

1. Vibrational Motion, Infrared (In)active Modes & Degeneracy (8 points)

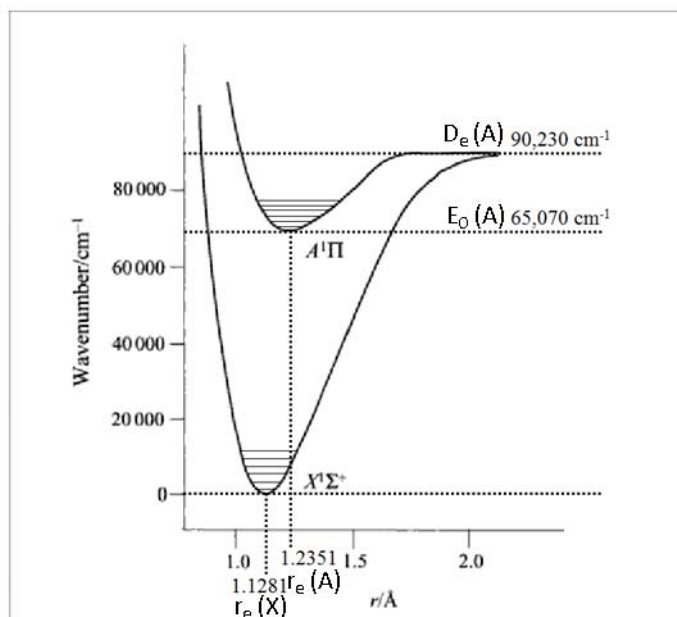
a) There are just enough diagrams. A nonlinear molecule has $3N-6$ vibrational modes. For four atoms, $3N-6 = 6$, the same number of modes shown. (1 points answer, 2 points explanation. No credit for an explanation longer than two sentences)

b) Only the first mode, ν_1 , is infrared inactive; all other modes are infrared active. The molecule has no permanent dipole moment and the symmetric stretch in ν_1 does not cause a dipole moment. All other motions, $\nu_2 - \nu_6$, produce a dipole moment. (2 points answer, 3 points explanation. Full credit for explicitly sketching the dipole derivative for each mode. -0.5 per incorrectly assigned mode, max deduction -2 . No credit for an explanation longer than three sentences)

c) GaI_3 has no permanent dipole, so no modes will appear in the rotational spectrum. (2 points, no need to explain answer)

2. Molecular Electronic Spectroscopy (25 points)

a)



8 points total:

- 1 point for general shape of curves (not just parabolas)
- 2 point for labeling curves with words or symbol to denote the state
- 1 points for minimum of excited state slightly to right of ground state minimum
- 2 points for labeling equilibrium radii (1 point each)
- 1 points for labeling the values of the energy levels in some way*
- 2 points for vibrational spacing in ground state larger than in excited state

*It is not important if the student uses energy or wavenumber for the y-axis. It is not important if the student puts the zero energy mark at the bottom of the well for the ground state or at the dissociation level, so long as the energy differences are consistent.

b) The $v=0$ state is most likely to be populated at 298 K. (2 points)

Either of the two justifications below will receive the remaining 3 points.

Direct calculation

The Boltzmann distribution is,

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} \exp\left[\frac{-\Delta E}{k_B T}\right]. \quad (1 \text{ points})$$

The difference in energies of the first two vibrational states ($v=0$, $v=1$) is

$$G_1 = (2170.21 \text{ cm}^{-1})(1.5) - (13.46 \text{ cm}^{-1})(1.5)^2 = 3225.03 \text{ cm}^{-1}$$

$$G_0 = (2170.21 \text{ cm}^{-1})(0.5) - (13.46 \text{ cm}^{-1})(0.5)^2 = 1081.74 \text{ cm}^{-1} \quad (0.5 \text{ points})$$

$$\Delta E = G_1 - G_0 = 2143.29 \text{ cm}^{-1}$$

Both $v=0$ and $v=1$ are singly degenerate, so $g_1 = g_0 = 1$.

