# CSO202A—Atoms, Molecules & Photons

## Homework – 4

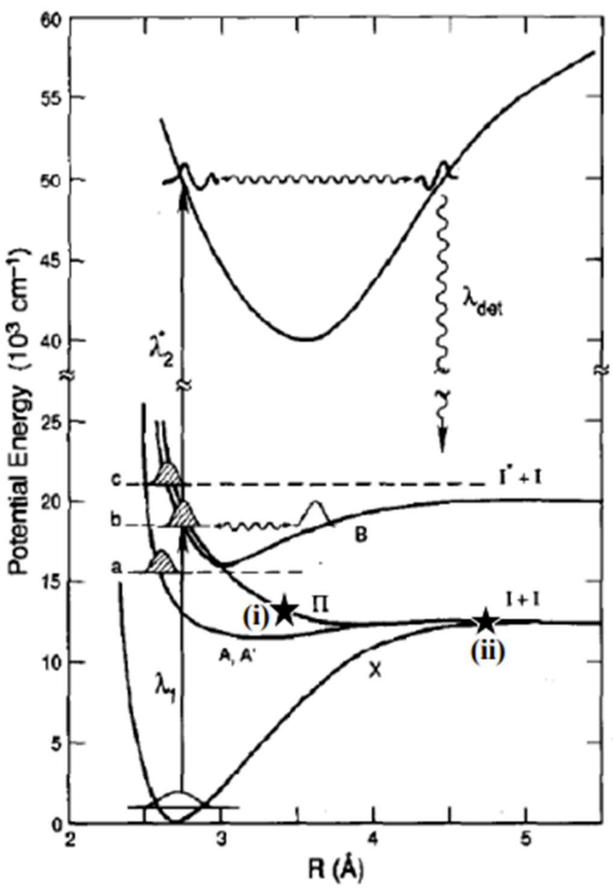
**Problem-I**

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:

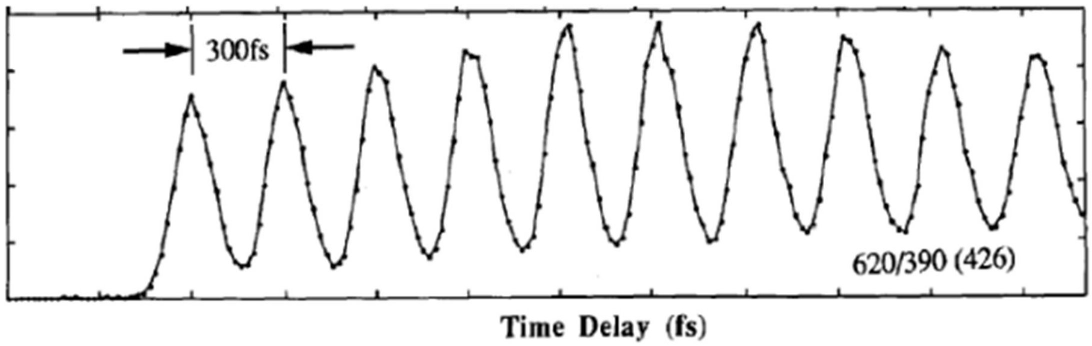
$I_2 \rightarrow I + I$

$I_2 \rightarrow I + I^*$

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 $I_2$.



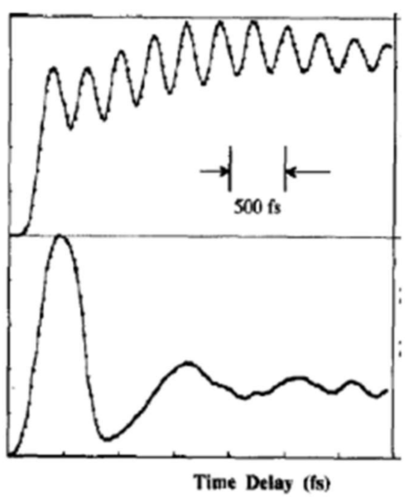
Note that in the PES diagram, there are 3 excited states, which can be populated by the pump beam $\lambda_1$. These states are denoted by AA*, B and $\Pi$.
The FTS signal obtained for the B state is shown below. In the figure, the notation used is $\lambda_1$ / $\lambda_2$* ( $\lambda_{det}$).




**Q1.** Estimate the fundamental vibrational wavenumber (in $cm^{-1}$) of $I_2$ in the B excited state.

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.




