

15.E: Lasers, Laser Spectroscopy, and Photochemistry (Exercises)

These are homework exercises to accompany [Chapter 15](#) of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q15.9

The Einstein coefficient of a ground and excited state with a degeneracy of g_1 and g_2 is given by

$$A = \frac{16\pi^3\nu^3 g_1}{3\epsilon_0 h c^3 g_2} |\mu|^2$$

where $|\mu|$ is the transition dipole moment. Consider the $1s \rightarrow 2p$ absorption of H(g), which is observed at 121.8 nm. The radiative lifetime of the triply degenerate excited 2p state of H(g) is 1.6×10^{-9} s. Determine the value of the transition dipole moment of this transition.

S15.9

Using the expression given in the problem, we can isolate $|\mu|$ to be given as

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 \nu^3 g_1}} \quad (15.E.1)$$

Since we know the wavelength and the radiative lifetime, we can find frequency (ν) and amplitude (A) with the following equations, respectively.

$$\nu = \frac{c}{\lambda} = 2.46 \times 10^{15} \text{ s}^{-1} \quad (15.E.2)$$

$$A = \frac{1}{\tau} = 6.25 \times 10^8 \text{ s}^{-1} \quad (15.E.3)$$

where τ represents radiative lifetime.

The 2p orbital is threefold degenerate $g_2 = 3$ and the 1s orbital is singly degenerate $g_1 = 1$. Therefore, we can plug the corresponding numbers into the equation below in order to yield the transition dipole moment, which would be

$$|\mu| = \sqrt{\frac{3A\epsilon_0 h c^3 g_2}{16\pi^3 \nu^3 g_1}} \quad (15.E.4)$$

$$|\mu| = 1.1 \times 10^{-29} \text{ C} \cdot \text{m} \quad (15.E.5)$$

Q15.10

$$A = \frac{16\pi^3 \nu^3 g_1}{3\epsilon_0 h c^3 g_2} |\mu|^2 \quad (15.E.6)$$

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3} B_{21} \quad (15.E.7)$$

Use the equations above to derive the quantum mechanical expression for the Einstein B coefficient. Consider the $5s^1 P_1 \rightarrow 3p^1 S_0$ transition of neon at 730.0 nm. Einstein A coefficient is $0.48 \times 10^6 \text{ s}^{-1}$. Determine the values of the Einstein B coefficient and the transition moment dipole for this transition.

S15.10

$$\mu = \frac{h\nu}{4\pi} n_2 A_{21} \quad (15.E.8)$$

$$A = \frac{32h\pi^3 \nu^7}{c^3 \epsilon_0} n_2 B_{21} \quad (15.E.9)$$

$$B_{21} = \frac{c^3 \epsilon_0}{n_2 A 32 h \pi^3 \nu^7} \quad (15.E.10)$$

$$730 \text{ nm} = 7.3 * 10^{-7} \text{ m} \quad (15.E.11)$$

$$\lambda = 7.3 * 10^{-7} \text{ m} \text{ and thus } \nu = c\lambda = 2.189 * 10^{16} \text{ s}^{-1}$$

$$B_{21} = \frac{c^3 \epsilon_0}{n_2 A 32 h \pi^3 \nu^7} \quad (15.E.12)$$

$$B_{21} = \frac{c^3 A}{8 h \pi \nu^3} \quad (15.E.13)$$

$$B_{21} = \frac{(2.998 * 10^8 \text{ m} * \text{s}^{-1})^3 * (0.48 * 10^6 \text{ s}^{-1})}{8 h \pi (2.189 * 10^{16})^3} \quad (15.E.14)$$

$$B_{21} = 7.420 * 10^{13} \text{ kg}^{-1} \text{ m} \quad (15.E.15)$$

Q15.11

Given

$$N_{total} = N_1(t) + N_2(t) + N_3(t) \quad (15.E.16)$$

find the rate equation for each N_i .

S15.11

For each one we must look at the excitation energy, and the stimulated and spontaneous emissions energies.

