

1. (a) What is the Larmor (precession) frequency of a ^{17}O nucleus in a 5.1 T magnetic field? (3 pts)

(b) Calculate the magnitude of the spin angular momentum vector ($|I|$) for a (i) ^{39}K and (ii) ^{18}O nucleus. (2 pts)

$$|I| = \left(\frac{h}{2\pi} \right) \sqrt{I(I+1)}$$

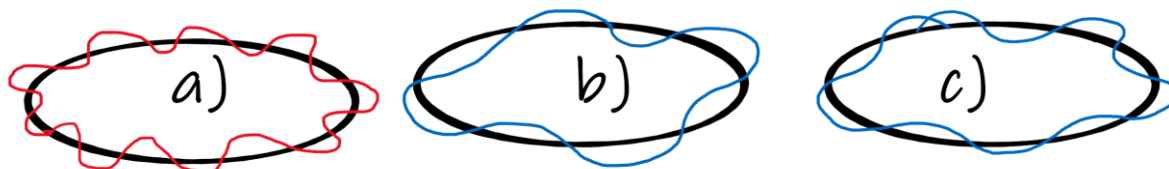
(c) The polarisation, p , of ^1H nuclei in a magnetic field at 600 K is 0.000023. What is the ^1H resonance frequency in this (unrealistically strong) field? (2 pts)

(d) What temperature would be required to get the same polarisation using a 300 MHz spectrometer? (2 pt)

2. Which of the following are functions are eigenfunctions of the operator for angular momentum where the potential is constant over all x ? Justify your answers in terms of the recovery of an eigenfunction and a proper eigenvalue (2 pts)

$$\hat{H}\varphi = -\frac{\hbar}{2m} \frac{d^2\varphi}{dx^2} + V(x)\varphi$$

3. (i) The diagrams below show the wavefunctions for three states of a particle in a ring.

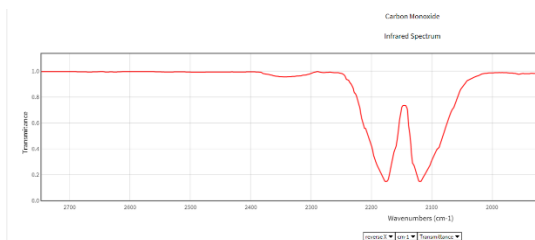


- (a) Which of the states are eigenstates (states whose wavefunction is an eigenfunction of the operator, in this case the Hamiltonian). Justify your answer clearly. (2 pts)
- (b) Of the eigenstates, which is highest and which is lowest in energy. Explain your reasoning clearly (2 pts)
- (c) How should we interpret the amplitude of the waves? (1 pt)

(ii) Explain briefly (use diagrams where appropriate) how Einstein's interpretation of the photoelectric effect implies quantisation of the energy of photons. (2 pts)

(iii) Describe how a molecule interacts with light with frequencies (i) 30 GHz and (ii) 900 GHz (hint convert frequency to wavenumber (cm^{-1}) or wavelength (nm)) (2 pt)

4. Carbon monoxide (CO) is toxic but in low concentrations is a signalling molecule in biological systems. Spectroscopy can be used to obtain data such as bond length.



- Explain the shape of the FTIR absorption spectrum shown above (1 pt)
 - Calculate the force constant for the bond of CO if it absorbs infrared light at 2150 cm^{-1} . (2 pts)
 - Assume that the bond strength is unchanged in the $^{14}\text{C}^{18}\text{O}$ isotopologue of CO. At what **wavelength (in nm)** would the absorption be expected to be observed? (2 pts)
 - Calculate the wavelength of the 1st and 2nd overtones of CO that would be expected if it behaved as a perfect harmonic oscillator. Would this be at lower or higher frequency in reality? Give reasons for your answer (2 pt)
- 5 a. Estimate the most populated rotational level of $^{12}\text{C}^{16}\text{O}$ at (i) $-20\text{ }^{\circ}\text{C}$ and (ii) $900\text{ }^{\circ}\text{C}$? Take $B = 57.635\text{ GHz}$. (3 pts)

- Sketch the expected rotational absorption spectrum of $^{12}\text{C}^{16}\text{O}$.
 - Indicate the gap between successive lines in terms of B
 - the approximate relative intensity of the lines
 - the line of maximum intensity at 300 K .

