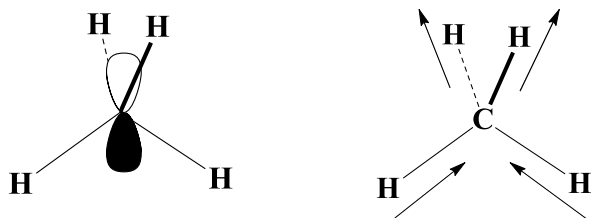


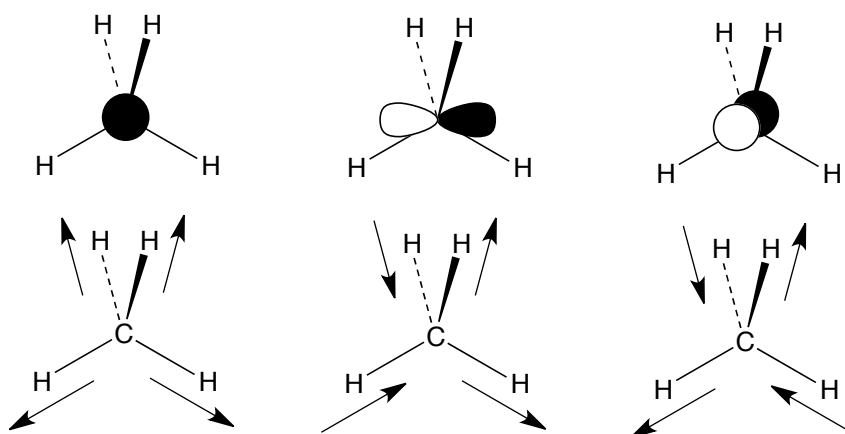
The infrared spectrum of $\text{CH}_4(\text{g})$ contains a single strong band in the C-H stretching region, at 3020 cm^{-1} . The Raman spectrum shows a band at 2914 cm^{-1} .

The form of the vibrational modes can be obtained using their relationship to the atomic orbitals on the central atom. The example below illustrates this relationship using one of the stretching modes and one of the carbon p -orbitals.



- (a) Sketch the form of the remaining stretching modes for methane.

[P: 3 marks]



- (b) Three of the stretching modes have the same vibrational frequency. Clearly identify these vibrations on your sketch and briefly explain why this occurs.

[P: 2 marks]

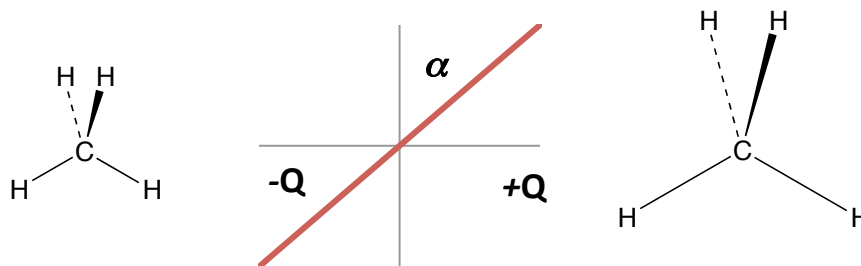
The 3 vibrations which are analogous to the 3 p -orbitals have the same vibrational frequency (i.e. they are degenerate). Each of these vibrations involve the same motions, with 2 C-H bonds compressing whilst 2 C-H bonds are stretching, and only differ in the pairs of bonds doing this.

- (c) Identify which of the vibrational mode(s) corresponds to the infrared band at 3020 cm^{-1} and which mode(s) correspond to the Raman band at 2914 cm^{-1} . Briefly explain your assignment.

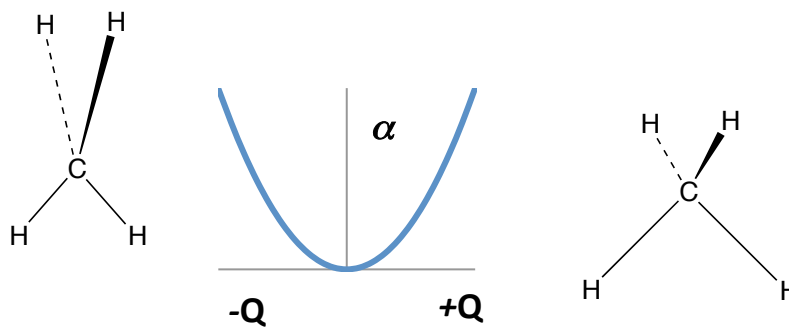
[P: 3 marks]

To be infrared active, the vibration must give rise to a *change* in dipole moment. The dipole moment does change along each of the degenerate vibrations.

To be Raman active, there must be a non-symmetrical change in the polarisability during the vibration. The polarisability depends on the size of the molecule and so it changes for a CH₄ molecule which is undergoing the breathing mode:



For the other 3 vibrations, the change in polarisability is symmetrical along the vibration motion:



The infrared band at 3020 cm⁻¹ corresponds to the 3 vibrations which are analogous to the *p*-orbitals. The Raman band at 2914 cm⁻¹ corresponds to the breathing mode (i.e. the vibration which is analogous to an *s*-orbital).

- (d) Briefly explain why there is only one band in the C-H region of the infrared spectrum, even though there are four C-H bonds in methane.

[CR: 2 marks]

The 4 C-H bonds in methane are identical. They couple together to give 4 normal modes. 3 of these normal modes are degenerate. These 3 are infrared active but occur at the same frequency. The 4th mode is not infrared active.

