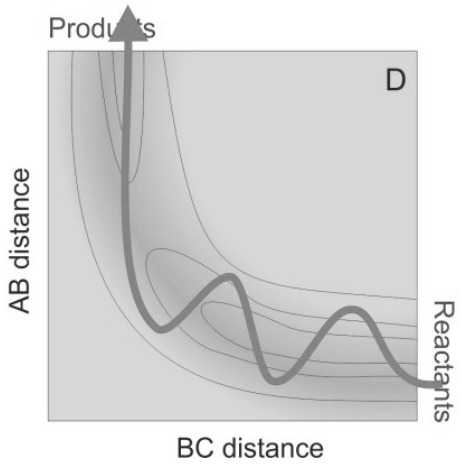
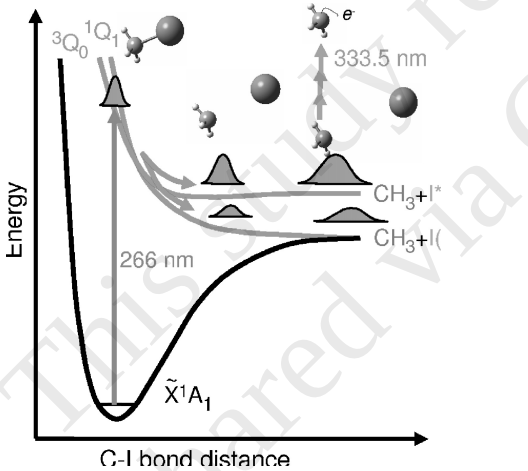
Module – II
Tutorial – 2 (for 9th February, 2018)

1. Shown below is a PES for a reaction and example classical trajectories on this surface.

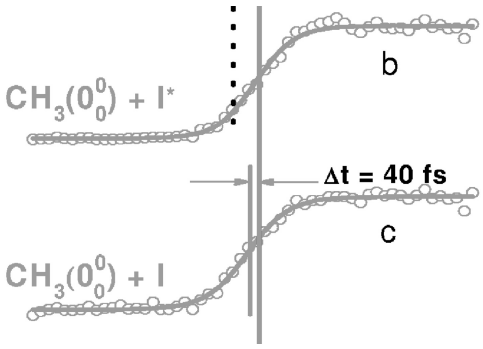


(a) Identify the nature of these trajectory i.e., reactive, nonreactive.
(b) Which reaction is being studied?

2. Shown below is a schematic PES for dissociation of CH_3I into CH_3 and I. The pump laser is at 266 nm. The probe laser at 333.5 nm detects the methyl radicals being formed.

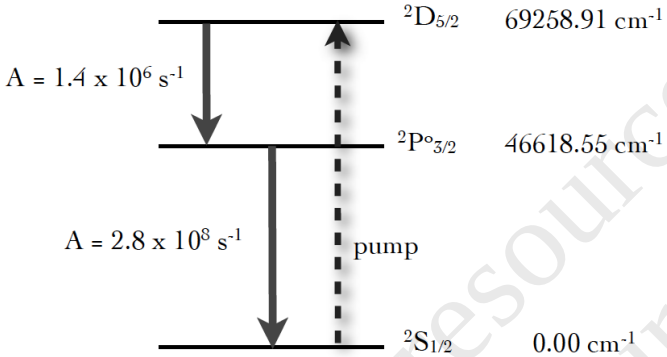


Shown below is the CH_3 transient signal as a function of the delay time. This gives us an idea of which reaction channel is faster.



