

Homework 4, Due: Tuesday, April 29

Potential Energy Surfaces, Frank-Condon Factors, Absorption, Fluorescence and Wavepackets in Iodine Vapor:

In this problem you will work with a model of iodine gas to calculate steady-state absorption, fluorescence, and time-domain dynamics of iodine gas. I_2 is a solid that sublimates to a vivid purple vapor (Find videos of it on Youtube, if you need entertainment). This problem will involve the following:

- Modeling the ground and excited state potential energy surfaces (PES) of I_2 as Morse oscillators.
- Calculating the nuclear wavefunctions for the ground and excited states by direct numerical solution of the Schrodinger's equations.
- Calculating the Frank-Condon Factors (FCF) between the nuclear wavefunctions of the ground and excited electronic states.
- Predicting steady-state absorption and fluorescence spectra.
- Predicting the time-domain behavior of the nuclear wavefunctions after an electronic excitation.

1)- The Potential Energy Surfaces:

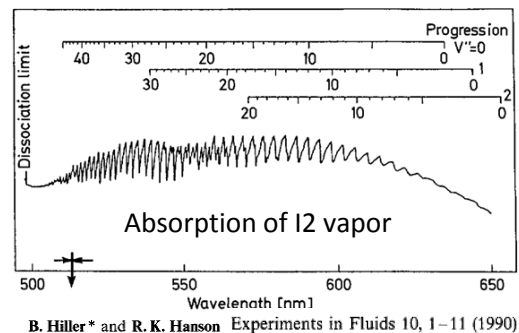
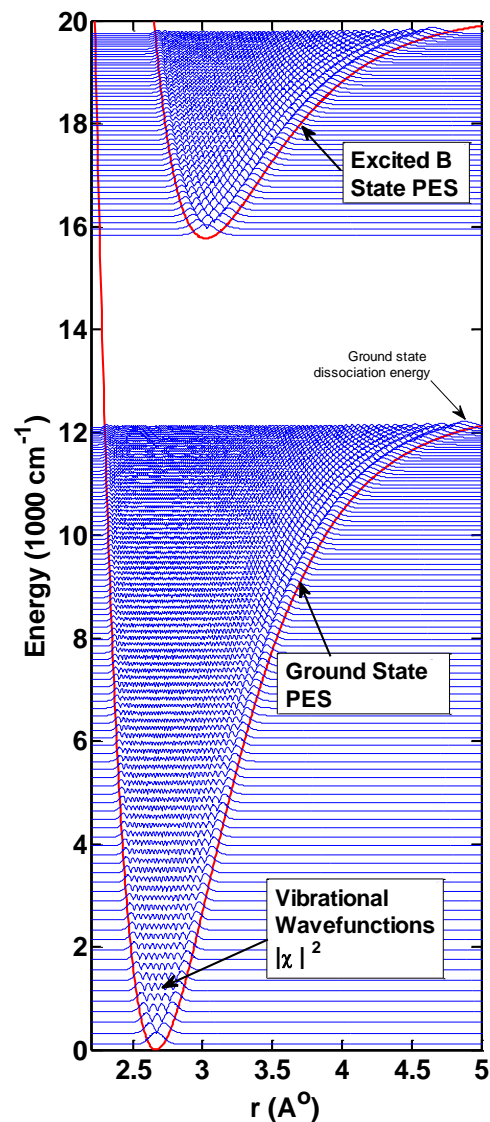
We will model the ground and excited state PES of iodine using the Morse oscillator potential:

$$PES(R) = D_e(1 - e^{-\beta(R-R_0)})^2$$

Here R_0 is the equilibrium bond length and D_e is the dissociation energy with respect to the bottom of the well.

- The parameter β is related to the curvature at the bottom of the well (i.e. the harmonic frequency). To find this relation, expand the Morse potential in a power series around R_0 to show that:

$$D_e\beta^2 = \frac{1}{2}k_e$$



where k_e is the force constant at the bottom of the well and you know its relation to the harmonic frequency ω_e .

b)- The parameters for the ground and excited potential energy surfaces of I_2 are given in the table below:

	Ground State	Excited State
Energy offset (cm^{-1})	0	15769
R_0 (\AA)	2.666	3.024
$\hbar\omega_e$ (cm^{-1})	214.50	125.69
D_e (cm^{-1})	12440	4349

Using these parameters plot the ground and excited PES. Your plot should look like the PESs shown in the previous page.