Justify your answers. (4 pts)

6. a. Work out how many normal (i.e. vibrational) modes the following compounds have (you need to work out the compound's molecular shapes!) (3 pts)

Indium trichloride (InCl_3)

calcium sulphate (CaSO_4)

ammonia borane (NBH_6)

b. In the equation for the transition dipole moment operator for infrared absorption is shown below.

(i) Explain why the first term in the expansion is zero. (2pt)

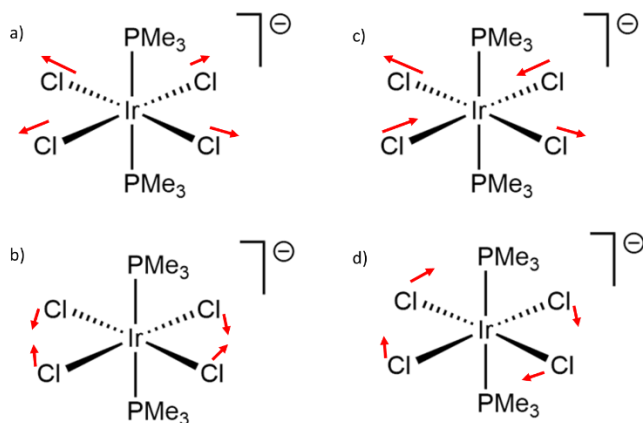
(ii) For CO_2 show, by consideration of the derivative $\left(\frac{d\mu}{dx}\right)_0$, that (a) the asymmetric stretch of CO_2 is infrared active while (b) the symmetric stretch is not. (2pt)

$$\mu_{fi} = \mu_0 \int \psi_{v_f}^* \psi_{v_f} dx + \left(\frac{d\mu}{dx}\right)_0 \int \psi_{v_f}^* x \psi_{v_f} dx$$

7. The iridium complex shown below has approximately D_{4h} symmetry. The small arrows to indicate the motion of atoms during one half cycle of a mode.

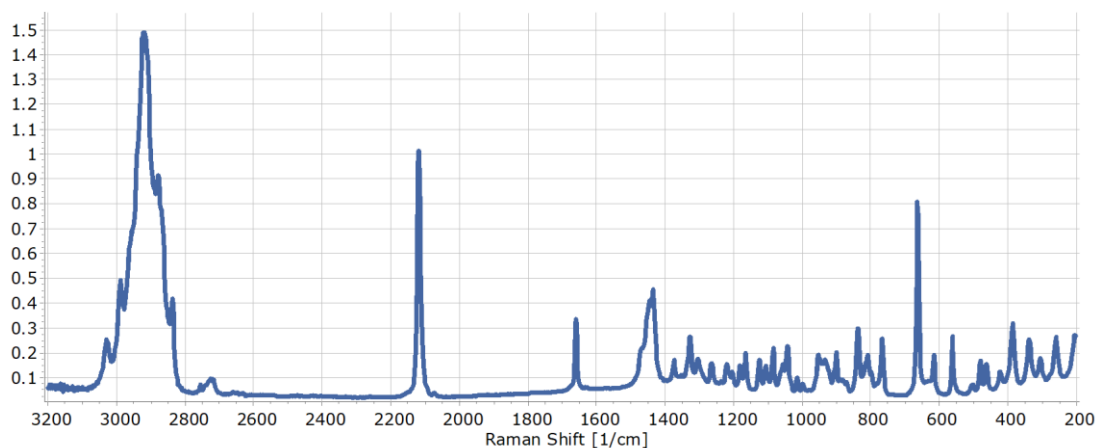
The symmetry species for the modes are in random order **a_{1g}**, **a_{2g}**, **b_{1g}**, **b_{2g}**,

