Problem Set PS06

ISSUED: 2/22/01 **Due: 3/8/01**

Prof. Darin J. Ulness Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Exercises

1. Three distinct laser beams are used to perform a four wave mixing experiment. For beam 1, $\omega = 21000\text{cm}^{-1}$; for beam 2, $\omega = 20000\text{cm}^{-1}$; and for beam 3, $\omega = 19000\text{cm}^{-1}$. What is the signal frequency along the following signal wavevectors. Identify the signals that would be considered nearly degenerate four wave mixing (that is, the signal frequency is close to the fundamental frequencies).

   (a) $\vec{k}_{sig} = \vec{k}_1 + \vec{k}_2 + \vec{k}_3$

   (b) $\vec{k}_{sig} = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$

   (c) $\vec{k}_{sig} = \vec{k}_1 + \vec{k}_2 - \vec{k}_3$

   (d) $\vec{k}_{sig} = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$

2. The coherent Raman scattering (CRS) spectroscopies are an important class of nearly degenerate four wave mixing processes. In a typical CRS experiment two fundamental beams (beams 1 and 2) are identical and a third beam (beam 3) is chosen such the difference between frequencies of beam 1or 2 and that of beam 3 matched a vibrational transition of the sample. When the beams are in the BOX beam geometry, the CRS signal emerges along the wavevector $\vec{k}_{sig} = \vec{k}_1 + \vec{k}_2 - \vec{k}_3$.

   (a) Draw the beam configuration for a CRS experiment.

   (b) There are two types of CRS experiments i) CARS (coherent anti-Stokes Raman scattering) and CSRS (coherent stokes Raman scattering). Based on what you know to be the definition of Stokes scattering, How do these two experiments differ? Draw a spectrum which shows the fundamental and signal beam frequencies.

   (c) Say you wanted to do a CARS experiment to study the C–Cl stretching mode of carbon tetrachloride (460cm^{-1}). Which dyes would you use for your laser beams (see figure below)? Where in frequency would your signal come out?

   (d) Say you wanted to do a CARS experiment to study the C–N symmetric stretching mode of acetonitrile (2253cm^{-1}). Which dyes would you use for your laser beams (see figure below)? Where in frequency would your signal come out?

3. Read sections 1.9 and 1.11 of Laidler & Meiser and work problems 1.31, 1.36, 1.37, 1.39, 1.41 and 1.45

Conceptual Problems

4. How does a laser work?

5. Use the Boltzmann distribution to show that no matter how hot it gets an ensemble of two level systems in thermal equilibrium will never have a larger population in the excited state then in the ground state. (This is a very important concept to understand because we must get around this to make a laser work).

6. In the previous problem you showed that an ensemble of two level systems in thermal equilibrium can never have what is called *population inversion* (a higher population in the excited state than in the ground state). One sometimes sees in the literature authors saying that an ensemble has "negative temperature" (a temperature below absolute zero) when a population inversion situation exists. Use the Boltzmann distribution to explain why they might use this phrase.

Reflective Questions

7. Read the following excerpt from an article entitled "A few modest prescriptions for widening the path to politics" written by Journalist D.S. Greenberg.

   (a) Do you agree with Greenberg fully, somewhat, not at all?

   (b) What is the difference between a scientist getting involved in politics versus a politician becoming well versed on science issues.

   (c) It seems to me that very few science students at Concordia get involved with student government. Do you think this is apathy, lack of time or something more fundamental having to do with either how we are trained or what type of personalities we have?

   (d) Greenberg suggests that "the laboratory is a poor launching pad for politics." Why might this be so?

(e) Greenberg uses the fact that only four members of congress are scientists to represent over half a million scientists. Does this congressman to constituient ratio deviate significantly from the average (there are 500 and some members of Congress)?

Science finds advantage and claims virtue in its detachment and aloofness from politics. But politics is the medium through which a society decides upon and implements its values and its choices. That the political system frequently goes awry and fails to work to its full potential of beneficial effects is a reason for increased involvement, not withdrawal. And this is especially so for an enterprise that draws heavily on the public purse and radiates powerful effects in all directions and on all things - while denying responsibility for the consequences of its work.

In its retreat into political isolation, science cannot detach itself from relations with the outside world. But increasingly, these relations are with industry seeking profits from academe's scientific strength and prestige, distressingly often to the detriment of scientific integrity and public well-being. Science is too powerful, too potent in its effects on society, and too arcane, to be entrusted to the expanding alliance between a profession that has retreated into a ghetto and the commercial sector, with their shared focus on making money. While this relationship flourishes, a deadening complacency has settled over the institutions that should be protecting and advancing the public interest in science. With rare exceptions the public is satisfied to leave science to the scientists. Politicians put hands on science mainly to get a share for their voters. None of the professional sectors concerned with science are inclined to push for change on their own, and there is little expectation that the necessary correctives to the scientific enterprise will come from within.