For example, the excitation from 1 to 3, stimulated emission from 3 to 1 and the spontaneous emission from 3 to 1 and 2 to 1.

$$\frac{dN_1}{dt} = -B_{31} \rho_\nu \nu_{31} N_1 + B_{31} \rho_\nu \nu_{31} N_3 + A_{31} N_3 + A_{21} N_2 \quad (15.E.17)$$

the others follow as

$$\frac{dN_2}{dt} = -B_{32} \rho_\nu \nu_{32} N_2 + B_{32} \rho_\nu \nu_{32} N_3 + A_{32} N_3 - A_{21} N_2 \quad (15.E.18)$$

and

$$\frac{dN_3}{dt} = -B_{31} \rho_\nu \nu_{31} N_1 + -B_{31} \rho_\nu \nu_{31} N_3 - A_{32} N_3 - A_{31} N_3 - B_{32} \rho_\nu \nu_{32} N_3 + B_{32} \rho_\nu \nu_{32} N_2 \quad (15.E.19)$$

where we estimate the emission from level 3 to level 2.

Q15.12

Consider a nondegenerate 3-level system. Suppose that an incident light beam of energy $h\nu = E_3 - E_1$ is turned on for a while and then turned off. Show that the subsequent decay of the E_3 is given by

$$N_3(t) = N_3^0 e^{-(A_{32} + A_{31})t} \quad (15.E.20)$$

Where N_3^0 is the number of atoms in state 3 at the instant the light source is turned off. What will be the observed radiative lifetime of this excited state?

S15.12

After the light is turned off, no stimulated processes will occur and the rate equation of N_3 becomes:

$$N_3 = C e^{-(A_{32} + A_{31})t} \quad (15.E.21)$$

At $t = 0$ (when the light is turned off), $N_3(t) = N_3^0 = C$, so

$$N_3(t) = N_3^0 e^{-(A_{32} + A_{31})t} \quad (15.E.22)$$

The observed radiative lifetime will be $(A_{32} + A_{31})^{-1}$. (The radiative lifetime is the reciprocal of the coefficient of the t in the exponential term.)

Q15-14

An excited state of Lithium has the electron configuration,



Define the lowest energy term symbol.

S15-14

Construct a micro state table with spin (M(S)) across the top and angular momentum (M(L)) down the left side.

		-1/2	1 (+)
-1		-1(-)	0 (+)
0		0(-)	1 (+)
1		1(-)	

The highest spin value is +1/2, while the highest angular momentum value is 1. As a result, J can range from 3/2 (L+S) to 1/2 (L-S). Because the p-orbital is less than half-full, the term symbol with the lowest J value will be lower in energy.

Term symbol:



Q15.15

The ground state energy of the He atom is -2.904 hartrees. Use this value to determine the energy of He⁺

S15.15

(good job however you could have shown more steps as it us unclear how you made the jumps from energy to He⁺ and then that the energy was 0.904, it took me some time to fiddle with what you gave me as a solution to arrive to that number so more in between steps are need --RM)

$$E = \frac{-Z^2}{2n^2} \quad (15.E.25)$$

$$He^+ = -2E_h \quad (15.E.26)$$

Therefore the energy of He⁺ is 0.904 hartrees above that of He.

There isn't too many steps in solving the problem. It would have been great to compare it to another method or the actual energy of an H⁺ hydrogen, such as, using the Rydberg formula to evaluate the energy....

Q15.19

A laser operating at 640 nm produces pulses at a rate of 85 MHz. Calculate the radiant power of each pulse if the pulses last 15 fs each and the average radiant power of the laser is 2.6 W. How many photons are produced by the laser per second?

S15.19

We can first calculate the amount of energy per pulse:

$$\frac{2.6W}{85 \frac{\text{pulses}}{\text{MHz}}} = \frac{2.6 \frac{J}{s}}{85 \cdot 10^6 \frac{\text{pulses}}{s}} = 3.059 \cdot 10^{-8} \frac{J}{\text{pulse}} \quad (15.E.27)$$

Using this, we can then calculate the radiant energy of each laser pulse:

$$\frac{3.059 \cdot 10^{-8} \frac{J}{\text{pulse}}}{15 \cdot 10^{-15} s} = 2039.216 \frac{kW}{\text{pulse}} \quad (15.E.28)$$

Finally, we can calculate the radiant energy of a single photon:

