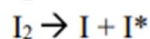
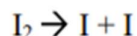


## CSO202A—Atoms, Molecules & Photons

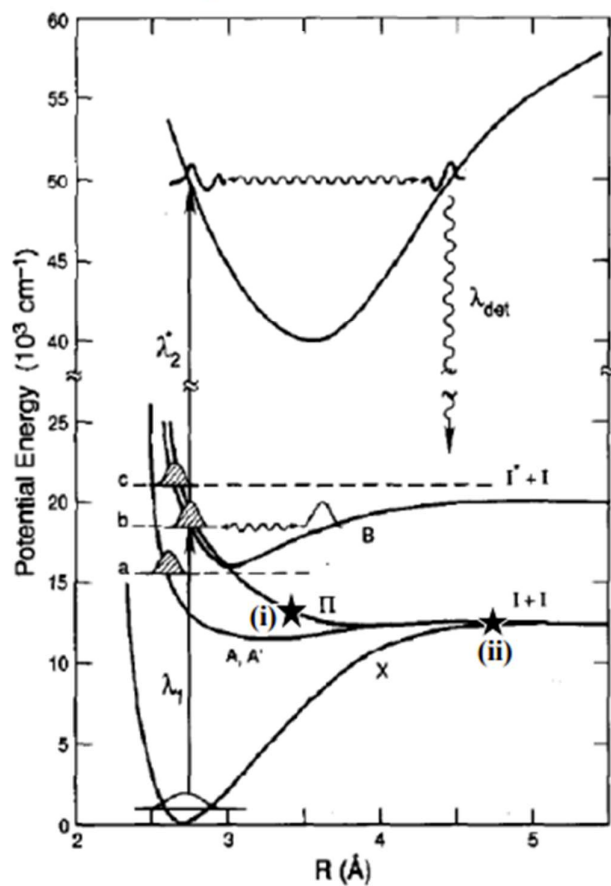
### Homework – 4

#### Problem-I

In one of the articles of Zewail included in the resources: Bowman, Dantas and Zewail, *Chem. Phys. Lett.* **1989**, 161, 297; there is a description of their study of the femtosecond transient spectroscopic study of  $I_2$ . There are two channels for the reaction and are given by:

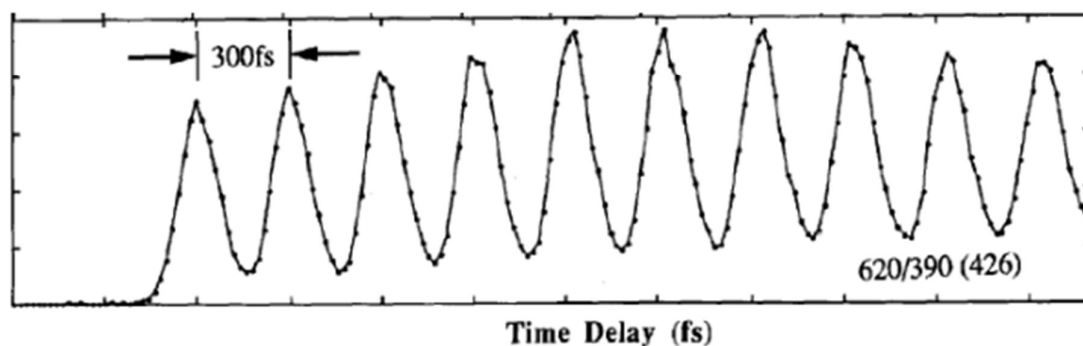


The PES for the reaction is given below. The ground state is denoted by “X”. Note that the probe beam takes the system to a bound state, which fluoresces at a wavelength  $\lambda_{det}$ , that is different from  $\lambda_2^*$ . This happens to be a feature of a well characterized fluorescent state in  $I_2$ .



Note that in the PES diagram, there are 3 excited states, which can be populated by the pump beam  $\lambda_1$ . These states are denoted by  $AA^*$ , B and  $\Pi$ .