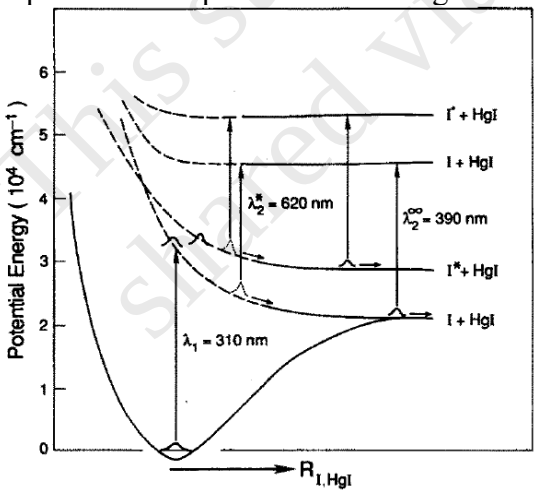
(a) Which reaction channel do you expect to be faster? Why?
(b) The experiments involved a Ti:sapphire laser of 1kHz repetition rate producing 80 fs pulses with 1 mJ energy. Calculate the power of each pulse and the number of photons in a single pulse.

3. Three electronic levels of Cd^+ ion, relevant to the He-Cd laser, are shown (not to scale) below with relevant data.

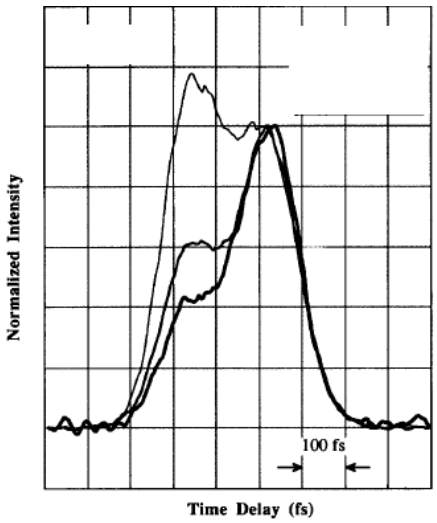


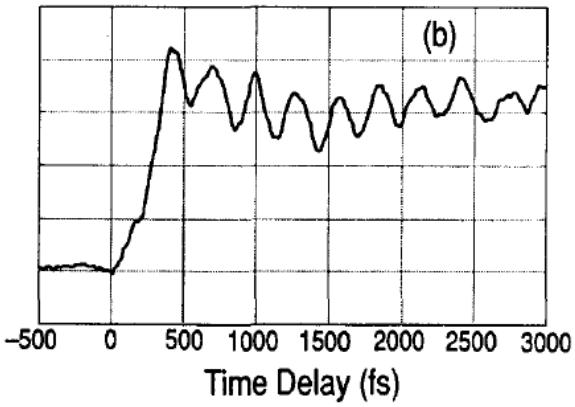
What wavelength laser light (in nm) should you expect? Why?

4. Dantus et al. [J. Chem. Phys. 91, 7437 (1989)] studied the linear triatomic molecule HgI_2 using femtosecond pump-probe spectroscopy. A simplified version of their experiment is represented in the figure below.



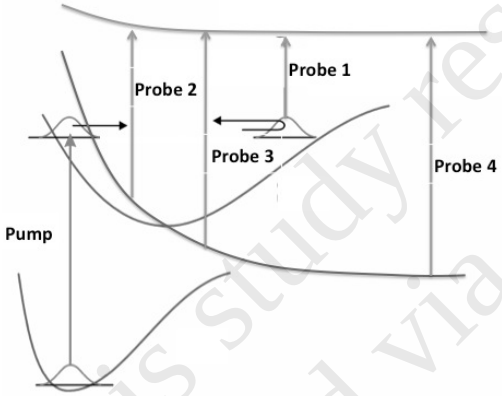
Two femtosecond transient signals are shown below for the same pump wavelength but two different probe wavelengths.





(a) Identify which one corresponds to "on-resonance'' transient signal. Write down the corresponding probe wavelength and provide a brief reason for your answer.
(b) Estimate the timescale (in fs) by which the reaction is complete. Justify your answer.
(c) The laser setup used in the experiment yields pulses of 50 fs with 0.3 mJ energy at 20 Hz repetition rate. Calculate the power of each pulse and the average power of the laser.

5. Consider the following PES for a dissociation reaction. The pump and probe laser pulses are of 50 fs pulse width.



(a) Sketch the transient signal for all the 4 different probe lights with different wavelengths with relative accuracy.
(b) Briefly discuss how the transients will change if the pump wavelength is changed to half of the wavelength used in above figure.