

MODEL SOLUTIONS

NAME:

ROLL NO:

CSO 202A: ATOMS, MOLECULES AND PHOTONS MID-SEMESTER EXAM

18TH FEBRUARY 2018

TOTAL MARKS: 80

DURATION: 120 MINUTES

ANSWER THE QUESTIONS IN THE SPACE PROVIDED.

BLANK SHEETS WILL BE PROVIDED FOR ROUGH WORK BUT WILL NOT
BE EVALUATED

Fundamental constants: $k_B=1.38\times10^{-23}$ J/K , $N_A=6.02\times10^{23}$ mol⁻¹
 $1 \text{ eV} = 1.60\times10^{-19}$ J, $1\text{u} = 1.66\times10^{-27}$ kg mol⁻¹, $h=6.63\times10^{-34}$ Js, $c=3\times10^8$ ms⁻¹

	MARKS	MAXIMUM
PROBLEM 1		15
PROBLEM 2		15
PROBLEM 3		10
PROBLEM 4		25
PROBLEM 5		15
TOTAL		80

Total no of pages = 20

PROBLEM 1 – Molecular Beam Set-up (15 marks)



This reaction was studied using an elementary crossed molecular beam set-up. Answer the questions below regarding the set-up of the experiment. You can use the following data

Atomic masses: K = 39.0 u , I = 127 u

Dissociation energy: $I_2 = 149 \text{ kJ/mol}$ $KI = 319 \text{ kJ/mol}$

Vibrational Frequency: $I_2 = 214.5 \text{ cm}^{-1}$ $KI = 186.5 \text{ cm}^{-1}$

Rotational Constant B: $I_2 = 0.037 \text{ cm}^{-1}$ $KI = 0.061 \text{ cm}^{-1}$

The initial beams were chosen to be perpendicular to each other with relative velocity of 1000 ms^{-1} .

(a) (4 marks) Assuming that the iodine beam is moving with the most probable velocity at 500K, what is the speed of the K beam ?

Since I_2 and K beams are perpendicular to each other, we have

$$v_{\text{rel}}^2 = v_K^2 + v_{I_2}^2$$

$$v_K^2 = 1000^2 - v_{I_2}^2$$

$$v_{I_2}^2 = v_{mp}^2 = \frac{2RT}{M_{I_2}} = \frac{2 \times 8.314 \frac{\text{J}}{\text{mol K}} \times 500 \text{ K}}{254 \times 10^{-3} \frac{\text{kg}}{\text{mol}}}$$

Solving, we get $v_K = 983.5 \text{ m/s}$

(b) (4 marks) What is the most populated rotational state of iodine at 500 K? Show all steps in the calculation.

Probability of state J is given by

$$P_J = (2J+1) e^{-\frac{BJ(J+1)}{k_B T}}$$

Most populated state $\Rightarrow \left. \frac{dP_J}{dJ} \right|_{J_{\max}} = 0$

$$\Rightarrow (2J_{\max}+1) \left(-\frac{B}{k_B T} \right) (2J_{\max}+1) + 2 = 0$$

$$\frac{B_{I_2}}{k_B T} = \frac{hc \bar{B}}{k_B T} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 0.037}{1.38 \times 10^{-23} \times 500}$$

Solving, we get $J_{\max} = 68$

(c) (3 marks) Assuming that all the reactants are in their most probable states, calculate the total energy of the reactants in the center of mass frame.

$$E_{\text{react}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

$$= \frac{1}{2} \mu (1000)^2 + hc \bar{B}_{I_2} \times \quad + \frac{hc \bar{v}_{I_2}}{2} - D_e(I_2)$$

We have used the idea that the most probable state of vibration is the ground state.

$$\text{In kJ/mol : } E_{\text{react}} = 16.9 + 2.08 + 1.29 - 149 \\ = -128.7 \text{ kJ/mol}$$

(d) (4 marks) Calculate the possible vibrational quantum numbers of the KI molecule.

$$-128.7 = E_{\text{trans}}' + E_{\text{rot}}' + E_{\text{vis}}' + E_{\text{el}}' \quad \text{kJ/mol}$$

$$-128.7 = E_{\text{trans}}' + E_{\text{rot}}' + E_{\text{vib}}' - 319 \quad \text{kJ/mol}$$

$$E_{\text{trans}}' \geq 0 \quad E_{\text{rot}}' \geq 0$$

Thus, maximum vibrational energy is obtained when

$$E_{\text{trans}}' = E_{\text{rot}}' = 0$$

$$\Rightarrow h c \bar{\nu}_{\text{KI}} \left(v_{\max} + \frac{1}{2} \right) = 190.3 \text{ kJ/mol}$$

$$\text{Solving, we get } v_{\max} = 84.7$$

Possible vibrational states of KI have quantum nos

$$v = 0, 1, 2, \dots, 84$$

PROBLEM 2 – Analysis of Results of Molecular Beam Experiment (15 marks)

In this problem we focus on the results and analysis of the molecular beam experiment of the same reaction as in Problem 1 i.e. : $K + I_2 \rightarrow KI + I$

Answer the questions below regarding the set-up of the experiment. You can use the following data

Atomic masses: $K = 39.0 \text{ u}$, $I = 127 \text{ u}$

Dissociation energy: $I_2 = 149 \text{ kJ/mol}$ $KI = 319 \text{ kJ/mol}$

Vibrational Frequency: $I_2 = 214.5 \text{ cm}^{-1}$ $KI = 186.5 \text{ cm}^{-1}$

Rotational Constant B: $I_2 = 0.037 \text{ cm}^{-1}$ $KI = 0.061 \text{ cm}^{-1}$

(a) (4 marks) Assume that both the K and the I_2 beams have a velocity of 566 m/s and are collided in perpendicular direction in the laboratory frame of reference. Further, assume that iodine is in its ground rotational and vibrational state. Based on this information, calculate the maximum speed of KI in the center of mass frame of reference.

$$E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} = E'_{\text{trans}} + E'_{\text{rot}} + E'_{\text{vib}} + E'_{\text{el}}$$

$$\frac{1}{2} \mu v_{\text{rel}}^2 + 0 + \frac{hc \tilde{B}_{I_2}}{2} - 149 = E'_{\text{trans}, \text{max}} + 0 + \frac{hc \tilde{B}_{KI}}{2} - 319$$

