

Theoretical Photochemistry WiSe 2017/18 – Exercise 5

Vibronic absorption spectra. Consider the two harmonic potential surfaces depicted in Fig. 1. The Hamiltonian is given as follows,

$$\hat{H}_{\text{mol}} = \hat{H}_G |G\rangle\langle G| + \hat{H}_E |E\rangle\langle E| \quad (1)$$

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

$$\begin{aligned} \hat{H}_G &= -\frac{\hbar^2}{2m} \frac{d^2}{dq^2} + \frac{1}{2}kq^2 + E_g \\ \hat{H}_E &= -\frac{\hbar^2}{2m} \frac{d^2}{dq^2} + \frac{1}{2}k(q-d)^2 + E_e \end{aligned} \quad (2)$$

To include the interaction with light, the Hamiltonian is augmented as follows with an interaction part \hat{H}_{int} :

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{int}} \quad ; \quad \hat{H}_{\text{int}} = -\mathcal{E}(t)\hat{\mu} \quad (3)$$

where $\mathcal{E}(t)$ is a time-dependent electric field and $\hat{\mu}$ is the electric dipole moment operator. We assume here that $\hat{\mu}$ is independent of vibrational coordinates and induces an electronic transition between the ground and excited electronic states,

$$\hat{\mu} = \mu_e(|G\rangle\langle E| + |E\rangle\langle G|) \quad (4)$$

where μ_e is a constant, i.e., the so-called transition dipole moment.

(a) Assume that the ground-state wavefunction is given as $|\psi_G\rangle = \phi_G(q)|G\rangle$. What is the electronically excited state $|\psi_E\rangle = \phi_E(q)|E\rangle$ that is created by light absorption? To this end, consider the action of \hat{H}_{int} on $|\psi_G\rangle$. Indicate the electronic *and* vibrational components of the resulting excited-state wavefunction.

(b) Explain why the picture of a “vertical”, or Franck-Condon transition describes the light absorption process correctly.

(c) Explain why the excited-state vibrational wavefunction $\phi_E(q)$ is generally *not* an eigenfunction of \hat{H}_E . (Also, identify a special case where $\phi_E(q)$ is an eigenfunction of \hat{H}_E .)

(d) Re-write the matrix element $\langle\psi_E|\hat{\mu}|\psi_G\rangle$ in the vibrational eigenstate representation. Note that $|\psi_G\rangle = \phi_G(q)|G\rangle$ and $|\psi_E\rangle = \phi_E(q)|E\rangle$ as above, and use the notation $\phi_{G,v}(q)$ and $\phi_{E,v'}(q)$ for the vibrational eigenstates.

- (e) Based upon the result of (d), introduce the overlap integrals $S_{v'v} = \langle \phi_{E,v'} | \phi_{G,v} \rangle$. How does the matrix element $\langle \psi_E | \hat{\mu} | \psi_G \rangle$ depend upon the $S_{v'v}$'s?
- (f) The squares of the overlap integrals, $|S_{v'v}|^2$, are called Franck-Condon factors and provide a measure of the relative intensity of the transition. Show that summing Franck-Condon factors over v' is equal to 1.
- (g) Draw a schematic absorption spectrum, indicating the dependence of the frequency-dependent intensities on the Franck-Condon factors.
- (h) What does the absorption spectrum look like if $d = 0$ in Fig. 1?

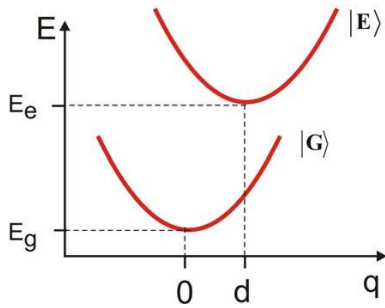


Fig. 1. *Model of two displaced harmonic potential surfaces representing the ground (G) and excited (E) states. It is assumed that the force constants are identical for the two potentials but the equilibrium position of the E state is shifted by d . The vibrational coordinate is denoted as q .*