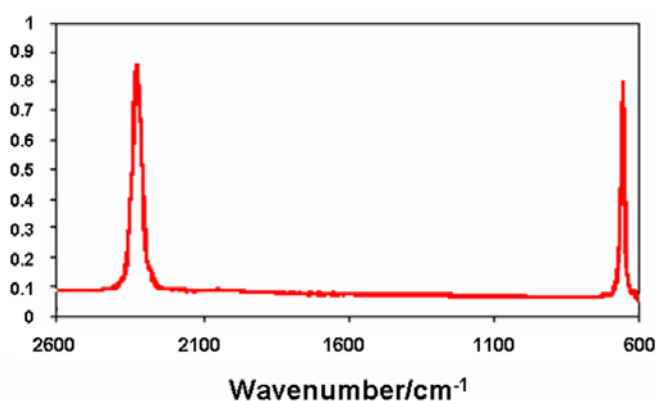


Question 3

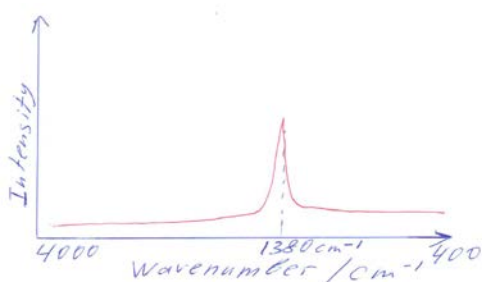
[40 marks]

- (a) The Infrared spectrum of liquid CO_2 present two absorption bands, one corresponding to antisymmetric vibrational mode ν_3 at ca. 2340 cm^{-1} and another band at ca. 670 cm^{-1} corresponding to two double degenerate bending modes ν_2 of CO_2 . The main selection rule for infrared active vibrations is that the dipole moment should change during the corresponding vibrations, which is the case for vibrations ν_3 and ν_2 . There is no rotational structures in these spectral bands because rotations are hindered in liquid phase of CO_2 . Both these vibrations are IR active because dipole moment changes during vibrations. x-axis shows values of Wavenumber/ cm^{-1} while y-axis shows absorbance (no units).



The Raman spectrum of liquid CO_2 present one absorption band (as Fermi resonance was not taught in this course) of symmetric vibration ν_1 CO_2 ca. 1380 cm^{-1} . The main selection rule in Raman spectroscopy requires change of polarisability during molecular vibration: $\frac{\partial \alpha}{\partial r} \neq 0$

Symmetric vibration of CO_2 ν_1 exhibits change in polarizability during vibration, while other vibrations do not change polarizability, so Raman inactive. [10 marks]



- (b) Solution should include discussion of diatomic molecule as harmonic oscillator.

Frequency of vibration of diatomic molecule is $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ We need to

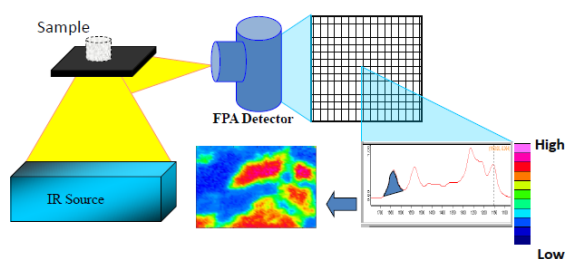
determine the reduced masses of ^{56}FeH and ^{54}FeH , assuming a mass of 1 for hydrogen:
 For ^{56}FeH , it is $1 \times 56 / 57 = 0.9825\text{g}$, for ^{54}FeH it is $1 \times 54 / 55 = 0.9818\text{g}$. $(0.9825 / 0.9818)^{1/2} = 1.00036$; so, wavenumber for $^{54}\text{FeH} = 1661.0 \text{ cm}^{-1} \times 1.00036 = 1661.6 \text{ cm}^{-1}$.
 Frequency $\nu = c \times \text{wavenumber}$, so frequency is $5 \times 10^{13} \text{ Hz}$. There is no need to know exact value of atomic mass unit as it will be cancelled in the ratio of square root of reduced masses.

