Julius-Maximilians-
UNIVERSITÄT WÜRZBURG

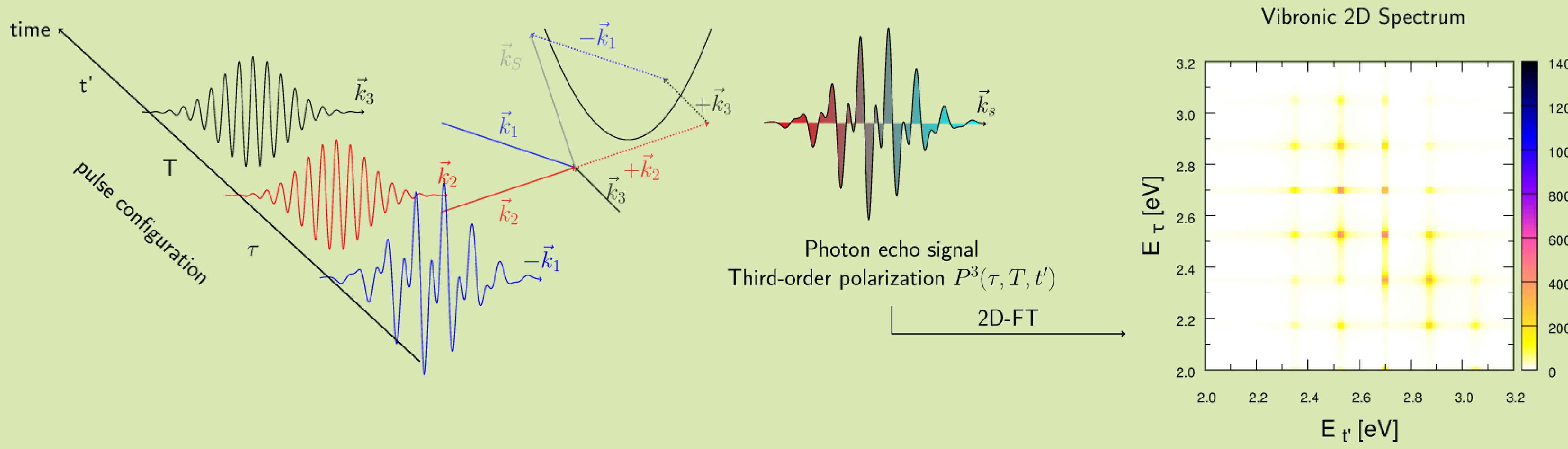
Fakultät für Chemie und Pharmazie
PHYSIKALISCHE UND THEORETISCHE CHEMIE

