How Can Photosynthetic Light-Harvesting Have a Quantum Efficiency Approaching Unity?

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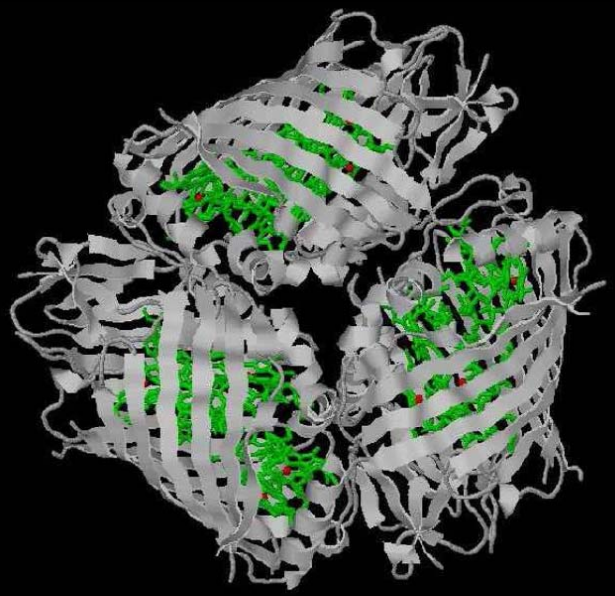
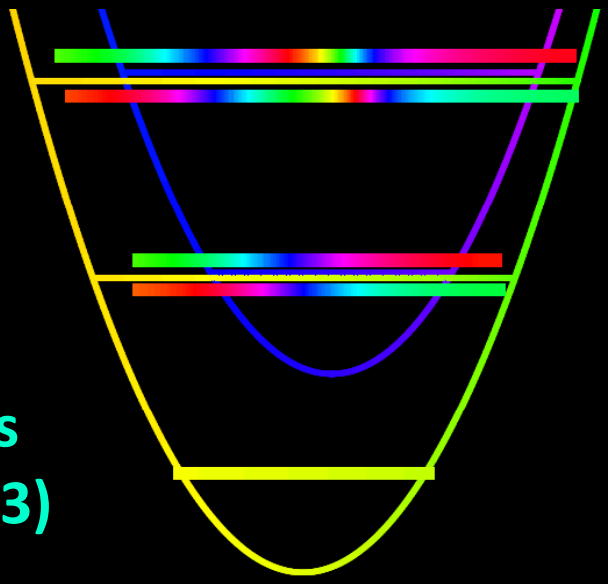
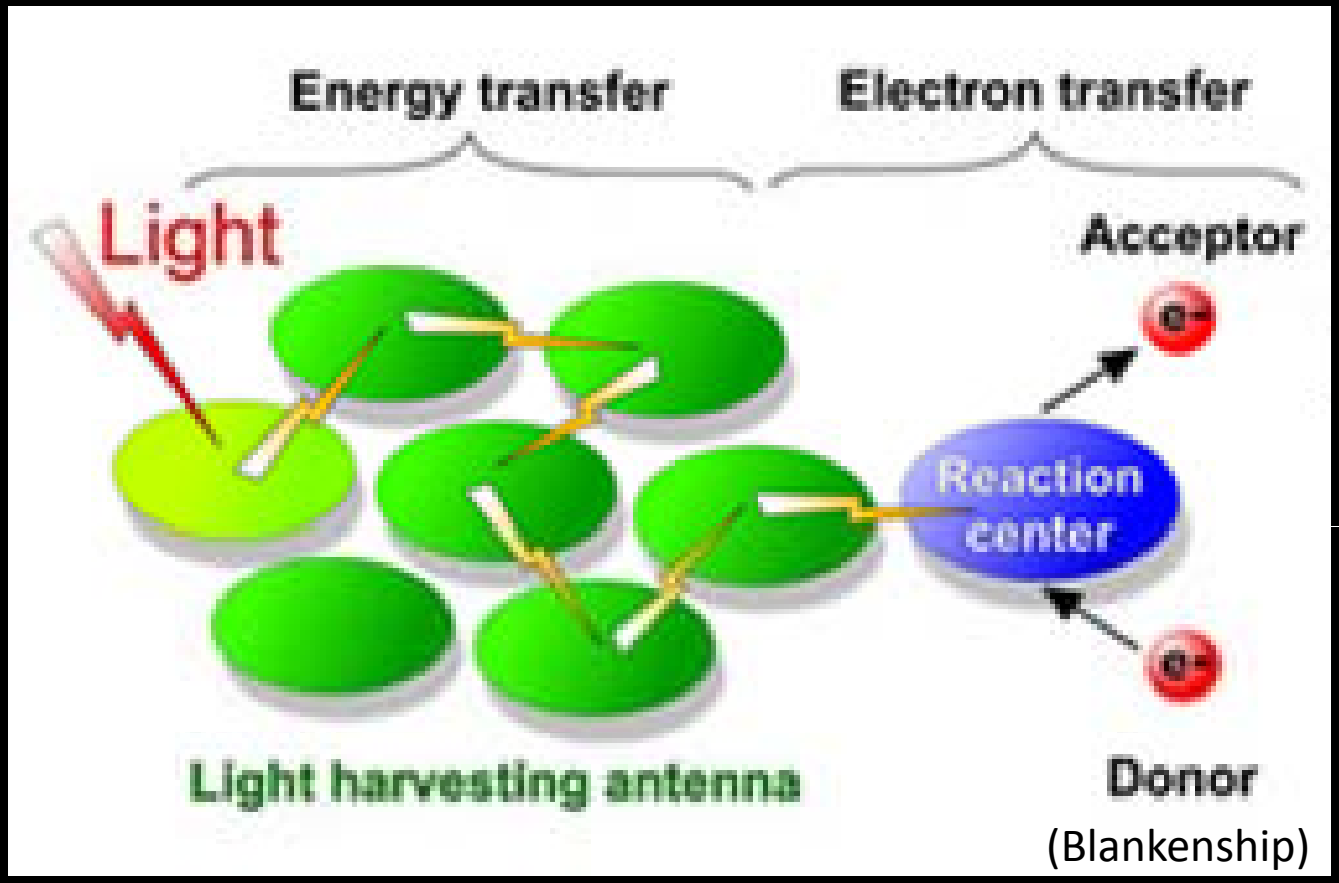




Tiwari, Peters & Jonas
PNAS 110, 1203 (2013)



(Blankenship)

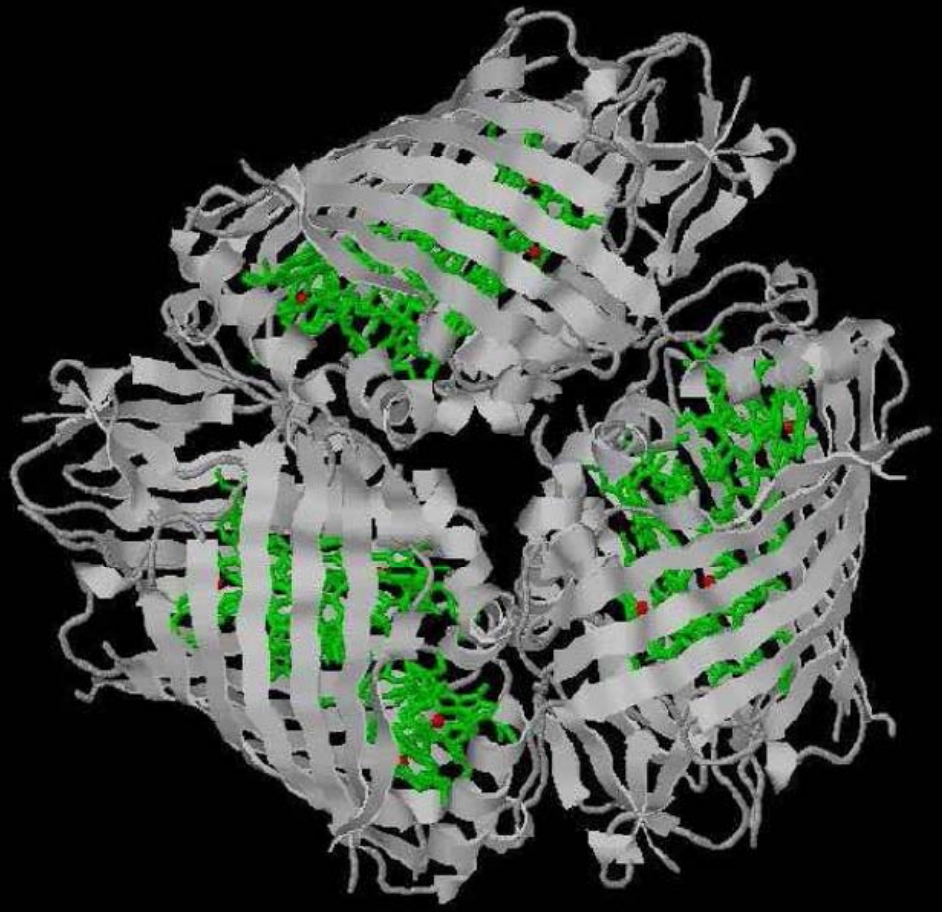
Overall Energetic Efficiency

= chemical energy stored/incident light energy ≈ 2%

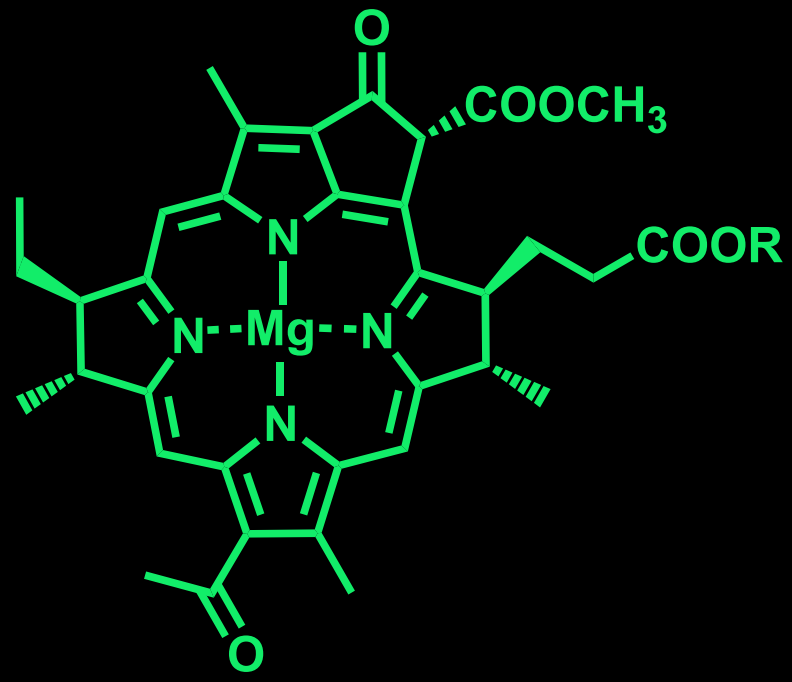
Light Harvesting Efficiency of the Antenna

= photons to RC/photons absorbed ≈ 100%

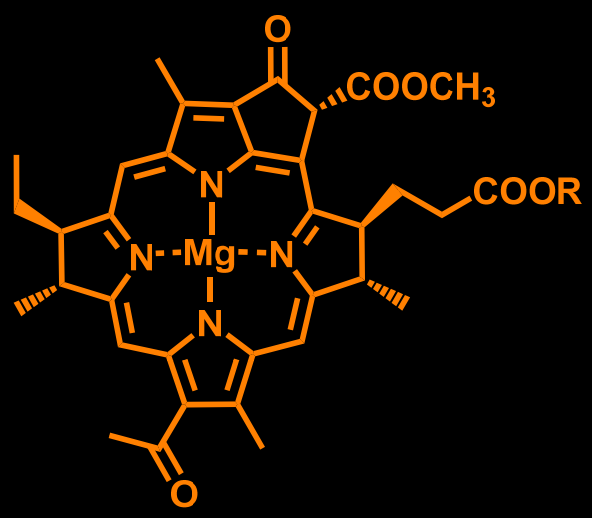
FMO trimer

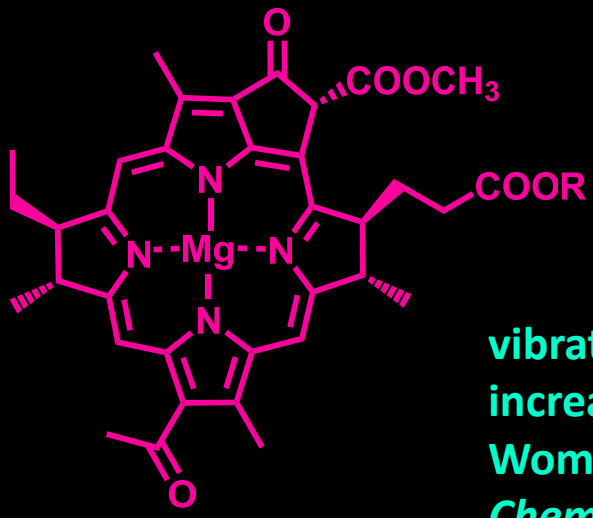


Each sub-unit contains 7 *bacteriochlorophyll a* pigments



Protein adjusts pigment energies …

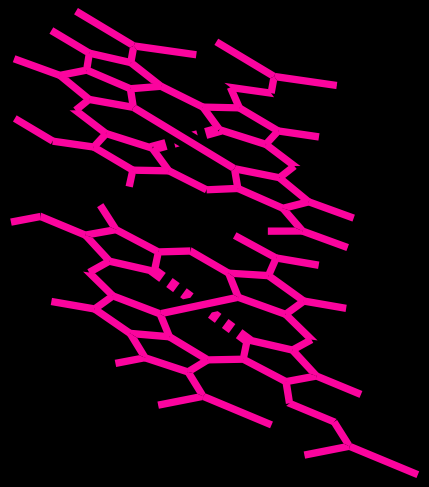




Energy flows downhill …

vibrational resonance increases speed: Womick & Moran, *J Phys Chem B* 115, 1347 (2011).

