CHEM 6147/8147 Molecular Photochemistry/Photophysics Chapter 1 Homework
Due Sept. 1 Thursday 5:30 P.M.

Planck's constant h = 6.626×10^{-34} Js speed of light c = 2.998×10^{8} ms^{-1}

1 J = 1 Kg m^2 s^{-2} $1\text{Å} = 10^{10}\,m$ m_e=9.109×10^{-31} Kg

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

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

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1. Redraw the below Jablonski energy level diagram, but add vibrational and rotational levels to all 4 electronic energy levels. Illustrate the following transition:
$S_2(\upsilon=2, J=1) \leftarrow S_1(\upsilon=0, J=2)$

_____ T_2

_____ S_1

_____ T_1

_____S_0,

2.. A laser emits radiation at λ = 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 λ = 532 nm.
a. If the laser output is 25 mJ per pulse, how many photons are emitted per pulse?
b. What is the frequency of this radiation?
c. 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.
d. How many wavenumbers corresponds a 532 nm photon?
e. 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 ($H^{35}Cl$) has an equilibrium rotational constant (B_e) of 10.44 cm^{-1}. Assuming a rigid rotor model: $F(J) = \tilde{B}J(J+1)$
(a) For $H^{35}Cl$ 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}$^{-1}$*.
(b) What is the rotational period for $H^{35}Cl$ in the J = 2 state?
(c) What is the cm^{-1} of $H^{35}Cl$ in the J = 2?
(d) What is the frequency of $H^{35}Cl$ 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 υ=0 and υ=1 levels of the harmonic oscillator model: $\tilde{\nu} = \tilde{\nu}_0\left(u + \frac{1}{2}\right)$ in cm^{-1}

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

6. Given the following enthalpies of rxn :

$NO_2(g) + h\nu \rightarrow NO(g) + O(g,{}^3P)$ if the ΔH of rxn = 71.86 Kcal/mol

$NO_2(g) + h\nu \rightarrow NO(A^2\Sigma^+,g) + O(g,{}^3P)$ if the ΔH of rxn = 198.3 Kcal/mol

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

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

7. Utilizing the Arrhenius expression for rate constant: $k = A \exp(-E_a/RT)$,
With $A = 10^{13}$ s^{-1}, T=298 K, what approximate value of E_a in cm^{-1} (per molecule) will lead to excited state lifetimes on the order of hours?