Wave-packet approach to two-dimensional vibronic spectroscopy

J. Albert, M. Falge, M. Keß, J. Wehner and V. Engel
Julius-Maximilians-Universität Würzburg

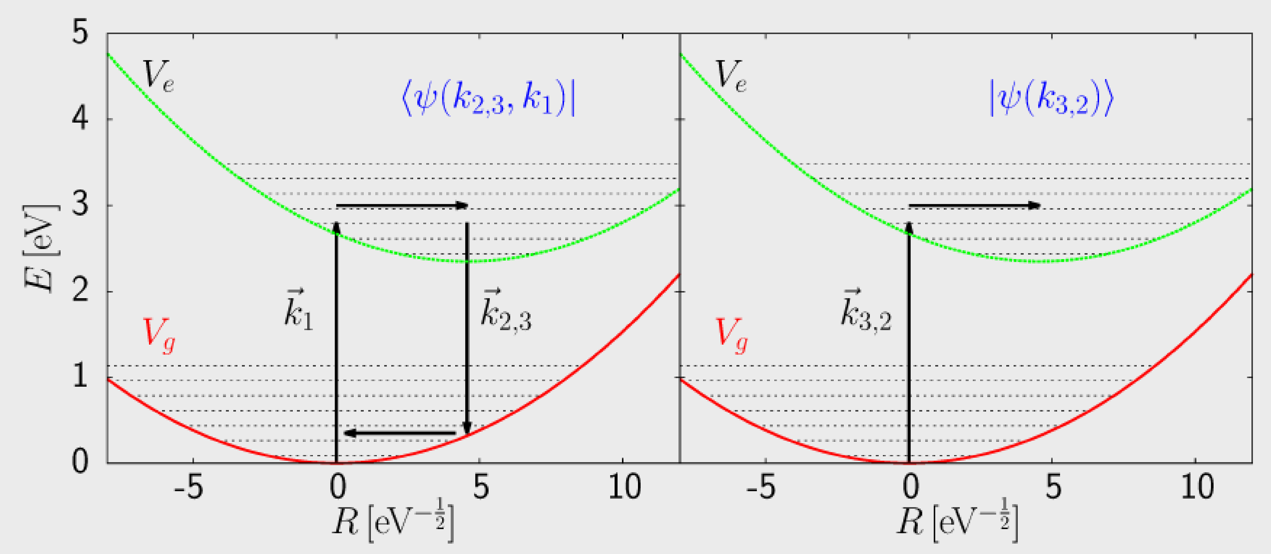
DFG GRK1221

Overview: Two-Dimensional (2D) vibronic Spectroscopy

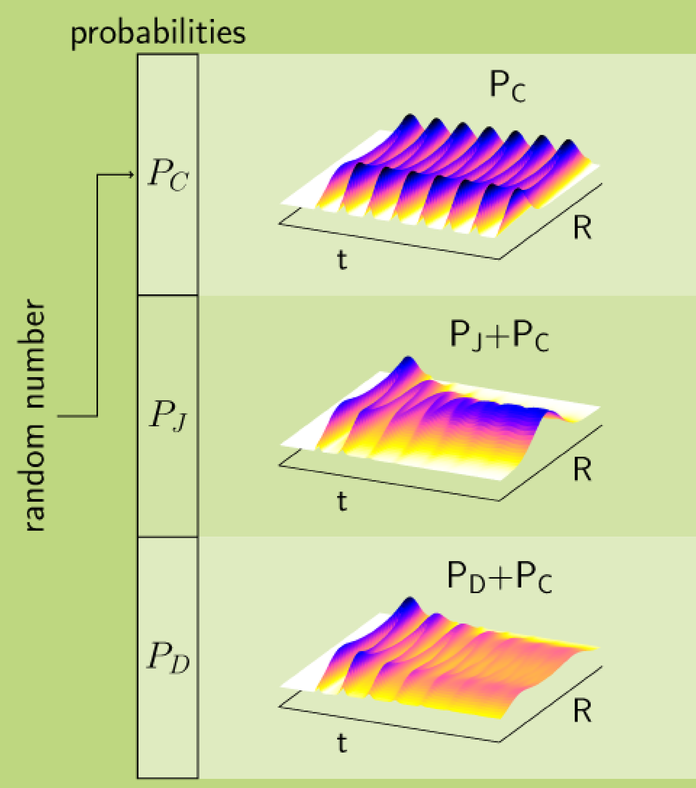


Vibronic Model System (Monomer)

Contribution to Third-order Polarization $P^{(3)} = \langle \psi(k_{3,2}, k_1) \,|\, \hat{\vec{\mu}} \,|\, \psi(k_{3,2}) \rangle$



Quantum Jump Approach



Coherent Evolution (P_C):

$$|\psi(t+dt)\rangle = \frac{\sum_n c_n(t)|n\rangle \, e^{-\frac{iE_n dt}{\hbar}} \, e^{-\frac{\Gamma_n dt}{2}} \, e^{-\frac{\gamma dt}{2}}}{\sqrt{C}}$$

