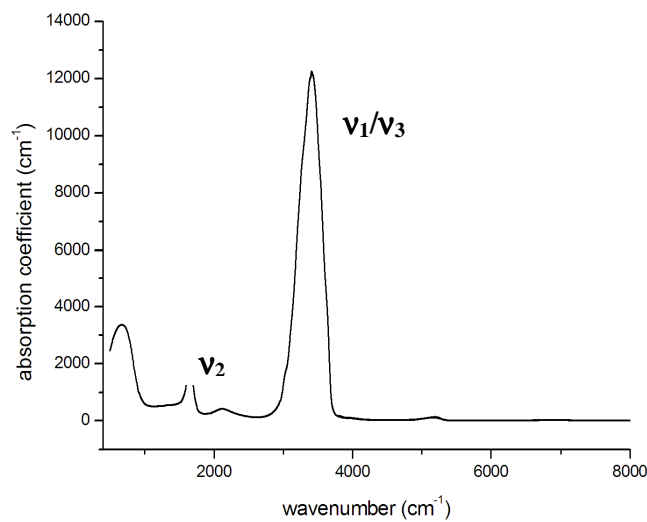


The vibrational absorption spectrum of liquid water extends from the infrared into the visible region. The spectrum of the liquid is largely explained by that of the water monomer, albeit in a hydrogen-bonded environment. The water molecule (in water) has three vibrational modes:

mode	frequency	description
ν_1	3277	symmetric stretch
ν_2	1645	bend
ν_3	3490	asymmetric stretch

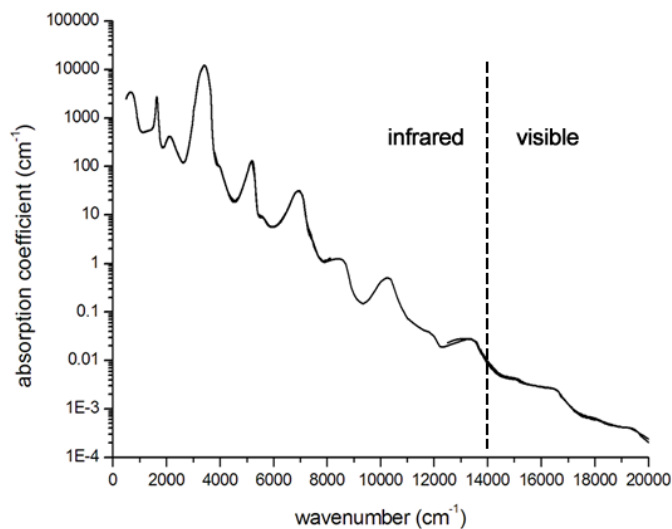
Additionally, there are *librations* – vibrations of the entire framework of H₂O about its equilibrium position in the liquid environment. Important librations occur at 396 cm⁻¹ and 686 cm⁻¹.

The highly heterogeneous environment causes the symmetric and antisymmetric O-H stretches to blend into one feature, while the bend remains distinct. Indicate these features as ν_1/ν_3 and ν_2 on the following spectrum.



[2 marks]

The smaller features are much more easily shown using a logarithmic absorption axis. The following spectrum extends into the visible region.



Indicate on this spectrum the onset of visible light (700 nm).

A wavelength of 700 nm corresponds to 700×10^{-9} m or 700×10^{-7} cm. This wavelength corresponds to a wavenumber:

$$\bar{\nu} = 1 / \lambda = 1 / (700 \times 10^{-7} \text{ cm}) = 14300 \text{ cm}^{-1}.$$

This is indicated by the dotted line on the spectrum above.

[2 mark]

The following table assigns the observed vibrational absorption features of liquid water, noting that multiple quanta of ν_1 and ν_3 are not resolved, and simply denoted ν_S . There are five features left unassigned. Write assignments for these features in the table, using the assigned features as a guide.

Assignment of the IR vibrational absorption spectrum of liquid water					
Wavelength	cm^{-1}	Assignment	Wavelength	cm^{-1}	Assignment
0.2 mm	50	intermolecular bend	1470 nm	6800	$2\nu_S$
55 μm	183.4	intermolecular stretch	1200 nm	8330	$2\nu_S + \nu_2$
25 μm	395.5	L_1 , librations	970 nm	10310	$2\nu_S + 2\nu_2$
15 μm	686.3	L_2 , librations	836 nm	11960	$2\nu_S + 3\nu_2$
6.08 μm	1645	ν_2 , bend	739 nm	13530	$2\nu_S + 4\nu_2$
4.65 μm	2150	$\nu_2 + L_2$	660 nm	15150	$2\nu_S + 5\nu_2$
3.05 μm	3277	ν_1 , symmetric stretch	606 nm	16500	$2\nu_S + 6\nu_2$
2.87 μm	3490	ν_3 , asymmetric stretch	514 nm	19460	$6\nu_S$
1900 nm	5260	$\nu_S + \nu_2$			

[5 marks]

It turns out, that if one looks at white light through a long pathlength of pure water, one perceives a blue coloration. What is responsible for this blue colour?