Protein positions pigments to couple them …

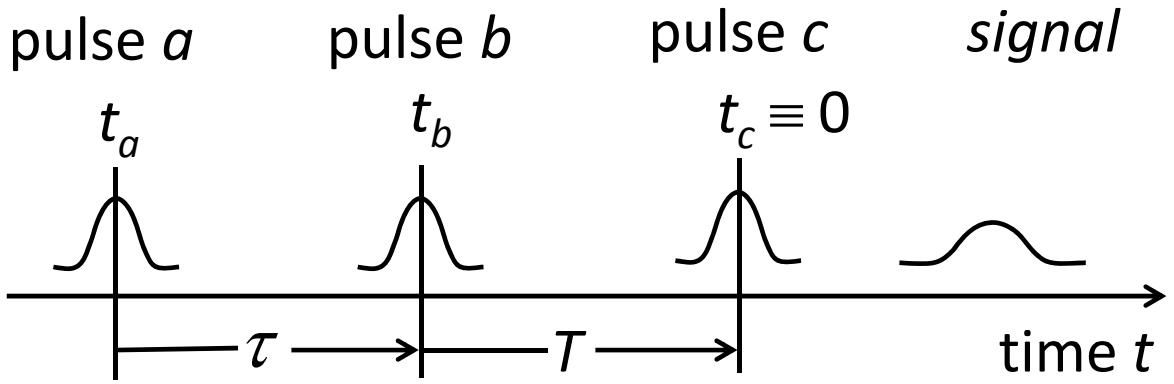


Protein damps pigment motions …
Electronic decoherence
Vibrational relaxation
(“It ain’t over ‘til it’s over.”)

Efficiency is maximum when vibrational relaxation rate = $2J/\hbar$ (J is coupling)

A.S. Davydov and A.A. Serikov “Energy Transfer between Impurity Molecules in Crystal in the Presence of Relaxation” *phys. stat. sol. b* 51, 57 (1972)

2D Fourier Transform Spectra



Femtosecond 4-wave mixing - background free signal by phase matching: $k_s = k_c + k_b - k_a$.

Measure signal field *E* by interferometry as a function of both time *t* and delay τ (fixed *T*).

Fourier transform 2D time domain fields twice:

$E(t, \tau, T) \xrightarrow{\text{2D FT}} E(\omega_t, \omega_\tau, T)$ is the 2D spectrum.

Rephasing 2D:
$\tau > 0$ (*a* 1st, *b* 2nd)

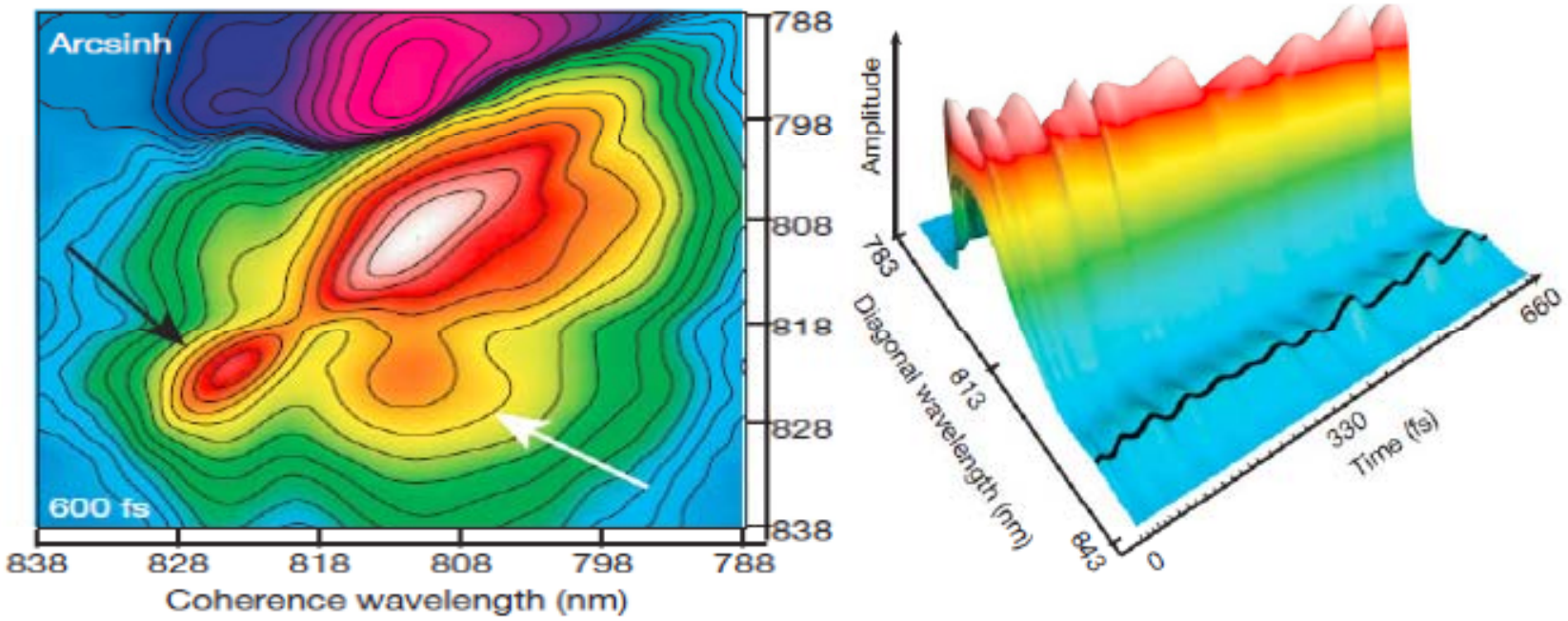
Non-Rephasing 2D:
$\tau < 0$ (*b* 1st, *a* 2nd)

Absorptive 2D:
all τ

J.D. Hybl, A. W. Albrecht, S. M. Gallagher Faeder & D. M. Jonas
Chem. Phys. Lett. 297, 307-313 (1998).

Signatures of Photosynthetic Energy Transfer

FMO Complex: Green Sulfur Bacteria

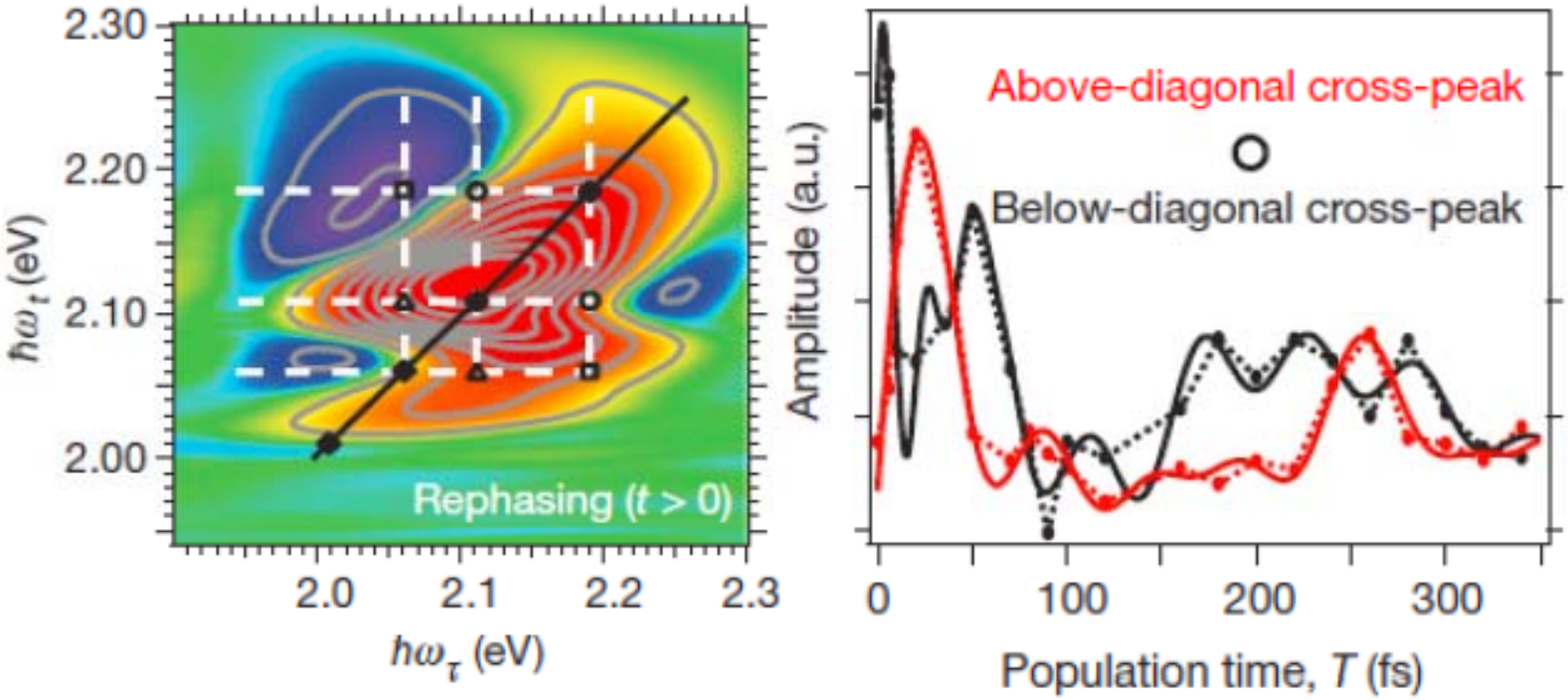


- **DP & CP beating in absorptive 2D**

Engel et al., Nature (2007) Vol. 446, 782-786

Signatures of Photosynthetic Energy Transfer

PC645: Cryptophyte marine algae



- 180° phase between CP in rephasing 2D

Collini et al., Nature (2010) Vol. 463, 644-648

Signatures of Photosynthetic Energy Transfer

180° phase between CP in rephasing 2D

is not

a consequence of electronic coherence.

Butkus, Zigmantas, Valkunas & Abramavicius

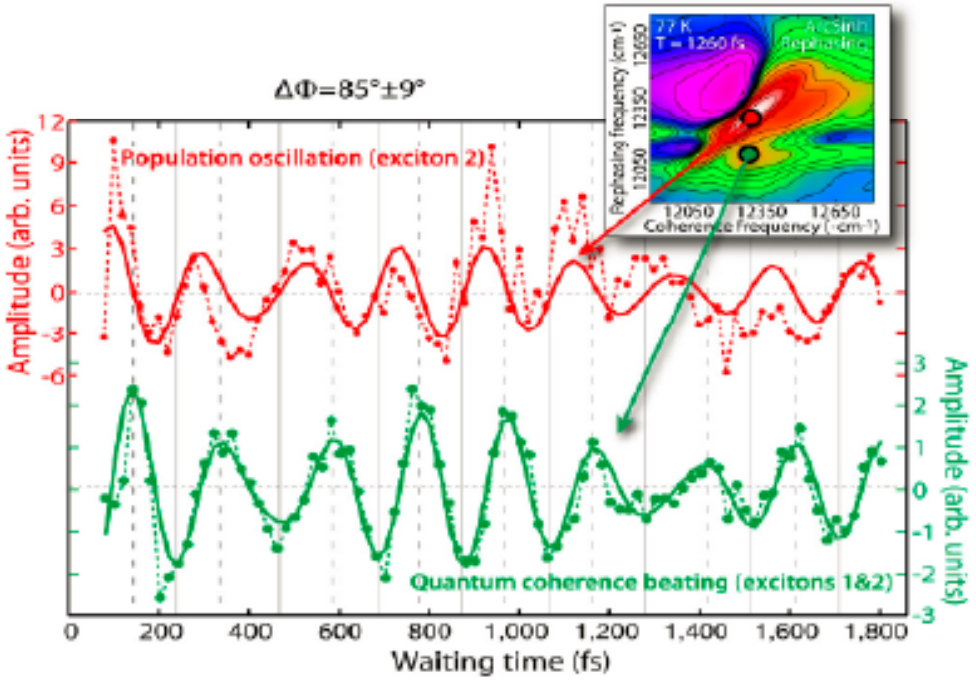
Chem. Phys. Lett. **545, 40–43 (2012) .**

Sampling - location matters.

"The spectral beats with t_2 can thus only have the same phases in the k_I [R] or k_{II} [NR] spectrum, when measured at peak centers."

Signatures of Photosynthetic Energy Transfer

FMO Complex: Green Sulfur Bacteria



NOT predicted by electronic coherence - oscillatory Quantum energy Transport (QT)?