Using $k_B = 0.69503476 \text{ cm}^{-1} \text{ K}^{-1}$ and $T = 298 \text{ K}$, we obtain

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} \exp\left[\frac{-\Delta E}{k_B T}\right] = \exp\left[\frac{-2143.29 \text{ cm}^{-1}}{(0.69503476 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}\right] = 3.21 \times 10^{-5} \quad (0.5 \text{ points})$$

The first vibrational state is barely populated, and higher states (with greater $E_1 - E_0$) will be even less populated. Therefore, the $v=0$ state is most likely to be populated. (1 point)

Order of magnitude calculation

The Boltzmann distribution is,

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} \exp\left[\frac{-\Delta E}{k_B T}\right]. \quad (1 \text{ points})$$

We know that $k_B T \approx 200 \text{ cm}^{-1}$ at room temperature (0.5 point, from lecture notes) and that a typical vibrational frequency is on the order of 1000 cm^{-1} . (0.5 point) Since the ratio of $\Delta E / k_B T$ is large (order 10^1), the Boltzmann distribution predicts that the population ratio between the excited state and the ground state is very small; so mostly just the ground state is populated at room temperatures. (1 point)

c) The lines in rotational spectroscopy are separated by $2B$,

$$2B = \frac{h}{4\pi^2 I} ,$$

and the moment of inertia is $I = \mu R^2$ and $\mu = m_1 m_2 / (m_1 + m_2)$

Using the above three equations, we can obtain

$$2B = \frac{h}{4\pi^2} \frac{m_1 + m_2}{m_1 m_2} \frac{1}{R^2} \quad (1.5 \text{ points for using the three equations above in some way})$$

Since $2B$ is a frequency and we want to express this result in wavenumbers, divide both sides by the speed of light,

$$2\tilde{B} = \frac{h}{4\pi^2 c} \frac{m_1 + m_2}{m_1 m_2} \frac{1}{R^2}$$

(1 point for dividing by speed of light somewhere in problem to convert to wavenumbers, or other valid conversion to wavenumbers)

Remember to use the isotope masses from OGC ($m_{C-12}=12$ amu exactly, $m_{O-16}=15.994914622$ amu)

$$2\tilde{B} = \left(\frac{6.6260688 \times 10^{-34} \text{ J} \cdot \text{s}}{4\pi^2 (2.9979925 \times 10^8 \text{ m/s})} \right) \left(\frac{27.994914622 \text{ amu}}{(12 \text{ amu})(15.994914622 \text{ amu})} \right) \left(\frac{1 \text{ amu}}{1.6605387 \times 10^{-27} \text{ kg}} \right) \left(\frac{1}{(1.1281 \text{ \AA})^2} \right) \left(\frac{10^{10} \text{ \AA}}{\text{m}} \right)^2$$

$$2\tilde{B} = 386.40 \text{ m}^{-1} = 3.8640 \text{ cm}^{-1}$$

(1.5 points, -1.5 for incorrect sig figs or units, -1 for not using the correct masses of ^{12}C and ^{16}O)

Side note: Why are there so many sig figs for an equilibrium internuclear distance? If you remember, we usually estimate the internuclear distance from the rotational constants (not the other way around as we did in this problem). If you look at tables of rotational constants for molecules, you'll even see numbers with more sig figs – sometimes even nine or ten. “No measurement can be made as precisely as frequency, so when utmost accuracy is important, one should strive to measure the phenomenon of interest in terms of a frequency.” (H.A. McGee, Jr., “Molecular Engineering”)

d) Starting with the equation for the anharmonic oscillator,

$$E_{\text{vib},v} = h\omega_e \left(v + \frac{1}{2}\right) - h\omega_e x_e \left(v + \frac{1}{2}\right)^2 .$$

The zero-point energy can be found from the $v=0$ state and the equation for vibrational energy levels,

$$E_0 = h \left[\omega_e \left(\frac{1}{2} \right) - \omega_e x_e \left(\frac{1}{2} \right)^2 \right]. \quad (2 \text{ points})$$

