

Deadline: lecture Thursday (2017-07-06)

- 1.) (4 points) Using Kubo's stochastic theory in the limits of a) $\Delta\tau_c \ll 1$ with $T_2=1/(\Delta^2\tau_c)$ and b) $\Delta\tau_c \gg 1$. Show that a) represents the homogeneous limit with Lorentian line width, and b) the inhomogeneous limit with Gaussian line width.
- 2.) (2 points) A vibration with the frequency ν_b couples via its overtone $2\nu_b$ with the vibration ν_a . This process is called Fermi resonance. The coupling strength is V . Calculate the frequency splitting ν_{\pm} of both interacting states. $E_a = h\nu_a$ and $E_b = h\nu_b$.
- 3.) (2 points) Calculate the 3rd order response function of the $R1^*$ diagram for excited state absorption in a pump probe experiment with well separated pump and probe pulses. Pulses can be represented as delta functions. Neglect population relaxation.
- 4.) (3 points) Below a contour plot of VIS pump – VIS probe data are shown on Al(tpfc)(py)₂. Negative signals indicate an increase of signal at the detector (negative absorption signals), while positive signals indicate a loss of signal at the detector (positive absorption). The upper panel shows the linear absorption spectrum (violet line) and fluorescence spectrum (red line). The absorbance differences are depicted as a function of pump-probe delay time and probe wavelength. Identify the positive and negative signals. Sketch the dynamics in a Jablonski diagram. Are there any dynamics visible in the measured time window? Note, the time scale from -200 fs to 200 fs is blurred by nonlinear artefacts.

