Name: MODEL SOLUTIONS Tutorial Section:
Roll No:

CSO 202A: Atoms, Molecules and Photons
Mid-Semester Exam 3rd March 2017
35 Marks Total Total Time: 2 Hours

Instructions: Answer all the questions in the space provided. You may use additional sheets for rough work but they will not be graded. Read the questions carefully and give precise answers. You may use calculators, but you are not allowed to share with others. In case you do not have a calculator, estimate the answer the best you can.

Unless indicated otherwise, all symbols have their usual meanings. Some fundamental constants and conversion of units are given below.

1 u = 1.66×10^{-27} kg
$k_B = 1.38 \times 10^{-23}$ J/K
$R = 8.314$ J/mol K
$h = 6.63 \times 10^{-34}$ J s
$c = 3.00 \times 10^{10}$ cm/s

Q. No	Marks	Maximum
1		15
2		10
3		10
Total		35

This Question paper has a total of 18 pages

Question No 1: FTS-study of $I_2 \rightarrow I + I$ reaction (15 marks total)

This is taken from an the article R.M. Bowman, M. Dantus and A.H. Zewail, *Chem. Phys. Lett.*, **161**, 297 (1989). Here we will analyze some features of this reaction. There are two *channels* for the reaction and are given by:

$I_2 \rightarrow I + I$

$I_2 \rightarrow I + I^*$

where the * is used to indicate an excited state of the product I atom. These will be probed using the FTS experiment.

(a) Write the atomic term symbol for the ground state of I atom (with the largest J value), and the first excited state (I*). (1 mark)

I: p^5 → Same as p^{-1} $L = 1$ $S = 1/2$

Ground State $J = 3/2$ $^2P_{3/2}$

1st Excited State $J = \frac{1}{2}$ $^2P_{1/2}$

(b) Write the molecular term symbol corresponding to the ground state of I_2, and the term symbol(s) corresponding to excited state configuration(s) where 1 electron moves from the Highest occupied molecular orbital to the lowest unoccupied molecular orbital. (2 marks)

I_2 : MO configuration $\pi_u^4 \pi_g^{*4}$ ⇒ $\Lambda = 0$ $S = 0$

Ground state : $^1\Sigma_g^+$

Excited state configuration $\pi_u^4 \pi_g^{*3} \sigma_u^{*1}$

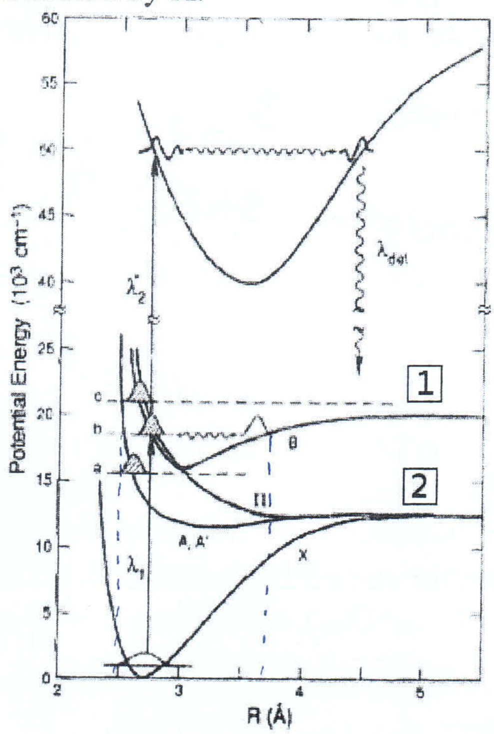
$\Lambda = 1$ $S = 1$ (or 0)

↑

Hund's Rule

$^3\Sigma_u^-$

(c) Consider the schematic diagram below showing the potential energy surfaces involved in this reaction. This diagram will be referred to in subsequent parts of the question as the PES diagram.
The ground state is denoted by X.