Plug in numbers, realizing that you must convert from cm^{-1} to s^{-1} via the speed of light.

$$E = (6.6260688 \times 10^{-34} \text{ J s}) \left(\frac{1}{2} (1515.61 \text{ cm}^{-1}) - \left(\frac{1}{2} \right)^2 (17.25 \text{ cm}^{-1}) \right) (2.9979925 \times 10^{10} \text{ cm s}^{-1})$$

$$E = 1.497 \times 10^{-20} \text{ J}, \text{ limited to four sigfigs by } \omega_e x_e.$$

(2 points, -2 for incorrect units or sig figs)

e) Start with the relationship between the frequency and the force constant.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1 \text{ point})$$

Solving for the force constant,

$$k = 4\pi^2 \mu \nu^2.$$

We want to find the percent increase in the force constant after fluorescence and use the fact that the reduced mass does not change during this transition,

$$\% \text{Change} = \frac{k_X - k_A}{k_A} \times 100 = \frac{4\pi^2 \mu \nu_X^2 - 4\pi^2 \mu \nu_A^2}{4\pi^2 \mu \nu_A^2} \times 100 = \frac{\nu_X^2 - \nu_A^2}{\nu_A^2} \times 100$$

(1 point: definition of percent increase)

(1 point: recognizing reduced mass doesn't change)

$$\% \text{Change} = \frac{k_X - k_A}{k_A} \times 100 = \frac{(2170.21 \text{ cm}^{-1})^2 - (1515.61 \text{ cm}^{-1})^2}{(1515.61 \text{ cm}^{-1})^2} \times 100$$

$$\frac{k_X - k_A}{k_A} \times 100 = 105\%$$

The force constant increases by about 105%.

(1 point, no credit for non-percentage answer or one without three sig figs)

3. ^1H NMR: Number of Peak Groupings and Relative Areas (12 points)

Molecule	Relative Areas	Molecule	Relative Areas
$\begin{array}{c} (\alpha) \quad (\beta) \\ \text{H}_3\text{C}-\text{OH} \\ \text{methanol} \end{array}$	$\alpha:\beta$ 3:1	$\begin{array}{c} (\alpha) \quad (\beta) \quad (\beta) \quad (\alpha) \\ \text{H}_3\text{C}-\text{C}(\text{H}_2)-\text{O}-\text{C}(\text{H}_2)-\text{CH}_3 \\ \text{ethoxyethane} \end{array}$	$\alpha:\beta$ 3:2
$\begin{array}{c} (\alpha) \quad (\beta) \quad (\gamma) \\ \text{H}_3\text{C}-\text{C}(\text{H}_2)-\text{CH}_2\text{Br} \\ \text{1-bromopropane} \end{array}$	$\alpha:\beta:\gamma$ 3:2:2	$\begin{array}{c} (\alpha) \\ \text{CH}_3 \\ \\ (\alpha) \text{CH}(\text{H}_3)-\text{C}(\text{H}_2)-\text{CH}_2\text{Cl} \\ \text{1-chloro-2-methylpropane} \end{array}$	$\alpha:\beta:\gamma$ 6:1:2
$\begin{array}{c} (\alpha) \quad (\beta) \quad (\beta) \quad (\alpha) \\ \text{OH}-\text{CH}_2-\text{CH}_2-\text{OH} \\ \text{ethane-1,2-diol} \end{array}$	$\alpha:\beta$ 1:2	$\begin{array}{c} \text{CH}_3 (\alpha) \\ \\ (\beta) \text{HC}=\text{C}-\text{CH}(\beta) \\ \quad \quad \quad \\ (\beta) \text{HC}=\text{C}-\text{CH}(\beta) \\ \\ \text{CH}_3 (\alpha) \\ \text{p-xylene} \end{array}$	$\alpha:\beta$ 3:2
$\begin{array}{c} (\alpha) \quad (\beta) \quad (\gamma) \quad (\beta) \quad (\alpha) \\ \text{H}_3\text{C}-\text{C}(\text{H}_2)-\text{CH}_2-\text{C}(\text{H}_2)-\text{CH}_3 \\ \text{pentane} \end{array}$	$\alpha:\beta:\gamma$ 3:2:1	$\begin{array}{c} \text{O} \quad \quad \text{H}(\gamma) \\ \quad \quad \quad \\ (\alpha) \text{C}-\text{C}(\text{H})=\text{C}-\text{H}(\delta) \\ \quad \quad \quad \\ \text{H}_3\text{C} \quad (\beta) \text{H} \\ \text{but-3-en-2-one} \end{array}$	$\alpha:\beta:\gamma:\delta$ 3:1:1:1