- **DP beating in rephasing 2D**
- **90° phase between DP and CP**

Panitchayangkoon et al., PNAS (2011) Vol. 108(52), 20908-20912

- **COHERENCE SPANS MORE THAN ONE PIGMENT (*not seen in one-pigment proteins*)**

- ***NOT* A FRANCK-CONDON (ADIABATIC or BORN-OPPENHEIMER) EXCITED VIBRATION – *too weak in photosynthetic pigments***

- **Beats over ~2 ps have led to discussion of MIXED VIBRATIONAL-ELECTRONIC (VIBRONIC) BEATS on the EXCITED ELECTRONIC STATE**

Standard dimer model - the two isolated pigment Hamiltonians are:

$$\hat{H}_A = \frac{1}{2}\omega_A(\hat{q}_A^2 + \hat{p}_A^2)\hat{I} + (E_A - \omega_A d_A \hat{q}_A)\,|A\rangle\langle A|$$

$$\hat{H}_B = \frac{1}{2}\omega_B(\hat{q}_B^2 + \hat{p}_B^2)\hat{I} + (E_B - \omega_B d_B \hat{q}_B)\,|B\rangle\langle B|$$

an excited pigment is Coulombically coupled to the other

$$\hat{H}_{\text{dimer}} = \hat{H}_A + \hat{H}_B + J(|A\rangle\langle B| + |B\rangle\langle A|)$$

2 crucial coordinates for energy transfer:

$q_+=(q_A+q_B)/2^{1/2}$

correlated vibration

(adiabatically separable)

survives energy transfer. NOT THIS

$q_-=(q_A-q_B)/2^{1/2}$

anti-correlated vibration

(non-adiabatic tuning coordinate)

drives energy transfer.

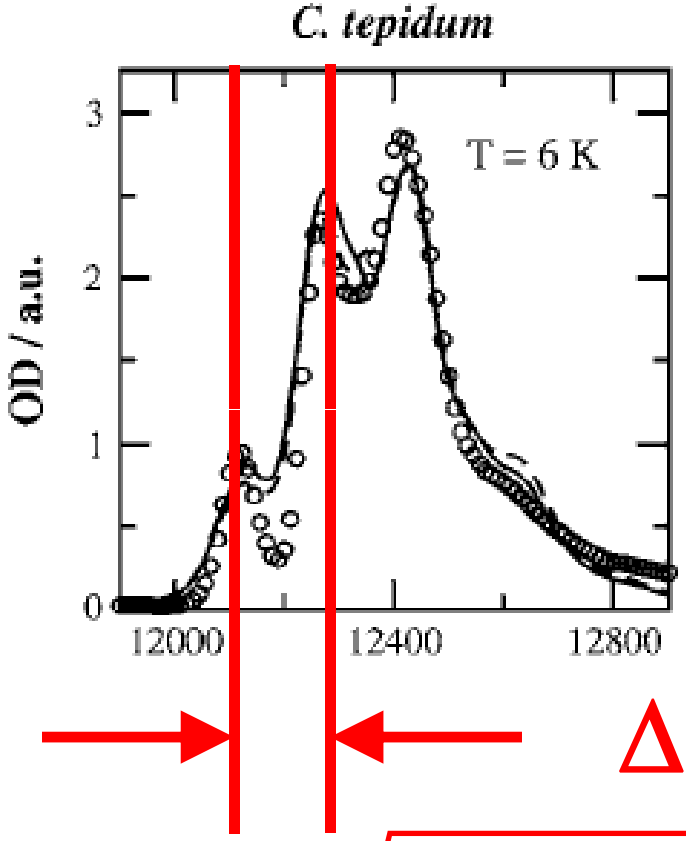
$$\hat{H}_1 = \hat{H}_{corr} + \hat{H}_{int}$$

$$\hat{H}_{corr} = \frac{1}{2}[(E_A + E_B) + \omega(\hat{q}_+^2 + \hat{p}_+^2) - \sqrt{2}\omega d q_+]\hat{I}$$

$$\hat{H}_{int} = \frac{1}{2}\omega(\hat{q}_-^2 + \hat{p}_-^2)\hat{I}$$

$$+\begin{bmatrix} \left(-\frac{\Delta}{2} - \frac{\omega d \hat{q}_-}{\sqrt{2}}\right) & J \\ J & \left(+\frac{\Delta}{2} + \frac{\omega d \hat{q}_-}{\sqrt{2}}\right) \end{bmatrix}$$

DIMER MODEL (loosely based on FMO)



Coupling Range:

$J \approx 30\text{-}110\ \text{cm}^{-1}$

[J.Phys.Chem. B 109, 10542(2005)]

pick $J = 66\ \text{cm}^{-1}$

← Biophys.J. 91, 2778(2006)

$$\Delta_{EX}(3-1) \approx 200\ \text{cm}^{-1}$$

$$\Delta_{EX} = \sqrt{\Delta^2 + 4J^2} \Rightarrow \Delta = 150\ \text{cm}^{-1}$$

BChl a **vibration at ω_{vib} = 195 cm^{-1} (±2) with λ = 4 cm^{-1} [J.Phys.Chem. B 105,12410(2001)]**

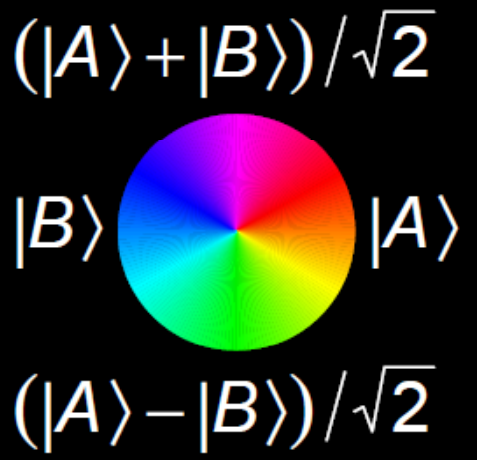
ISOLATED PIGMENTS

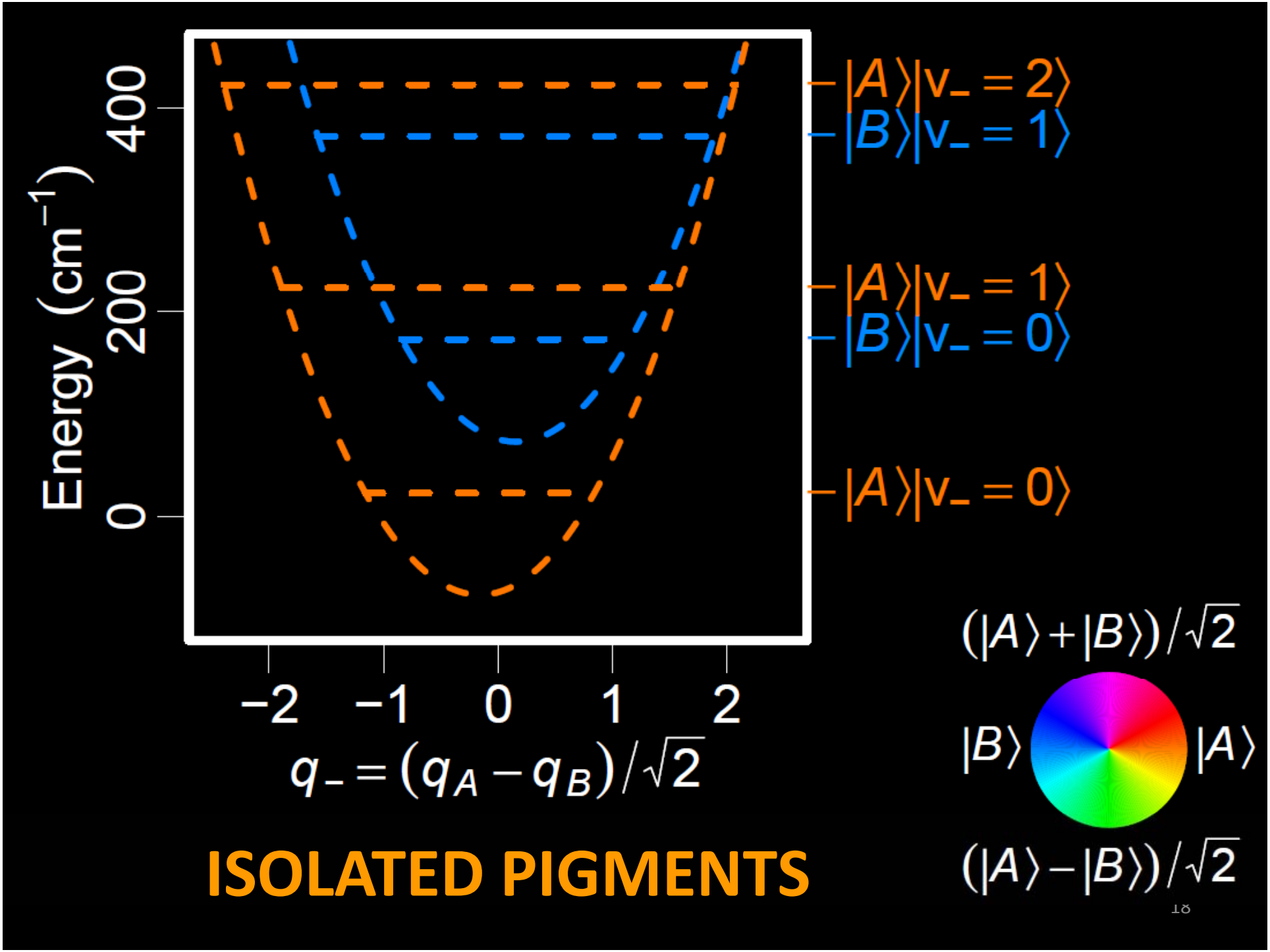
neglect coupling J

$$V_A(q_-) = (1/2)[\omega q_-^2 - (\Delta + \sqrt{2}\omega d q_-)]$$

$$V_B(q_-) = (1/2)[\omega q_-^2 + (\Delta + \sqrt{2}\omega d q_-)]$$

$$\hat{H}_{vib}^{A(B)} = (1/2)\omega(\hat{p}_-^2) + V_{A(B)}(\hat{q}_-)$$




Energy (cm^{-1})
400
200
0
$|A\rangle|v_- = 2\rangle$
$|B\rangle|v_- = 1\rangle$
$|A\rangle|v_- = 1\rangle$
$|B\rangle|v_- = 0\rangle$
$|A\rangle|v_- = 0\rangle$
−2
−1
0
1
2
$q_- = (q_A - q_B)/\sqrt{2}$
$(|A\rangle + |B\rangle)/\sqrt{2}$
$|B\rangle$
$|A\rangle$
$(|A\rangle - |B\rangle)/\sqrt{2}$
ISOLATED PIGMENTS

ADIABATIC APPROXIMATION (EXCITONS)

neglect $\hat{p}_-$, treat operator $\hat{q}_-$ as parameter q_-

$$\hat{H}_{elec}(q_-) = \begin{bmatrix} V_A(q_-) & J \\ J & V_B(q_-) \end{bmatrix}$$

$$\hat{H}_{elec}(q_-)\left|\psi^{+/-}_{elec}(q_-)\right\rangle = E^{+/-}_{elec}(q_-)\left|\psi^{+/-}_{elec}(q_-)\right\rangle$$

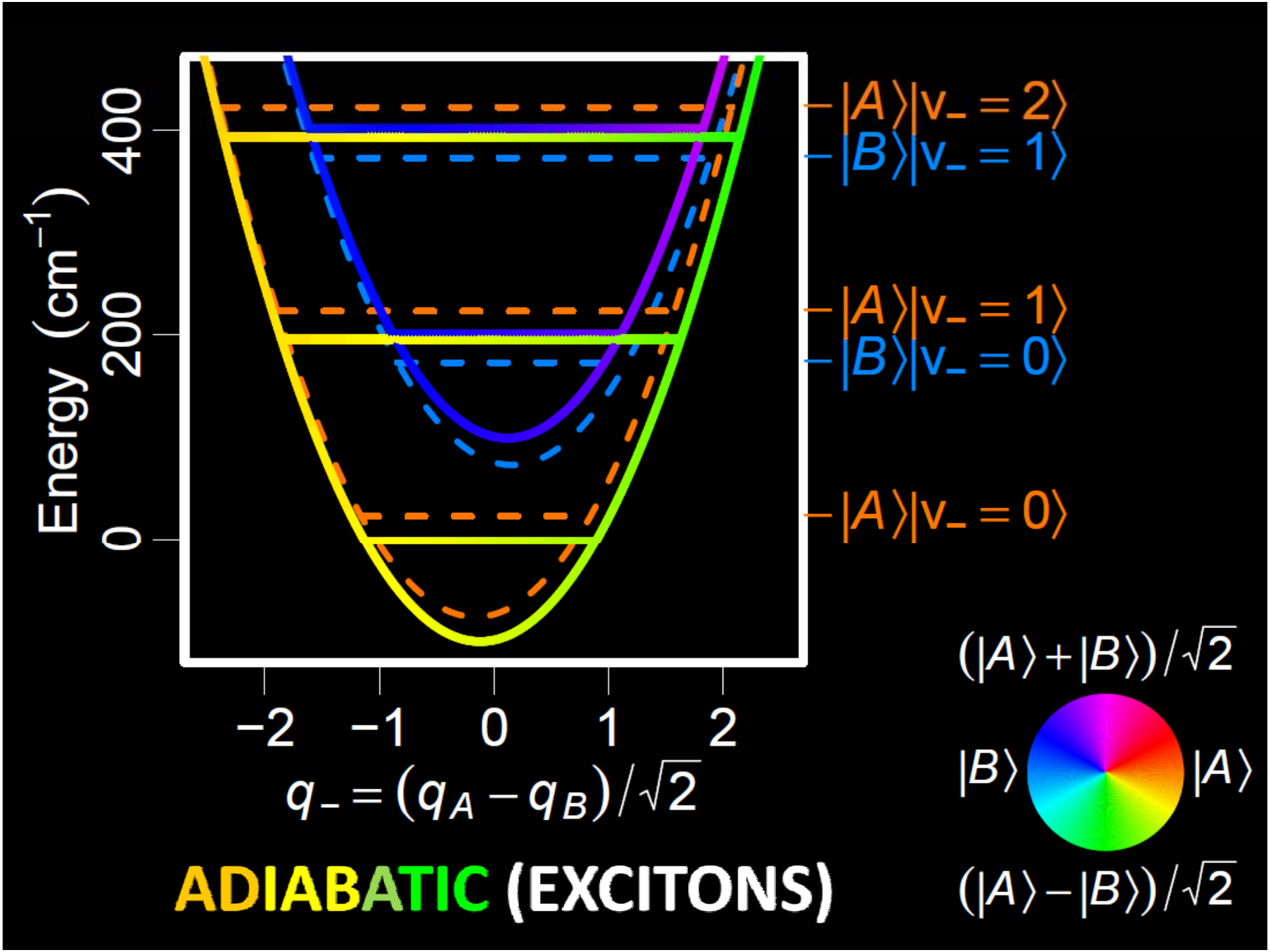
$$E^{+/-}_{elec}(q_-) = [V_A(q_-) + V_B(q_-)]/2 \pm \sqrt{(\Delta/2 + \omega d q_-/\sqrt{2})^2 + J^2}$$