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \cdot 10^{-34} J \cdot s)(2.988 \cdot 10^8 \frac{m}{s})}{640 \cdot 10^{-9} m} = 3.094 \cdot 10^{-19} J \quad (15.E.29)$$

Using this energy, we can calculate the the number of photons produced per second by the laser:

$$\frac{E_{\text{laser}}}{E_{\text{photon}}} = \frac{2.6 \frac{J}{s}}{3.094 \cdot 10^{-19} \frac{J}{\text{photon}}} = 8.40 \cdot 10^{18} \frac{\text{photons}}{\text{second}} \quad (15.E.30)$$

Q15.21

Which laser pulse contains more photons, a 945 ns, 9.45 mJ pulse at 945 nm or a 23 ns, 2.30 mJ at 230 nm? Does the speed of the pulse effect the number of photons?

S15.21

- E = energy per photon
- \hbar = plancks constant = $6.626 \cdot 10^{-34} J \cdot s$
- c = speed of light = $3.00 \cdot 10^8 \frac{m}{s}$
- λ = wavelength = 945 nm or 230 nm = $945 \cdot 10^{-9} m$ or $230 \cdot 10^{-9} m$

$$E_{\text{photon}} = \frac{(6.626 \cdot 10^{-34} J \cdot s) * (3.00 \cdot 10^8 \frac{m}{s})}{945 \cdot 10^{-9} m} = 2.104 \cdot 10^{-19} J/\text{photon}$$

$$E_{\text{pulse}} = 9.45 \text{ mJ} = 9.45 \cdot 10^{-3} J$$

$$\#_{\text{photon}} = \frac{E_{\text{pulse}}}{E_{\text{photon}}} = \frac{9.45 \cdot 10^{-3} J}{2.104 \cdot 10^{-19} J/\text{photon}} = 4.493 \cdot 10^{16} \text{ photons}$$

$$E_{\text{photon}} = \frac{(6.626 \cdot 10^{-34} J \cdot s) * (3.00 \cdot 10^8 \frac{m}{s})}{230 \cdot 10^{-9} m} = 8.64 \cdot 10^{-19} J$$

$$E_{\text{pulse}} = 2.30 \text{ mJ} = 2.30 \cdot 10^{-3} J$$

$$\#_{\text{photon}} = \frac{E_{\text{pulse}}}{E_{\text{photon}}} = \frac{2.30 \cdot 10^{-3} J}{8.64 \cdot 10^{-19} J/\text{photon}} = 2.66 \cdot 10^{15} \text{ photons}$$

First and foremost, the speed of the laser DOES NOT effect the number of photons! The 9.45 mJ at 945 nm laser pulse has more photons than the 2.30 mJ at 230 nm pulse.

The pulse duration does not affect the number of photons a laser pulse contains. Energies of both laser pulses are equivalent. Energy per pulse is proportional to the number of photons and inversely proportional to the wavelength of the emitted photons. Therefore, the 945 pulse contains more photons.

Q15.22

Given the following laser pulses: a $10 \times 10^{-9} s$, $1.6 \times 10^6 J$ pulse at $76 \times 10^{-10} m$ or a $5 \times 10^8 s$, $1.6 \times 10^6 J$ pulse at 5.32×10^{-11} , which one has the most photons?

S15.22

For 10-ns, 1.60-mJ pulse at 760 nm:

$$Q_p = \frac{hc}{\lambda} \quad (15.E.31)$$

$$= \frac{(6.626 \times 10^{-34})(3 \times 10^8)}{760 \times 10^{-9}} \quad (15.E.32)$$

$$= 2.62 \times 10^{-19} \quad (15.E.33)$$

Number of photon in 1.6 mJ pulse is:

$$N_1 = \frac{Q}{Q_p} = 6.12 \times 10^{15} \quad (15.E.34)$$

For 500-ms, 1.60-mJ pulse at 5320 nm:

$$Q_p = 3.75 \times 10^{-18} \quad (15.E.35)$$

Number of photon in 1.6 mJ pulse is:

$$N_2 = \frac{Q}{Q_p} = 0.4 \times 10^{15} \quad (15.E.36)$$

Thus, 10-ns, 1.60-mJ pulse at 760 nm contain more photon.