Solving, we get $E'_{\text{trans}, \text{max}} = 182.1 \frac{\text{kJ}}{\text{mol}}$

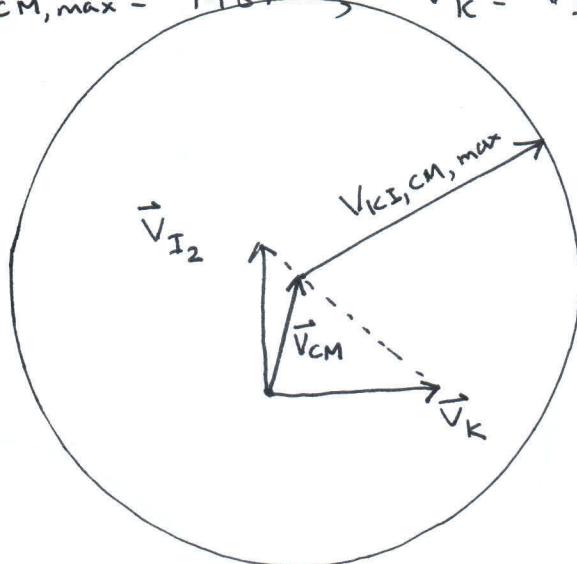
Maximum speed of KI in C.M. frame satisfied

$$\frac{1}{2} m_{KI} v'_{\text{max, cm}}^2 = \frac{182.1 \times 10^3}{6.023 \times 10^{23}}$$

Solving, we get $v'_{\text{max, cm}} = 1481 \text{ m/s}$

(b) (3 marks) Draw the Newton diagram for the above collision. Clearly indicate the region showing the possible velocity vector of the KI molecule. Make sure that your drawing is to scale.

Note: $v_{KI, CM, max} = 1481 \rightarrow v_K = v_{I_2} = 566$



Final velocity of KI can be in any point inside the circle but not outside it.

(c) (4 marks) For the beams used above, it is observed that most of the scattered KI is in the forward direction with respect to the incident KI beam. Further it is observed that KI is produced in excited rotational and vibrational states. Using this basic information, draw the velocity flux contour map of KI.

As in Problem 1(d), we can calculate v_{max} for KI.

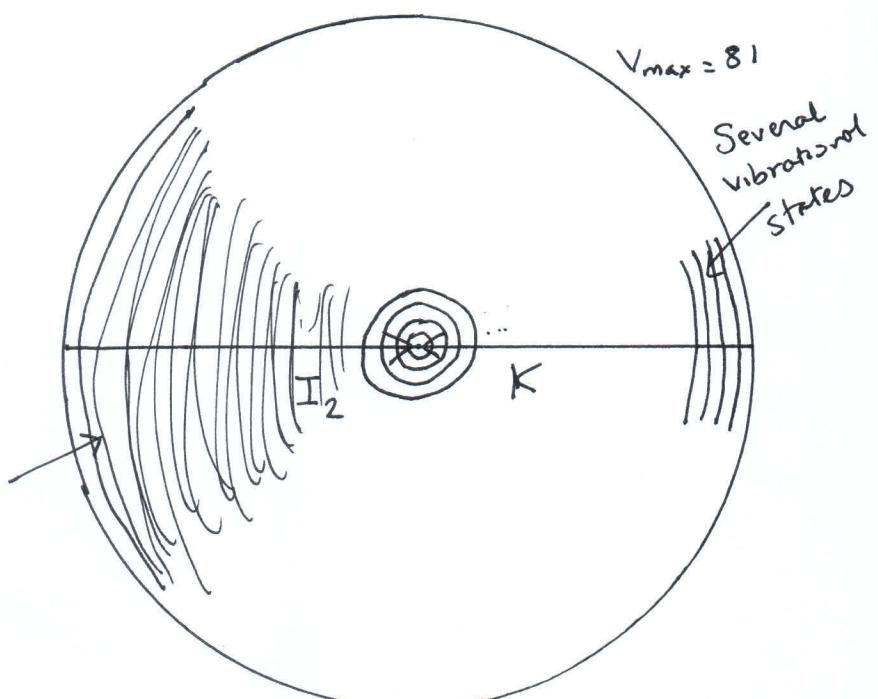
From problem 2(a)

