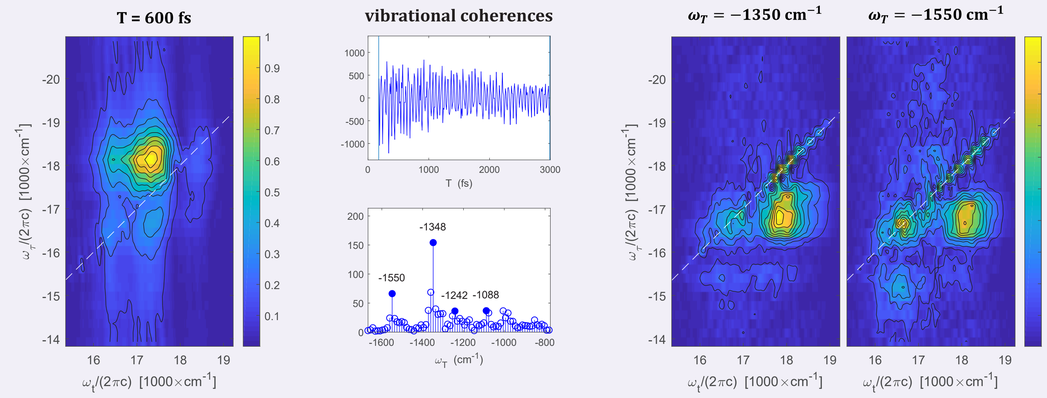
$$\sum_{i=1}^{n} A_i(\omega_\tau, \omega_t) \exp(\hat{s}_i T)$$

3DFT spectra

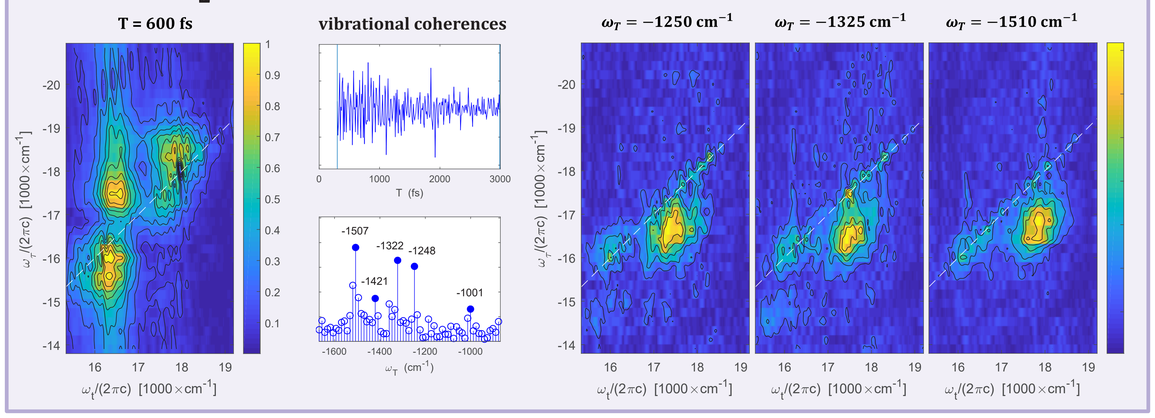


3DFT electronic spectra of porphyrins

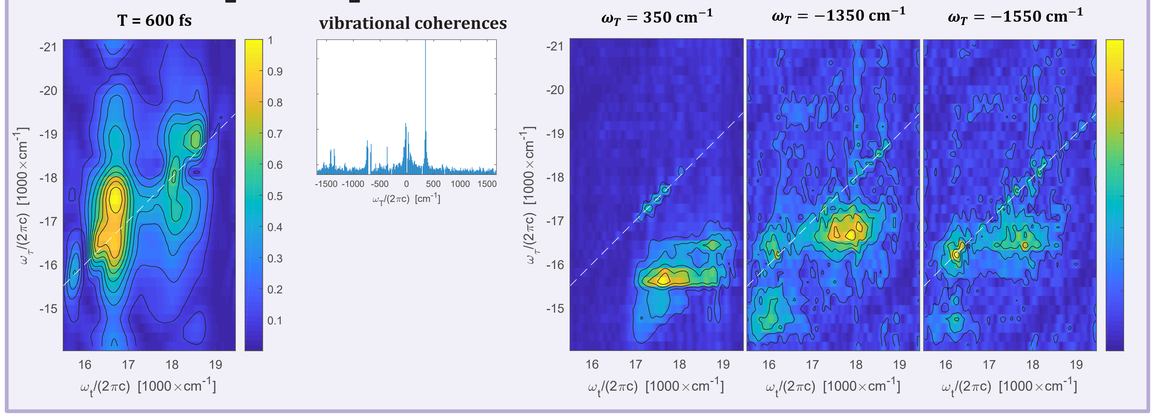
ZnTPP



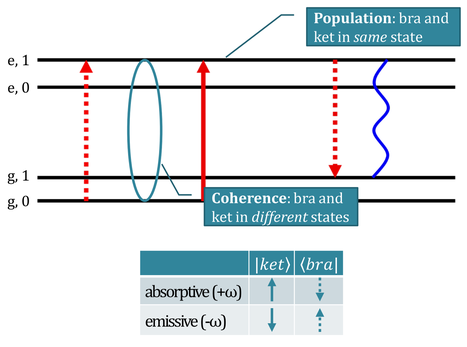
PZn(ETIPS)$_2$

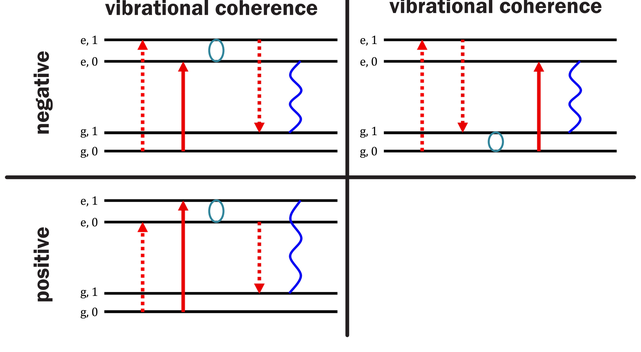


Cofacial PZn$_2$(ETIPS)$_2$ dimer



Coherence pathways





Conclusions

Porphyrin oligomers serve as an ideal framework for exploring the influence of electronic–vibrational coupling on energy and charge transfer using 2DFT electronic spectroscopy. 3DFT spectra of porphyrin monomers exhibit rich vibronic beating signatures that allude to a complex interplay between vibrational and electronic degrees of freedom. Likewise, porphyrin dimers contain intense vibronic beating features whose dependence on electronic coupling will be a target of continued research.