Notice that the probe beam takes the molecule to a bound state which fluoresces at a wavelength λ_{det} that is different from λ_2* . This happens to be a feature of a well-characterized fluorescent excited state in I_2. What are the species present on the flat regions of the potential energy curves at the points denoted by 1 and 2 in the figure ? (2 marks)

1 I + I*

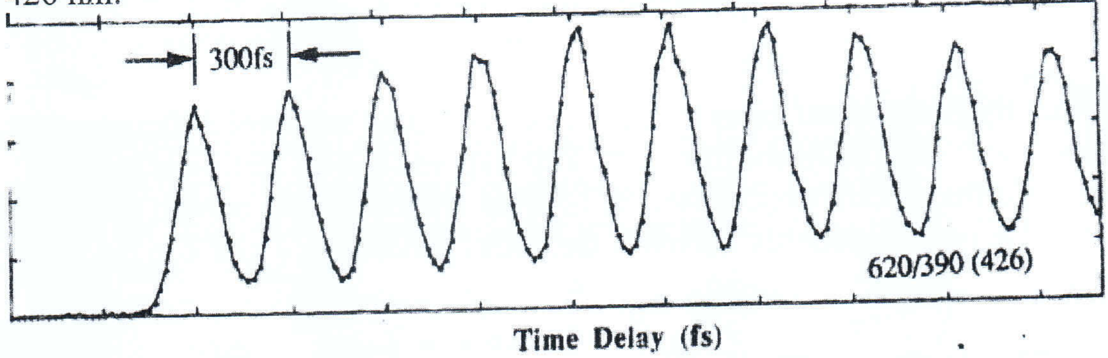
2 I + I

(d) Notice in the PES diagram, that there are 3 excited states which can be populated by the pump beam λ_1. These states are denoted by AA*, B and Π. One of these corresponds to a bound state, one to a strongly dissociative state, and one to a repulsive surface that is weakly dissociative. Identify which of the states above corresponds to the bound state, and the strongly dissociative state. (1 mark)

Bound state : B

Strongly Dissociative State : Π

(e) The FTS signal obtained for one of the excited states is shown below. In the figure, the notation used is λ_1/λ_2^* (λ_{det}), so we have λ_1=620 nm , λ_2^* = 390 nm and λ_{det}=426 nm.



Identify the excited state that will give this FTS signal. Justify your answer (1 mark)

Bound State B.

Only bound state can give oscillations in FTS signal

(f) If we take the fundamental vibrational frequency in state B in the PES diagram as 122 cm^{-1}, what is the time period of oscillation of the state B. (1 mark)

$$T = \frac{1}{\nu} = \frac{\lambda}{c} = \frac{1}{c\bar{\nu}} = \frac{1}{122 \times 3 \times 10^{10}}$$

$$T = 273 \text{ fs}$$

(g) The minimum of state B in the PES diagram is 637 nm above the minimum of the state X from where the ~~probe~~ pump beam excites the molecule. Using the fundamental vibrational frequency of 122 cm^{-1}, calculate the vibrational state of B that is populated by a 620 nm pump beam when it excites state X from its ground state. (2 marks)

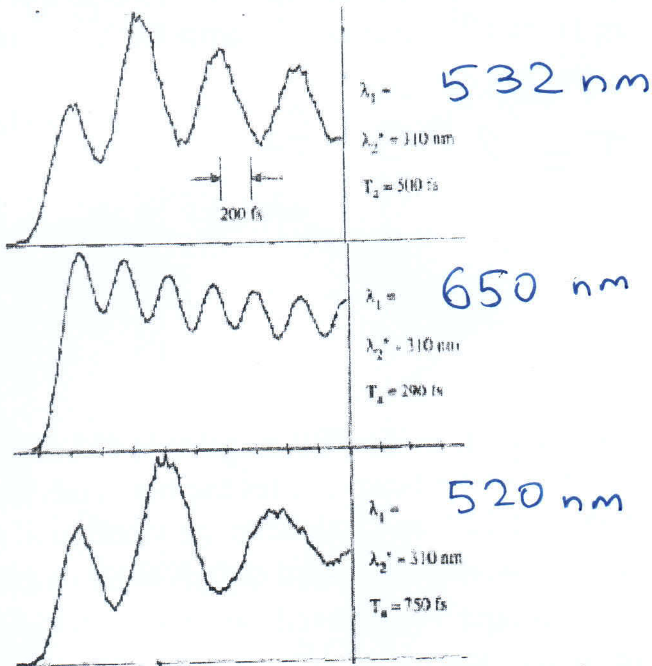
$$\frac{hc}{620\text{ nm}} - \frac{hc}{637\text{ nm}} = \left(v + \frac{1}{2}\right) hc\,(122\text{ cm}^{-1})$$