(1.5 point per correct labeling of non-equivalent hydrogens, 0.5 points per ratio consistent with labeling. Can label α , β , and γ differently as long as the ratios match the key. No credit for any ratio that is not reduced to the smallest set of integer values, because we specifically asked you to!)

4. ^1H NMR: Interpreting Chemical Shifts (6 points)

In all of these molecules, the halogen withdraws electron density from the rest of the molecule, including the hydrogens. This effect deshields the hydrogen atoms, resulting in a greater chemical shift. Halogens with higher electronegativities withdraw the most electron density, so we expect chemical shift to increase with the halogen's electronegativity. For the halogens, electronegativity follows $\text{F} > \text{Cl} > \text{Br} > \text{I}$, and we therefore observe the same pattern for the chemical shifts of the hydrogens on CH_3X .

2 point for recognizing halogen series (or that all atoms are in a single column of the periodic table, or that the molecules only differs by one atom)

2 point for recognizing effect of electronegativity on deshielding

2 points for discussion of deshielding and effect on chemical shift

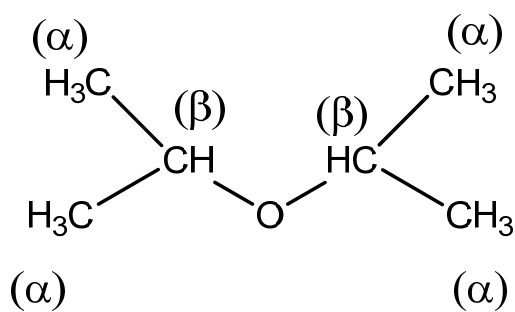
5. ^1H NMR: Interpreting Spectra (16 points)

a) Since there are two groups of peaks, there are only two types of hydrogen atoms. **(1 point)** In this solution, we call them types α and β .

Since the peak area is 6:1 and there are 14 total hydrogen atoms in the molecule, there must be 12 hydrogen atoms of type α and two hydrogen atoms of type β . **(2 points)**

The first group (type α) is a doublet, which means that there is only one hydrogen atom attached to adjacent atom(s) that exhibit spin-spin coupling. The second group (type β) is a septet, which means that six hydrogen atoms are attached to the adjacent atom(s) that exhibit spin-spin coupling. **(2 points; NOTE: students don't need to use the term spin-spin coupling – they may use splitting or discuss neighboring atoms.)**

Diisopropyl ether (2-isopropoxypropane) satisfies these three criteria. **(2 points for structure)**



2-isopropoxypropane

(Students do not need to label hydrogens as α or β , as long as their argument can be followed)

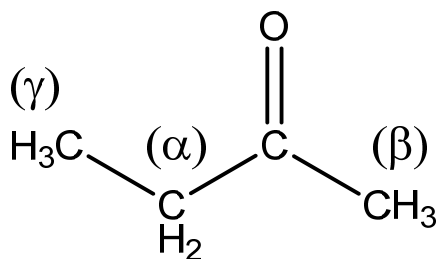
b) Since there are three groups of peaks, there are three types of hydrogen atoms. Call them types α , β , γ . (2 points)

From the plot (words or the red line), you know that the relative peak areas are 2:3:3 for α : β : γ , moving left to right along the chemical shift axis (x-axis).