[2 marks]

It is the weak absorptions due to the overtones and combinations of the vibrations that are responsible for the colour. The absorption is very weak in the red region but even weaker at higher frequencies. Thus the coloration is very weak but, with enough water, leads to a blue colour (i.e. the complementary colour of red).

Using that data in the above table, calculate effective spectroscopic constants, ω_e and $\omega_e x_e$, for the OH stretching motion for water (in water). Use the average of the symmetric and antisymmetric stretches, $(3277+3490)/2$, as the fundamental anharmonic frequency.

[4 marks]

The fundamental occurs at $(3277+3490)/2 \text{ cm}^{-1}$: fundamental = 3384 cm^{-1} .

The first overtone corresponds to $2\nu_s$. This occurs at 6800 cm^{-1} in the table.

From the data sheet, the Morse potential gives the vibrational energy levels as:

$$G(v) = (v + 1/2)\omega_e - (v + 1/2)^2\omega_e x_e$$

The fundamental corresponds to $G(1) - G(0)$:

$$G(1) - G(0) = [(1 + 1/2)\omega_e - (1 + 1/2)^2\omega_e x_e] - [(0 + 1/2)\omega_e - (0 + 1/2)^2\omega_e x_e] = \omega_e - 2\omega_e x_e$$

The first overtone corresponds to $G(2) - G(0)$:

$$G(2) - G(0) = [(2 + 1/2)\omega_e - (2 + 1/2)^2\omega_e x_e] - [(1 + 1/2)\omega_e - (1 + 1/2)^2\omega_e x_e] = 2\omega_e - 6\omega_e x_e$$

Thus:

$$\omega_e - 2\omega_e x_e = 3384 \text{ cm}^{-1} \quad (\text{A})$$

$$2\omega_e - 6\omega_e x_e = 6800 \text{ cm}^{-1} \quad (\text{B})$$

These simultaneous equations can be solved to give the values of ω_e and $\omega_e x_e$:

$$(\text{B}) - 2(\text{A}) = [2\omega_e - 6\omega_e x_e] - 2[\omega_e - 2\omega_e x_e] = (6800 - 2 \times 3384) \text{ cm}^{-1}$$

$$-2\omega_e x_e = 32 \text{ cm}^{-1}$$

$$\omega_e x_e = -16 \text{ cm}^{-1}$$

Substituting this value into (A) gives ω_e :

$$\omega_e = 3384 + 2\omega_e x_e = 3352 \text{ cm}^{-1}$$

Using the first overtone gives a *negative* value for $\omega_e x_e$. This is unphysical: it suggests a *negative* dissociation energy and vibrational energy levels that get further apart. This is clearly *not* happening – the table shows that $6\nu_s$ occurs at a *lower* frequency than 6 times the fundamental. This result is in fact due to the averaged value used for the fundamental.

It would be better to use a higher overtone. From the table, $6\nu_s$ occurs at 19460 cm^{-1} . It corresponds to $G(6) - G(0)$:

$$G(6) - G(0) = [(6 + 1/2)\omega_e - (6 + 1/2)^2\omega_e x_e] - [(0 + 1/2)\omega_e - (0 + 1/2)^2\omega_e x_e] = 6\omega_e - 42\omega_e x_e$$

Thus:

$$\omega_e - 2\omega_e x_e = 3384 \text{ cm}^{-1} \quad (\text{A})$$

$$6\omega_e - 42\omega_e x_e = 19460 \text{ cm}^{-1} \quad (\text{C})$$

These simultaneous equations can be solved to give the values of ω_e and $\omega_e x_e$:

$$(C) - 6(A) = [6\omega_e - 42\omega_e x_e] - 6[\omega_e - 2\omega_e x_e] = (19460 - 6 \times 3384) \text{ cm}^{-1}$$

$$-30\omega_e x_e = -844 \text{ cm}^{-1}$$

$$\omega_e x_e = +28 \text{ cm}^{-1}$$

Substituting this value into (A) gives ω_e :

$$\omega_e = 3384 + 2\omega_e x_e = 3440 \text{ cm}^{-1}$$

Total = 15