2)- The Vibrational Wavefunctions:

The wavefunctions for a Morse potential can be found analytically. However, in general you will face potentials with no analytical solutions. To prepare you for such cases, you will numerically solve the 1D Schrodinger's equation for the ground and excited PES. The procedure is outlined below:

a)- To numerically solve the 1D Schrodinger's equation:

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi = E\psi$$

First, discretize the position with discrete steps Δx . Then show that the second derivative can be approximated by the difference equation.

$$\frac{d^2\psi}{dx^2} \rightarrow \frac{1}{\Delta x^2} (\psi(x_{n+1}) - 2\psi(x_n) + \psi(x_{n-1}))$$

where $\psi(x_n)$ is the value of the wavefunction at location x_n .

b)- For each one of the ground and excited state PES, write the Schrodinger's equation in matrix form and find its eigenvalues E_j and eigenfunctions χ_j . Plot the wavefunctions on top of the PES, shifting each wavefunction vertically at a location corresponding to its energy. You should arrive a plot similar to what is shown in page 1.

2)- Frank-Condon Factors, absorption and fluorescence:

a)- Calculate the FCF between the ground state $v=0$ and all excited states vibrational energy levels. Present the results as a plot of FCF versus the energy gaps between states.

b)- Repeat the above step, but this time between four vibrational states in the ground PES and all vibrational states in the excited PES. Furthermore, weight each FCF by the corresponding thermal

population in the ground state (Notice that the vibration of I_2 is quite soft, necessitating this treatment). Plot the FCFs as a function of wavelength (between 500 nm and 650 nm) as a bar graph (in Matlab use the `bar(x,y)` function). Compare your result with the absorption spectrum of I_2 shown in the first page.

c)- Calculate the fluorescence lines of I_2 and present the result as a bar graph versus wavelength.

3)- Time-domain Dynamics in I_2 :

A short laser pulse can promote the ground vibrational state to excited state PES. Here you will calculate the dynamics of the vibrational wavepacket in the excited PES after such excitation.

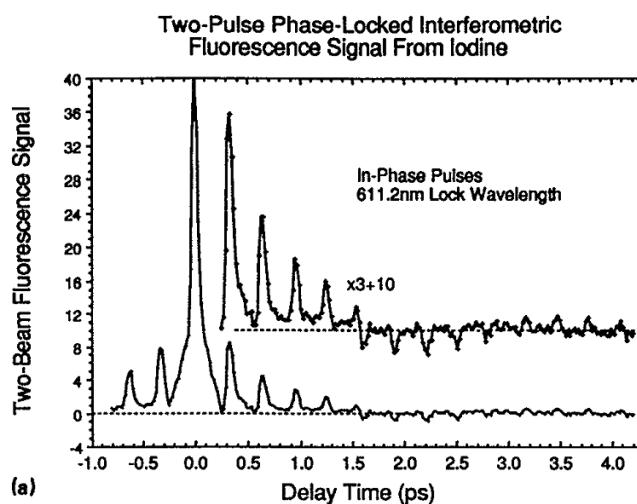
a)- The suddenly promoted ground vibrational wavefunction must be expanded in terms of excited state vibrational wavefunctions. Find the corresponding coefficients, assuming that only the $v=0$ ground vibrational state is promoted to the excited state.

$$c_j = \langle \chi_{g0} | \chi_{ej} \rangle$$

b)- Once the coefficients are known, the time-dependence of the wavefunction can be calculated as:

$$\Psi(t) = \sum_j c_j e^{-\frac{i}{\hbar} E_j t}$$

Plot the wavefunction in space and show the dynamics of the wavepacket by repeating the plot inside a time loop. Vary the time from 0 fs to 2000 fs. To see the wavepackets recurring, we will have to modify two parameters of the excited state PES. Set $D_e = 7000 \text{ cm}^{-1}$ and $R_0 = 2.9 \text{ \AA}$. Compare your results with the result from ultrafast spectroscopy of iodine shown below.



[Fluorescence-detected wave packet interferometry: Time resolved molecular spectroscopy with sequences of femtosecond phase-locked pulses.](#) N. F. Scherer, R. J. Carlson, A. Matro, M. Du, A. J. Ruggiero, V. Romero-Rochin, J. A. Cina, G. R. Fleming, and S. A. Rice, *J. Chem. Phys.* **95**, 1487 (1991).