Q15.24

A CO_2 laser operating at $9.0 \mu m$ uses an electrical power of 5.20 kW. If this laser produces 100-ns pulses at a repetition rate of 20Hz and has an efficiency of 29%, how many photons are in each laser pulses?

S15.24

The pump energy per pulse is:

$$\frac{5200 J * s^{-1}}{20 s^{-1}} = 260 J * pulse^{-1}$$

Given that the laser is 29% efficient, the radiant per pulse is $(260 J)(0.29) = 67.6 J$.

The number of photons per pulse, n is

$$n = \frac{E\lambda}{hc},$$

by plugging in the values into this equation, we have

$$\begin{aligned} n &= \frac{(260 J)(0.29)(9.0 * 10^{-6} m)}{(6.626 * 10^{-34} J * s)(2.998 * 10^8 m * s^{-1})} \\ &= 3.42 * 10^{21} \text{ photons} \end{aligned}$$

My calculation reveals the final answer to be 3.42×10^{21} photons (Aaron Choi)/ I believe you accidentally calculated using the speed of light as $2.998 \times 10^{-8} \frac{m}{s}$

Q15.25

Figure 15.10 displays the energy levels of the CO_2 laser. Given the following spectroscopic data for $CO_2(g)$, calculate the spacing between the $J' = 3 \rightarrow 2$ laser lines for the $001 \rightarrow 100$ vibrational transition.

$$\text{Fundamental frequency}(J' = 0 \rightarrow 0)_{100 \rightarrow 001} = 960.80 \text{ cm}^{-1} \quad (15.E.37)$$

$$\tilde{B}(001) = 0.3871 \text{ cm}^{-1} \quad \tilde{B}(100) = 0.3902 \text{ cm}^{-1} \quad (15.E.38)$$

The fundamental frequency is 960.80 cm^{-1}

S15.25

Using the following equation $F(J)$ for $J = 2$ and $J = 3$ can be calculated:

$$F(J) = \tilde{B}J(J+1) \quad (15.E.39)$$

$$F_{001}(3) = (0.3871 \text{ cm}^{-1})(3)(3+1) = 4.645 \text{ cm}^{-1} \quad (15.E.40)$$

$$F_{100}(2) = (0.3902 \text{ cm}^{-1})(2)(2+1) = 2.341 \text{ cm}^{-1} \quad (15.E.41)$$

Therefore the spacing is

$$960.80 \text{ cm}^{-1} + 4.645 \text{ cm}^{-1} - 2.341 \text{ cm}^{-1} = 963.10 \text{ cm}^{-1} \quad (15.E.42)$$

Q15.26

The upper level of the $H_2(g)$ laser is the lowest excited state of the molecule, the $B^1 \sum_u^+$ state, and the lower level is the $X^1 \sum_g^+$ ground state. The lasing occurs between the $v' = 6$ level of the excited state and the $v'' = 13$ level of the ground state. Use the following spectroscopic data to determine the wavelength of the laser light from $H_2(g)$ laser.

State	$\tilde{T}_e / \text{cm}^{-1}$	$\tilde{\nu}_e / \text{cm}^{-1}$	$\tilde{\nu}_e \tilde{x}_e / \text{cm}^{-1}$
$B^1 \sum_u^+$	91,689.9	1356.9	19.93
$X^1 \sum_g^+$	0	4401.2	121.34

A 3.0 ns pulse can be generated with a pulse radiant power of 200 kW. Calculate the radiant energy of such a laser pulse. How many photons are there in this pulse?

S15.26

To calculate the energy of the upper and lower lasing levels the following equation is used:

$$G(v) = \tilde{\nu}_e \left(v + \frac{1}{2} \right) - \tilde{x}_e \tilde{\nu}_e \left(v + \frac{1}{2} \right)^2 \quad (15.E.43)$$

$$G''(13) = (4401.2 \text{ cm}^{-1})(13.5) - (121.34 \text{ cm}^{-1})(13.5)^2 = 37,301.98 \text{ cm}^{-1} \quad (15.E.44)$$

$$G''(6) = (1356.9 \text{ cm}^{-1})(6.5) - (19.93 \text{ cm}^{-1})(6.5)^2 = 7,977.81 \text{ cm}^{-1} \quad (15.E.45)$$

