

Problem Set PS06

ISSUED: 2/17/99 Due: 2/24/00

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, $\omega = 20000\text{cm}^{-1}$; 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 1 or 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 ring breathing mode of benzene (992cm^{-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-H symmetric stretching mode of benzene (3063cm^{-1}). Which dyes would you use for your laser beams (see figure below)? Where in frequency would your signal come out?

(e) Say you wanted to do a CSRS experiment to study the ring breathing mode of benzene (992cm^{-1}). Which dyes would you use for your laser beams (see figure below)? Where in frequency would your signal come out?

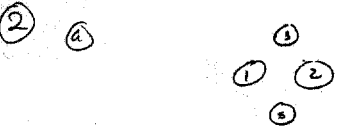
- (f) Say you wanted to do a CSRS experiment to study the C–H symmetric stretching mode of benzene (3063cm^{-1}). Which dyes would you use for your laser beams (see figure below)? Where in frequency would your signal come out?

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

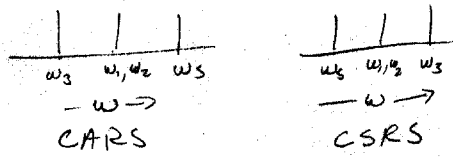
4. How does a laser work?
5. Use the Boltzmann distribution to show that no matter how hot it gets an ensemble of two level systems in thermal equilibrium will never have a larger population in the excited state than in the ground state. (This is a very important concept to understand because we must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

- ① (a) $\omega_s = 59000 \text{ cm}^{-1}$ Not NDFWM
 (b) $\omega_s = 19000 \text{ cm}^{-1}$ NDFWM
 (c) $\omega_s = 21000 \text{ cm}^{-1}$ NDFWM
 (d) $\omega_s = 19000 \text{ cm}^{-1}$ NDFWM

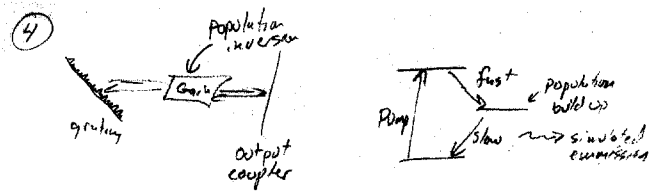


(b) Stokes scattering - Raman shifted to the red (longer) wavelengths by the vibrational frequency
 Anti-Stokes scattering - Raman shifted to the blue (shorter) wavelengths by the vibrational frequency.

So, since $\omega_s = \omega_1 + \omega_2 - \omega_3$ for CSRS
 We want $\omega_3 - \omega_1 \approx \omega_v$ where ω_v is the vibrational frequency. For CARS we want $\omega_1 - \omega_3 \approx \omega_v$

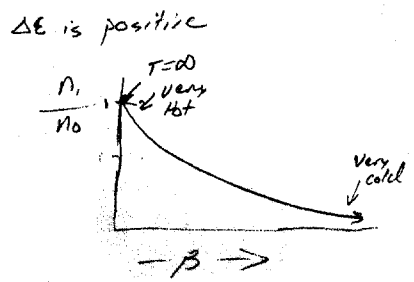


3 of 3



⑤ $n_1 = \frac{e^{-\beta E_1}}{Z}$ $n_0 = \frac{e^{-\beta E_0}}{Z}$

$$\frac{n_1}{n_0} = \frac{\frac{e^{-\beta E_1}}{Z}}{\frac{e^{-\beta E_0}}{Z}} = e^{-\beta \Delta E} \quad \Delta E = E_1 - E_0$$



⑥ from above $\frac{n_1}{n_0} = e^{-\beta \Delta E}$
 for $\frac{n_1}{n_0}$ to be greater than 1 β must be negative
 k is a constant so T must be negative.

② cont

(c) Need to find any pair of dyes who's output frequency ranges allow for $|\omega_1 - \omega_2| = \omega_s$. There are many of these.

For example Rh 610 tuned to 585 nm $\Rightarrow 17094 \text{ cm}^{-1}$
 $17094 + 992 = 18086 \Rightarrow 552 \text{ nm Rh 590}$
 signal comes out at $18086 + 992 = 19078 \text{ cm}^{-1} \Rightarrow 524 \text{ nm}$

(d) For example
 EDS698 tuned to 700 nm $\Rightarrow 14285 \text{ cm}^{-1}$
 $14285 \text{ cm}^{-1} + 3063 \text{ cm}^{-1} = 17348 \text{ cm}^{-1} \Rightarrow 576 \text{ Rh 610/615 mix 1:1}$
 signal comes out at $17348 + 3063 = 20411 \text{ cm}^{-1} \Rightarrow 480 \text{ nm}$

(e) Could use the same as in (c) but reverse the roles. Now the CARS signal will come out at $16194 \text{ cm}^{-1} \Rightarrow 617 \text{ nm}$

(f) For example
 Coem in 480 tuned to 480 nm $\Rightarrow 20833 \text{ cm}^{-1}$
 $20833 \text{ cm}^{-1} - 3063 = 17770 \text{ cm}^{-1} \Rightarrow 562 \text{ Rh 590}$
 signal: $17770 \text{ cm}^{-1} - 3063 = 14707 \text{ cm}^{-1} \Rightarrow 680 \text{ nm}$

③ see solution manual L + M