$$\Delta_{EX} = E^{+}_{elec}(q_- = 0) - E^{-}_{elec}(q_- = 0)$$

$(|A\rangle + |B\rangle)/\sqrt{2}$

$|B\rangle$ $|A\rangle$

$(|A\rangle - |B\rangle)/\sqrt{2}$


Energy (cm^{-1})
400
200
0
$|A\rangle|v_- = 2\rangle$
$|B\rangle|v_- = 1\rangle$
$|A\rangle|v_- = 1\rangle$
$|B\rangle|v_- = 0\rangle$
$|A\rangle|v_- = 0\rangle$
−2
−1
0
1
2
$q_- = (q_A - q_B)/\sqrt{2}$
$(|A\rangle + |B\rangle)/\sqrt{2}$
$|B\rangle$
$|A\rangle$
$(|A\rangle - |B\rangle)/\sqrt{2}$
ADIABATIC (EXCITONS)

ADIABATIC APPROXIMATION (EXCITONS)

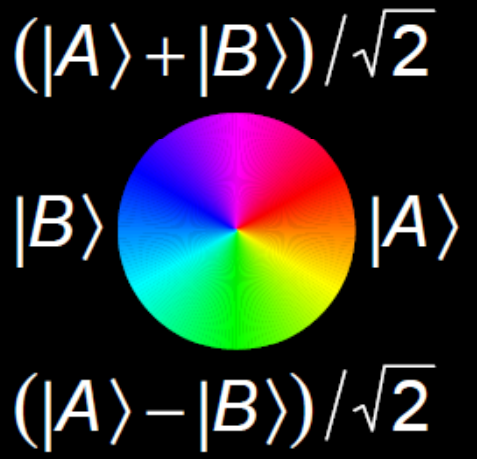
$$\left|\psi^{+}_{elec}(q_{-})\right\rangle = s(q_{-})\left|A\right\rangle + c(q_{-})\left|B\right\rangle$$

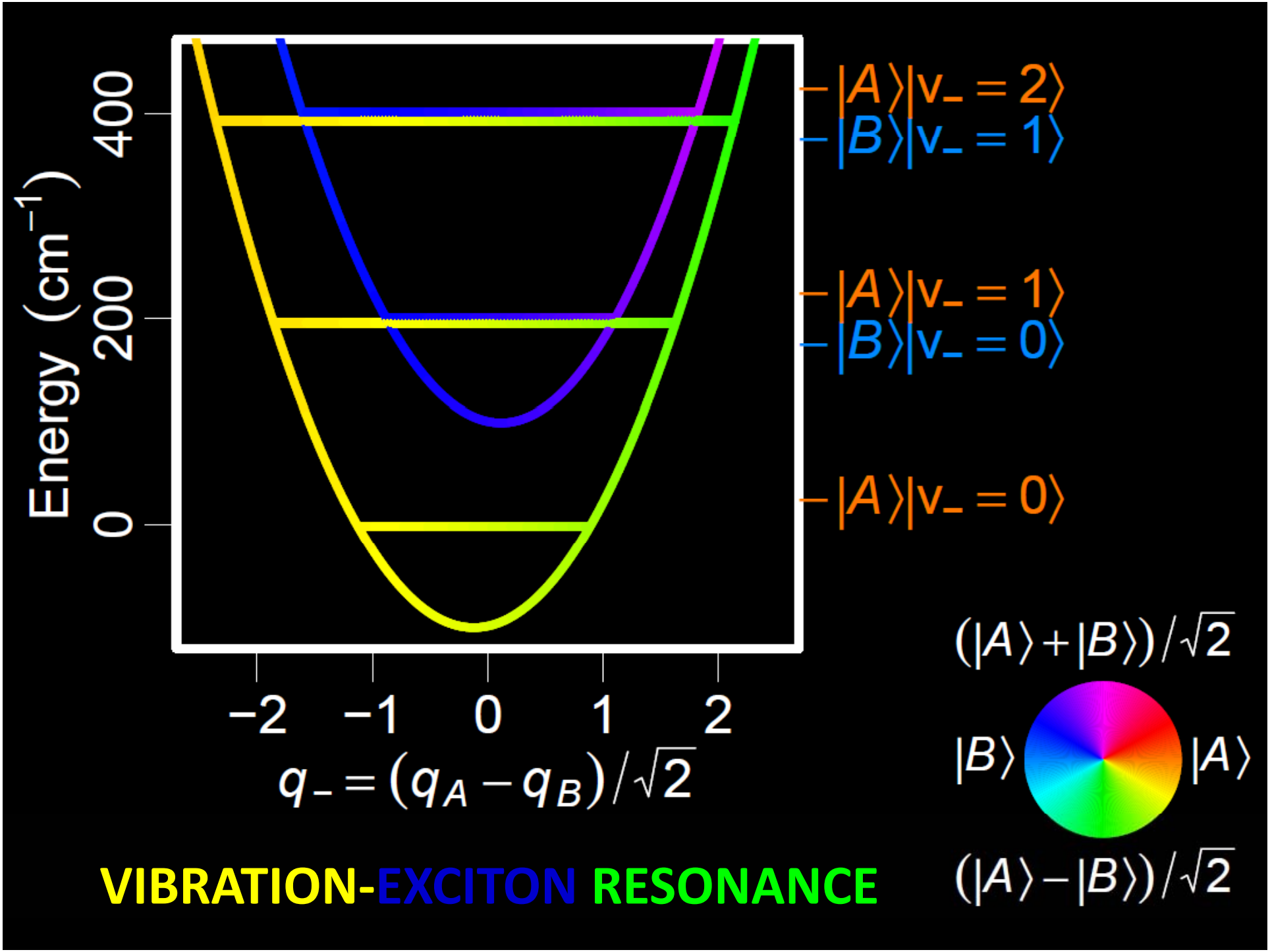
$$\left|\psi^{-}_{elec}(q_{-})\right\rangle = c(q_{-})\left|A\right\rangle - s(q_{-})\left|B\right\rangle$$

$$\hat{H}^{+/-}_{vib} = (1/2)\omega(\hat{p}^{2}_{-}) + E^{+/-}_{elec}(\hat{q}_{-})$$

$$\left|\psi^{+}_{vib-elec}(q_{-})\right\rangle = \left|\psi^{+}_{elec}(q_{-})\right\rangle\left|\psi^{+}_{v}(q_{-})\right\rangle$$

$$\left|\psi^{-}_{vib-elec}(q_{-})\right\rangle = \left|\psi^{-}_{elec}(q_{-})\right\rangle\left|\psi^{-}_{v}(q_{-})\right\rangle$$




Energy (cm^{-1})
0
200
400
−2
−1
0
1
2
$q_- = (q_A - q_B)/\sqrt{2}$
$|A\rangle|v_- = 2\rangle$
$|B\rangle|v_- = 1\rangle$
$|A\rangle|v_- = 1\rangle$
$|B\rangle|v_- = 0\rangle$
$|A\rangle|v_- = 0\rangle$
$(|A\rangle + |B\rangle)/\sqrt{2}$
$|B\rangle$
$|A\rangle$
$(|A\rangle - |B\rangle)/\sqrt{2}$
VIBRATION-EXCITON RESONANCE

NON- ADIABATIC

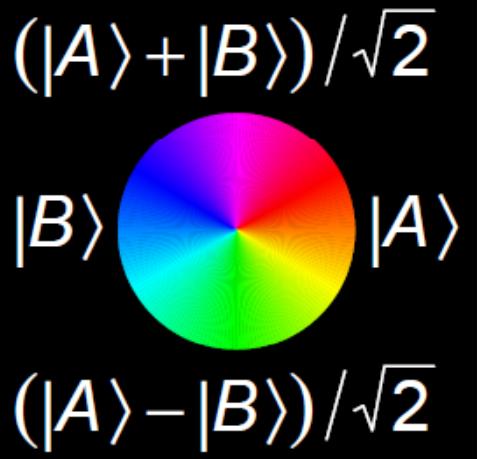
$$(1/2)\omega(\hat{p}_-^2)\left|\psi_{elec}^-(q_-)\right\rangle\left|\psi_v^-(q_-)\right\rangle$$

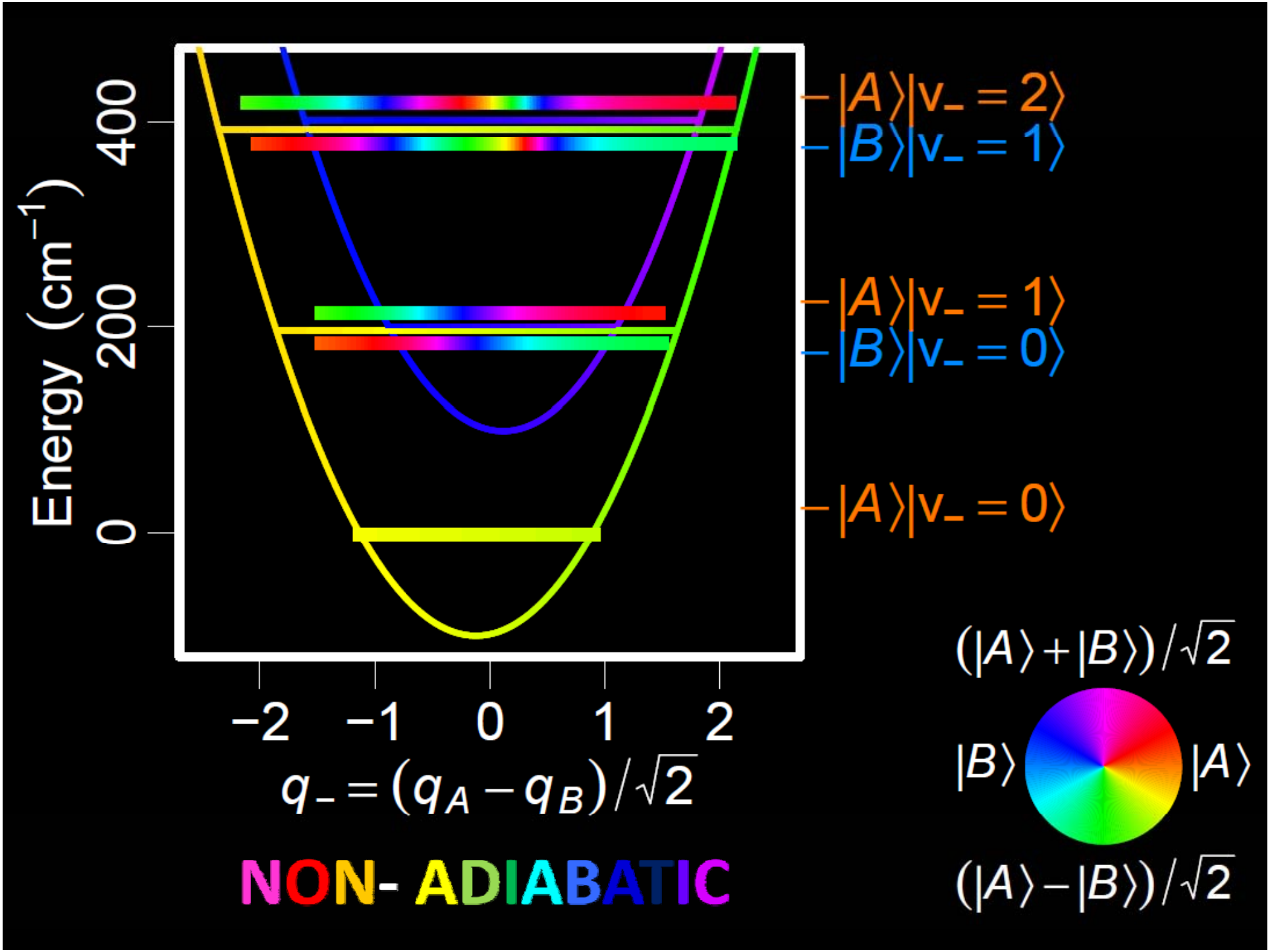
$$=(1/2)\omega(-\hbar^2)\left|\frac{\partial^2}{\partial^2 q_-}\psi_{elec}^-(q_-)\right\rangle\left|\psi_v^-(q_-)\right\rangle$$