$$h \tilde{c} B_{KI} v_{max} = 182.1 \frac{\text{kJ}}{\text{mol}}$$

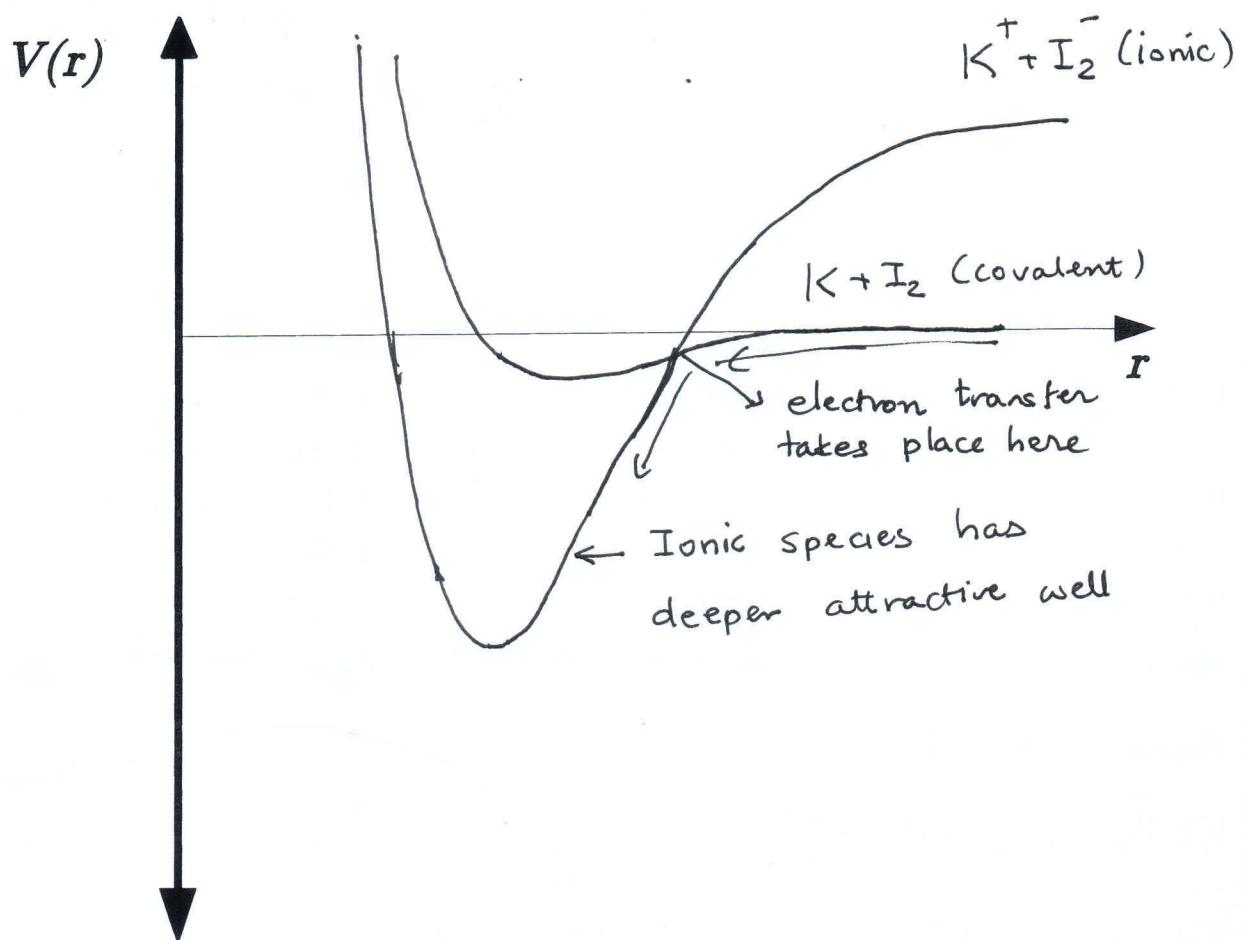
Solving, we get

$$v_{max} = 81$$

forward scattered products

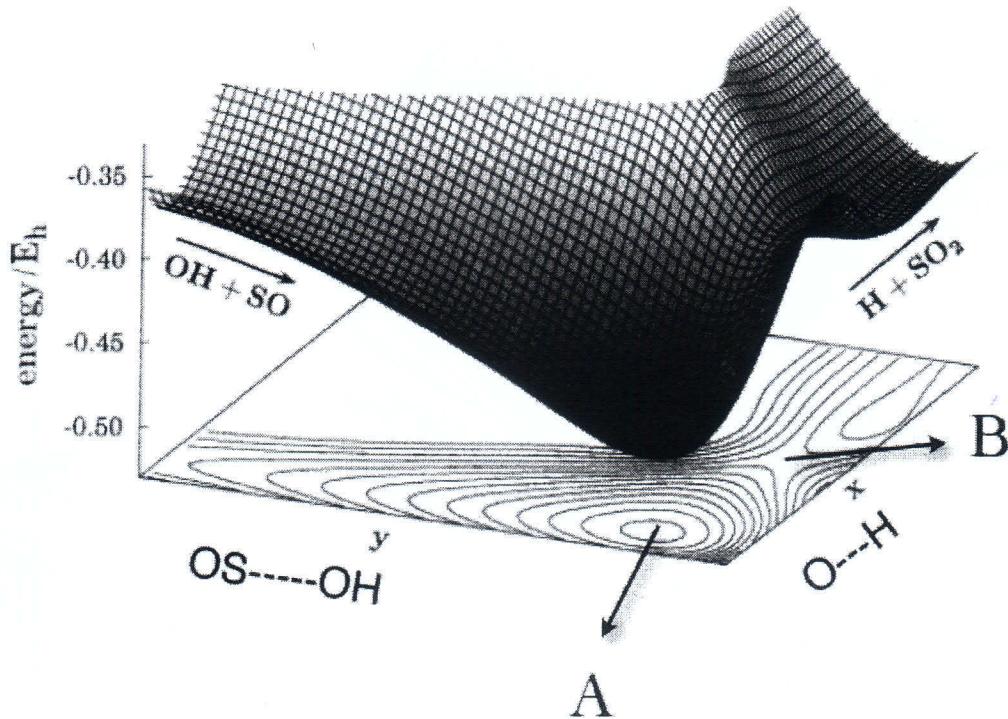


(d) (4 marks) One of the major triumphs of this experiment was to calculate the reactive scattering cross-section and show that it is several times greater than the cross-section calculated using hard sphere scattering theory. This is justified using the harpoon mechanism of the reaction where there is an electron hop from K to I₂ before the collision which steers the incoming potassium atom towards the center of I₂. Show two non-reactive potential energy curves for K + I₂ and K⁺ + I₂⁻ as a function of the intermolecular/interionic distance.



PROBLEM 3 – Potential Energy Surfaces (10 Marks)

A part of the Potential Energy Surface(PES) of interaction of OH and OS is shown below, both as a surface and as a contour plot. The contours shown above start at -0.48 au and go up in steps of 0.01 au.



Answer the questions below. You can use the following information.