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



**Q1.** Estimate the fundamental vibrational wavenumber (in  $\text{cm}^{-1}$ ) of  $\text{I}_2$  in the B excited state.

fundamental vibrational  
wave number  $= \bar{\nu} = 1/\lambda = \frac{\nu}{c}$   
 $= \frac{1}{\tau c}$

Given that  $\tau = 300 \text{ fs}$   
 $c = 3 \times 10^8 \text{ ms}^{-1}$

Then,  $\bar{\nu} = \frac{1}{300 \times 10^{-15} \times 3 \times 10^8 \times 10^{-2}} \text{ cm}^{-1}$

$\boxed{\bar{\nu} = 111 \text{ cm}^{-1}}$

$\bar{\nu} = f/c$

$\Rightarrow \bar{\nu} = \frac{10^{15}}{300 \times 3 \times 10^8} \text{ m}^{-1}$

$= \frac{10^5}{9} \text{ m}^{-1} = \frac{10^3}{9} \text{ cm}^{-1}$

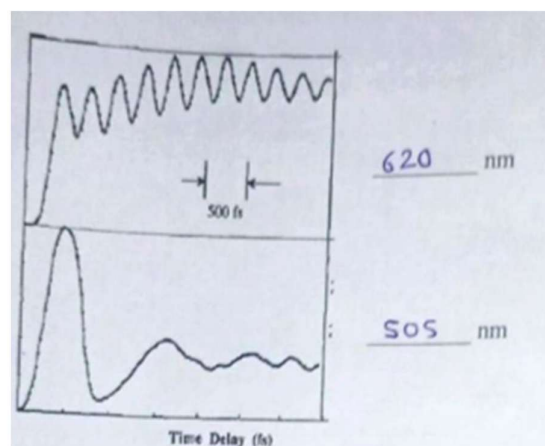
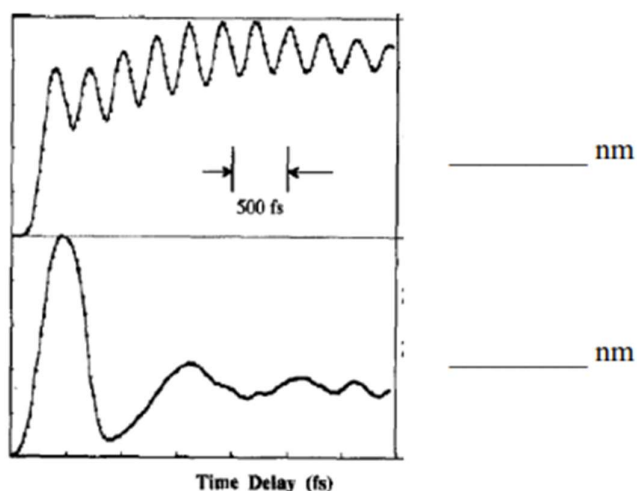
$\bar{\nu} = \frac{10^3}{9} \text{ cm}^{-1} = 111.11 \text{ cm}^{-1}$

$f = \frac{1}{300 \text{ fs}} = \frac{10^{15}}{300} \text{ sec}^{-1}$

$c = 3 \times 10^8 \text{ m/s}$

Note that 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).

**Q2.** Identify the pump wavelength that corresponds to each of the transients below.

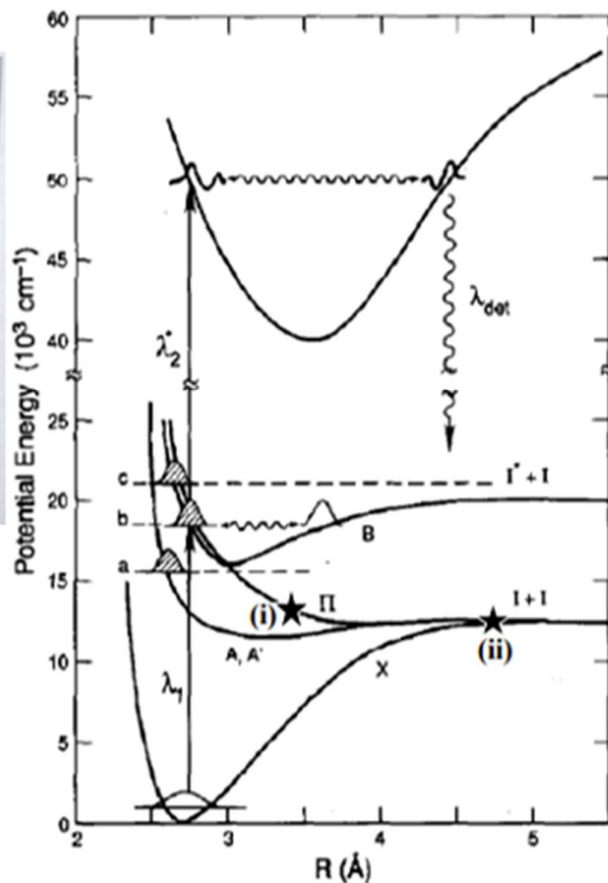


It is observed that the oscillation of the wave packet prepared this way lasts for longer than 40 ps.