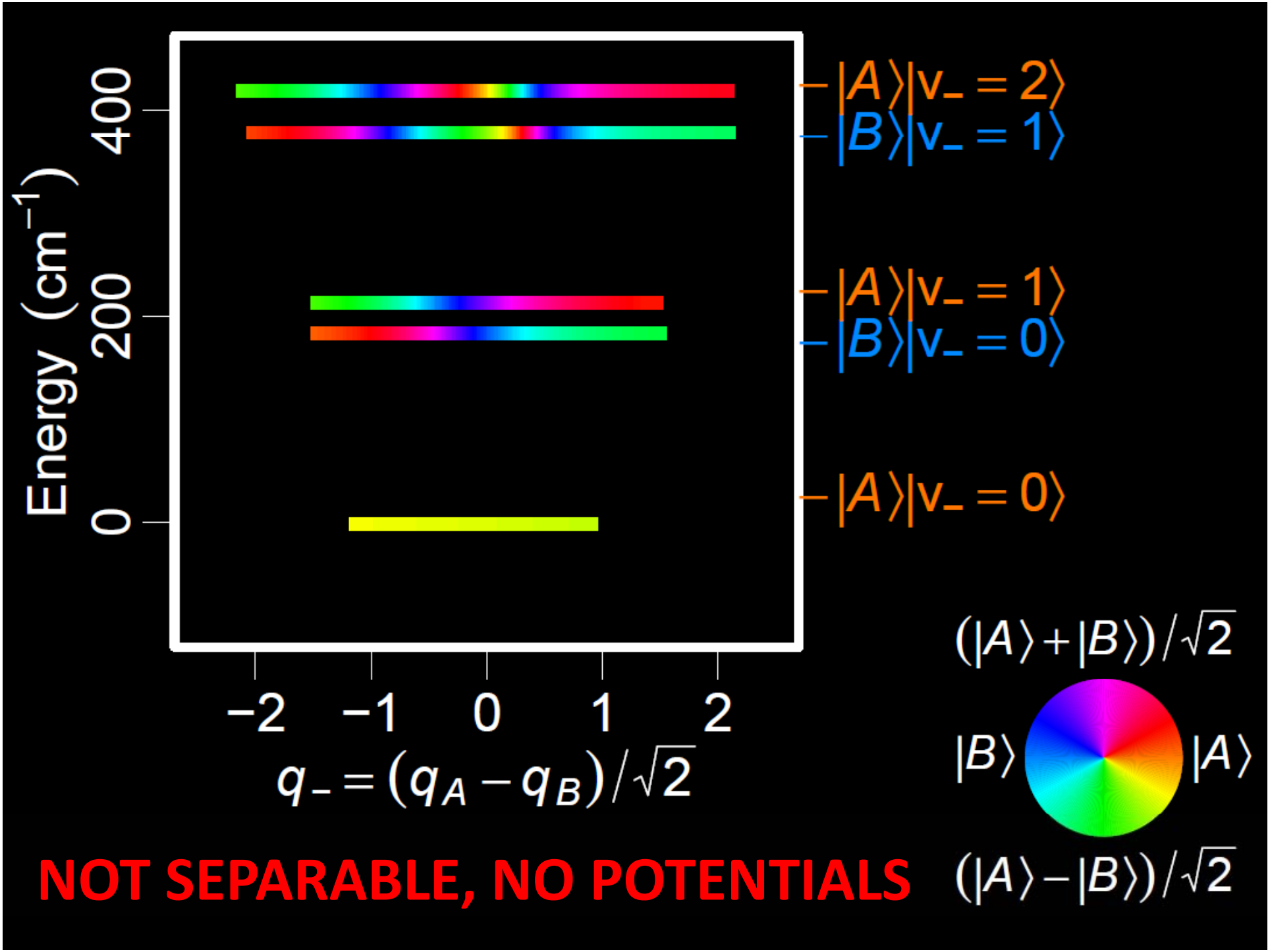
$$+(2/2)\omega(-\hbar^2)\left|\frac{\partial}{\partial q_-}\psi_{elec}^-(q_-)\right\rangle\left|\frac{\partial}{\partial q_-}\psi_v^-(q_-)\right\rangle+\ldots$$

$$\left|\psi_{vib-elec}^n(q_-)\right\rangle=\chi_A^n(q_-)|A\rangle$$

$$+\chi_B^n(q_-)|B\rangle$$

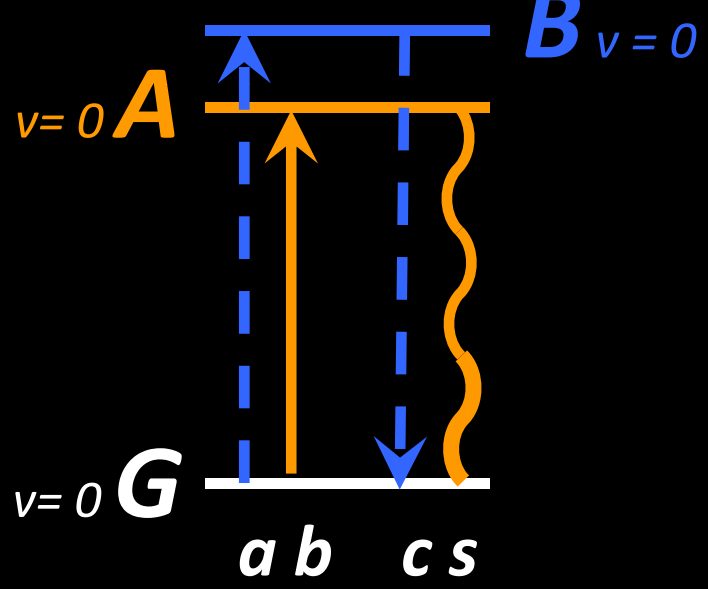



Energy (cm^{-1})
400
200
0
−2
−1
0
1
2
$q_- = (q_A - q_B)/\sqrt{2}$
$|A\rangle|v_- = 2\rangle$
$|B\rangle|v_- = 1\rangle$
$|A\rangle|v_- = 1\rangle$
$|B\rangle|v_- = 0\rangle$
$|A\rangle|v_- = 0\rangle$
$(|A\rangle + |B\rangle)/\sqrt{2}$
$|B\rangle$
$|A\rangle$
$(|A\rangle - |B\rangle)/\sqrt{2}$
NON- ADIABATIC


Energy (cm^{-1})
400
200
0
−2
−1
0
1
2
$q_- = (q_A - q_B)/\sqrt{2}$
$|A\rangle|v_- = 2\rangle$
$|B\rangle|v_- = 1\rangle$
$|A\rangle|v_- = 1\rangle$
$|B\rangle|v_- = 0\rangle$
$|A\rangle|v_- = 0\rangle$
$(|A\rangle + |B\rangle)/\sqrt{2}$
$|B\rangle$
$|A\rangle$
$(|A\rangle - |B\rangle)/\sqrt{2}$
NOT SEPARABLE, NO POTENTIALS

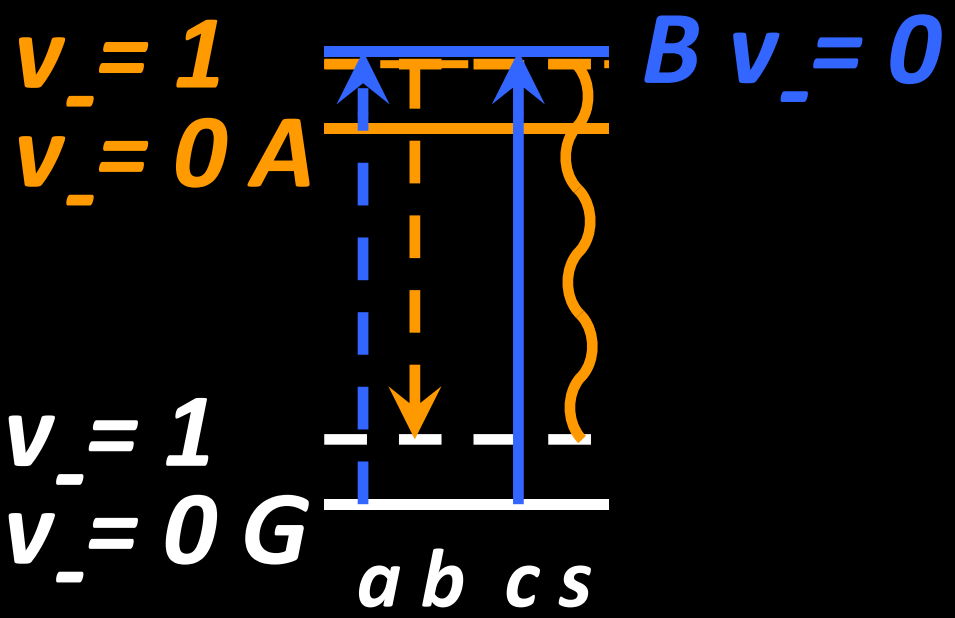
WAVE MIXING DIAGRAMS

ELECTRONIC COHERENCE



EXCITED ELECTRONIC STATE

ANTI-CORRELATED VIBRATION



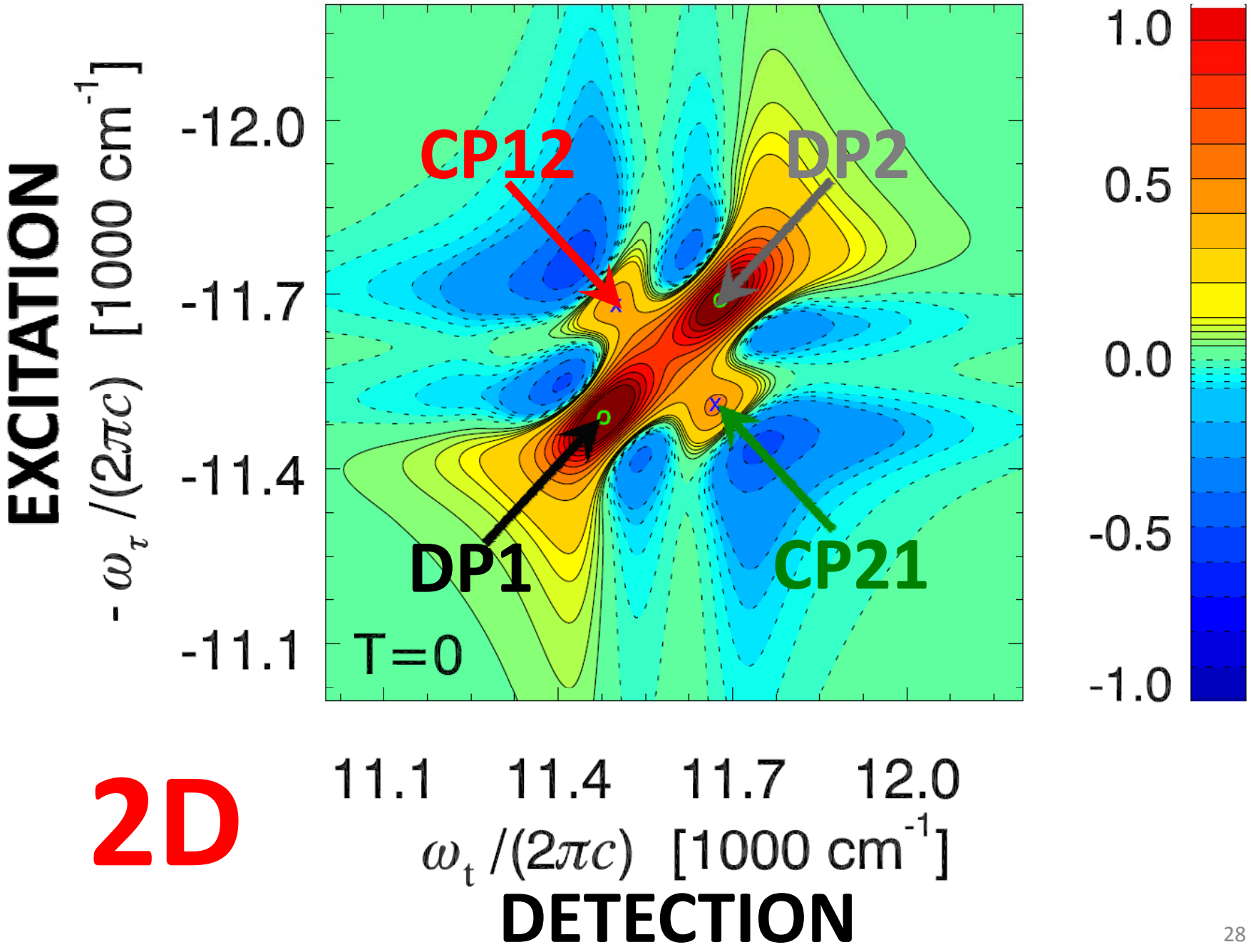
GROUND ELECTRONIC STATE

DIMER MODEL (loosely based on FMO)

correlated dephasing for 2D peakshape
critically damped Brownian oscillator
λ = 30 cm^{-1} (Stokes' shift)
ω = 70 cm^{-1} (*BChl a* phonon sideband)