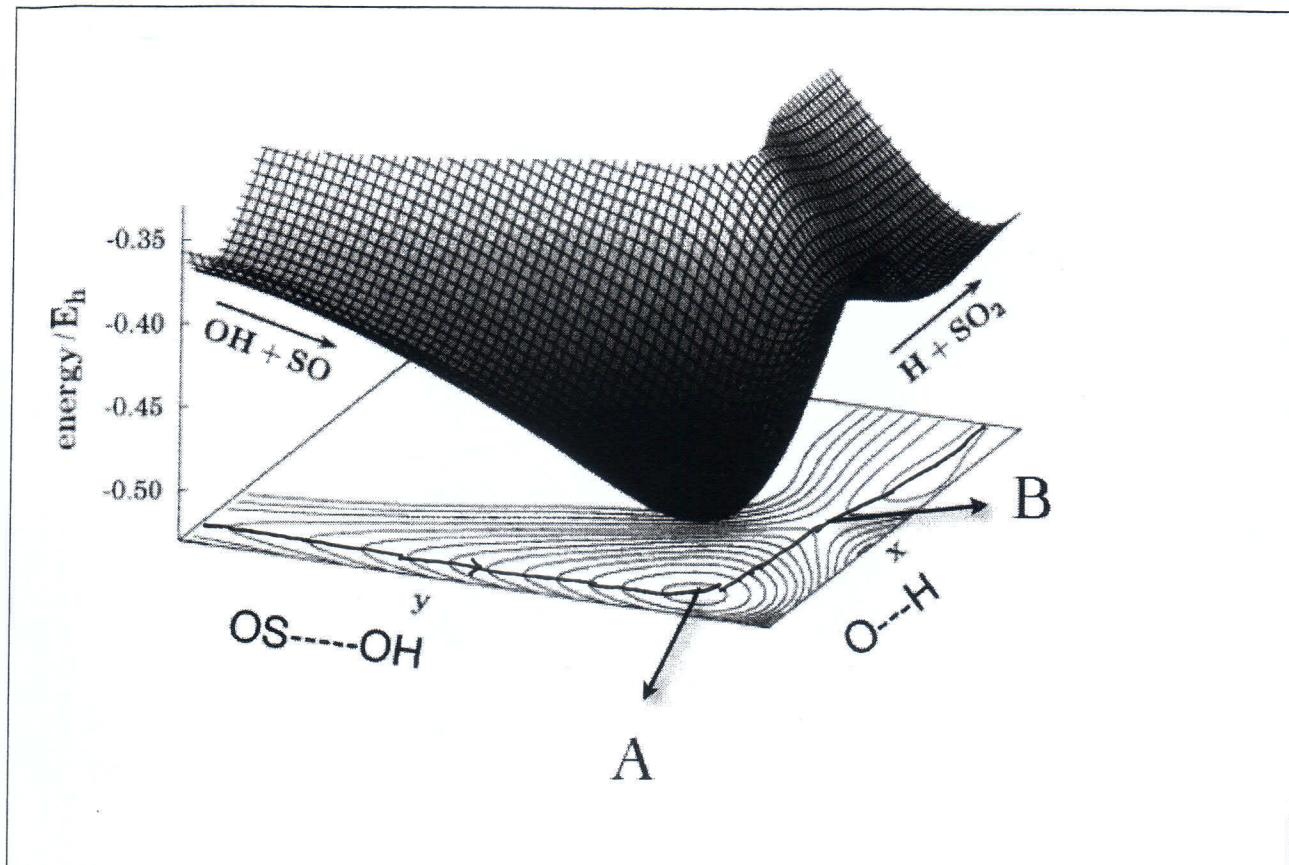
1 au of energy = 1 hartree = 4.360×10^{-18} J = 27.211 eV = 2625 kJ/mol = 627.5 kcal/mol

(a) (4 marks) Does the point **A** correspond to a minimum, a transition state or a maximum? Estimate the energy of **A** relative to OH+SO in kcal/mol ? Answer both the questions above for point **B**.

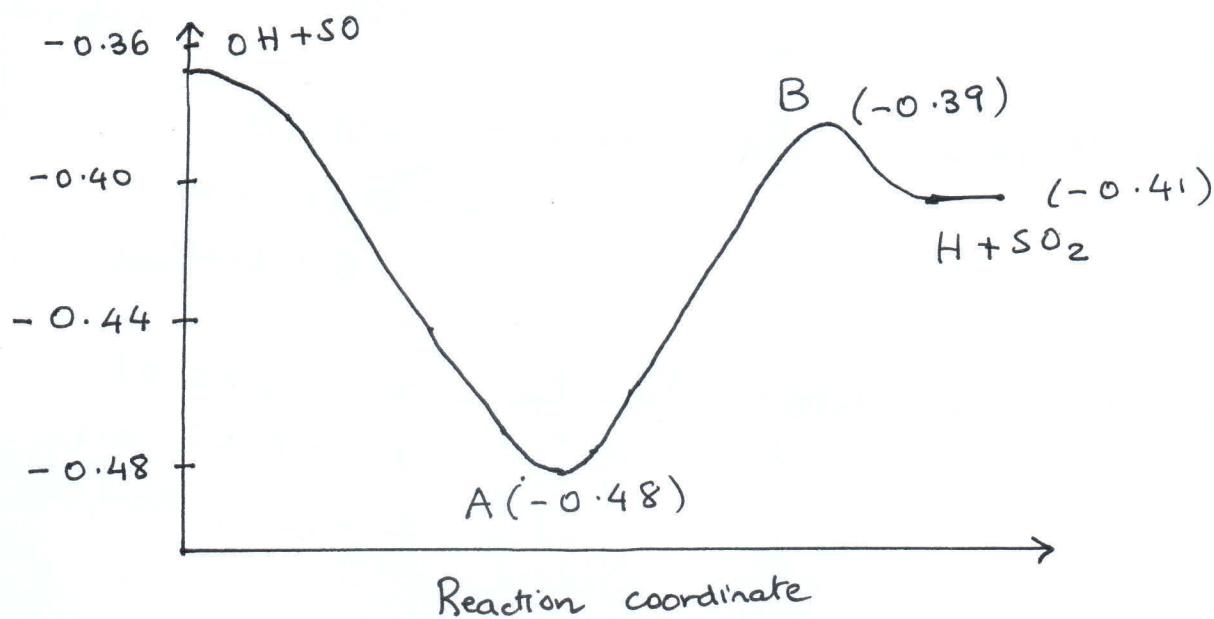
$$\begin{aligned} A : \text{Minimum} \quad E_A - E_{\text{OH}+\text{SO}} &= -11 \times 0.01 \\ &= -0.11 \text{ a.u.} \\ &= -69 \text{ kcal/mol} \end{aligned}$$

$$\begin{aligned} B : \text{Transition state} \quad E_B - E_{\text{OH}+\text{SO}} &= -2 \times 0.01 \\ &= -0.02 \text{ a.u.} \\ &= -12.6 \text{ kcal/mol} \end{aligned}$$

(b) (2 marks) Sketch the minimum energy path on the contour plot. i.e. the 2D plot in the figure.

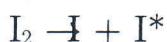
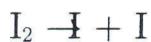


(d) (4 marks) Draw the potential energy curve (1D) for the above reaction. Draw your diagram approximately to scale and indicate the energy values of the species involved.