[5 marks]

(c) Beer-Lambert Law: $A = \epsilon c l$, where ϵ is molar absorptivity, c is concentration and l is pathlength; A is absorbance (measured as a peak of the infrared band or as a area under the band, called integrated absorbance). Schematic diagram would also be helpful. $0.1 = 0.5 \times 10^6 \text{ cm}^2/\text{mol} \times c \times 0.02 \text{ cm}$; $c = 0.01 \text{ mol/L}$

[5 marks]

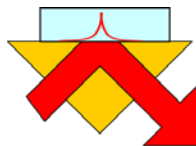
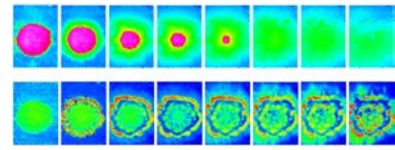
(c) First, principles of FTIR imaging should include discussion and a brief description of a combination of FTIR spectrometer with infrared array detector to measure thousands of spectra simultaneously from different locations within the sample. The simplest way to obtain chemical images is plotting absorbance of specific infrared bands as a function of all pixels:



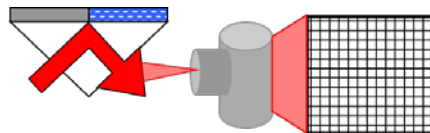
Combining FTIR spectrometer with a Focal Plane Array detector
 (64 x 64 or 128 x 128 pixels)

The main approach to study tablet dissolution is macro ATR-FTIR imaging that uses ATR accessories with inverted prism (figure below) accommodated in a large sample compartment (or macro chamber) of a spectrometer. The main reason for the choice of ATR is because water strongly absorb IR radiation while ATR probes layer of only few micrometer thick (appropriate equation would be useful here). The inverted prism crystals made of ZnSe, diamond, Si or Ge. This results that macro ATR-FTIR imaging

measures different areas of studied tablets (from ca. 1 mm² to a few cm squared). This approach is suitable for studies of dynamic systems (e.g. dissolving tablet) to detect concentration profiles of drug, polymer and water within interfacial areas of tablet/aqueous medium. Main applications of macro ATR-FTIR imaging include studies of dissolution of tablets for understanding mechanism of drug release as it is capable detection drug crystallisation (figure below) during dissolution (because of shift of spectral bands).

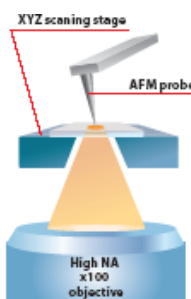
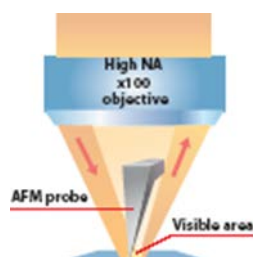
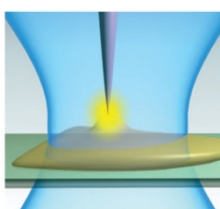


Macro ATR



[10 marks]

(d) The technique that can differentiate carbon nanotubes (SWCNT) of different diameters is TERS – tip-enhanced Raman spectroscopy, which is a novel technique that combines the high spatial resolution of atomic force microscopy (AFM) with the chemical information of Raman spectroscopy, thus breaking diffraction limit associated with confocal Raman microscopy. Brief discussion of principles of tip-enhanced Raman spectroscopy should include description of metal-tip covered with nano-particles gold (or silver) that produce surface-enhanced effect at the edge of the tip, as show in the figure on the left below. Therefore, the signal measured (yellow area in the figure) will be localised significantly better than the focus of laser beam in Raman microscopy, thus achieving spatial resolution on the order of nanometers, suitable for differentiation of carbon nanotubes (SWCNT). Discussion may also include mention of two approaches: upright illumination (for non-transparent samples) and inverted illumination (for transparent samples) and examples of differentiation of different carbon nanotubes by obtaining TERS spectra from the small area of dispersed nanotubes, where different Raman signals from bundles of carbon nanotubes of different diameters provided opportunity to differentiate their locations within the mixture. This is possible because wavenumber of the corresponding radial breathing modes (RBM) are directly related to the diameters of SWCNT, thus plotting distribution of intensity of RBM would allow to obtain image showing distribution of SWCNT of a particular diameter.



[10marks]



Question 3

[40 marks]

a) (a)

IR: All molecules apart from $^{37}\text{Cl}^{35}\text{Cl}$ will show IR spectra because those molecules will have vibrations that change dipole moment of these molecules. The nonpolar $^{37}\text{Cl}^{35}\text{Cl}$ molecule has one vibration which does not produce change of dipole moments because isotopes of Cl have the same charges.

Raman: All molecules will be active in Raman because their corresponding vibrations would change size or shape of molecules, thus leading to the change of polarizability.