**Q3.** Why does the signal detected above NOT decay rapidly?

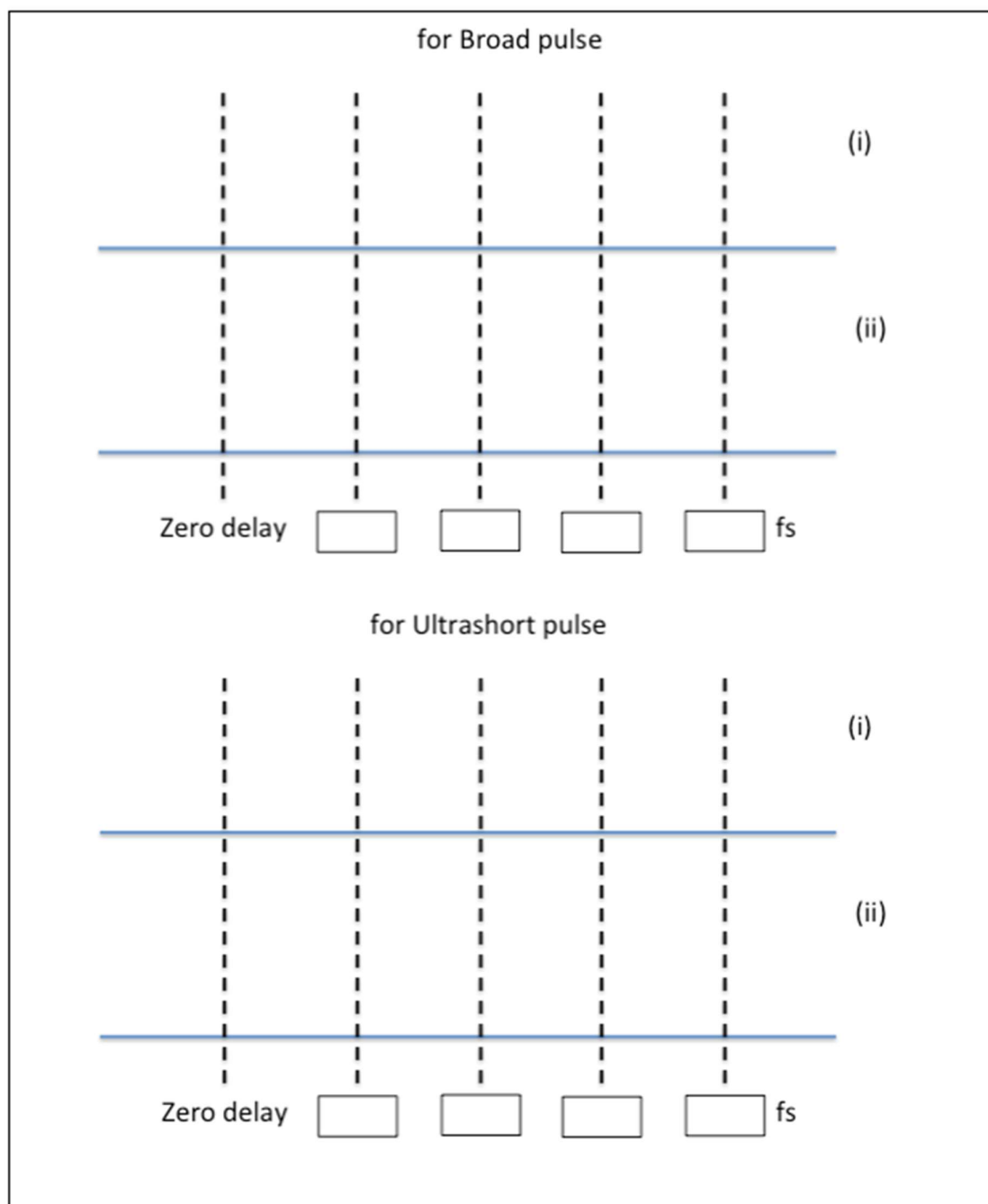
Note that it is also possible to probe the  $\Pi$  state by selecting a proper probe pulse, which will lead the system to B state. In the PES diagram please notice the two positions (i) and (ii) on the  $\Pi$  state.