But coming from several directions, small impulses for change can reverberate through the various sectors with energizing effects beyond their original strength. The goal should be more involvement of science with politics, rather than less, because more would benefit society by opening science to public view and controversy. More involvement with politics would surely be uncomfortable for science, because it would threaten the reigning combination of support without scrutiny or responsibility. But it would be beneficial for society in its dependence on science, and possibly even helpful for science itself. The aim is to dislodge science from its comfortable ghetto and move it into the rough waters of the political mainstream.

No amount of sermonizing can compel a flood of mathematicians, physicists and biochemists into seeking elective office. The laboratory is a poor launching pad for politics. However, the prevailing anti-political culture of science encourages the field to stick to the ghetto, and perhaps even to strengthen its walls. In 2000, over half a million holders of PhDs in the natural and physical sciences and in engineering were employed in the US. Only four were members of Congress.

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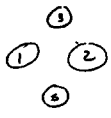
(1) (a) $\omega_s = 57000\ cm^{-1}$ Not NDFWM

(b) $\omega_s = 19000\ cm^{-1}$ NDFWM

(c) $\omega_s = 21000\ cm^{-1}$ NDFWM

(d) $\omega_s = 19000\ cm^{-1}$ NDFWM

(2) (a)

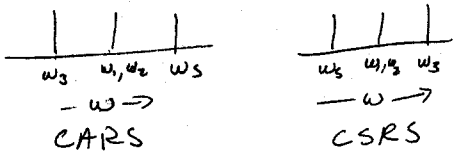


(b) Stokes scattering – Raman shifted to the red (longer) wavelengths by the vibrational frequency

Anti-Stokes scattering – Raman shifted to the blue (shorter) wavelengths by the vibrational frequency.

So, since $\omega_s = \omega_1 + \omega_2 - \omega_3$ for CSRS

We want $\omega_3 - \omega_1 \cong \omega_v$ where ω_v is the vibrational frequency. For CARS we want $\omega_1 - \omega_3 \cong \omega_v$



(2 cont)

(c) Need to find any pair of dyes who's output frequency range allow for $|\omega_1 - \omega_3| = \omega_v$ There are many of these

For example Rh 610 $585 \Rightarrow 17094\ cm^{-1}$

$17094 + 460 = 17554 \Rightarrow 570$ nm Rh 590

Signal at $17534 + 460 = 18014\ cm^{-1} = 555$ nm

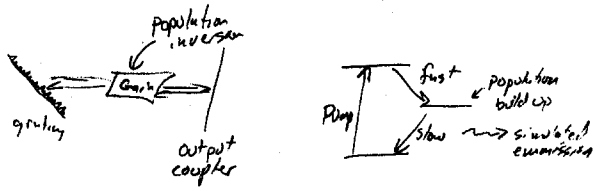
(d) For example DCM $627\ nm \Rightarrow 15,929\ cm^{-1}$

$15,929 + 2253 = 18,182\ cm^{-1} \Rightarrow 550$ Rh 5?c

Signal at $18,182 + 2253 = 20,435\ cm^{-1} \Rightarrow 489$ nm

(3) see soln manual / L+M

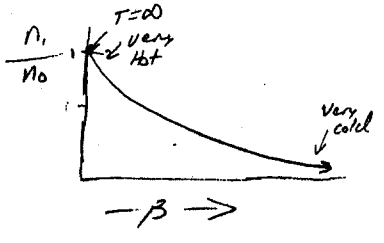
(4)



(5) $n_1 = \frac{e^{-\beta\varepsilon_1}}{z}$ $n_0 = \frac{e^{-\beta\varepsilon_0}}{z}$

$$\frac{n_1}{n_0} = \frac{\frac{e^{-\beta\varepsilon_1}}{z}}{\frac{e^{-\beta\varepsilon_0}}{z}} = e^{-\beta\Delta\varepsilon} \qquad \Delta\varepsilon \equiv \varepsilon_1 - \varepsilon_0$$

$\Delta\varepsilon$ is positive



(6) from above $\frac{n_1}{n_0} = e^{-\beta\Delta\varepsilon}$

for $\frac{n_1}{n_0}$ to be greater than 1 β must be negative

k is a constant so T must be negative