

CHEM 6147/8147 Molecular Photochemistry/Photophysics Chapter 1 Homework

Due Sept. 1 Thursday 5:30 P.M.

Planck's constant $h = 6.626 \times 10^{-34}$ Js

speed of light $c = 2.998 \times 10^8$ ms⁻¹

1 J = 1 Kg m² s⁻²

$1 \text{ \AA} = 10^{10} \text{ m}$

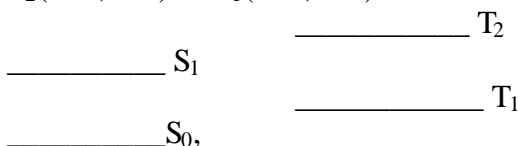
$m_e = 9.109 \times 10^{-31}$ Kg

$R = 1.987 \text{ Cal mol}^{-1} \text{ K}^{-1}$

5 equations to memorize: $(D)E = nh\nu$, $c = \lambda\nu$, $\tilde{\nu} = 1/\lambda$, $\lambda = h/p$ where $p = mv$, $t = 1/\nu$

1. Redraw the below Jablonski energy level diagram, but add vibrational and rotational levels to all 4 electronic energy levels. Illustrate the following transition:

$S_2(\nu=2, J=1) \leftarrow S_1(\nu=0, J=2)$



2. A laser emits radiation at $\lambda = 589.250$ nm with a linewidth (FWHM) of 0.04 nm. What is the linewidth in cm⁻¹ units. Hint: Differentiate $\tilde{\nu} = \frac{1}{\lambda}$ to obtain a relationship between $d\tilde{\nu}$ and $d\lambda$.

3. A laser (Nd:YAG 2nd harmonic) emits radiation at $\lambda = 532$ nm.

- If the laser output is 25 mJ per pulse, how many photons are emitted per pulse?
- What is the frequency of this radiation?
- If the laser pulse in part **a** passes through a 8.0 mm iris, what is the fluence in units of mJ cm⁻² pulse⁻¹? In your own words explain why it might be more useful to readers if an experiment reported the laser fluence rather than the laser energy.
- How many wavenumbers corresponds a 532 nm photon?
- What is the average power in watts (1 watt = 1 J s⁻¹) for the laser with a repetition rate 10 pulses per second?

4. Hydrochloric acid (H³⁵Cl) has an equilibrium rotational constant (B_e) of 10.44 cm⁻¹.

Assuming a rigid rotor model: $F(J) = \tilde{B}J(J+1)$

- For H³⁵Cl in the (J=1) rotational state, how long does it take to complete one revolution about the rotational axis, i.e. what is the rotational period?. *Hint: rotational period = {rotational frequency}⁻¹.*
- What is the rotational period for H³⁵Cl in the J = 2 state?
- What is the cm⁻¹ of H³⁵Cl in the J = 2?
- What is the frequency of H³⁵Cl in the J = 1 to J = 2 transition in MHz?

5. The C-H stretch of an organic molecule is ~3000 cm⁻¹. For a vibrational normal mode

dominated by the C-H stretch determine the period for this stretch in the $v=0$ and $v=1$

levels of the harmonic oscillator model: $\tilde{\nu} = \tilde{\nu}_0 \left(v + \frac{1}{2} \right)$ in cm^{-1}

note $\tilde{\nu}_0 = 3000 \text{ cm}^{-1}$ the fundamental frequency in wavenumbers.

6. Given the following enthalpies of rxn :

$\text{NO}_2(\text{g}) + h\nu \rightarrow \text{NO}(\text{g}) + \text{O}(\text{g}, ^3\text{P})$ if the ΔH of rxn = 71.86 Kcal/mol

$\text{NO}_2(\text{g}) + h\nu \rightarrow \text{NO}(\text{A}^2\Sigma^+, \text{g}) + \text{O}(\text{g}, ^3\text{P})$ if the ΔH of rxn = 198.3 Kcal/mol

(a) Determine the maximum wavelength (in nm) necessary for: $\text{NO}(\text{g}) \rightarrow \text{NO}(\text{A}^2\Sigma^+, \text{g})$

(b) The minimum cm^{-1} necessary for the relative kinetic energy of $\text{NO}(\text{A}^2\Sigma^+, \text{g})$ and $\text{O}(\text{g}, ^3\text{P})$ to be at least 50 Kcal/mol

7. Utilizing the Arrhenius expression for rate constant: $k = A \exp(-E_a/RT)$,

With $A = 10^{13} \text{ s}^{-1}$, $T=298 \text{ K}$, what approximate value of E_a in cm^{-1} (per molecule) will lead to excited state lifetimes on the order of hours?