Since there are a total of eight hydrogen atoms in the molecule, you can deduce from the peak areas that there are two hydrogen atoms of type α , three hydrogen atoms of type β , and three hydrogen atoms of type γ . (2 points)

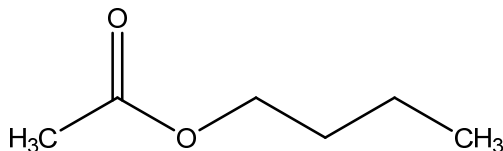
The first group (type α) is a quartet, which means that three hydrogen atoms are attached to adjacent atom(s) that exhibit spin-spin coupling. The second group (type β) is a singlet, which means that no hydrogen atoms are attached to the adjacent atom(s) that exhibit spin-spin coupling. The third group (type γ) is a triplet, which means that two hydrogen atoms are attached to adjacent atom(s) that exhibit spin-spin coupling. (3 points; NOTE: students don't need to use the term spin-spin coupling – they may use splitting or discuss neighboring atoms.)

Methyl ethyl ketone (MEK, or 2-butanone) satisfies these criteria. (2 points for structure)



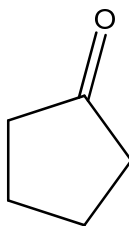
butan-2-one

(Students do not need to label hydrogens as α , β , or γ , as long as their argument can be followed)

6. IR/NMR Combination Analysis (16 points)**a) Butyl Acetate**

From the IR we can confirm CH₃, C=O, and C-O stretches. The NMR shows a singlet at 1.9 ppm from the carbonyl methyl group, a triplet at $\delta(\text{ppm})$:3.9 due to the CH₂ next to the ester oxygen atom, and multiplets at decreasing values depending on the distance from the ester oxygen.

(4 points for structure and 4 for explanation)