The number of normal vibrations: **1** for $^{37}\text{Cl}^{35}\text{Cl}$ and **4** for $\text{H}-\text{C}\equiv\text{N}$ (hydrogen cyanide), as these both are linear molecules. For C_{60} fullerene one may expect **174** vibrations (mostly in far-infrared region with many generate vibrations) and there are **3** normal vibrational modes for H_2O .

[12 marks, 3 marks for each molecules with explanation]

b) In Infrared spectroscopic measurements the high-spatial resolution of micro-ATR

should be mentioned, which is defined is given by the Rayleigh criterion $r = \frac{0.61\lambda}{NA}$

Where, NA is the numerical aperture of the system (the product of the refractive index, n , and $\sin\theta$ and θ is half the angle of the collection of light, thus $NA = n \sin\theta$), λ is the wavelength of light and r is the minimal distance required to have a contrast of 26.4 % between two nearby objects (just resolved). Refractive index of Ge crystal is 4, thus it results in numerical aperture NA four times greater than it was in air, thus overcoming diffraction limit of IR measurements in transmissions by 4 times. Schematics of such microscope objective would be useful here.

In Raman spectroscopy it is possible to overcome diffraction limit of light by using near-field approaches, such as tip-enhanced Raman spectroscopy (TERS), which is a novel technique that combines the high spatial resolution of atomic force microscopy (AFM) with the chemical information of Raman spectroscopy, thus breaking diffraction limit associated with confocal Raman microscopy.

Discussion of principles of tip-enhanced Raman spectroscopy should be included. The schematic would be useful here.

[13 marks]

- c) One of the methods to obtain depth profile information about polymeric samples is **confocal Raman** microscopy, which provided a possibility of non-destructive approach. Measurements recorded below the surface, so Raman spectra and thus chemical information are obtained as a function of depth. Restriction of out of focus regions entering the detector is achieved by using a pin-hole that the light from other depths blocked. **Schematic** of confocal Raman microscope would be helpful here.

Spatial resolution for depth profiling ca. 2-3 micrometers and the probing depth for polymeric materials is ca 50-100 micrometers. A brief discussion of immersion lenses is needed here.

The depth profiling is achieved by using aperture and moving microscope stage in z-direction by selected distance, e.g. 2 micrometers. Stating the depth range of this approach should be included (ca. 100 micrometre deep). Alternatively, a polymeric sample may be cut and surface of cross-section to be mapped by steps of 1 micrometre.

A different vibrational spectroscopic method for obtaining information about depth information of polymeric samples would be FTIR spectroscopic imaging. First, micro ATR-FTIR spectroscopic imaging can be applied to study polymeric sample with high spatial resolution of few micrometres. Therefore, principles of FTIR imaging should include brief discussion and a brief description of a combination of FTIR spectrometer with infrared array detector to measure thousands of spectra simultaneously from different locations within the sample. The way to obtain chemical images should be briefly stated.

When imaging in ATR mode, IR light approaches the sample through a high refractive index material which provides an opportunity to increase the NA and thereby improve the spatial resolution, for example refractive index of Ge is 4 and it is infrared transparent materials, so using it will enhance spatial resolution by four times. This is achieved in micro ATR-FTIR spectroscopic imaging for studies of cross-section of polymeric sample. The cross-section provides insight into distribution of substances within the sample, but it is invasive approach. The depth profiling is achieved non-destructively using variable angles of incidence by gradually increasing the angle probing layers of different thickness within 1-3 micrometres

range. It is also possible to probe polymeric materials (such as laminates) using different angles of incidence in macro ATR imaging with different apertures (schematics is required)

[15 marks]

Answers/Solution for Question 3

(a)

