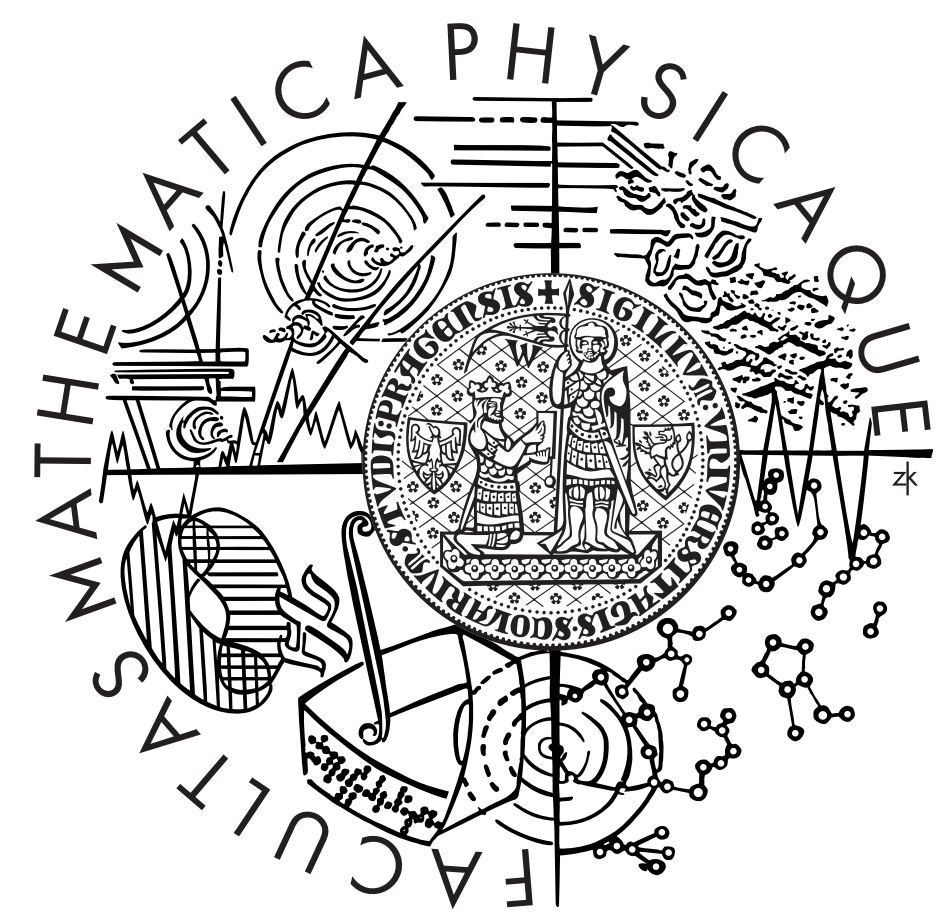




VIBRATIONAL RELAXATION BEYOND THE LINEAR DAMPING LIMIT IN TWO-DIMENSIONAL OPTICAL SPECTRA OF MOLECULAR AGGREGATES

V. PERLÍK¹ AND F. ŠANDA¹



¹ Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, Prague 121 16, Czechia

INTRODUCTION

We present a computational model for the spectra of molecular aggregates with signatures of vibronic progression. Vibronic dynamics is implemented by coupling the dynamics of Frenkel excitons with underdamped vibrations. Vibrational dynamics includes linear damping resulting in the exponential decay and quadratic damping inducing subexponential or power law relaxation and increasing vibrational decoherence as demonstrated on line-shapes of the absorption spectrum. Simulations of the third-order coherent response account for bath reorganization during excitonic transport, which allows us to study the line-shape evolution of cross peaks of 2D spectra.

VIBRONIC DYNAMICAL MODEL

Vibronic aggregate is modeled as coupled two 2-level electronic systems (exciton operators $\hat{A}_i^\dagger, \hat{A}_i$), high frequency vibrational modes (bosonic $\hat{V}_{i,z}^\dagger, \hat{V}_{i,z}$) are taken into account

$$\hat{H} = \sum_i \varepsilon_i \hat{A}_i^\dagger \hat{A}_i + \sum_{i \neq j} J_{ij} \hat{A}_i^\dagger \hat{A}_j + \sum_{i,z} \omega_{i,z} (\hat{V}_{i,z}^\dagger \hat{V}_{i,z} + 1/2) \quad (1)$$