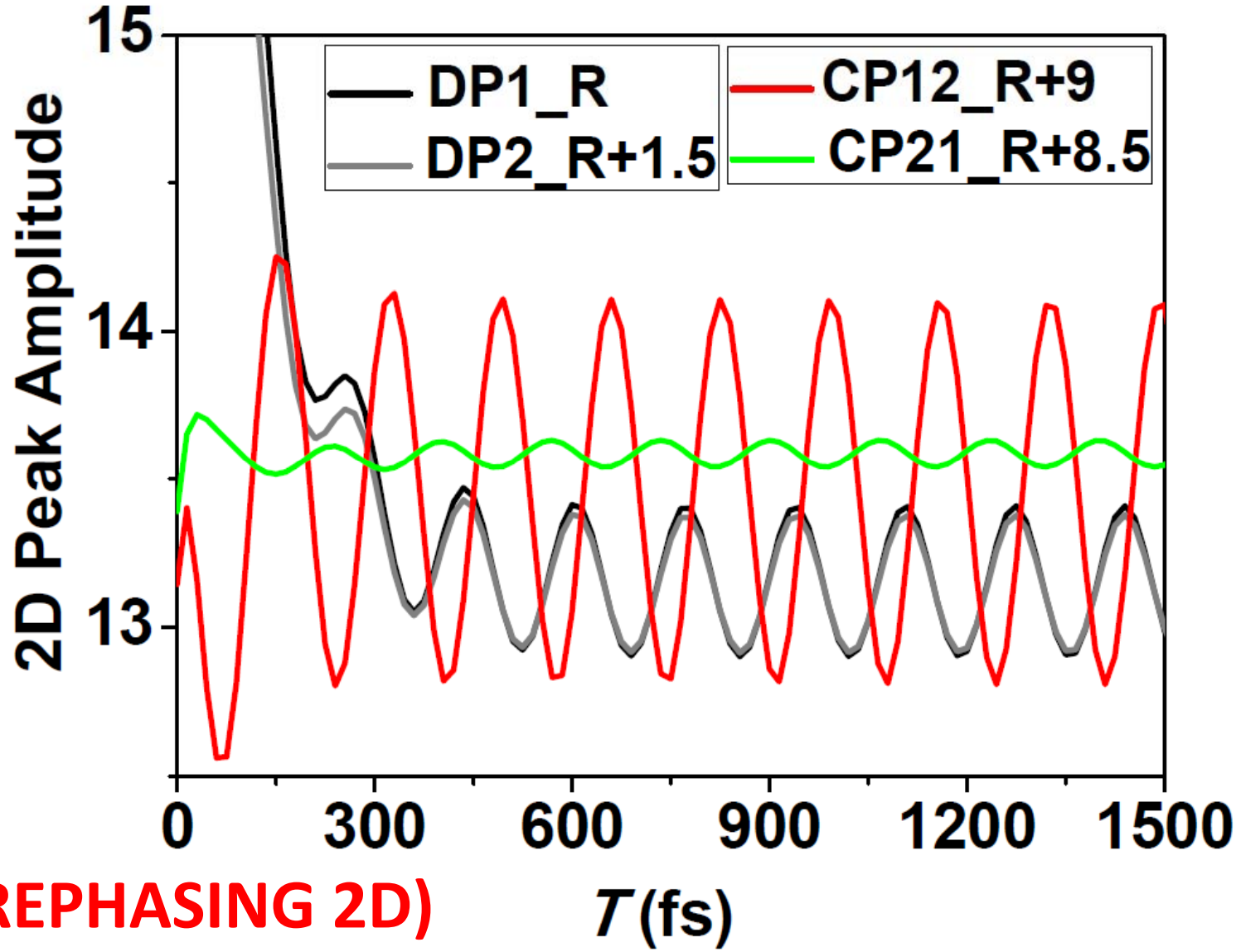
anti-correlated inhomogeneity
(Struve FMO anisotropy beat decay)

$$\sigma_{\Delta}^{2} = \left\langle (\Delta - \overline{\Delta})^{2} \right\rangle \approx \mathbf{34\ cm^{-1}}$$


CP12
DP2
DP1
CP21
T=0
EXCITATION
$-\omega_\tau/(2\pi c)$ [1000 cm^{-1}]
-12.0
-11.7
-11.4
-11.1
1.0
0.5
0.0
-0.5
-1.0
11.1
11.4
11.7
12.0
$\omega_t/(2\pi c)$ [1000 cm^{-1}]
DETECTION

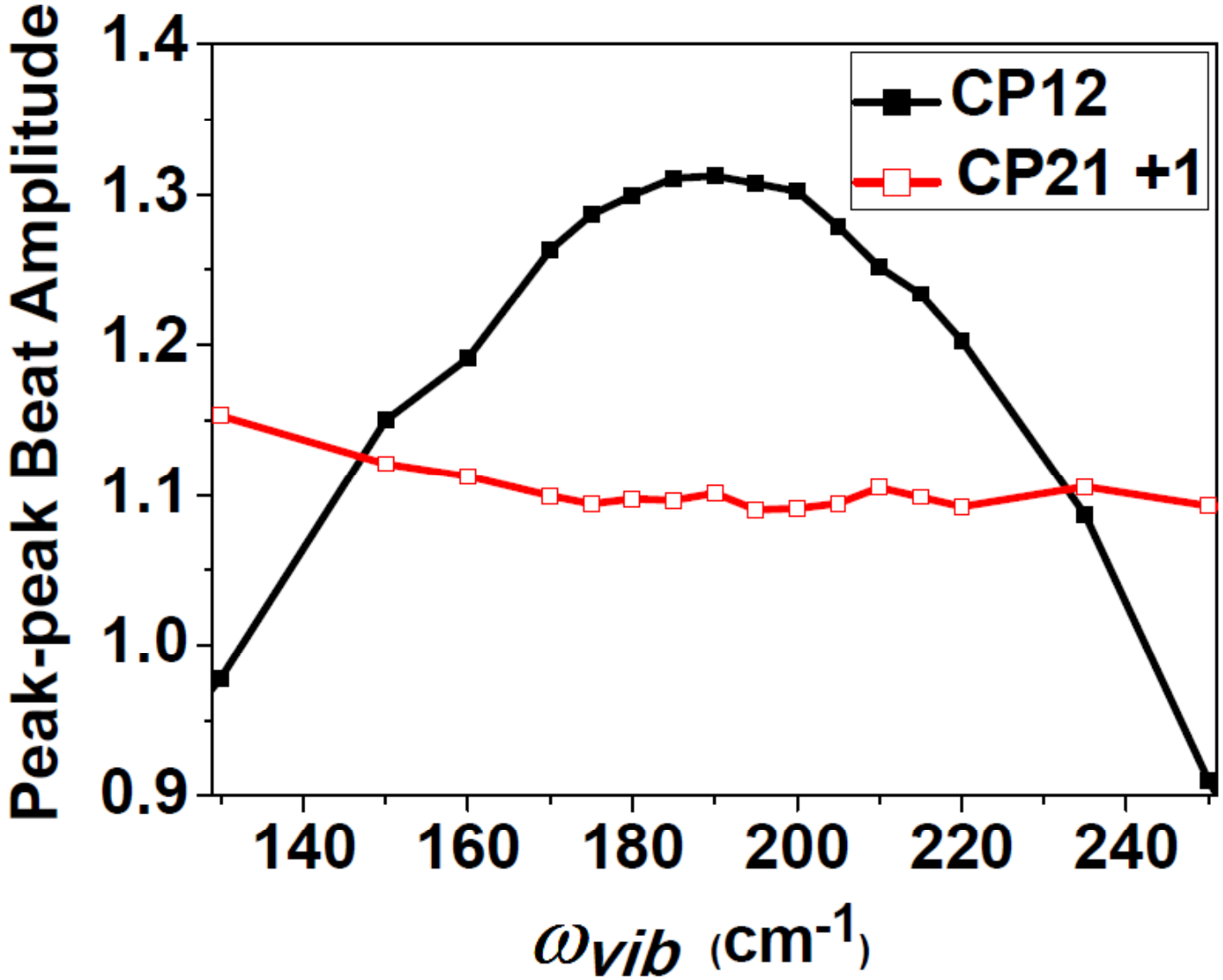
2D

BEATS ON GROUND ELECTRONIC STATE: CP12/CP21 180°, DP beat, DP/CP 90°

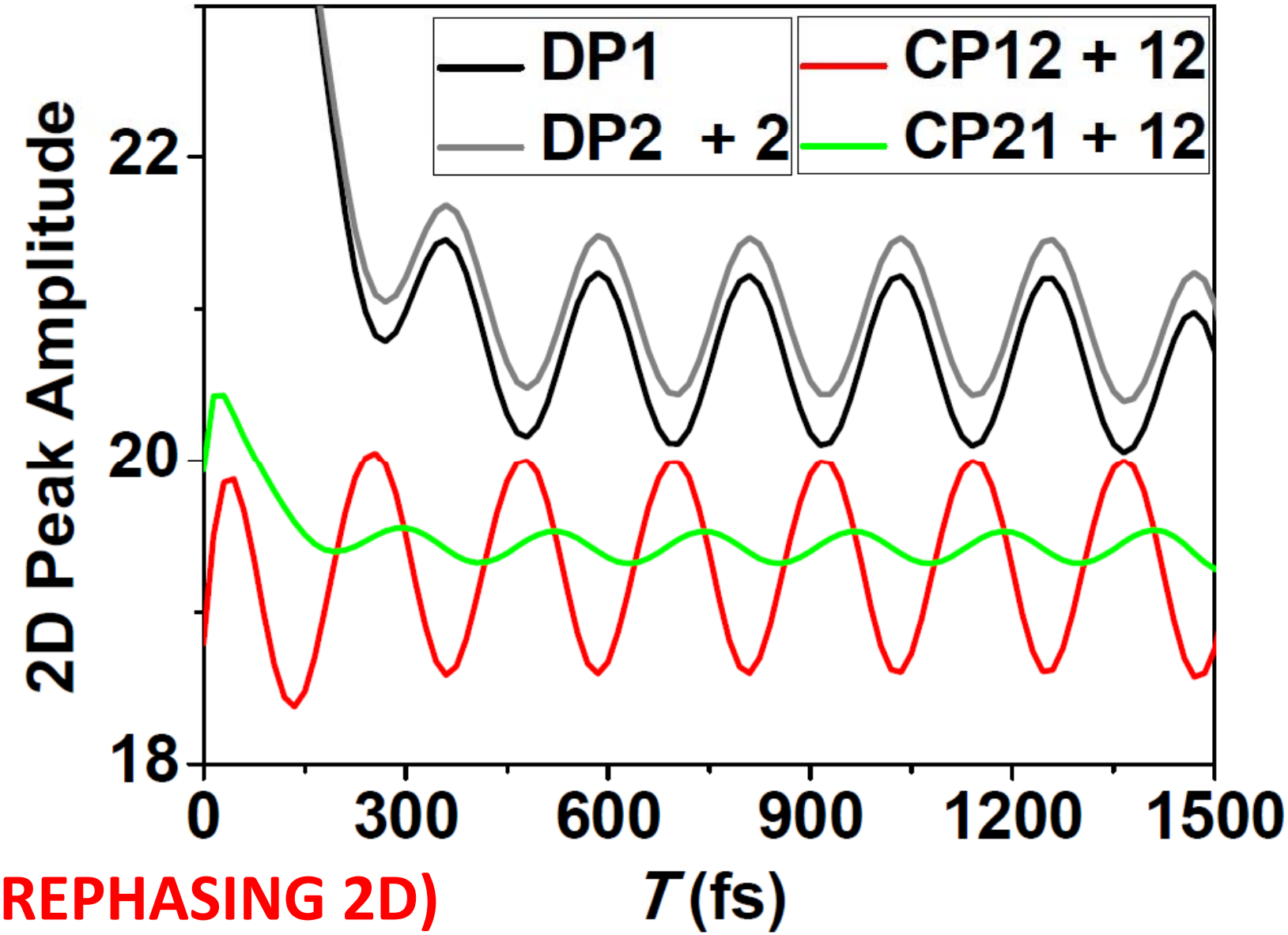


(REPHASING 2D)

Enhancement of cross-peaks at Δ_{EX} = 200 cm^{-1}



Δ_{EX} = 230 cm^{-1} **NON-RESONANT** ω = 150 cm^{-1}



(REPHASING 2D)