$$\frac{10^7}{620} - \frac{10^7}{637} = 122\left(v + \frac{1}{2}\right)$$

$$v = 3.03$$

$$\Rightarrow \quad v_{max} = 3$$

(h) Consider the three FTS transients below, all corresponding to state B (in figure from part c). The three transients correspond to three different pump ~~probe~~ wavelengths, 520 nm, 532 nm and 650 nm.



Identify the pump wavelength that corresponds to each of the transients above. Write your answer next to λ_1 in each subfigure above. Remember that when the available energy is lower, the molecule has to traverse a smaller distance during each oscillation.

Briefly justify your answer below. (2 marks)

When $\lambda = 650$ nm, only the lower vibrational states are excited. Molecule moves a smaller distance during each oscillation. Hence frequency of oscillation is highest.

(i) What is the recoil velocity (from the relative translational energy) of a molecule excited to state B by a pump of wavelength 520 nm ? Recall that potential energy minimum of state B is 637 nm above the ground state of X. Assume that both X and B are in their ground vibrational state and neglect rotational energy of the molecule. (1 mark)

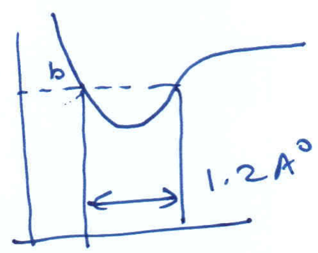
$$\frac{1}{2}\mu V_r^2 = \frac{hc}{520\,nm} - \frac{hc}{637\,nm} - \frac{hc\bar{\nu}}{2} = 6.9\times10^{-20}\,J$$

$$\mu = \frac{127}{2}\times 1.66\times10^{-27}\,kg$$

$$\therefore V_r = 1.14\times10^{3}\,m/s$$

(j) Based on the velocity above, *estimate* the time taken for the B molecule at point b in the PES diagram to oscillate back and forth. You can assume that the molecule moves with a constant velocity over the distance that you can estimate from the PES diagram. Clearly show the steps and the assumptions you are making (2 marks).

At b, molecule moves ~ 1.2 Å during vibration

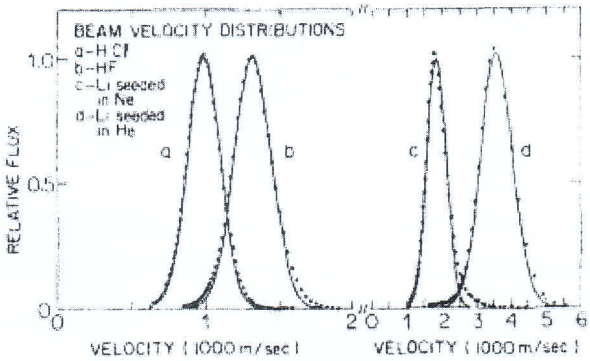


Assuming that molecule moves this distance at $V = V_r$, time taken for on round trip $= \frac{2.4\times10^{-10}\,m}{1.14\times10^{3}\,m/s}$

$= \underline{210}$ fs

Q. No. 2 : Crossed Molecular Beam study of Li + HF → LiF + H (10 marks)

This question is taken from the article : C.H. Becker, P. Casavecchia, P.W. Tiedemann, J.J. Valentini and Y.T. Lee, *J. Chem. Phys.* , 73, 2833 (1980). The reaction being explored by this experiment is Li + HF → LiF + H
The atomic masses are : Li: 7, H: 1, F: 19
The experiment uses supersonic jet expansion for creating beams of HF and Li. Li atoms are seeded in a carrier gas containing He or Ne. The beam velocity distributions are plotted in the figure below. The solid line is a fit of the data to the beam profile from a supersonic jet.