J_{ij} is the resonant coupling between i -th and j -th chromophore. The vibronic states are coupled to a gaussian bath $\hat{H}_B = \sum_k \Omega_k \hat{B}_k^\dagger \hat{B}_k$. System-bath interaction is responsible for damping of vibrational modes and electronic dephasing. Three different couplings are included

$$\begin{aligned} \hat{H}_A &= \sum_{k,i} \Omega_k \xi_{k,i}^{ED} (\hat{B}_k^\dagger + \hat{B}_k) \hat{A}_i^\dagger \hat{A}_i & \mathcal{A}_n(\omega) &\equiv \sum_k \Omega_k \xi_{k,i}^{ED} \xi_{k,i}^{ED} \delta(\omega - \Omega_k) \\ \hat{H}_V &= \sum_{k,i,z} \Omega_k \xi_{k,i,z}^V (\hat{B}_k^\dagger + \hat{B}_k) (\hat{V}_{i,z}^\dagger + \hat{V}_{i,z}) & \mathcal{V}_{i,z}(\omega) &\equiv \sum_k \Omega_k \xi_{k,i,z}^V \xi_{k,i,z}^V \delta(\omega - \Omega_k) \\ \hat{H}_W &= \sum_{k,i,z} \Omega_k \xi_{k,i,z}^W (\hat{B}_k^\dagger + \hat{B}_k) ((\hat{V}_{i,z}^\dagger + \hat{V}_{i,z})^2 - 1) & \mathcal{W}_{i,n}(\omega) &\equiv \sum_k \Omega_k \xi_{k,i,z}^W \xi_{k,i,z}^W \delta(\omega - \Omega_k) \end{aligned}$$

where the three terms V -constant, V -linear and V -quadratic are responsible for electronic dephasing, for exponential vibrational relaxation and for non-linear vibronic-bath couplings, respectively. Spectral density of the Brownian overdamped oscillator representing Gaussian-Markovian coordinate with single relaxation rate Λ was used

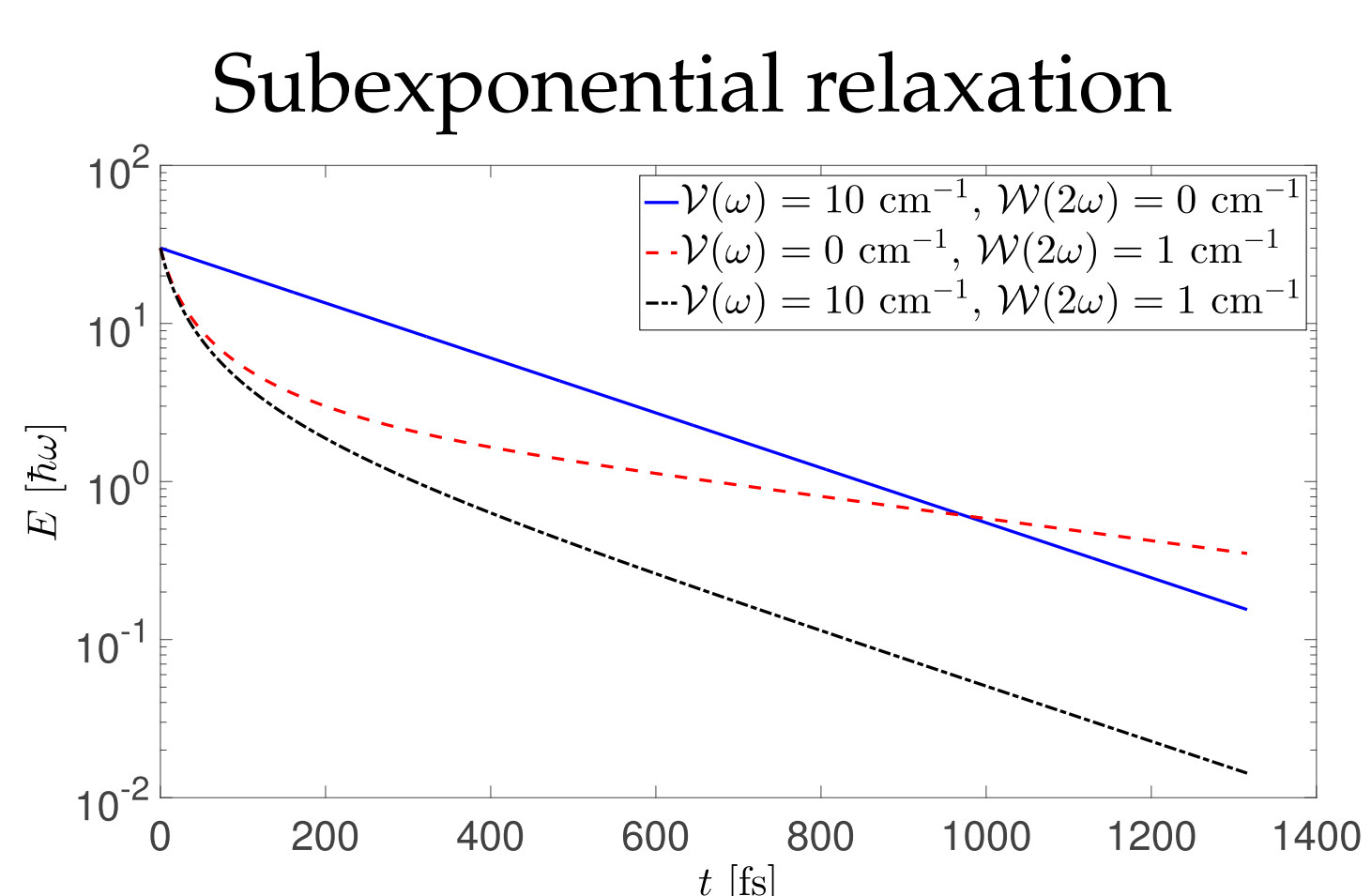
$$A_i(\omega) = \frac{2\lambda_A^i \Lambda_A^i \omega}{\omega^2 - \Lambda_A^i} \Theta(\omega)$$