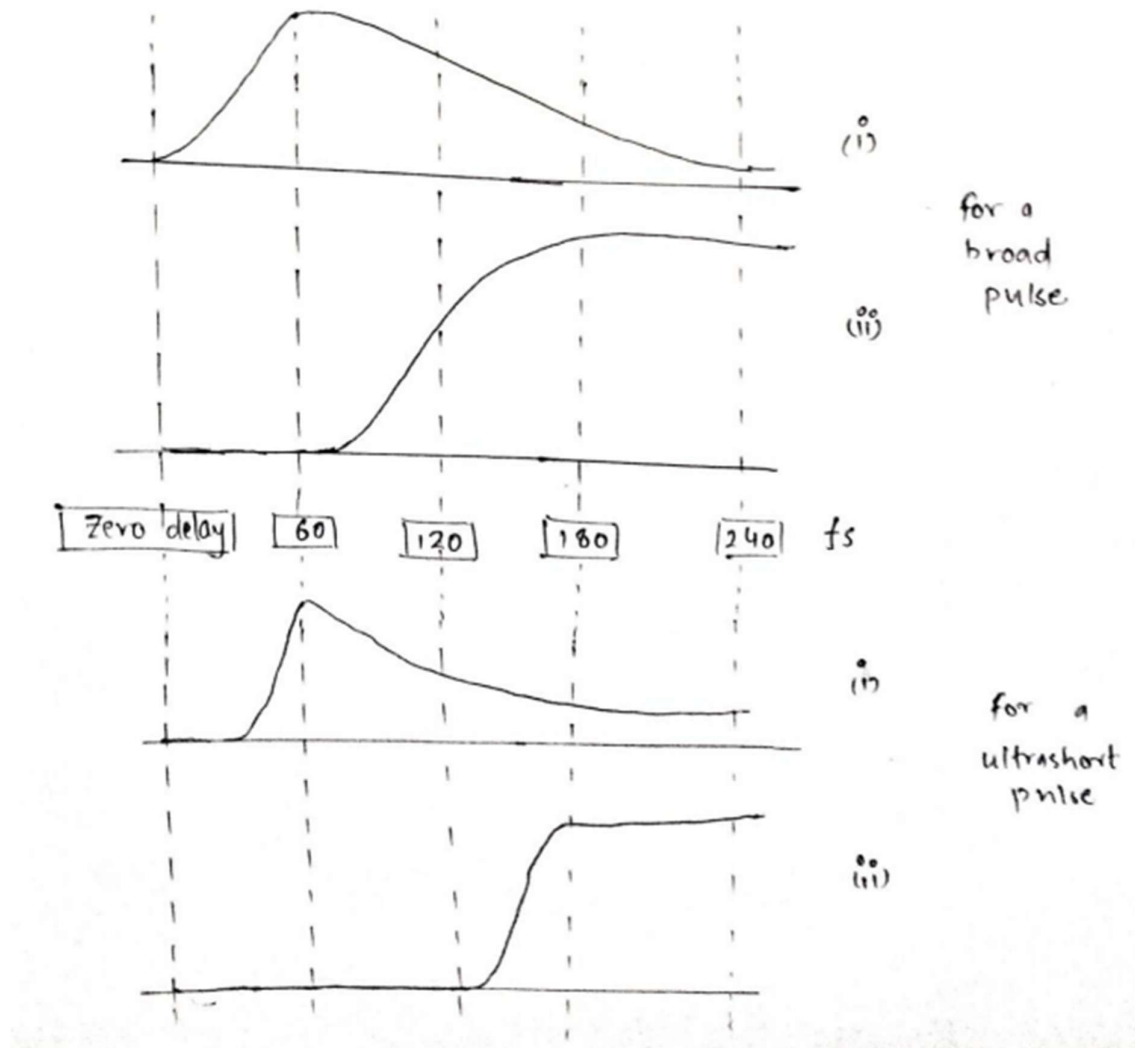
As observed, oscillation of wave packet this way lasts for longer than 40 ps. There is no sign of decay of the total signal since the ~~decay of the total signal~~ life-time of the 'B' state is very long compared to the femtosecond time scale of experiment. In B-excited state, pulse will again return to its original position without any noticeable loss of energy. That's why it is oscillating like that in B-excited state at  $\lambda_1 = 620 \text{ nm}$ .