(a) First focus on graph b. The peak of beam b can be taken as 1310 m/s. Calculate the source temperature of the HF beam using the peak value as the terminal velocity in the supersonic jet expansion expression given below

$u=\sqrt{\frac{2RT_s}{M}\frac{\gamma}{\gamma-1}}$ where γ is the ratio of heat capacities (=1.38 for HF). (1 mark)

$$1310 = \sqrt{\frac{2RT_s}{20\times10^{-3}} \cdot \frac{1.38}{0.38}}$$

$$T_s = 568\ K$$

(b) Now focus on graphs c and d. Why is the velocity distribution of d to the right of the velocity distribution of c ? (1 mark)

d hase He as carrier gas which is lighter than Ne. So d is to the right of c.

(c) The peak of graph d is at 3570 m/s. Assuming that the He carrier gas is in majority, estimate the source temperature of the He carrier gas. (1 mark) $\gamma = 5/3$

$$3570 = \sqrt{\frac{2RT_s}{4\times10^{-3}} \times \frac{5}{2}}$$

$$T_s = 1226\ K$$

(d) Now we again look at graph b, where the peak is at 1310 m/s. If this gas was distributed according to a Maxwell-Boltzmann distribution of speeds, estimate the temperature of the gas, and the relative FWHM $\frac{\Delta v}{v}$ of the gas. Clearly explain your work. (2 marks)

$$V_{mp} = \sqrt{\frac{2RT}{M}}$$

$$T = \frac{1310^2 \times 20\times10^{-3}}{2\times 8.314} = 2064\ K$$

According to MB distribution

$$P(v) \propto v^2 e^{-\frac{mv^2}{2k_BT}} \sim e^{-\frac{v^2}{2\sigma^2}}$$

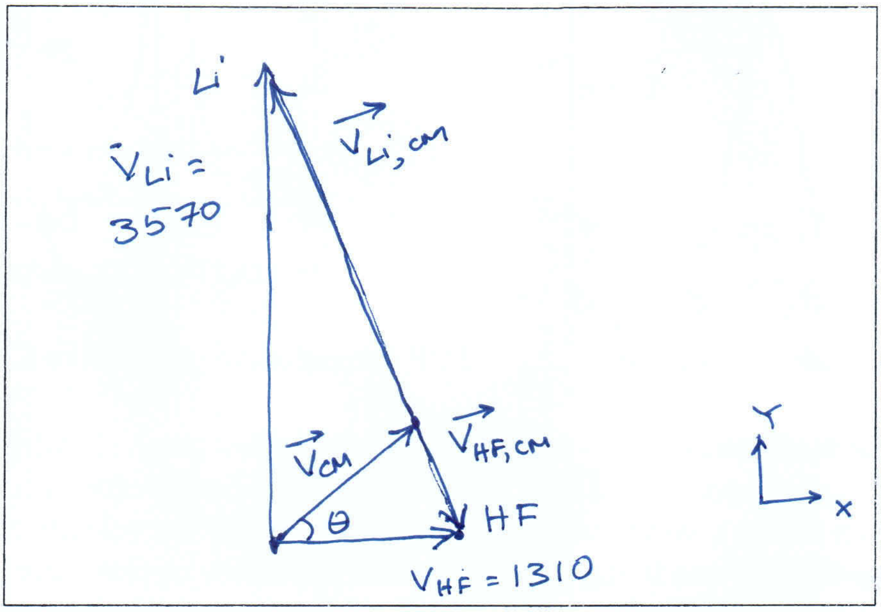
$$\sigma \sim \Delta v$$

$$P\left(\sqrt{\frac{2RT}{M}}\right) \propto \left(\frac{2RT}{M}\right)^2 e^{-1}$$