NONLINEAR BATH-VIBRATIONAL COUPLING

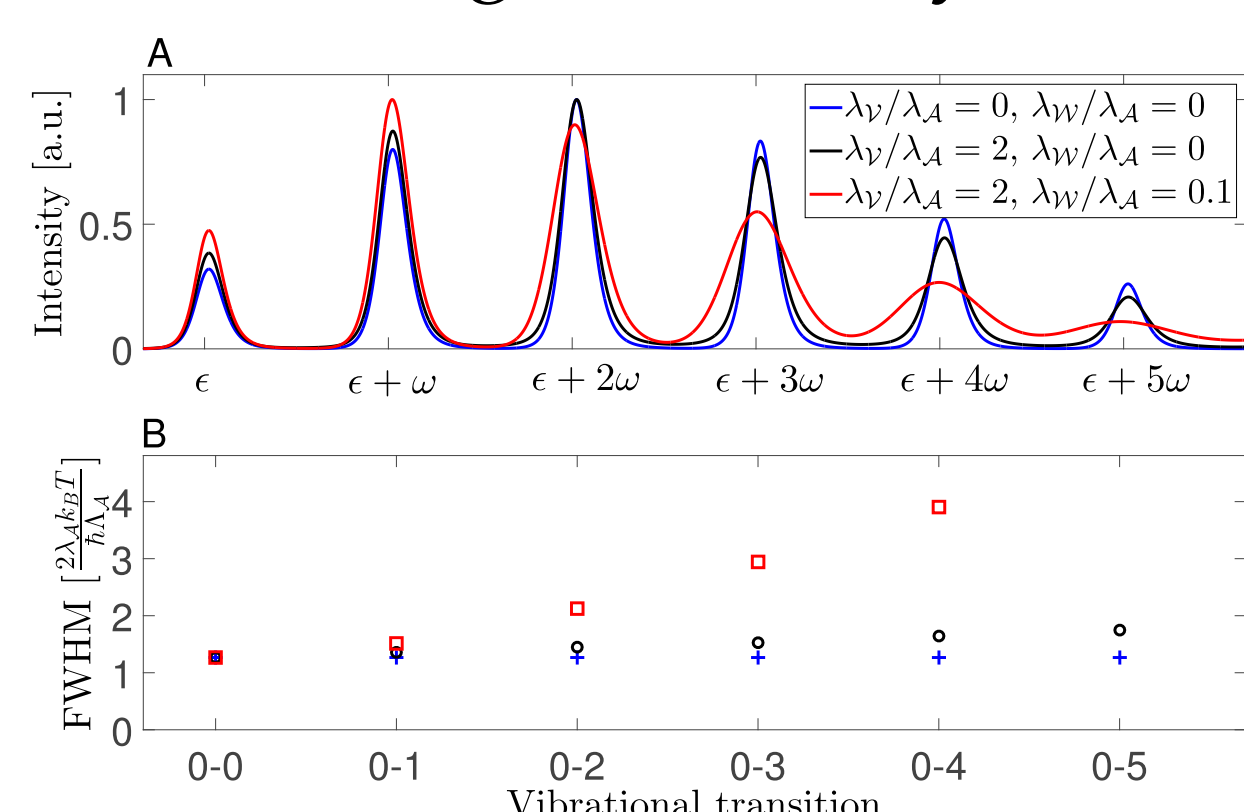
Dynamical effects of the system-bath coupling are accounted up to the second order using master equation [1]. Master equation for populations transformed into the evolution equation for energy $\langle E^2 \rangle \equiv \sum_n n(n-1) \omega^2 \rho_{nn}$