'B' is a bound state & has a higher lifetime & so it does not immediately break into  $I^* + I$ , but has wavepacket oscillation (pump: 620 nm: lower energy). Another possible excited state is the  $\Pi$ -state, which is a dissociative state into  $I + I$ , but this is weaker as it is a symmetry forbidden transition.

**Q4.** Draw the FTS signal for the two states (i) and (ii) with relative 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 the excitation wavelength is 620 nm.





To measure the FTS, they used a colliding pulse mode-locked (CPM) laser system of 50 fs pulse width (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 systems) is 2 m. This was further processed in a Nonlinear Optical Parametric Amplifier (NOPA) to get the desired pump and probe pulses. The pulse duration was measured by intensity autocorrelation using NLO crystal. To compensate the GVD prism was used.

Q5. Estimate the number of oscillations of the electric field of 600 nm light within the pump pulse.

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

$$\text{No. of oscillation per pulse} = \frac{\text{pulse width}}{\uparrow}$$

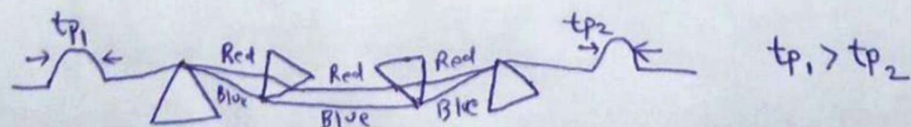
$$= \frac{50 \text{ fs}}{2 \text{ fs}}$$

$$\text{Oscillations per pulse} = 25$$

Q6. Draw a setup to compensate GVD and briefly explain.

As we know, speed of Red > speed of blue (except in vacuum)  
So, when pulse travels through any medium (eg. glass) then pulse width has increased.

To overcome this GVD, we apply compensate GVD by prism. Although our job is not to just generate pulse but also to maintain that



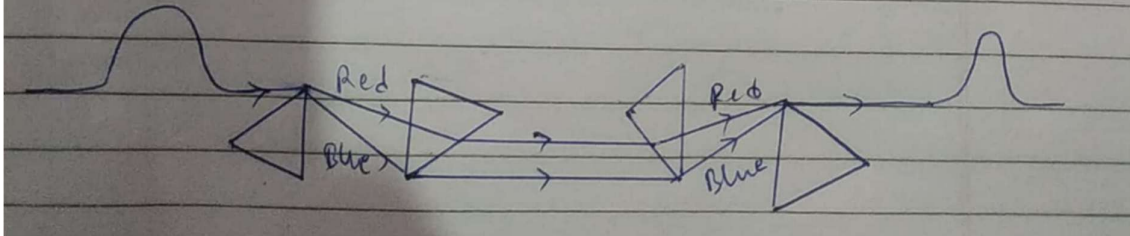
here we arrange ~~Red~~ prism like that path of blue ~~is~~ became greater than path of red.

means: arrange like:

path travelled by red < path travelled by blue

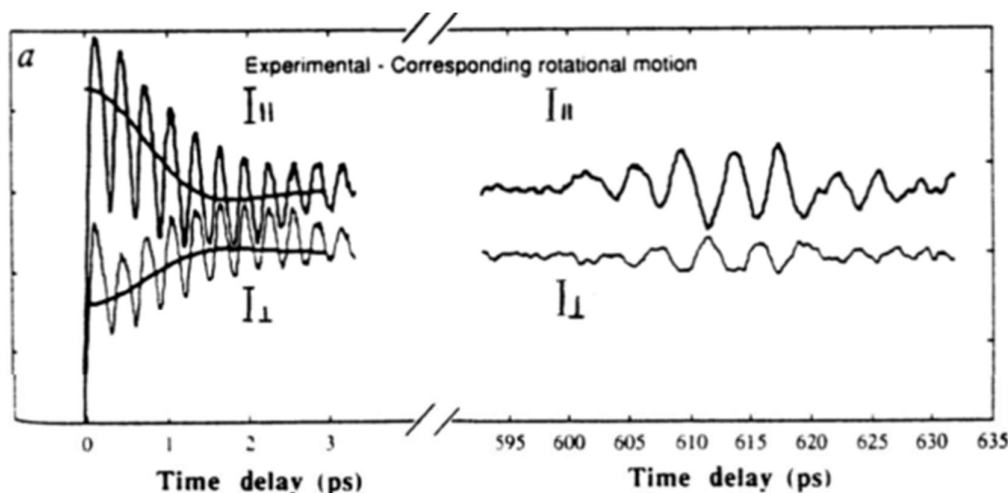


To again reduce the pulse width, prism assembly is used. Red light travels less than blue light due to which pulse width reduces.