the transition is as follows

$$\tilde{\nu} = \tilde{T}_e + G''(6) - G''(13) \quad (15.E.46)$$

$$= 91,689.9 \text{ cm}^{-1} + 7,977.81 \text{ cm}^{-1} - 37,301.98 \text{ cm}^{-1} = 62,365.73 \text{ cm}^{-1} \quad (15.E.47)$$

therefore

$$\lambda = 160.34 \text{ nm} \quad (15.E.48)$$

The radiant energy of the laser pulse is found using dimensional analysis

$$\left(200 \frac{\text{kJ}}{\text{s}} \right) (2 \times 10^{-9} \text{ s}) = 1 \times 10^{-4} \text{ J} \quad (15.E.49)$$

the number of photons per pulse is determined using $E = nh\nu = 8.06 \times 10^{13}$ photons.

Q15.27

Determine the excited-state rotational quantum number for $X \rightarrow A$ adsorption bands of $H_2(g)$. The transition is from the $v'' = 0$ of the X state to the excited vibrational level of the A state $v' = 3$. To accurately calculate the vibrational term $G(v)$ for the excited state A , a second-order anharmonic correction is made to account for the shape of the potential curve, while first-order corrections are sufficient for the ground level electron state.

$$G(v) = \tilde{\nu}_e(v + \frac{1}{2}) - \tilde{\nu}_e \tilde{x}_e(v + \frac{1}{2})^2 + \tilde{\nu}_e \tilde{y}_e(v + \frac{1}{2})^3$$

The need spectroscopic constants are tabulated below for the ground state X and the excited state A of $H_2(g)$.

State	\tilde{T}_e/cm^{-1}	$\tilde{\nu}_e/cm^{-1}$	$\tilde{\nu}_e \tilde{x}_e/cm^{-1}$	$\tilde{\nu}_e \tilde{y}_e/cm^{-1}$	\tilde{B}_e/cm^{-1}	$\tilde{\alpha}_e/cm^{-1}$
A	120952	2321.4	62.8	0	29.9	1.24
X	0	2291.7	62.4			

These values are from the NIST website for the H_2

Determine the value of $\tilde{\nu}$ corresponding to the transition $X(v'' = 0, j'' = 0) \rightarrow A(v' = 3, j' = 0)$. Given that the ground state levels are $v'' = 0, j'' = 1$ of the X state and that the rotational term for this level is $F(1) = 1.057 cm^{-1}$, determine the closest value of J' , the rotational number of the $v' = 3$ level of the excited A state.

S15.27

For the ground state, the $G(v)$ value is :

$$G''(0) = (\frac{1}{2})(2291 cm^{-1}) - (\frac{1}{2})^2 62.4 cm^{-1}$$

$$G''(0) = 1129.9 cm^{-1}$$

For the excited state $G(v)$ value is :

$$G''(3) = (2321.4 cm^{-1})(3 + \frac{1}{2}) - (62.8 cm^{-1})(3 + \frac{1}{2})^2$$

$$G''(3) = 7354 cm^{-1}$$

\tilde{T}_e is the difference in the minima of the electronic potential energy curve in wave numbers, so the transition will have the energy

$$\tilde{\nu}_e = \tilde{T}_e + G'(3) - G''(0)$$

$$\tilde{\nu}_e = 120952 cm^{-1} + 7354 cm^{-1} - 1129.9 cm^{-1}$$

$$\tilde{\nu}_e = 127176.1 cm^{-1}$$

\tilde{B}_v can be found for A state, $v = 3$ with this equation:

$$\tilde{B}_{32} = \tilde{B}_e - \tilde{\alpha}_e(v + \frac{1}{2})$$

$$\tilde{B}_{32} = 29.9 cm^{-1} - (1.24 cm^{-1})(3 + \frac{1}{2}) = 25.56 cm^{-1}$$

the observed lines are in between $35714.29 cm^{-1}$ and $3448.28 cm^{-1}$ recalling that $\tilde{E}_{v,j} = G(v) - F'(j)$;

$$35717.29 cm^{-1} = 127176.1 cm^{-1} - 1.057 cm^{-1} + F'(j)$$

$$35717.29 cm^{-1} = 127175.043 cm^{-1} + F'(j)$$

Therefore $91461 \approx F'(j)$ so j would be around 10 or higher.

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