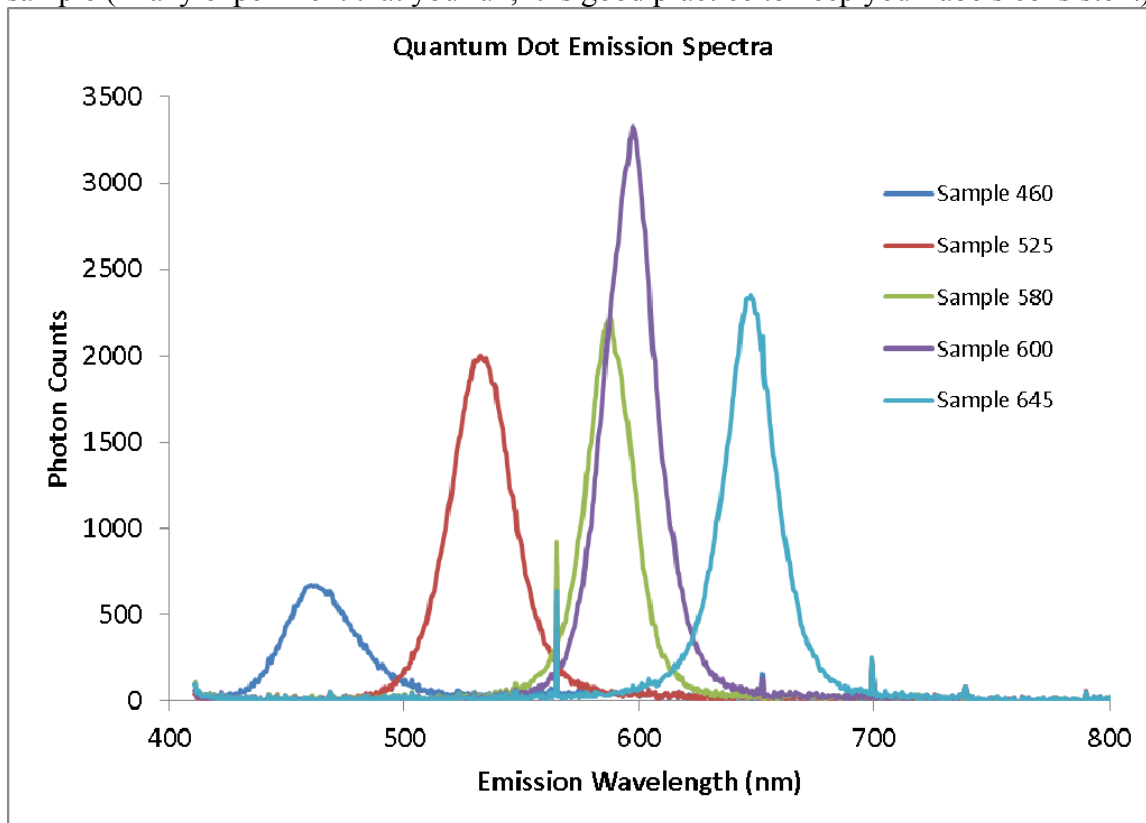
b) Cyclopentanone

From the IR we can identify the CH and C=O stretches as well as CH₂ bends. Most notably, the NMR shows only 2 multiplets, indicating that there are only 2 sets of chemically equivalent protons. Given the formula, the only structure that meets our requirements is cyclopentanone.

(4 points for structure and 4 for explanation)

7. Determining the size of quantum dots (15 points)

a) Below are the five emission spectra. The labels are the filenames of each quantum dot sample (in any experiment that you run, it is good practice to keep your labels consistent)



Note that there are sharp peaks in all of the spectra at 564.78 nm, 652.37 nm, and 699.24 nm. These features are from extraneous laser emissions (the laser pointer is not perfectly monochromatic).

(5 points for plot. -1 for each missing or unlabeled spectrum. No credit for the plot if the axes are not labeled, since we specifically told you to do so!)

b) You can either zoom in on each peak, or just use the VLOOKUP command in Excel to figure out where the maximum emissions occur. Remember that we asked for only three sigfigs, or ± 1 nm.

Sample	Emission maximum (nm)
460	462
525	532
580	587
600	597
645	647

(2 points. -0.5 pts per correct emission maximum. Award credit for any value ± 2 nm of the correct answer. No credit for incorrect sigfigs or units, since we told you how many to use!)

c) Start with the Brus equation:

$$\Delta E(r) = E_{\text{gap}} + \frac{h^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right),$$

where $\Delta E(r)$ is the emission energy as a function of radius, E_{gap} is the band gap energy, h is Planck's constant, r is the radius of the quantum dot, m_e^* is the effective mass of the excited electron, and m_h^* is the effective mass of the electron hole. For light, $\Delta E = \frac{hc}{\lambda}$, so make this substitution and solve for r .

$$r = \left[\frac{h^2}{8 \left(\frac{hc}{\lambda} - E_{\text{gap}} \right)} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \right]^{1/2}$$

Note that larger nanoparticles (larger r) exhibit a larger λ .

(3 points for correctly solving for r)

Convert our given values to SI units:

$$E_{\text{gap}} = (1.74 \text{ eV}) \left(\frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) = 2.79 \times 10^{-19} \text{ J}$$

$$m_e^* = (0.13)(9.109 \times 10^{-31} \text{ kg}) = 1.2 \times 10^{-31} \text{ kg}$$

$$m_h^* = (0.45)(9.109 \times 10^{-31} \text{ kg}) = 4.1 \times 10^{-31} \text{ kg}$$

Using $h = 6.62608 \times 10^{-34} \text{ J s}$, $c = 2.99792458 \times 10^8 \text{ m s}^{-1}$, and $1 \text{ Å} = 10^{-10} \text{ m}$, we obtain

Sample	Emission wavelength (nm)	Radius of dot (Å)
460	462	20
525	532	25
580	587	32
600	597	33
645	647	46

The radii are limited to two sigfigs by m_e^* and m_h^*

(5 points: 1 pt per correct radius. -2 if unit conversions were the only mistake. No credit for any answers not in Å, since we specifically asked for that unit! No credit for any answer with incorrect sigfigs.)