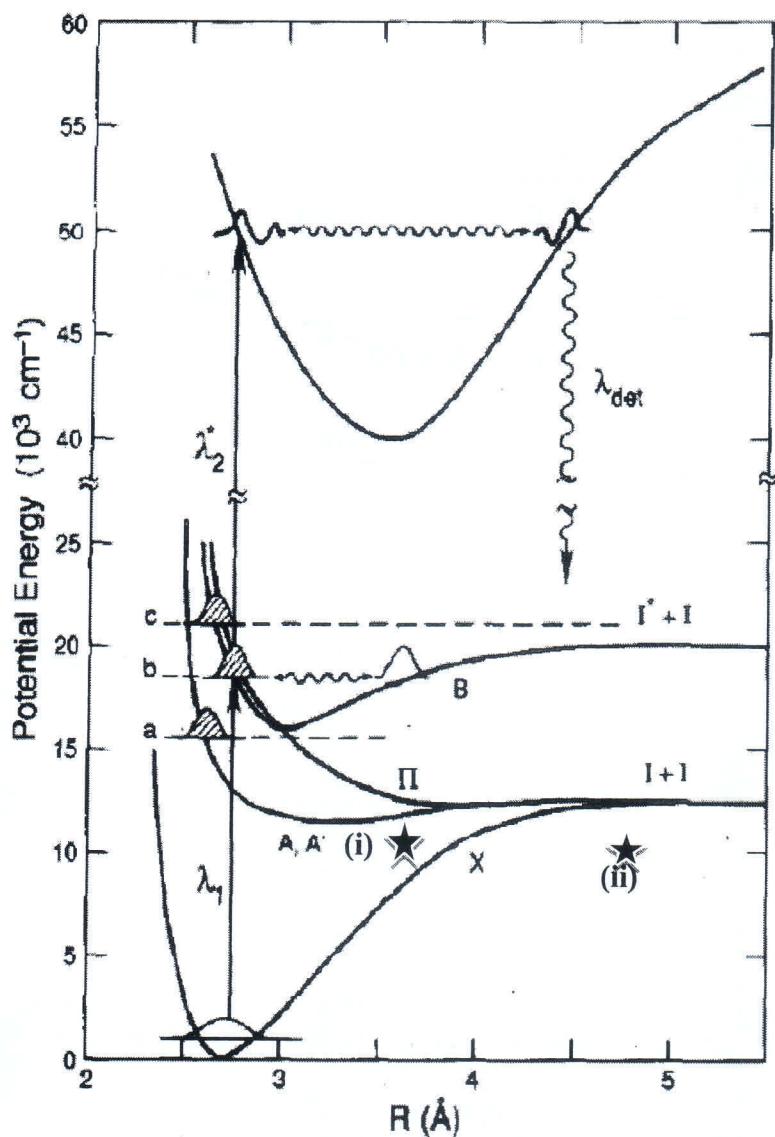


PROBLEM 4 – Femtosecond Transient Spectroscopy (25 marks)

This problem is taken from the article Bowman, R. M.; Dantus, M. and Zewail, A. H. *Chem. Phys. Lett.* **1989**, *161*, 297. The authors studied the Femtosecond Transient Spectroscopy(FTS) of I₂ (Atomic Mass No of I = 127). There are two channels for the reaction and are given by

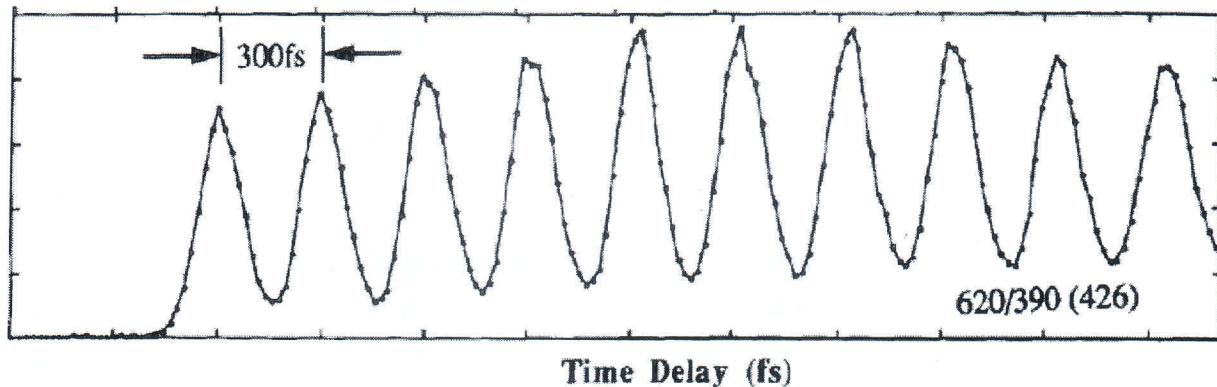


The PES for the reaction is given below. The ground state is denoted by "X". Note that the probe beam takes the system to a bound state, which fluoresces at a wavelength λ_{det} , that is different from λ_2^* . This happens to be a feature of a well characterized fluorescent state in I₂.



Note that in the PES diagram, there are 3 excited states, which can be populated by the pump beam λ_1 . These states are denoted by **AA***, **B** and **II**.

The FTS signal obtained for the B state is shown below. In the figure, the numbers on the bottom right denote $\lambda_1 / \lambda_2^* (\lambda_{\text{det}})$.

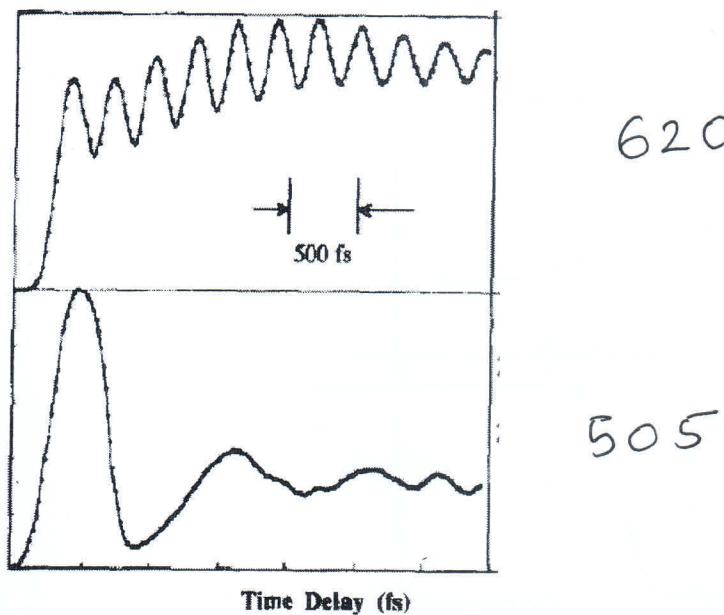


(a). (2 marks) Estimate the fundamental vibrational wavenumber (in cm^{-1}) of I_2 in the **B** excited state.

$$\begin{aligned}\bar{\nu} &= \frac{1}{\lambda} = \frac{\nu}{c} = \frac{1}{\tau c} \\ &= \frac{1}{300 \times 3 \times 10^{-5}} \text{ cm}^{-1} \\ &= 111 \text{ cm}^{-1}\end{aligned}$$

In order to confirm that the oscillations are due to the wave packet prepared by the pump pulse they used different pump pulses (620 nm and 505 nm).