- (i) Use the character table for D_{4h} and match each mode (a to d) to the correct symmetry species. In each case justify your answer clearly. (4 pts)
- (ii) Which of the four modes are not a vibration (normal mode). Justify your answer. (2 pts)
- (iii) For those modes that are vibrations, indicate with justification whether or not they are IR and/or Raman active. (2 pts)



8. The spectrum shown below (also available as Spectragryph file) is a mixture of two compounds.

- (i) Identify the major bands due to functional groups (3 pts)
- (ii) Identify the component compounds (2 pts)



9. (i) Calculate the total number of microstates described by each of the following term symbols (3 pts)
- (ii) order the 4 microstates from lowest to highest energy (degenerate). Justify your answer. (1 pt)
- (iii) in each case calculate the spin multiplicity (1 pt)

(a) \uparrow \uparrow \uparrow \uparrow ---

(b) \uparrow \uparrow --- --- \uparrow

(c) \downarrow \uparrow \uparrow --- ---

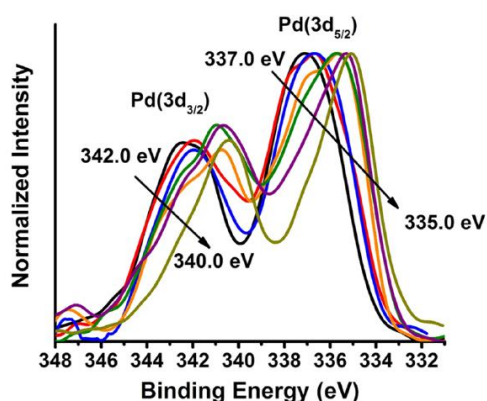
(d) \uparrow \uparrow --- --- \downarrow

10. X-ray Photo-electron Spectroscopy and X-ray Absorption Spectroscopy are two different techniques, both of which use X-rays to probe the electronic properties of a material.

- Explain the differences between the two techniques, i.e. (3 pts)
 - which orbitals are probed?
 - what is the detection method
 - what are the sample requirements
- Which of the two techniques is most sensitive to the oxidation state of a transition metal? Justify your answer. (2 pts)

In the figure below, the Pd(3d) XPS spectra are shown for a Pd(acac)₂ complex, supported on alumina (Al₂O₃), during reduction in octene at 25°C for 6 h (red), 24 h (blue), 48 h (orange), 72 h (green), 96 h (purple) and 120 h (yellow).

- Explain why there are two bands visible in the 3d Pd XPS. (2 pts)
- Explain the change in position of the bands upon reduction of the Pd complex. (1 pt)



11. The UV/Vis spectra of a solution of MnCl₂ in water shows a weak band at around 400 nm with a molar absorptivity of 350 M⁻¹ cm⁻¹

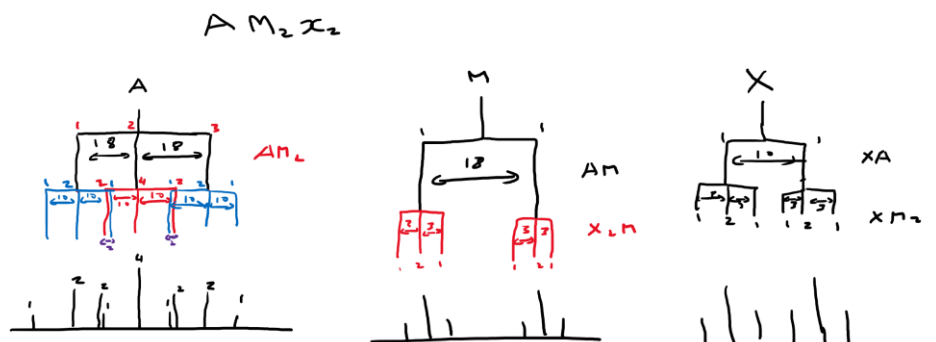
What is the %Transmittance of a 0.20 mmol dm⁻³ solution in a 1 mm pathlength cuvette (2 pt)

12. Draw a schematic (line) representation of the pure first order ¹H NMR spectrum of an AM₂X₂ spin system corresponding to the following parameters (7 pts):