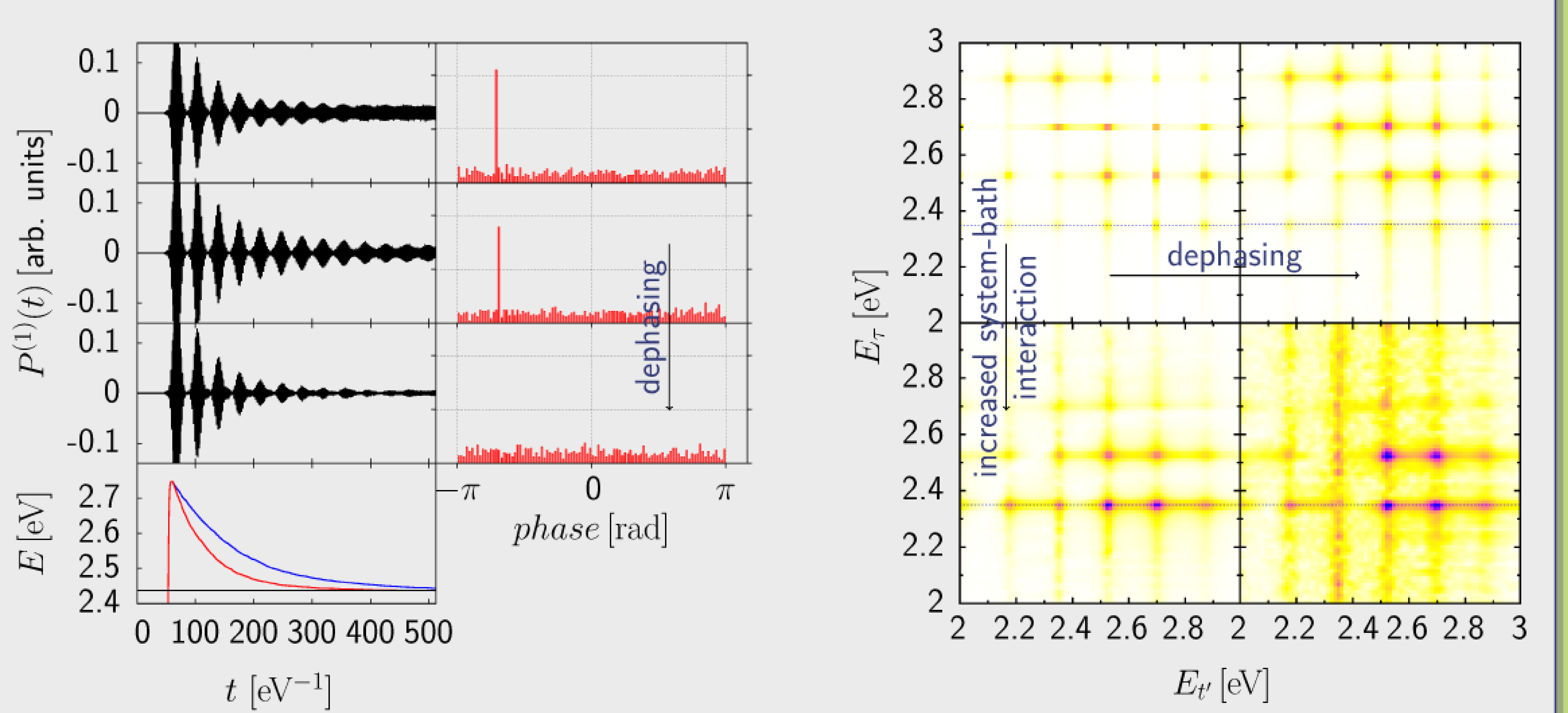
Quantum Jump (P_J):

$$|\psi(t+dt)\rangle = c_n(t) \frac{|m\rangle}{\sqrt{|c_n(t)|^2}}$$

Pure Dephasing (P_D):

$$|\psi(t+dt)\rangle = \sum_n c_n(t) \, e^{-i\delta_n} |n\rangle$$

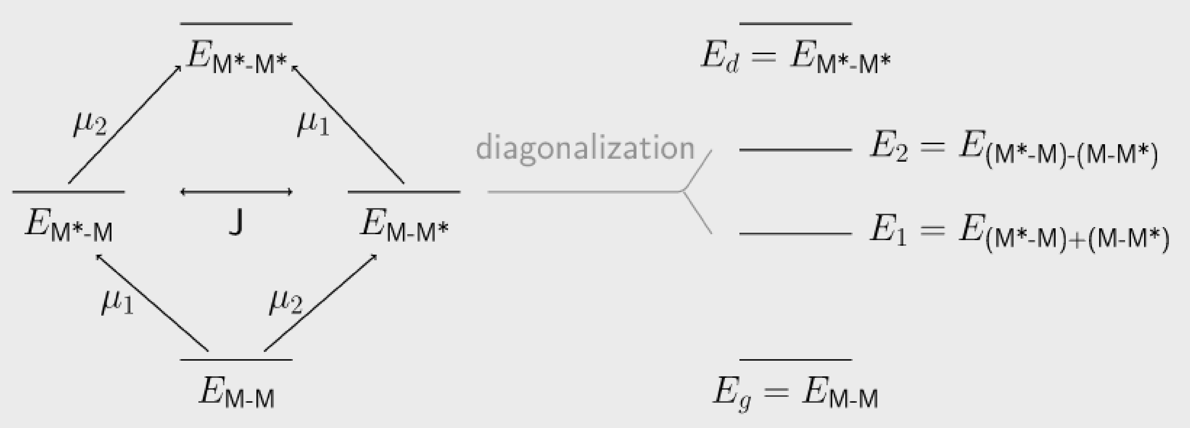
Results: First-order polarization and 2D-spectra



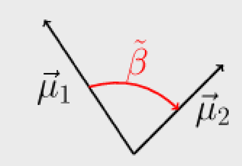
- For stronger system-bath coupling the decay of polarization and mean energy occurs faster.
- For long times the fast oscillation survives and is characterized by the electronic excitation energy.
- Effect of pure dephasing completely destroys polarization.
- Pure dephasing does not alter the peak position.
- Dissipation occurs mainly in E_τ-direction
- Coupling and pure dephasing cause decay and peak broadening of 2D signals.