(b). (3 marks) Identify the pump wavelength that corresponds to each of the transients below.



It is observed that the oscillation of the wave packet prepared this way lasts for longer than 40 ps.

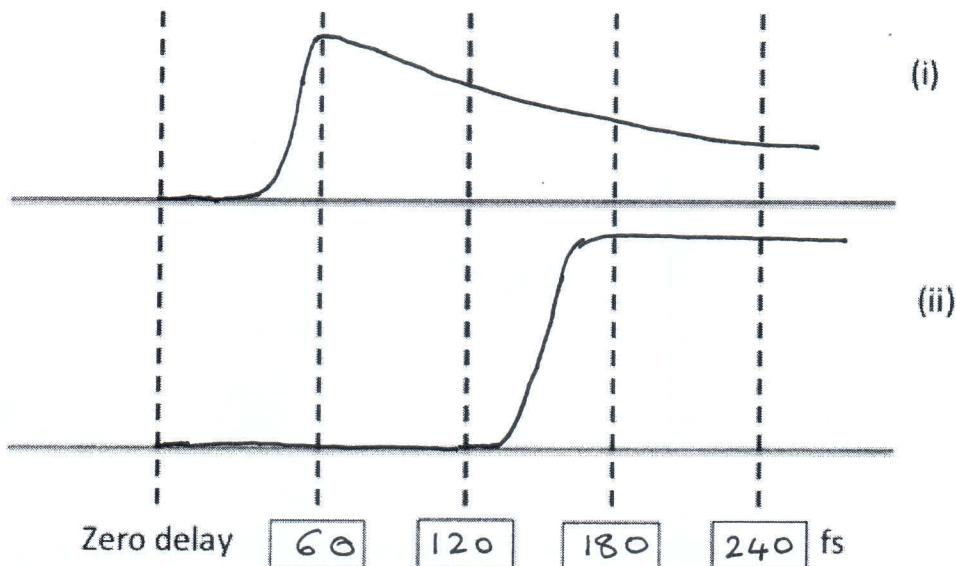
(c). (2 marks) Why does the signal detected above **NOT** decay rapidly ?

B is a bound state and thus it has a higher lifetime, so it does not easily go to $I^* + I$
 Another mode of relaxation is a transition from B to π , which is a weakly dissociative state. However, this transition is weak since it is forbidden by symmetry.

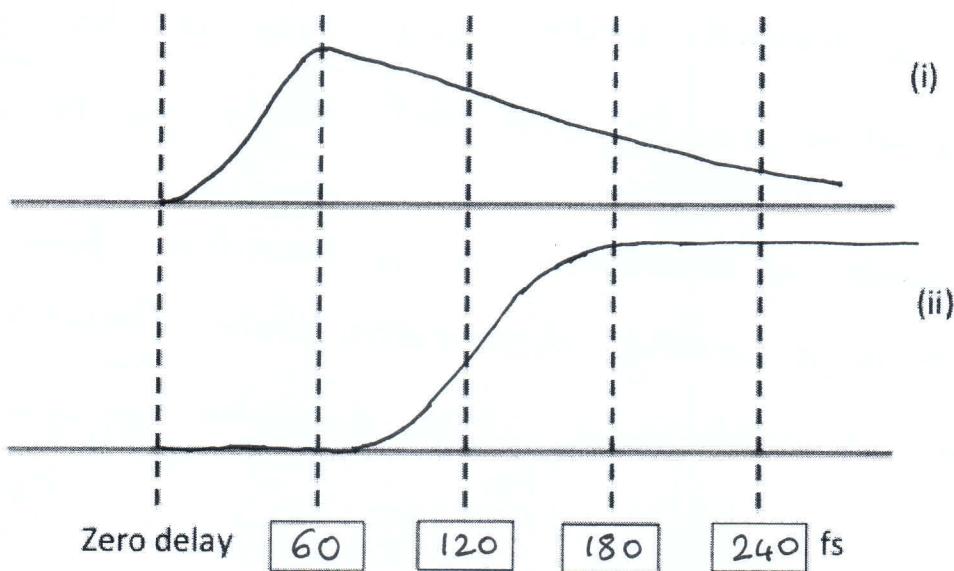
Note that it is also possible to probe the Π state by selecting a proper probe pulse, which will lead the system to B state. In the PES diagram please notice the two positions (i) and (ii) on the Π state.

(d) (7 marks) Draw the expected FTS signal for the two states (i) and (ii) with reasonable accuracy for an extremely ultrashort pulse (5 fs) and for a broad pulse (200 fs). The x-axis in both graphs is the delay time, which you should estimate in the boxes. Note that the recoil velocity is $1.14 \times 10^3 \text{ ms}^{-1}$ and excitation wavelength is 620 nm.

For an ultrashort pulse



For a broad pulse



To measure the FTS, they used a colliding pulse mode-locked (CPM) laser system of pulse width 50 fs (Gaussian profile) and 0.3 mJ per pulse energy with a central wavelength of 600 nm. The length of the laser cavity (i.e. two mirror system) is 2 m. This was further processed in NOPA to get the desired color of pump and probe pulses as discussed in the class. The pulse duration was measured by intensity autocorrelation using NLO crystal. To compensate the GVD, a grating system was used.