__________ nm

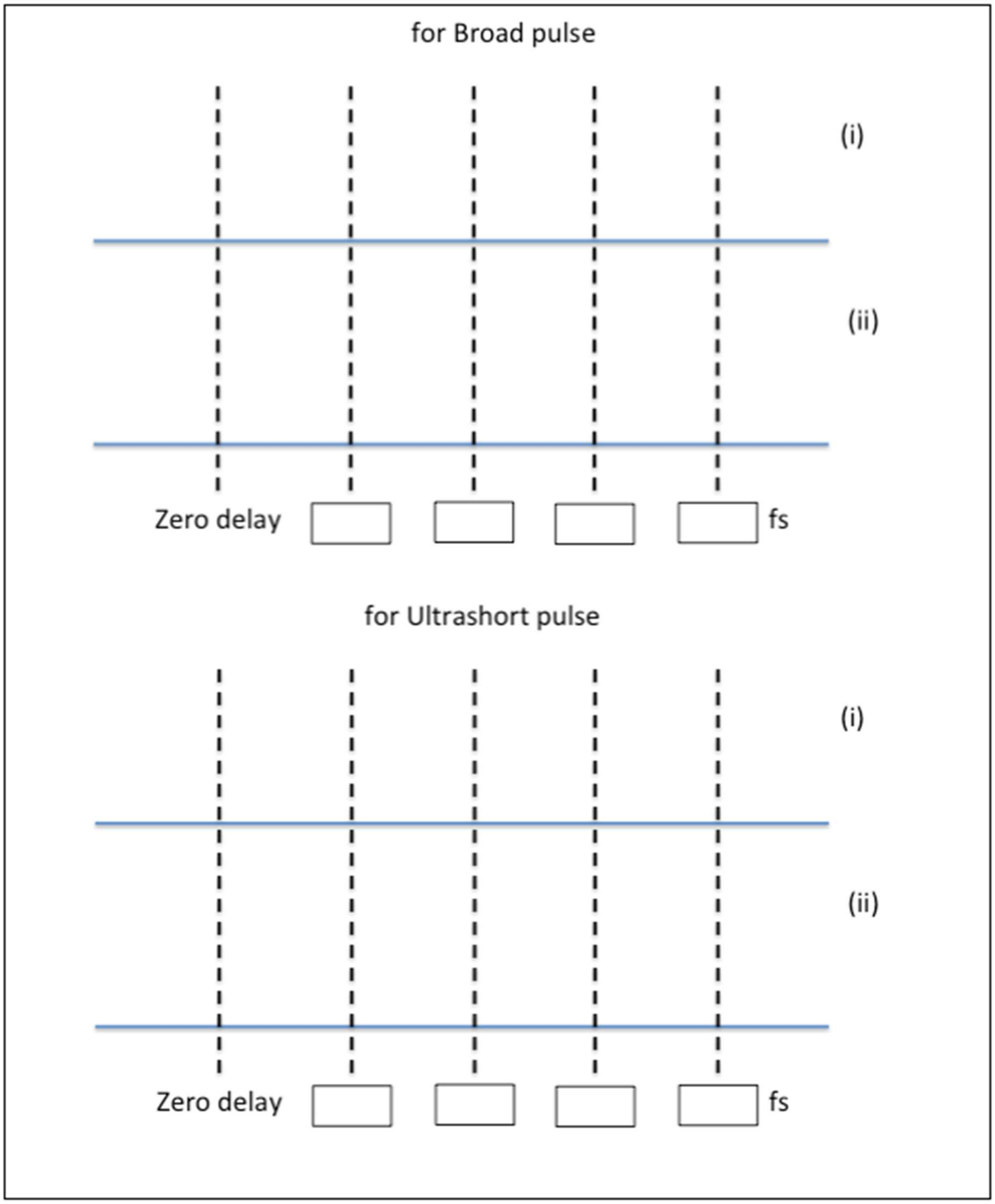
__________ nm

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.

**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 $1.14 \times 10^3$ $ms^{-1}$ and the excitation wavelength is 620 nm.



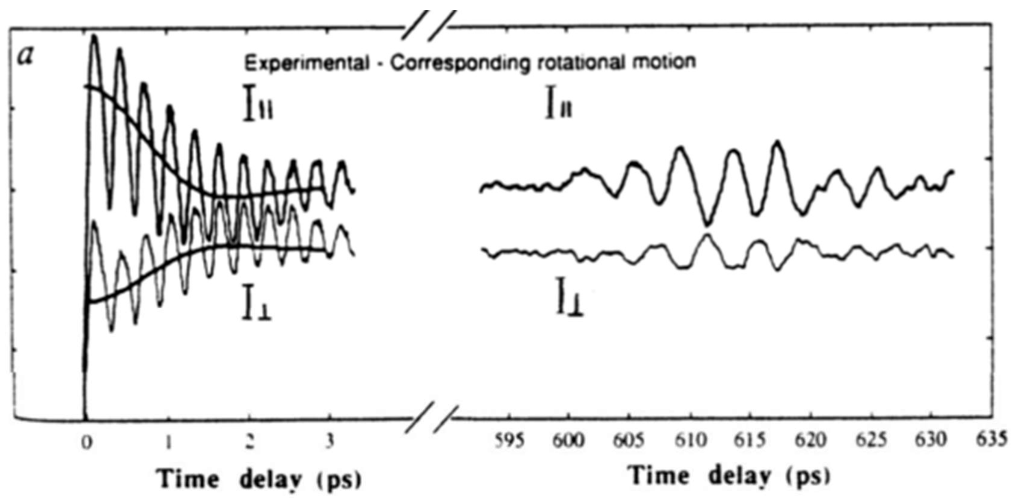

To measure the FTS, they used a colliding pulse mode-locked (CPM) laser system of 50 fs pulse width (Gaussian profile) and 0.3 mJ per pulse energy with a central wavelength of 600 nm. The length of the laser cavity (i.e. two mirror systems) is 2 m. This was further processed in NOPA to get the desired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

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

**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 ⊥ 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?

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

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