Estimate of $\Delta v^2 = \frac{\cancel{2}\, k_BT}{M}$ for Gaussian distribution ($\sim$ Maxwell-Boltzmann)

$$\frac{\Delta v}{v} \sim \frac{1}{\sqrt{2}}$$

(e) The Li and HF beams are perpendicular to each other. Consier the case where Li is seeded with He as the carrier gas. Using the peak velocities described in previous parts, draw a typical Newton diagram (in the box below) approximately to scale, showing the initial beams and the center of mass velocity. Also show the velocities of the incident beams in the center of mass frame. Calculate the angle of the center of mass velocity with the incident HF beam. (3 marks)



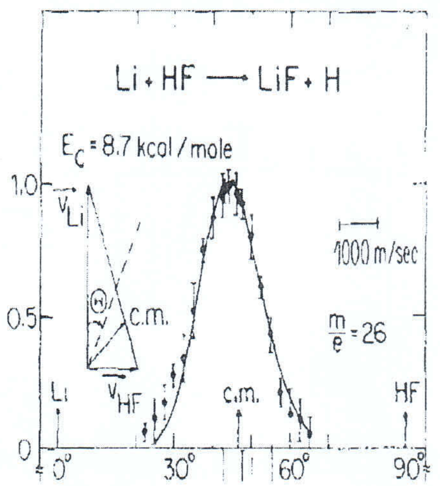
$$\vec{V}_{CM} = \frac{20}{27} \cdot 1310\,\hat{i} + \frac{7}{27} \times 3570\,\hat{j}$$

$$= 970.4\,\hat{i} + 925.6\,\hat{j}$$

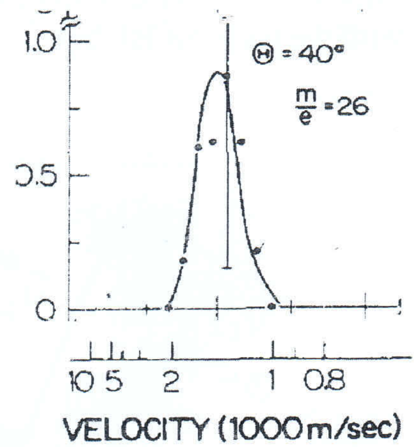
$$\cos\theta = 0.72$$

$$\theta = 43.6^\circ$$

(f) Now, let us look at the case where the relative kinetic energy is 8.7 kcal/mol. The graphs for the LiF angular distribution and the time of flight data at the angle maximum are shown below. The vertical lines are error bars and can be ignored.