(e) (3 marks) Compute the average power of the CPM laser output.

$$\Delta\nu = \frac{c}{2L} = \frac{3 \times 10^8}{2 \times 2} = 75 \text{ MHz}$$

$$\begin{aligned}\text{Average power} &= 0.3 \text{ mJ} \times 75 \text{ MHz} \\ &= 22.5 \text{ kW}\end{aligned}$$

(f) (3 marks) Estimate the spectral line-width (in nm) for the CPM laser output. Treat the laser pulses as Gaussian and recall that the product of time-width and band-width is 0.441.

$$\Delta\nu \times \Delta t = 0.441$$

$$\Delta\nu = \frac{0.441}{50 \times 10^{-15}} \text{ s}^{-1} = 8.82 \times 10^{12} \text{ s}^{-1}$$

$$\begin{aligned}\Delta\lambda &= \frac{\lambda^2}{c} \cdot \Delta\nu \\ &= \frac{(600 \times 10^{-9})^2}{3 \times 10^8} \times 8.82 \times 10^{12} \\ &= 10.6 \text{ nm}\end{aligned}$$

(g) (3 marks) Estimate the number of oscillation of the electric field of 600 nm light within the pump pulse.

$$T = \frac{\lambda}{c} = \frac{600 \times 10^{-9}}{3 \times 10^8} = 2 \text{ fs}$$

$$\text{No. of oscillations per pulse} = \frac{50 \text{ fs}}{2 \text{ fs}} = 25$$

(h) (2 marks) Estimate the number of modes being locked in the CPM laser.

$$\tau_p = \frac{1}{N \Delta v_{\text{cav}}}$$

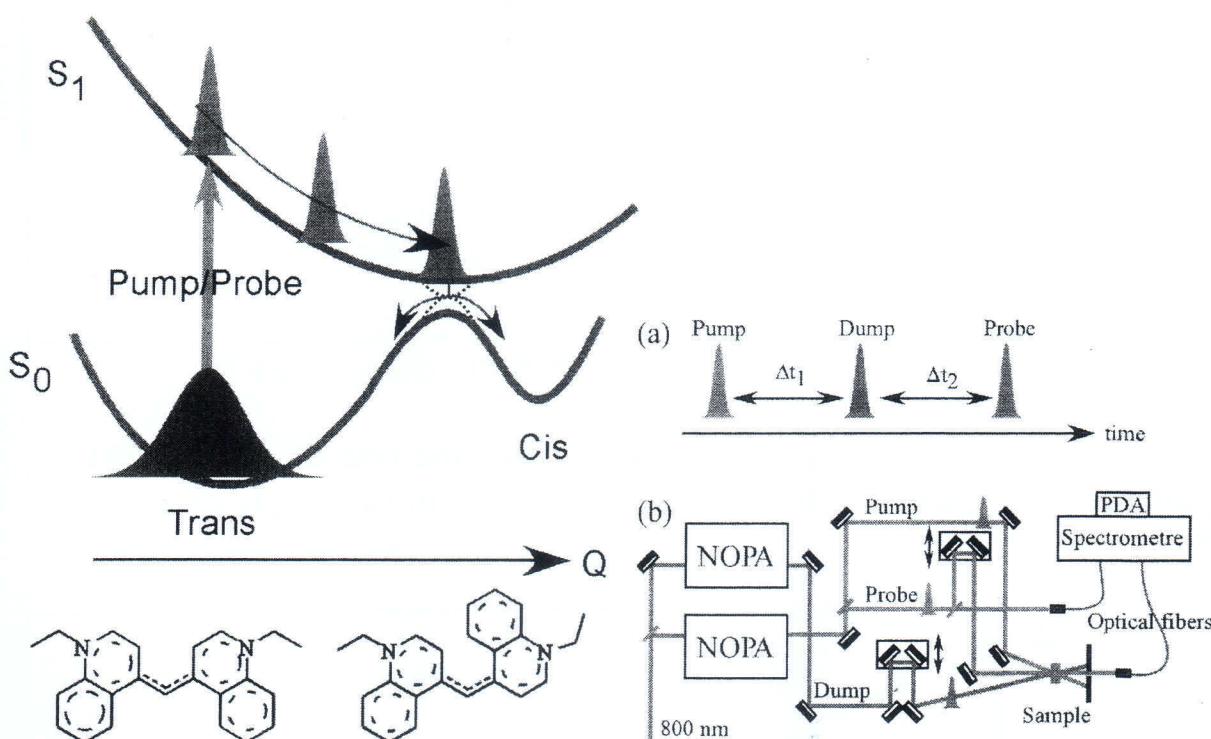
$$N = \frac{1}{\tau_p \times \Delta v_{\text{cav}}}$$

$$= \frac{1}{50 \text{ fs} \times 75 \text{ MHz}}$$

$$= 2.6 \times 10^5$$

PROBLEM 5: Pump-Dump-Probe (15 marks)

In an article by Wei *et al.* (*J. Am. Chem. Soc.* **2011**, *133*, 8205), the photoisomerization of a cyanine dye was studied by ultrafast pump-dump-probe spectroscopy. The Simplified model potential (before performing the femtosecond experiment) and reaction scheme for photoisomerization is given below. Note here that the pump and probe pulses are of the same color (590 nm). The time sequence of the pump, dump, and probe pulses and the experimental setup for the pump-dump-probe experiment are also shown.



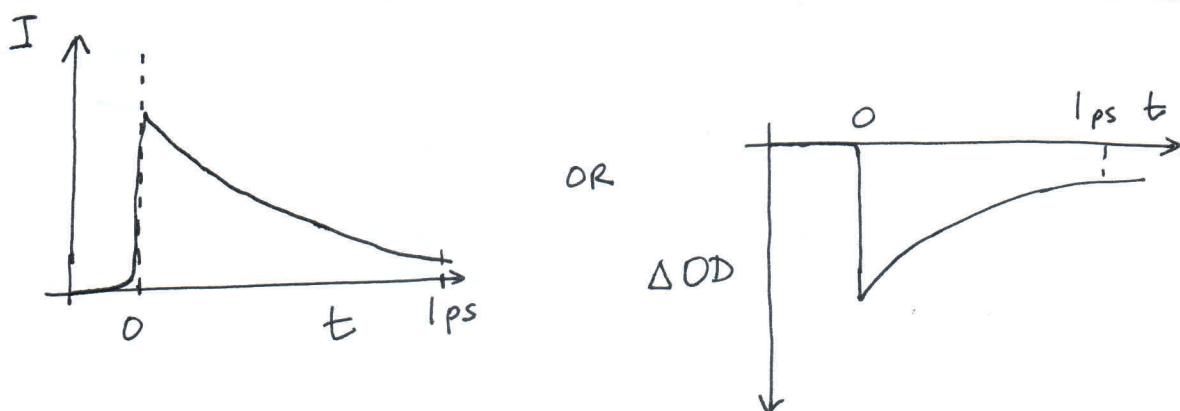
Here Q represents the twisting angle in the molecule. It can be assumed that for 180° rotation of the twisting angle (i.e. from the *Trans* to *Cis* conversion) the required time is 1 ps.