Frequencies (Hz from TMS) $\nu_a = 482$; $\nu_m = 646$; $\nu_x = 1356$ Hz

Coupling constants (Hz) $J_{AM} = 18$; $J_{AX} = 10$; $J_{MX} = 3$

- Give the chemical shifts in ppm for an instrument operating at 200 MHz **3 pts**
- Sketch in splitting diagrams above a schematic spectrum to indicate which splitting correspond to which coupling constants **3pts**



- iii. consider the rule for the first order coupling that the difference in chemical shift is at least 10 times the coupling constant $\Delta\delta > 10 J$. Would you expect the shape of spectrum you have drawn to be actually observed. Justify your answer. **1 pt**

13.

a) Two protons in a molecule undergo symmetric two-site conformational exchange. Their chemical shifts in the absence of exchange are 3.5 and 5.5 ppm each with a line width of 0.4 Hz. At 310 K a single signal with a line width of 20 Hz is observed with a 200 MHz spectrometer. What is the rate of exchange between the two sites at 310 K?

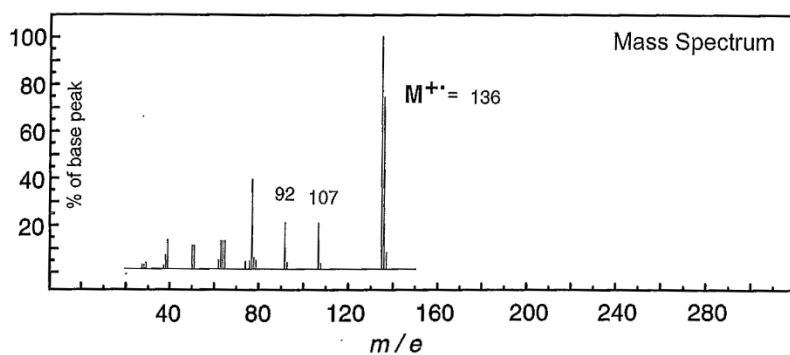
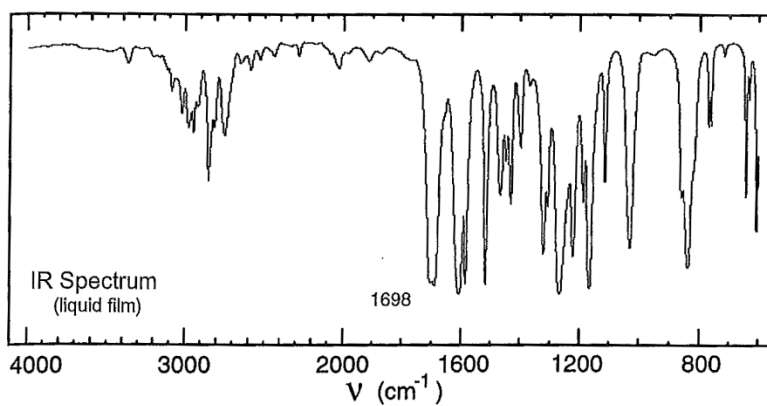
b) At 260 K to broad overlapping signals are observed with peaks at 4.1 and 6.9 ppm. What is the rate of exchange?

14. Propose a structure that is consistent with the spectrum and the molecular formula and show clearly what information can be extracted from the spectral data provided as follows.
you can answer in individual text boxes are upload a single answer here. The problem can be downloaded as a png file here.

Spectra as png [Exam spectroscopy 2020 multispectral.png](#)

Spectra as pdf [Exam spectroscopy 2020 multispectral.pdf](#)

- Assign features in the FTIR spectrum and Comment on the UV/Vis spectrum(3 pts).
- Comment on the identity of the ions observed in the mass spectrum(4 pts).
- Comment on the ^{13}C NMR spectrum (chemical shift, number and type of carbons) (4 pts).
- Comment on the ^1H NMR spectrum (chemical shift, coupling, integration and type of hydrogens. (4 pts).
- Give the structure of the compound and justify your answer(3 pts bonus).



UV Spectrum

λ_{max} 277 nm ($\log_{10} \epsilon$ 4.2)

solvent: methanol