$$\frac{d\langle E \rangle}{dt} = -2\mathcal{V}(\omega) \langle E \rangle - \frac{4\mathcal{W}(2\omega)}{\omega} \langle E^2 \rangle,$$

$$\langle E \rangle(t) = \begin{cases} \frac{\langle E \rangle(0)}{1 + t \left[\frac{4\langle E \rangle(0)\mathcal{W}(2\omega)}{\hbar\omega} + 2\mathcal{V}(\omega) \right]} & \text{power law decay at } t < 1/\mathcal{V}(\omega) \\ e^{-2\mathcal{V}(\omega)t} \langle E \rangle(0) & \text{asymptotic exponential decay} \end{cases}$$

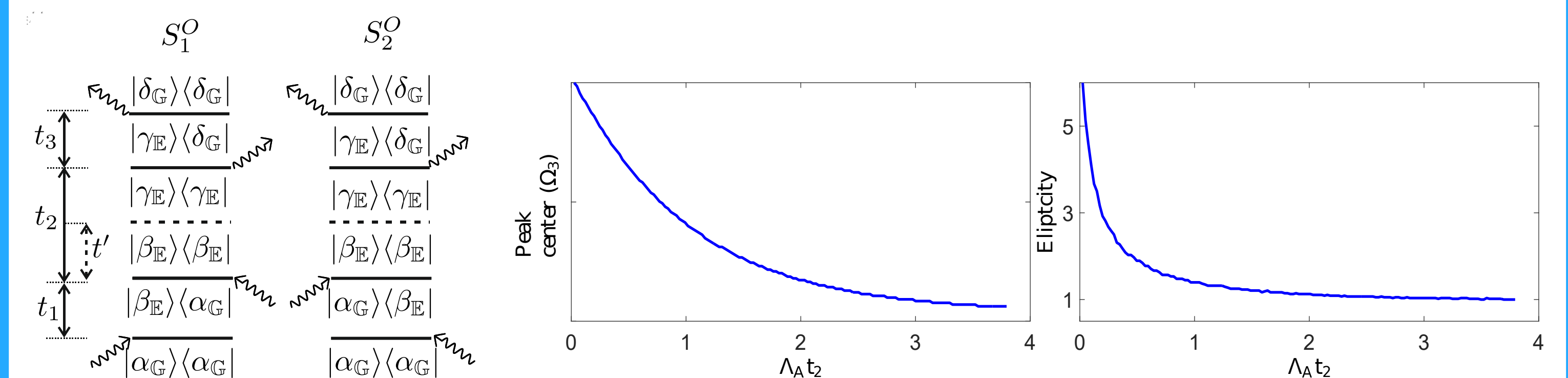
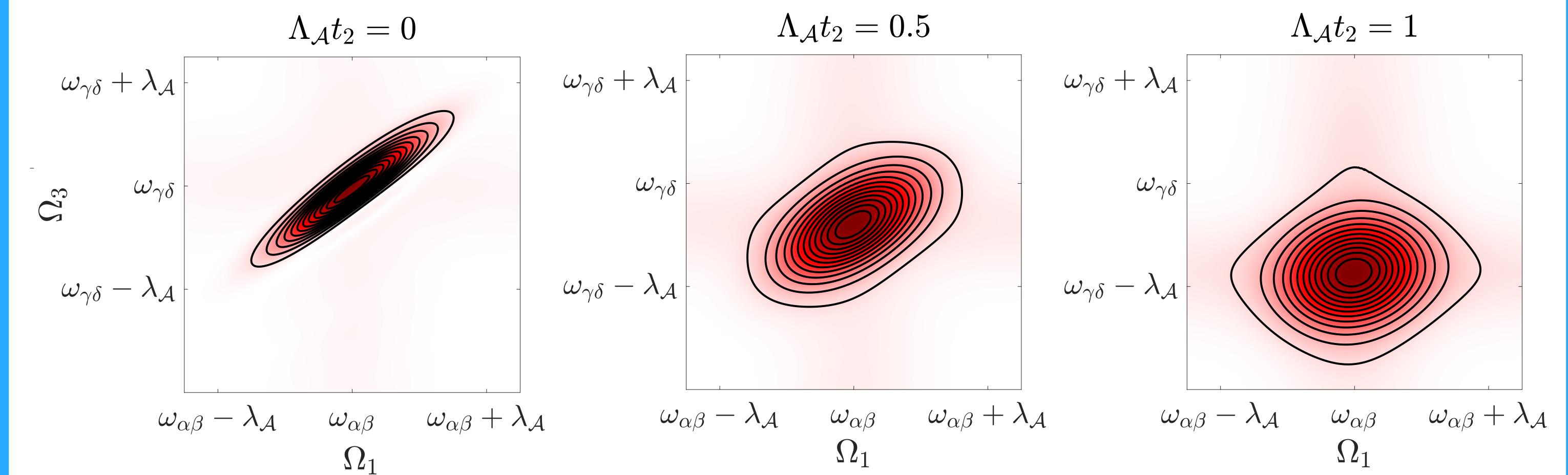