(i) C-H (ii) C-F (iii) N-H (iv) O-H

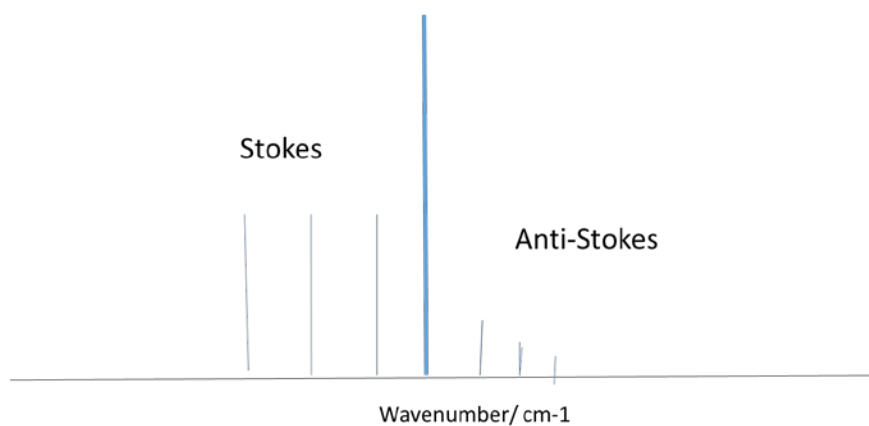
The position of wavenumber of stretching vibrations depends on masses of atoms involved and force constants, thus having heavy atom in (iii) will have lowest wavenumber (e.g. 1300-1100 cm^{-1}), followed by C-H (as much lighter atom H is involved), N-H has greater force constant than O-H.

So, the order should be (ii) C-F (i) C-H (iii) N-H (iv) O-H

(b) The depth of penetration in ATR depends on wavelength of the light (directly proportional).

Wavenumber of C=O band at around 1700 cm^{-1} , while wavenumber of C-O band is around 1000 cm^{-1} . Therefore, the depth of penetration for absorption at the C-O band will be $3\text{ }\mu\text{m} \times 1.7 = 5.1\text{ }\mu\text{m}$.

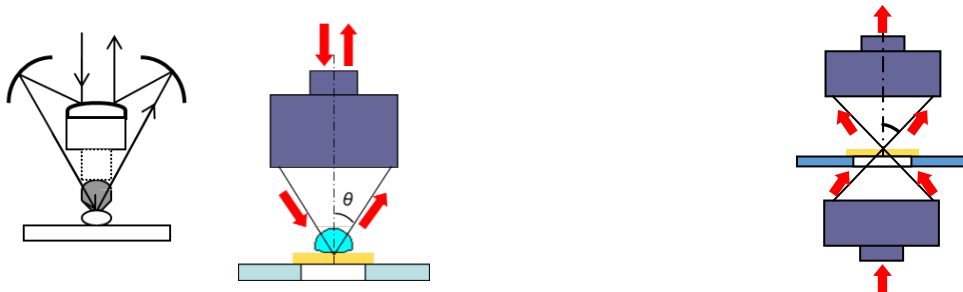
(c) The representation of incident line and corresponding Raman scattered lines should be presented, including Stokes and anti-Stokes (as in schematics below). The spacing from strong excitation line should be the same for both Stokes and anti-Stokes lines (which should have much smaller intensities because it involves vibrations at the first excitation level, $v=1$ that has fewer molecules unlike Stokes lines which involves vibrations in fundamental level, $v=0$). However, **Boltzmann distribution** will affect intensities of anti-Stokes because population of vibrational level with $v=1$ at 218 cm^{-1} will be greater than level at 314 cm^{-1} , which will be greater than at the level at 459 cm^{-1} .



(d) The micro ATR-FTIR imaging use microscope objective with Ge crystal (figure below on the left and centre) to increase numerical aperture and spatial resolution. This results that micro ATR-FTIR imaging provides a higher spatial resolution (2-3 micrometers) but images small area (50x50 or 60x60 micrometers squared).

Spatial resolution is defined is given by the Rayleigh criterion $r = \frac{0.61\lambda}{NA}$

Where, NA is the numerical aperture of the system (the product of the refractive index, n , and $\sin\theta$ and θ is half the angle of the collection of light, thus $NA = n \sin\theta$), λ is the wavelength of light and r is the minimal distance required to have a contrast of 26.4 % between two nearby objects (just resolved). When imaging in micro ATR-FTIR mode, IR light approaches the sample through a high refractive index material which provides an opportunity to increase the NA and thereby improve the spatial resolution, for example refractive index of Ge is 4 and it is infrared transparent materials, so using it will enhance spatial resolution by four times. This is achieved in micro ATR-FTIR spectroscopic imaging for studies of many different materials (polymer blends, cross-section of hair, live cells, etc.). In transmission, $n=1$ (air) and spatial resolution 4 times worse than in micro ATR. Schematics of transmission in the figure below on the right. It is possible increase spatial resolution in transmission using objective with high NA, but also using solid immersion lens (refractive index of CaF_2 is 1.4, thus 40% increase in spatial resolution), schematics is shown on the bottom.



Micro ATR