Thus, the infrared spectrum contains only 1 band in the C-H region of the spectrum. This band is due to the 3 degenerate vibrations drawn above.

- (e) For a harmonic oscillator, the wavenumber, $\bar{\nu}$, is given by the equation below.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Does the band in the Raman spectrum of deuterated methane, CD₄ occur at higher or lower wavenumber than that in the spectrum of CH₄? Briefly explain your answer.

[P: 2 marks]

The C-H and C-D bonds will be very similar so their force constants will be very similar: $k_{CD_4} = k_{CH_4}$.

As deuterium has a higher mass than hydrogen the reduced mass of CD₄ is higher than that of CH₄: $\mu_{CD_4} > \mu_{CH_4}$. Because of the higher reduced mass, CD₄ will have a lower vibrational frequency.

- (f) Use this equation to predict the wavenumber for the band in the Raman spectrum of CD₄.
[D: 2 marks]

The reduced mass is given by:

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

In atomic mass units,

$$\mu_{CH_4} = \frac{12 \times 1}{12 + 1} = \frac{12}{13} \quad \text{and} \quad \mu_{CD_4} = \frac{12 \times 2}{12 + 2} = \frac{24}{14}$$

From the equation above for the wavenumber:

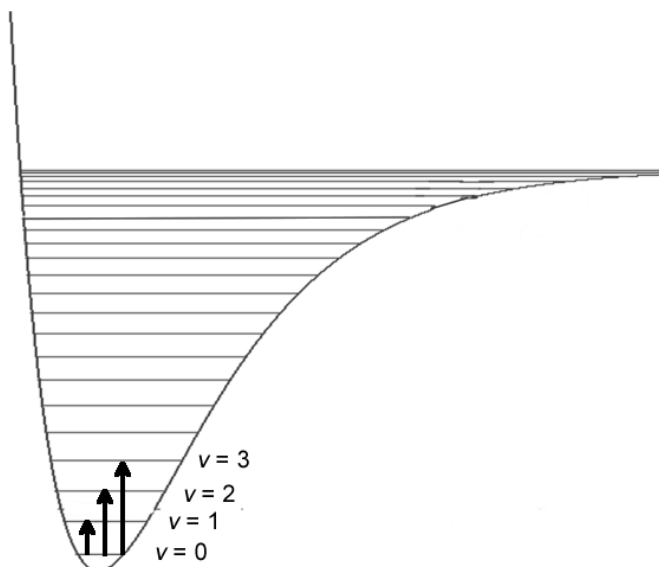
$$\frac{\bar{\nu}_{CD_4}}{\bar{\nu}_{CH_4}} = \sqrt{\frac{\mu_{CH_4}}{\mu_{CD_4}}} = \sqrt{\frac{12/13}{24/14}}$$

From above, the wavenumber for the Raman band of CH₄ is 2914 cm⁻¹. The wavenumber for the Raman band of CD₄ is thus predicted to occur at:

$$\bar{\nu}_{CD_4} = \sqrt{\frac{12/13}{24/14}} \times 2914 \text{ cm}^{-1} = 2138 \text{ cm}^{-1}$$

- (g) The first and second overtones of the infrared active mode occur at 6006 and 9047 cm⁻¹. Using a suitable energy level diagram, explain the origin of these transitions and qualitatively account for their energies.

[CR: 2 marks, D: 2 marks]



At normal temperatures, only the lowest vibrational level, $v = 0$, is significantly populated. All of the transitions arises from excitations from this level.

The fundamental at 3020 cm^{-1} corresponds to the transition $v = 0 \rightarrow v = 1$.

The first overtone at 6006 cm^{-1} corresponds to the transition $v = 0 \rightarrow v = 2$.

The second overtone at 9047 cm^{-1} corresponds to the transition $v = 0 \rightarrow v = 3$.

As shown on the energy level diagram, the vibrational levels are approximately equally spaced at low values of v . As v increases, anharmonicity becomes increasingly important leading to the levels becoming more closely spaced, until they converge at dissociation.

Thus, the first overtone occurs at approximately twice the wavenumber of the fundamental. The effect of anharmonicity is that it actually occurs at *slightly* less than this value.

Similarly, the second overtone occurs at approximately three times the wavenumber of the fundamental. Again, anharmonicity means that it actually occurs at *slightly* less than this value.

- (h) The main constituents of the atmosphere of the gas planet Uranus are methane, hydrogen and helium. The blue colour of this planet is thought to be due to methane. Explain how this colour arises and why the other atmospheric gases are not thought to contribute.

[HD: 4 marks]

As discussed in (g), the overtones occur at approximate multiples of the fundamental. The low mass of H leads to the C-H fundamental having a relatively high frequency. As a result, relatively few multiples are needed to produce an absorption in the visible region of the spectrum. The absorbance, however, decreases rapidly so that the

overtones in the red region absorb much more strongly than those in the rest of the visible spectrum. As the main absorption is in the red, the colour observed is blue (i.e. its complementary colour).

The absorbance in the visible region due to the C-H overtones is very weak but given a long enough path length, such as light travelling through the atmosphere of Uranus, it is enough to give a blue colour.

The other constituents of the atmosphere, H₂ and He, cannot absorb infrared light. H₂ is a homonuclear diatomic so that its stretch does not produce a dipole moment. He is an atom so has no bonds to vibrate.

P: 10, CR: 4, D: 4, HD: 4 and total = 22 marks