Homo- & Hetero-Dimer 2D-Spectra

Model System for Homo-Dimer



Dipole orientation



Calculation of Third-Order Polarization

$$\left\langle \psi(k_2,k_1) \middle| \hat{\vec{\mu}} \middle| \psi(k_3) \right\rangle_{\langle\downarrow\uparrow|\hat{\vec{\mu}}|\uparrow\rangle} = \frac{1}{(1+\eta^2)^2} \Big[a^2 \, e^{-it'(E_1-E_g)} \, e^{-i\tau(E_g-E_1)} + ab \, e^{-it'(E_1-E_g)} \, e^{-i\tau(E_g-E_2)} + ba \, e^{-it'(E_2-E_g)} \, e^{-i\tau(E_g-E_1)} + b^2 \, e^{-it'(E_2-E_g)} \, e^{-i\tau(E_g-E_2)} \Big]$$

$$\left\langle \psi(k_1) \middle| \hat{\vec{\mu}} \middle| \psi(k_2,k_3) \right\rangle_{\langle\uparrow|\hat{\vec{\mu}}|\uparrow\uparrow\rangle} = \frac{1}{1+\eta^2} \Big[c \, e^{-it'(E_d-E_1)} \, e^{-i\tau(E_g-E_1)} + d \, e^{-it'(E_d-E_2)} \, e^{-i\tau(E_g-E_2)} \Big]$$

Average over all orientations

$$\tilde{a}^2 = \frac{1}{5}\left(\mu_2^2 + \mu_1^2\eta^2 - 2\mu_1\mu_2\eta\cos\tilde{\beta}\right)^2$$

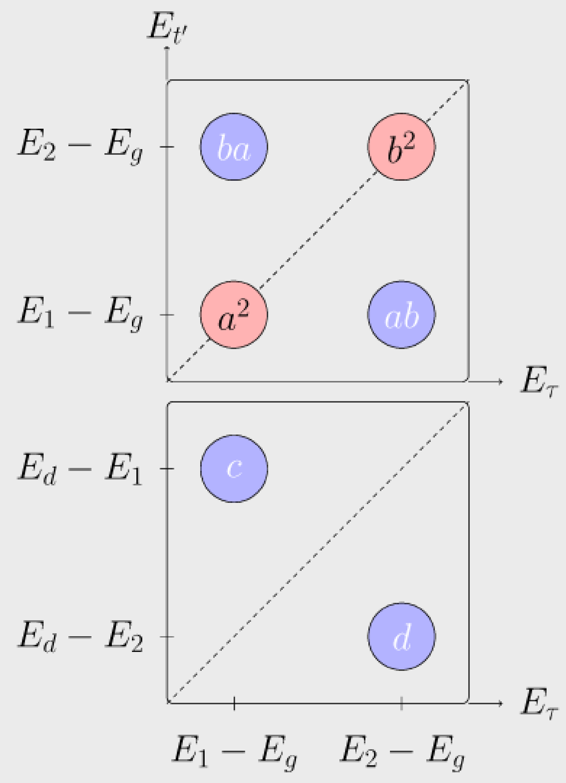
$$\tilde{ab} = \frac{1}{15}\Big(3\mu_1^4\eta^2 + 3\mu_2^4 + \mu_1^2\mu_2^2(1-4\eta^2+\eta^4)(2+\cos 2\tilde{\beta}) + 6\mu_1\mu_2(\mu_1^2-\mu_2^2)(\eta^3-\eta)\cos\tilde{\beta}\Big)$$

$$\tilde{b}^2 = \frac{1}{5}\left(\mu_1^2 + \mu_2^2\eta^2 + 2\mu_1\mu_2\eta\cos\tilde{\beta}\right)^2$$