For quantitative evaluation of the dump effect, they defined the dump efficiency (η) by using the transient absorption signals with (ΔA_{on}) and without (ΔA_{off}) the dump pulse:

$$\eta = \left| \frac{\Delta A_{on} - \Delta A_{off}}{\Delta A_{off}} \right| = \left| \frac{\Delta A_{diff}}{\Delta A_{off}} \right|$$

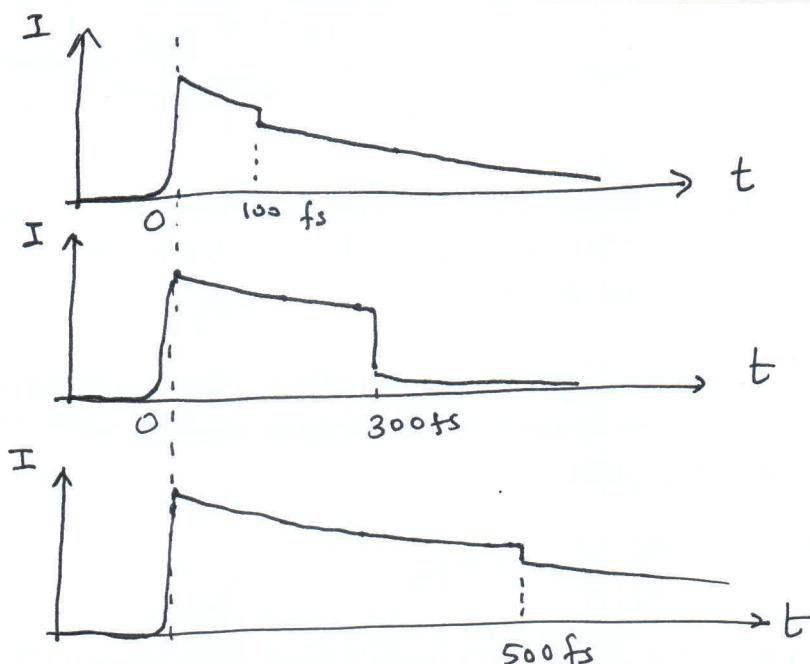
where $\Delta A_{diff} = \Delta A_{on} - \Delta A_{off}$ is a difference signal. This dump efficiency represents how much fraction of the S_1 population is transferred back to the ground state by the dump pulse.

(a) (2 Marks) Qualitatively sketch below the expected femtosecond transient in the absence of the dump pulse. No explanation required.



It is observed that the dump efficiency of a 690 nm dump pulse is maximum for a delay $\Delta t_1 = 300$ fs.

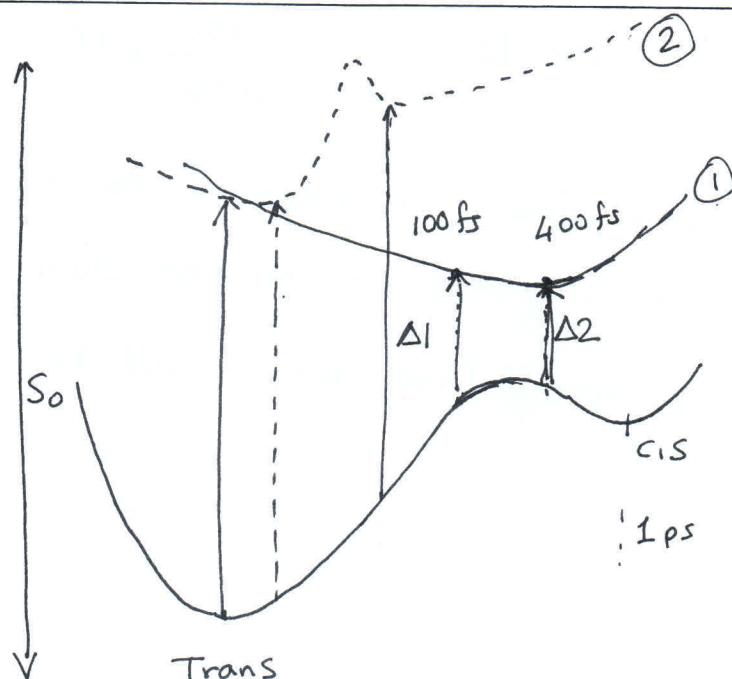
(b) (6 Marks) Qualitatively sketch the femtosecond transients with 690 nm dump pulse for $\Delta t_1 = 100$ fs, 300 fs and 500 fs in the graph given below.



ΔOD plots will be similar but -ve

The experiment revealed that for 620 nm dump pulse, the dumping efficiencies are same at $\Delta t_1=100$ and $\Delta t_1=400$ fs. Moreover they confirmed that $\frac{dE}{dQ}=0$ and $\frac{d^2E}{dQ^2}>0$ at 400 fs, where E is the potential energy.

(c) (4 Marks) The above information indicates that the potential energy curve for S_1 is not correct. Sketch the correct excited state (S_1) potential energy curve for the system. Explain your answer.



Energy difference at $\Delta t_1=100$ fs and $\Delta t_1=400$ fs are same

$\Delta t_1=400$ fs is a minimum.

2 possibilities shown above

(e) (3 Marks) Assuming that the rotation of the molecule takes place at a constant angular velocity, the twisting angle at 400 fs is expected to be 72° . However, the experimentally observed twisting angle at 400 fs is different. Is the expected twisting angle greater than or less than 72° ? Explain your answer.

Assuming angular rotation is at constant speed,
angle at 400 fs = $\frac{400}{1000} \times 180 = 72^\circ$

However since there is a barrier to rotation, the rotational velocity will be slower during the time when energy rises. Thus angle will be less than 72° .