FMO CP 90° frequencies *MUST* match BChl a

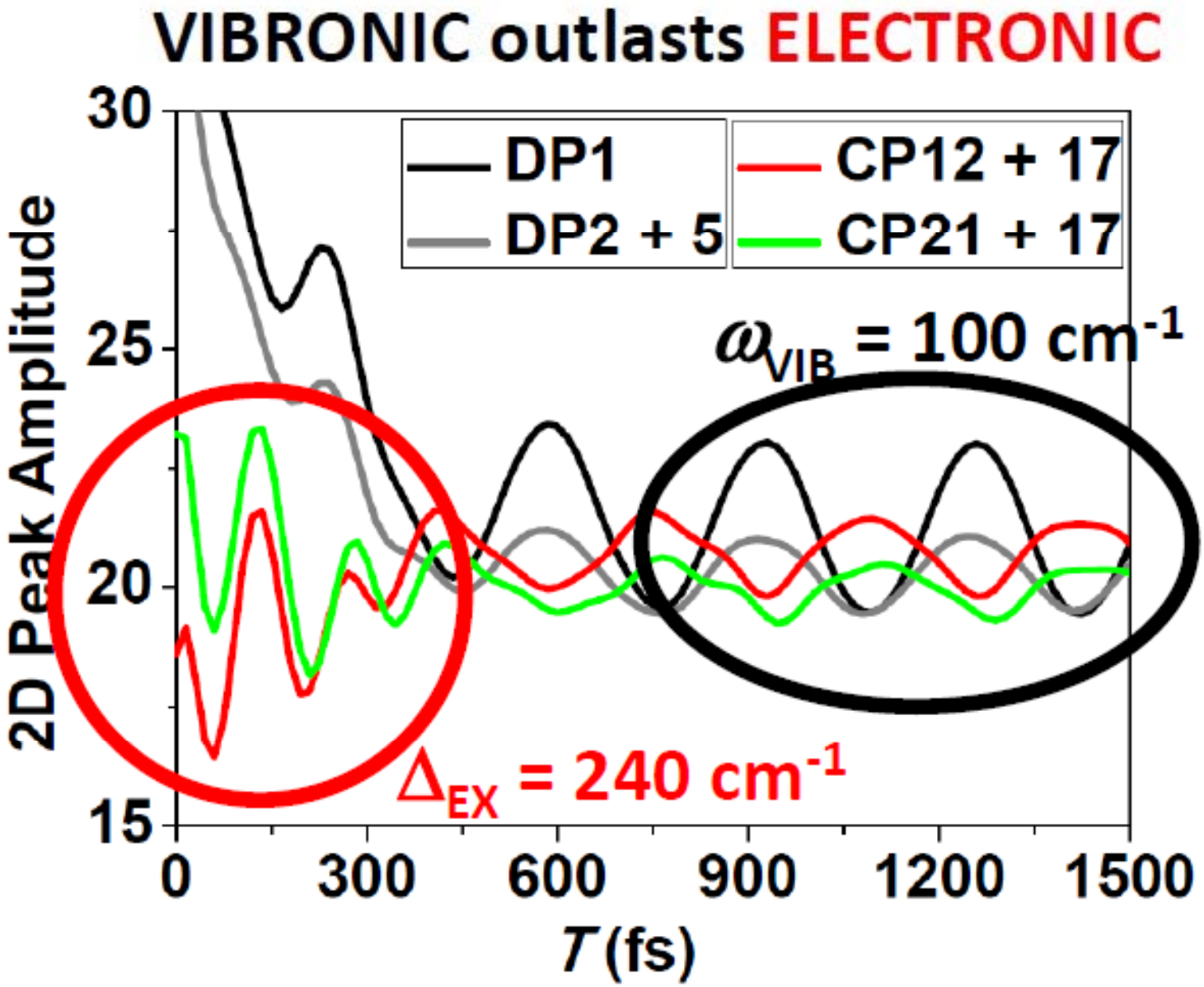
FMO 2D Cross-Peak	*BChl a* vibration ω
87 (CP35)	84(±2), 82(±3)
107(±2) (CP46)	
147 (±1) (CP24)	
161.3(±0.7) for CP12 159(±3) (CP36)	**164(±3)**
198.7(±1.4) for CP13	**196(±3)**
248 (CP13)	243(±2)
263(±2) (CP26) 264(±2) (CP37)	263(±2)

Bocian, Freiberg, Small, Avarmaa , van Grondelle and van Amerongen Groups

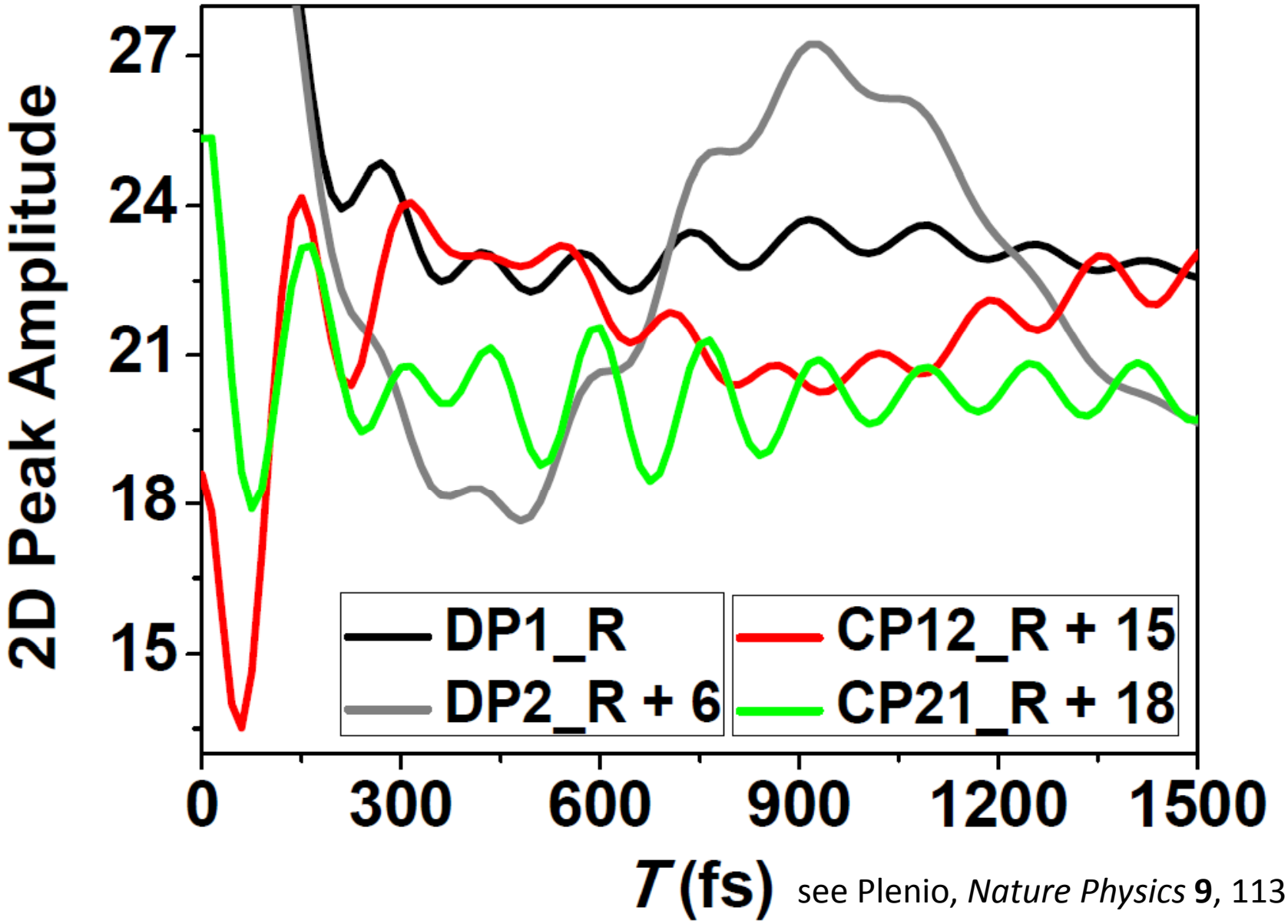
7 of 9 FMO CP frequencies match *BChl a*

FMO 2D Cross-Peak	*BChl a* vibration ω
87 (CP35)	84(±2), 82(±3)
107(±2) (CP46)	
147 (±1) (CP24)	
161.3(±0.7) for CP12 159(±3) (CP36)	164(±3)
198.7(±1.4) for CP13	196(±3)
248 (CP13)	243(±2)
263(±2) (CP26) 264(±2) (CP37)	263(±2)

Bocian, Freiberg, Small, Avarmaa , van Grondelle and van Amerongen Groups


VIBRONIC outlasts ELECTRONIC
DP1
DP2 + 5
CP12 + 17
CP21 + 17
ω_{VIB} = 100 cm^{-1}
Δ_{EX} = 240 cm^{-1}
2D Peak Amplitude
30
25
20
15
0
300
600
900
1200
1500
T (fs)

VIBRONIC obscures SIGNATURES



see Plenio, *Nature Physics* **9**, 113 (2013)

ELECTRONIC BEATS at Δ_{EX} FOR ~200 fs

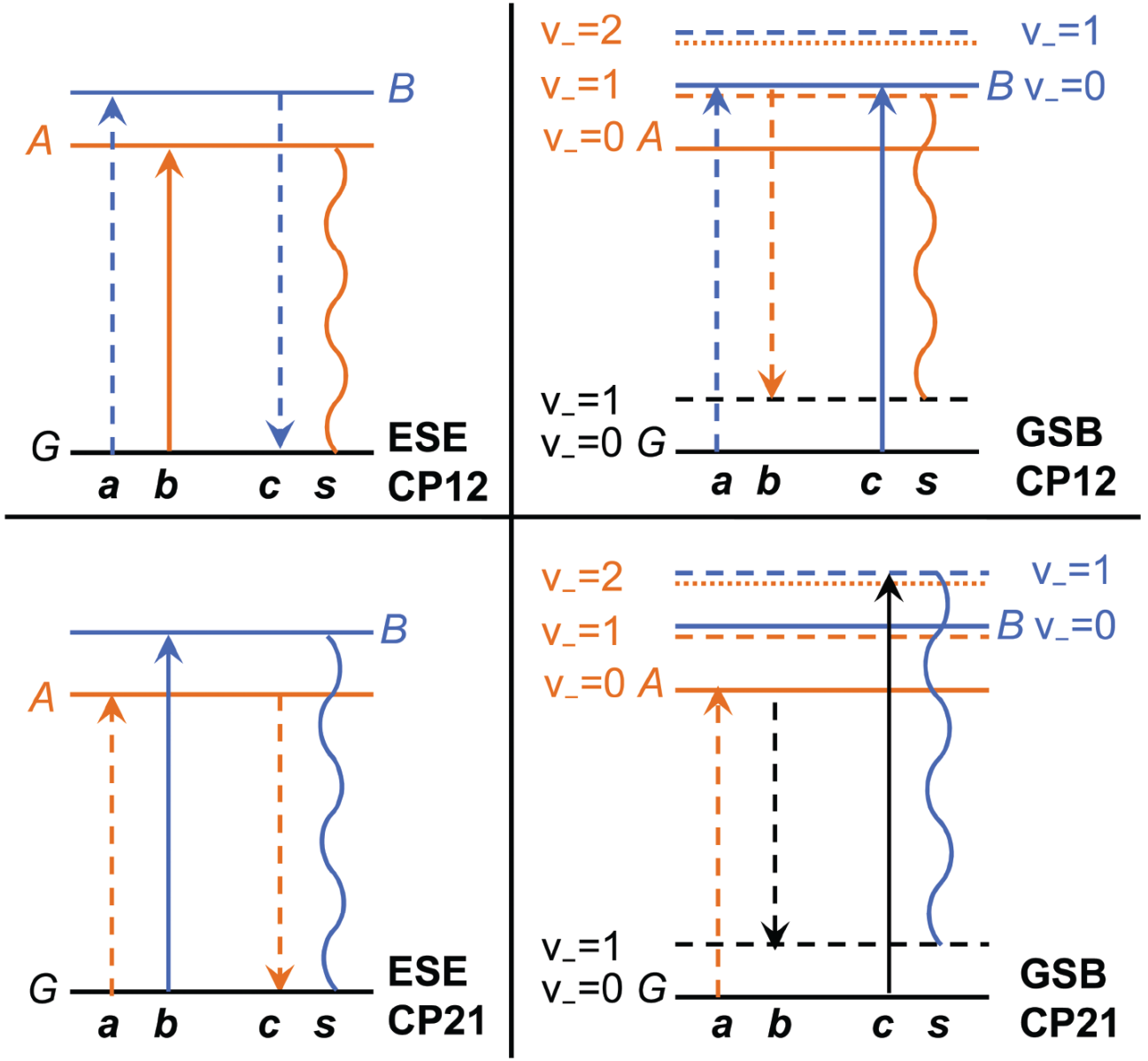
POSSIBLY SURVIVED BY VIBRONIC BEATS at $\Delta_{EX} \sim \omega_{vib}$

ANTI-CORRELATED VIBRATIONS at ω_{vib} on the GROUND ELECTRONIC STATE *OUTLIVE EVERYTHING ELSE OVER 2+ ps*

2D Signature	System	Theory	Computation	NA-GS-vib
DP diagonal and anti-diagonal widths anti-correlated (ABS)	PERY dye(44)	EC (13) FC-vib (40, 44)	EC (13) FC-vib (40, 44)	~ (Fig. S3)
DP amplitude anti-correlated to diagonal width osc. (ABS)	cyanine dye (45)	EC (13)	EC (13) FC-vib (45)	No (Fig. S3)
DP amplitude anti-correlated to ratio* of diagonal/anti-diagonal widths (ABS)	FMO (26) polymer (46)			~ (Fig. S3)
DP osc. (NR)	LHC II (63)	EC (64)	EC (64)	Yes (Fig. 4)
180^{o} phase between CP12 and CP21 osc. (R) †	PE545 (37) PC645 (37)	EC-No (38)	EC-No (38) FC-vib-No (38)	Yes (Fig. 4)
DP osc. (R)	FMO (51)	EC-No QT (65)	QT (65)	Yes (Fig. 4)
90^{o} phase between CP12 and DP2 osc. (R)	FMO (51)	EC-No QT (51)	QT (65)-No‡	Yes (Fig. 4)
Negative CP12 osc. frequency (R)	PC645 (30)	EC (30)		Yes (see Supporting Text & Fig. S1)
Polarization sequence (NR)	LHC II (33)			Yes (see Supporting Text & Fig. S1)