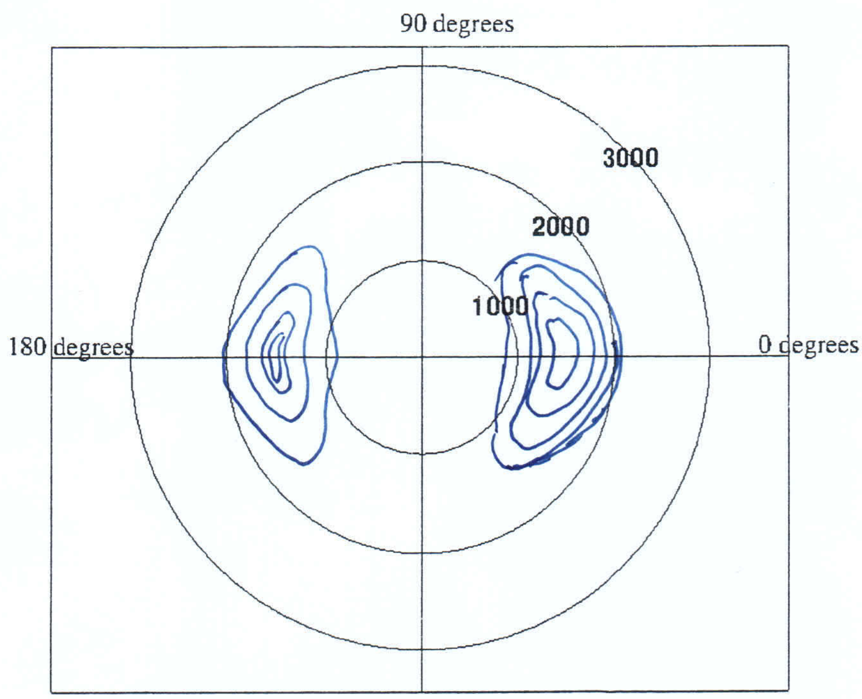


LiF angular distribution



TOF corresponding to relative KE=8.7 kcal/mol

Notice that the center of mass angle is shown in the left graph showing the angular distribution of the products. Using *just this basic information* (neglecting all convolution effects), sketch what the expected graph for the velocity flux contour map in the COM frame in the box below. The concentric circles correspond to the velocities in m/s indicated in the figure. Explain your answer clearly (~~3~~ 2 marks).



NOTICE $\Theta_{CM} \sim 45°$. $\Theta_{max} \sim 40°$ ⇒ scattering angle ~ 0°/180°

Peak velocity between 1000 and 2000 m/s.

Question 3: Lasers and Mode-locking (10 marks)

(a) Compute the mode-locked pulse width τ_p and the separation between pulses T for the following mode-locked 610 nm Rh6G dye laser operating over the gain bandwidth 570-640 nm with cavity mirrors separated by 2m. (3 marks)

We know that $T = \frac{2 \times L}{c}$

$$= \frac{2 \times 2}{3 \times 10^8} \text{ s} = 13.3 \text{ ns}$$

The bandwidth of the laser $= (640 - 570)\text{ nm} = 70 \text{ nm}$

This can be converted to frequency width by the relationship,

$$\Delta \nu = \frac{c}{\lambda^2} \Delta \lambda = \frac{3 \times 10^8 \text{ m/s}}{(6.1 \times 10^{-7} \text{ m})^2} \times (70 \times 10^{-9} \text{ m})$$

$$= 5.6 \times 10^{13} \text{ s}^{-1}$$

The ~~[illegible]~~ pulse width is then,

$$\tau_p = \frac{1}{\text{gain bandwidth}} = \frac{1}{\Delta \nu} = \frac{1}{5.6 \times 10^{13}} \text{ s} = 17.8 \text{ fs.}$$

(b) A laser delivers 10 fs pulses with 80 MHz repetition rate. The central wave length is 800 nm. What is the average power and peak power of this laser ? (2 marks)

Average power $=$ pulse energy $\times$ Rep. rate

$= 300 \times 10^{-3}\ \mathrm{J} \times 80 \times 10^{6}\ \mathrm{s}^{-1}$

$= 24 \times 10^{6}\ \mathrm{J/s} = 24\ \mathrm{MW}$

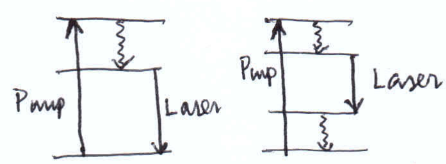
Peak power $= \dfrac{\text{Pulse energy}}{\text{pulse width}}$

$= \dfrac{300 \times 10^{-3}\ \mathrm{J}}{10 \times 10^{-15}\ \mathrm{s}}$

$= 3 \times 10^{13}\ \mathrm{W} = 30\ \mathrm{TW}$

(c) In general, between a 3-level laser and and 4-level laser, which laser is more efficient ? Explain your answer briefly. (1 mark)