Broadening induced by R rates



Dephasing rates $R_{\tilde{n}0, \tilde{n}0} = \tilde{n}\mathcal{V}(\omega) + \tilde{n}(\tilde{n}-1)\mathcal{W}(2\omega)$

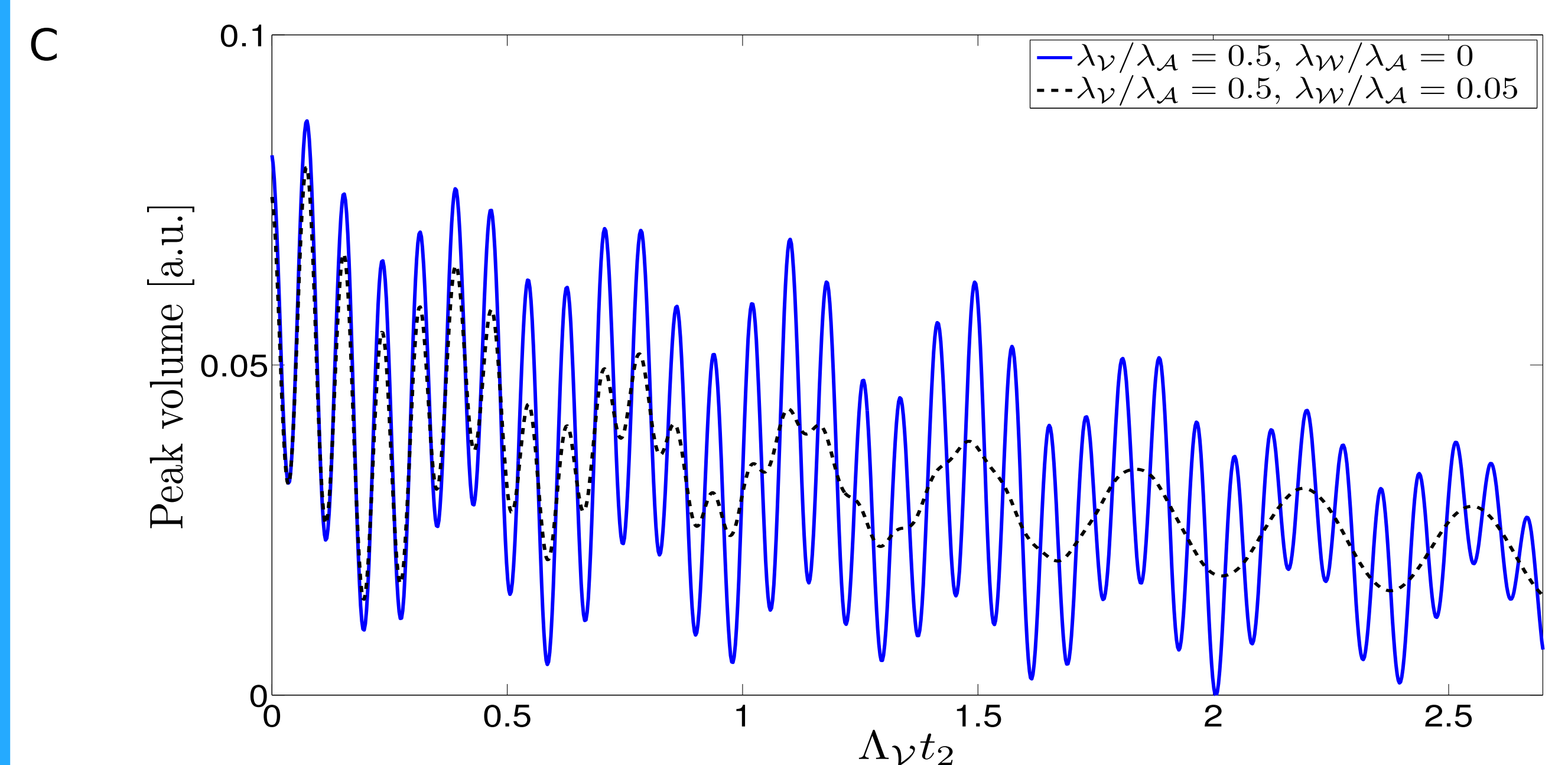
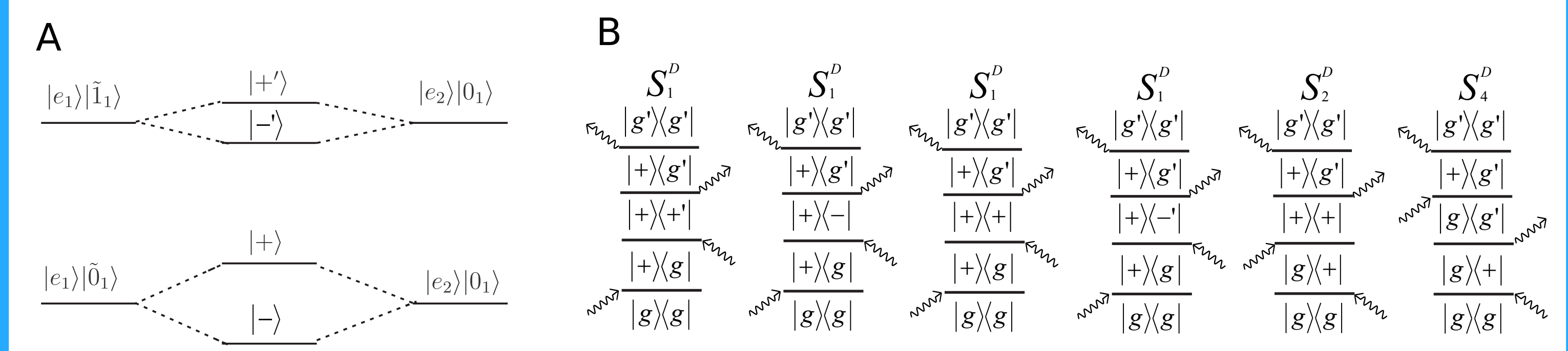
2D LINESHAPE EVOLUTION



Top: 2D peak shapes of transport emission pathways (diagrams S_1^0, S_2^0) for increasing delay times $\Lambda_A t_2 = 0, \Lambda_A t_2 = 0.5$ and $\Lambda_A t_2 = 2$.

Right bottom: Stokes shift and ellipticity defined as the ratio of diagonal and anti-diagonal FWHM of the peak as a function of delay time.

EFFECT OF NONLINEAR



A) Level scheme of the excited state manifold \mathbb{E} of vibronic dimer. States $|+\rangle$ and $|-\rangle$ are symmetric and anti-symmetric combinations of the local states.

B) Feynman diagrams for the vibrational cross peak (VCP) at frequencies $(\Omega_1, \Omega_3) = (\varepsilon_+, \varepsilon_+ - \omega)$, prime marks first vibrational level, e.g. $|g'\rangle \equiv |g\rangle |1_1\rangle$.

C) Modulation of the VCP peak. The blue line represents simulation with linear vibration bath coupling \hat{H}_V . For the black line, quadratic vibration-bath coupling \hat{H}_W is added.

CONCLUSIONS

- Vibronic model was successfully applied to model excitation transfer and (non)linear spectra of dyadic systems such as carotenoid-chlorophyll or rylene dyads.
- Relaxation dynamics beyond the exponential decay was obtained by employing quadratic vibrational-bath coupling.
- Effects of quadratic coupling on lineshape were investigated.

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REFERENCES

- [1] V. Perlík, F. Šanda, J. Chem. Phys. **147** 084104 (2017)