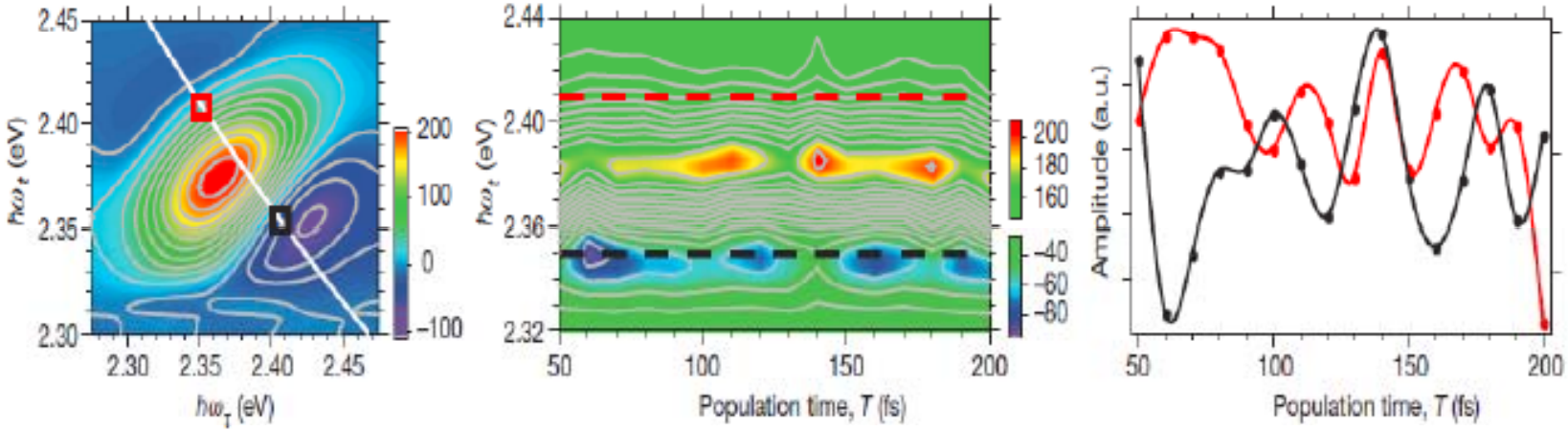
CAN WE DISTINGUISH GROUND STATE VIBRATIONS FROM ELECTRONIC COHERENCE?

CROSS-PEAK BEAT ASYMMETRY



CROSS-PEAK BEAT ASYMMETRY

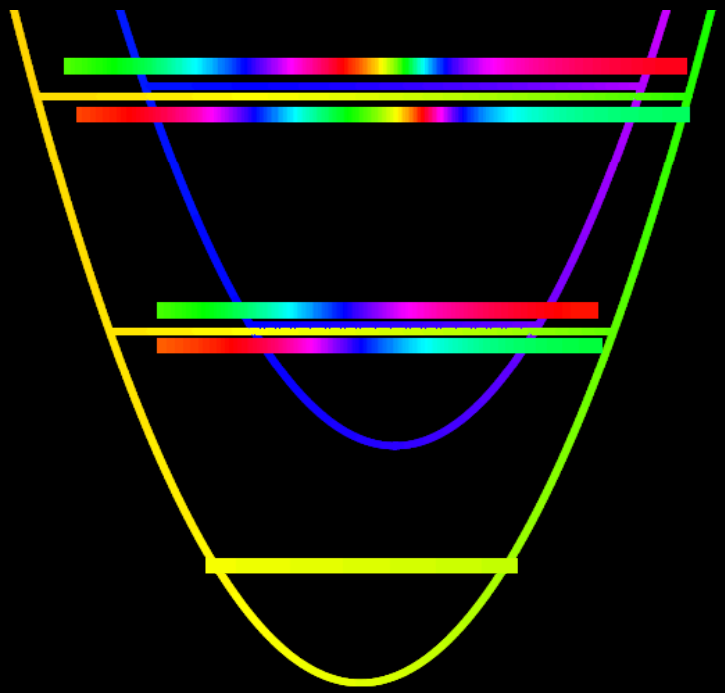
PE545: Cryptophyte marine algae



- *NOT predicted by electronic coherence or QT*
- CP12 is the cross-peak type reported in FMO
- asymmetry observed in PE545
- *anti-correlated vibrations dominate by 50 fs*

Collini et al., Nature (2010) Vol. 463, 644-648

PHOTOSYNTHETIC ENERGY TRANSFER *via* A NEW KIND OF NON-ADIABATIC FUNNEL



Tiwari, Peters & Jonas
PNAS 110, 1203 (2013)

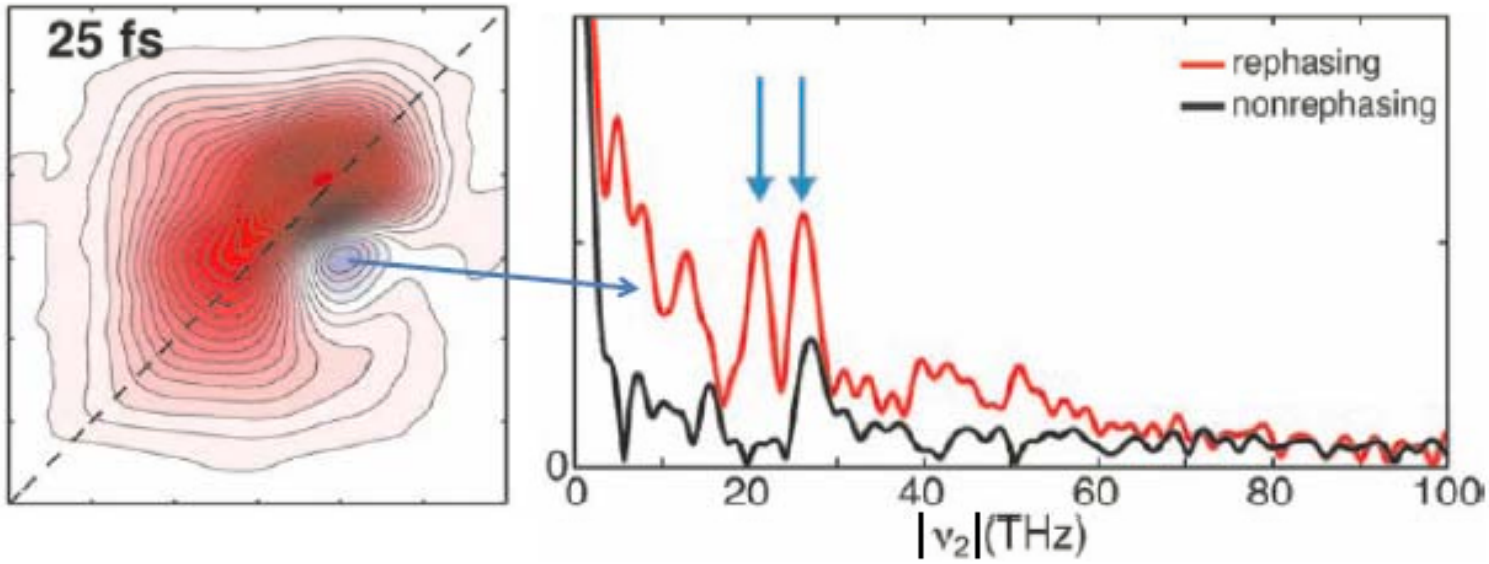
- not "conical" - adiabatic surfaces do not intersect because dipole-dipole coupling non-zero while pigments held by protein
- nested – small changes in vibrational equilibrium upon electronic excitation put surfaces inside each other
- unavoidable – change in electronic character within half a vibrational period everywhere

Acknowledgments

- National Science Foundation
- Janus Research Cluster – U. Colorado & NSF

Signatures of Photosynthetic Energy Transfer

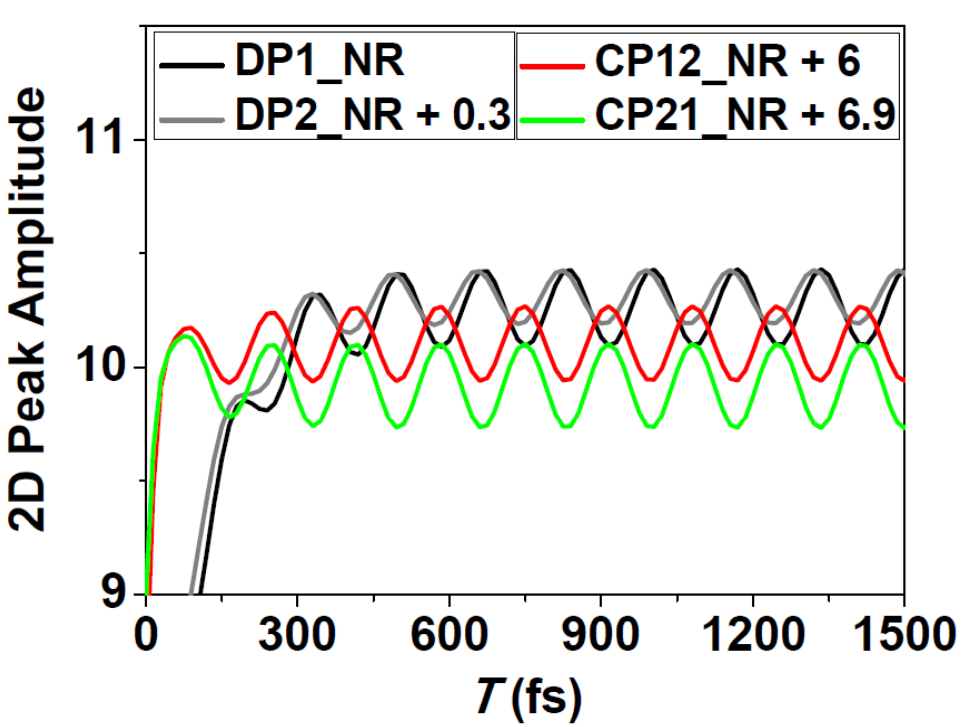
PC645: Cryptophyte marine algae

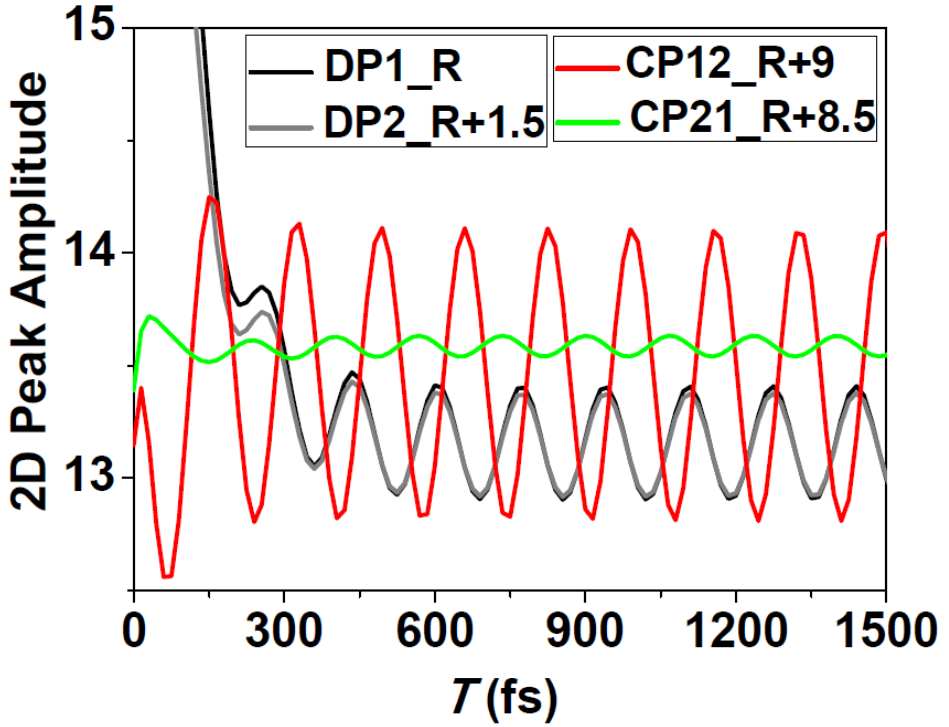


- CP *not* beating in non-rephasing 2D (S/N 2.5:1)

Turner et al., Phys. Chem. Chem. Phys. (2012) Vol. 14, 4857-4874

NON-REPHASING 2D *vs.* REPHASING 2D





Predicts that cross-peak beats will be seen in the non-rephasing 2D spectrum with amplitude about 5x less than rephasing 2D S/N currently 2.5:1 in rephasing …