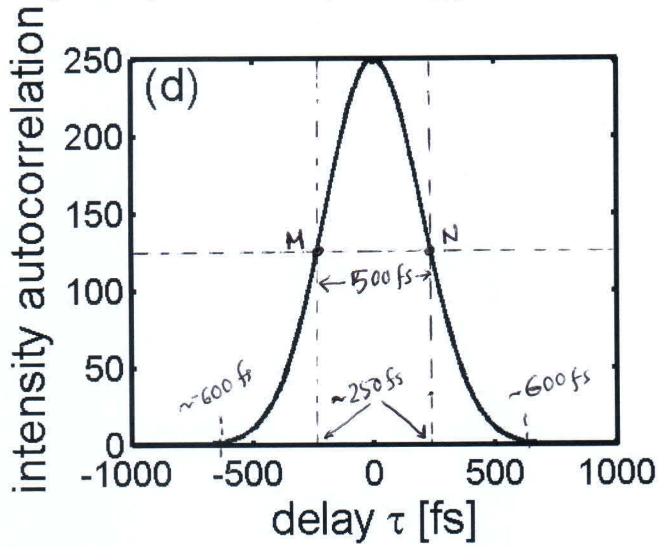
Four-level laser is more efficient.



3-level Laser 4-level Laser

Explanation : Laser gain with a much lower excitation is possible in 4-level system. Here the lower level of the laser transition is somewhat above the ground state, and a rapid nonradiative transfer from there to the groundstate keeps the population of the lower Laser level very small. Therefore, a moderate population in the third (upper laser level in a 4-level system) level, as achieved with a moderate pump intensity, is sufficient for laser amplification.

(d) The pulse-width of any ultrashort laser is determined by intensity autocorrelation technique. In a particular autocorrelator, it is known that the intensity autocorrelation width is $\sqrt{2}$ times greater than the actual laser pulse-width. A trace of the autocorrelation is shown below. Based on this trace, *estimate* the pulse-width τ_p. Clearly state any assumptions you make. (2 marks)



From the autocorrelation trace we have

'Half maximum' = 125 (intensity unit)

At 'half maximum' we can roughly estimate the τ - coordinates of the points M & N as −250 fs and 250 fs, respectively.

Therefore the FWHM of the autocorrelator trace is ~500 fs. (estimated)

$\therefore$ The pulse width $\tau_p \approx \frac{500}{\sqrt{2}}$ fs = 353·5 fs (estimated)

(e) Find the spectral line-width (in nm) for Gaussian laser pulses with central wavelength 800 nm, for two cases - $\tau_p=1$ ps, and $\tau_p=1$ fs.
Recall that the time band-width product is 0.441. (2 marks)

The time-bandwidth product $= \Delta\nu\,\Delta t = \Delta\nu\,\tau_p = 0.441$

$$\therefore \Delta\nu = \frac{0.441}{\tau_p}$$

For 1 ps pulse: $\Delta\nu = \frac{0.441}{10^{-12}}\,s^{-1} = 4.41 \times 10^{11}\,s^{-1}$

For 10 fs pulse: $\Delta\nu = \frac{0.441}{10^{-14}}\,s^{-1} = 4.41 \times 10^{13}\,s^{-1}$

Now, $\Delta\nu = \frac{c}{\lambda^2}\,\Delta\lambda$

or $\Delta\lambda = \Delta\nu\,\frac{\lambda^2}{c}$ [bandwidth in wavelength

So, for 1 ps pulse, the spectral bandwidth is

$$\Delta\lambda_{1ps} = \frac{4.41\times10^{11}\,s^{-1} \times (800\times10^{-9}\,m)^2}{3\times10^8\,m/s}$$

$$= 0.94 \text{ nm}$$

Similarly, for 10 fs pulse, the spectral bandwidth is

$$\Delta\lambda_{10fs} = \frac{4.41\times10^{13}\,s^{-1} \times (800\times10^{-9}\,m)^2}{3\times10^8\,m/s}$$

$$= 94 \text{ nm}$$