Theoretical Photochemistry WiSe 2017/18 – Exercise 7

Stimulated emission. Consider the two harmonic potential surfaces depicted in Fig. 1A. The Hamiltonian is given as follows,

$$\hat{H}_{\mathrm{mol}} = \hat{H}_G|G\rangle\langle G| + \hat{H}_E|E\rangle\langle E| \tag{1}$$

where $|G\rangle\langle G|$ and $|E\rangle\langle E|$ are projection operators with respect to the electronic ground state ($|G\rangle$) and excited state ($|E\rangle$), respectively, and the vibrational component Hamiltonians are given as

$$\begin{aligned} \hat{H}_G &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2 \\ \hat{H}_E &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}(x-a)^2 + \Delta \end{aligned} \tag{2}$$

The normalized Gaussian wave packet

$$\psi(x, t=0) = \left(\frac{\pi\hbar}{m\omega}\right)^{\frac{1}{4}} \mathrm{e}^{-\frac{m\omega}{2\hbar}x^2}$$

is prepared at time $t = 0$ by an impulsive excitation, and it evolves according to the time-dependent Schrödinger equation for the excited state,

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \hat{H}_E\psi(x,t)\ . \tag{3}$$

(a) Solve Eq. (3) using the Ansatz

$$\psi(x,t) = \mathrm{e}^{\eta(t)}\mathrm{e}^{-\frac{m\omega}{2\hbar}[x-\xi(t)]^2}\ ,$$

where $\eta(t)$ and $\xi(t)$ are complex time-dependent parameters (only $\xi(t)$ is required in the following).
OPTIONAL: Calculate the autocorrelation function $\langle\psi(x,0)|\psi(x,t)\rangle$ and, from its Fourier transform, the absorption spectrum.

(b) Calculate the expectation value of the position operator

$$\bar{x}(t) = \frac{\langle\psi(x,t)|x|\psi(x,t)\rangle}{\langle\psi(x,t)|\psi(x,t)\rangle}$$

and use it to calculate the time-dependent vertical emission energy, defined as $V_E(\bar{x}) - V_G(\bar{x})$
HINT: Use the following Gaussian integral formulas:

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\alpha x^2+\beta x}\mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}\mathrm{e}^{\frac{\beta^2}{4\alpha}}\ ; \qquad \int_{-\infty}^{+\infty} x\mathrm{e}^{-\alpha x^2+\beta x}\mathrm{d}x = \sqrt{\frac{\pi}{\alpha^3}}\frac{\beta\mathrm{e}^{\frac{\beta^2}{4\alpha}}}{2}$$

(c) Sketch the vibrationally-resolved spectra for the $|G\rangle \leftarrow |E\rangle$ emission, with the initial wave packet located at $\bar{x} = 0$ and at $\bar{x} = a$.

Now consider the system of Eq. (3) embedded in a 'solvent' which can dissipate the energy of the system and allow vibrational relaxation. Phenomenologically, relaxation can be described as a damping of the amplitude of the vibrational oscillations of the wave packet.

(d) Modify the expression for $\xi(t)$, including an exponential damping of oscillatory term. Derive a new expression for the vertical emission energy as a function of time, and compare the result with the position of the simulated emission peak in the pump-probe spectrum of Fig. 1B, as a function of pump-probe pulse delay.

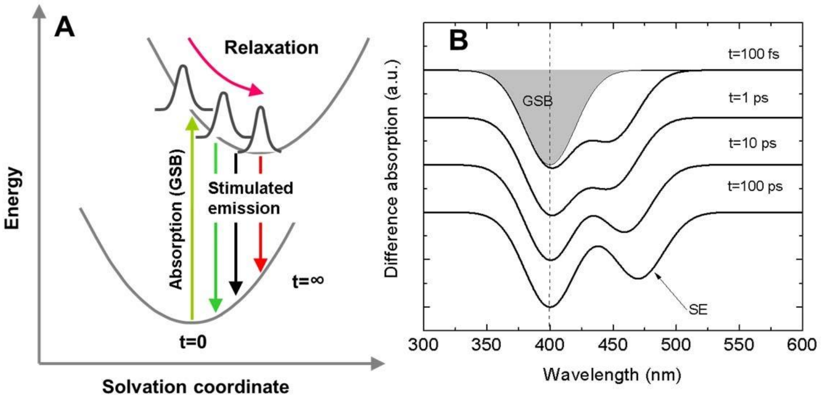

Fig. 1. *(A) Model of two displaced harmonic potential surfaces representing the ground (G) and excited (E) states. It is assumed that the force constants are identical for the two potentials but the equilibrium position of the E state is shifted by a. (B) Illustrative pump-probe spectra as a function of probe frequency and delay time between the pulses. The ground-state-bleach (GSB) and the stimulated emission (SE) contributions are indicated.*