## Problem – II

Shown below is a figure from the original work on  $I_2$  by Dantus, Bowman and Zewail, Nature 1990, 343, 737.



Initial orientation of the rotating molecules in the electronically excited state is obtained by use of linearly polarized light. Molecules whose transition dipole moment (oriented along the bond) is oriented along the direction of the electric field of the pump laser pulse are excited most efficiently, molecules oriented perpendicularly are not excited. The wavelength of the probe radiation is chosen such as to observe in the same Franck Condon region in which they were excited.

When the probe radiation is polarized parallel to the pump pulse (denoted  $||$  in the figure) then the signal is strong initially, before rotational motion reorients the transition dipoles away from the optimal direction. Signal then decreases as molecules turn away from this direction because of their thermal rotation. When the probe radiation is polarized perpendicularly to the pump pulse (denoted  $\perp$  in the figure) then the signal is weak initially, but then increases as molecules turn away from the perpendicular direction.

Consider the molecules to be rotators with a fixed axis of rotation.



**Q1.** Why at the shorter time the wave packet oscillations are superimposed, while they are not at a longer time?

Initially when the pump & probe light hits molecules excite and start rotation in some phase but as the ensemble evolves, molecules in higher rotational levels rotate quicker than the ones in lower  $J$  levels and the coherence decays. The coherence gradually decays & disappears by dephasing the alignment ( $180^\circ$  phase). In the above experiment at 600 ps,  $180^\circ$  phase change occurs.

Wave packet is formed by superimposition of waves. The oscillations are superimposed for shorter time, but at longer time rotational motion causes dephasing.

As the rotation evolves, higher  $J$  levels rotate more quickly than lower  $J$  levels due to which the coherence decays and hence no superimposition for ~~long~~ later time.

Q2. What is the classical period of rotation? Explain.

**Q2** Molecules exist at different J levels, hence have different angular velocities. But at  $t = 1/(2B)$ , all the molecules have performed an integral number of rotations so that a full classical rotation is completed (classically).

So after every  $t = \frac{1}{2B}$ , the whole setup would appear to have completed 1 rotation.

$B$  values wasn't known to me of  $I_2$

$$B = \frac{h}{8\pi^2 I} = \frac{h}{8\pi^2 M R^2}$$

$$= \frac{6.65 \times 10^{-34}}{8 \times \pi^2 \times \frac{127}{2} \times 1.66 \times 10^{-27} \times (2.665 \times 10^{-10})^2}$$

$$= 1127 \times 10^6$$

$$t = \frac{1}{2B} = 443.65 \text{ ps}$$

At time  $= \frac{1}{2B}$ , all molecules have performed integral number of rotations. Due to this there is a recurrence of the alignment. Hence, full rotational period is  $\frac{1}{2B}$ .

$$B = \frac{h}{8\pi^2 I} = \frac{h}{4\pi^2 M R^2}$$

$$\therefore B = \frac{h}{4\pi^2 M R^2} = \frac{h}{8\pi^2 M R^2}$$

$$= \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times \left(\frac{127}{2}\right) \times (2.665 \times 10^{-10})^2}$$

$$= 0.112 \times 10^{10} \text{ s}^{-1}$$

$\therefore$  Period of rotation  $= \frac{1}{2B} = \frac{1}{2 \times 0.112 \times 10^{10}}$

$$= 446.4 \text{ ps}$$

**Q3.** Estimate the period of oscillation from the experiment and comment on the possible reason if the numbers are not matching.

At 600 ps phase inversion occurs  
 $\Rightarrow \frac{T}{2} = 600 \text{ ps} - 3 \text{ ps}$  (3 ps A 3 ps system stabilised)  
 $T = 1194 \text{ ps}$

The numbers do not match because of our assumption that the molecules are rotors with fixed axis of rotation.

At 600 ps After 600 ps,  $I_{||}$  and  $I_{\perp}$  are ~~out~~  $180^\circ$  out of phase which occurs at half recurrence  
 $= \frac{1}{4B}$

$\therefore$  Time taken for half recurrence  
 $= 600 - 3$   
 $= 597 \text{ ps}$

$\therefore$  Time for complete rotation  $= 2 \times 597$   
 $= 1194 \text{ ps}$

Numbers are not matching ~~may~~ because vibration levels are also affecting the experimental time for rotation.