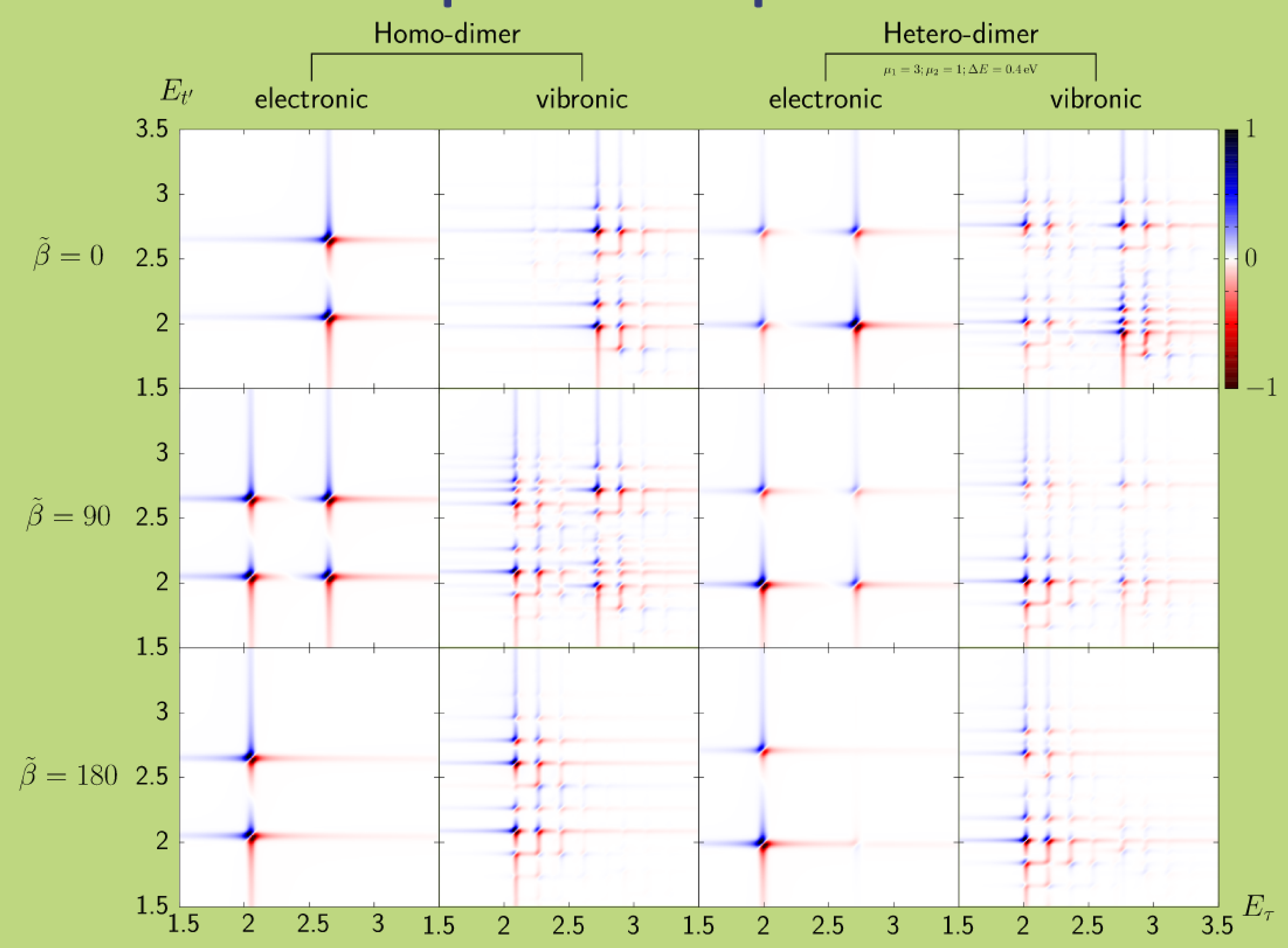
$$\tilde{c} = \frac{2}{15}\mu_1\mu_2\left(-3(\mu_1^2+\mu_2^2)\eta\cos\tilde{\beta} + \mu_1\mu_2(1+\eta^2)(2+\cos 2\tilde{\beta})\right)$$

$$\tilde{d} = \frac{2}{15}\mu_1\mu_2\left(3(\mu_1^2+\mu_2^2)\eta\cos\tilde{\beta} + \mu_1\mu_2(1+\eta^2)(2+\cos 2\tilde{\beta})\right)$$

Homo-dimer: $\eta = 1; \mu_1 = \mu_2$



Results: Comparison of Spectra



Symmetry breaking leads to richer spectra for Hetero-dimer

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References

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contact: julian.albert@uni-wuerzburg.de or johannes.g.wehner@uni-wuerzburg.de