Physical Chemistry Cumulative Exam

May 6th, 2016

Topic: general questions in spectroscopy

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(1) (25 points) For each brief description below, describe the relevant spectroscopy as microwave, infrared, Raman, UV-visible, fluorescence, phosphorescence, sum frequency generation, second harmonic generation …

a) A 250 nm photon is absorbed by a molecule, which then emits a 600nm photon.

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b) The absorption band is at 3000 cm^{-1}.

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c) A photon is emitted after intersystem crossing from a singlet state to a triplet state.

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d) A molecule absorbs a photon at 60 cm^{-1}, making a transition from J=4 to J=5

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e) A molecule absorbs a photon at 2000 cm^{-1}, producing a v=0 to v=1 transition in the symmetric stretch normal mode of molecule; there is no change in the dipole moment.

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(2) Molecules interacts with light in the following two ways:

Vibrational absorption → interaction of electric field of light with the molecule's oscillating dipole moment

Raman scattering → inelastic scattering of electric field of light through interaction with the molecule's induced dipole moment.

The dipole moment of the molecule, p, in an electric field is: $\mathbf{p} = \boldsymbol{\mu_0} + \alpha \cdot \mathbf{E}$, where μ_0 is the permanent dipole moment, α is the polarizability, and E is the electric field of the light wave, $E = E_0 \cos \omega t$.

For small vibrations (small quantum number v), the vibration is approximately harmonic and we can approximate the normal coordinates by $q_n(t) = q_{n0} \cos(\omega_n t)$. q_{n0} is the amplitude and ω_n is the vibration frequency.

(20 points) Please expand the dipole moment in a Taylor series in the normal coordinates q_n of the nuclear displacements to find the interaction between the light and the molecular vibrations.

p=_____

(hints: expand the permanent dipole moment and the polarizability separately)

The Taylor series:

$$f(x)=\sum_{n=0}^{\infty}\frac{f^{(n)}(a)}{n!}(x-a)^n$$

(15 points) Please point out which term indicates IR absorption and Raman scattering. Then what's the conditions to make Raman scattering active?

(3) In optics, a diffraction grating is an optical component with a periodic structure, which splits and diffracts light into several beams travelling in different directions. The directions of these beams depend on the spacing of the grating and the wavelength of the light so that the grating acts as the dispersive element. Because of this, gratings are commonly used in monochromators and spectrometers.

a. (20 points) You have been handed a transmission grating (5000 lines per centimeter) by your supervisor who wants to know how widely the red light and green light fringes. What's the distance, in **the second order**, is separated on a screen one meter from the grating between the red and green light? (The transmission grating is to be illuminated at normal incidence with red light at 707nm and green light at 500nm.) (√2=1.414, √3=1.732)

b. (20 points) A blazed grating containing 2000 blazes (lines) per millimeter was irradiated with a polychromatic beam at an incident angle of 60 degrees to the grating normal. Calculate the wavelengths of radiation that would appear at an angle of reflection of +30, 0, and -30 degrees for **the first order**, as can be seen in Figure 1. (√3=1.732)

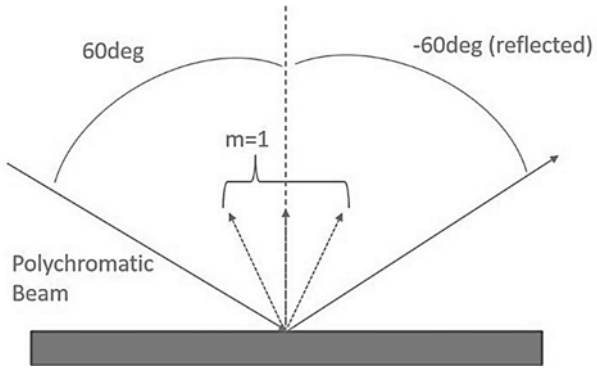

Figure 1