

**Sample: Physical Chemistry - Vibrational Spectrum of HCl**

1. Table of peaks

wavenumber, cm^{-1}	3059.0	3044.8	3029.8	3014.2	2997.8	2980.7	2963.1	2944.7
first difference, cm^{-1}	14.2	15.0	15.6	16.4	17.1	17.6	18.4	19.1

wavenumber, cm^{-1}	2925.6	2906.0	2864.8	2843.4	2821.3	2798.7	2775.5	2751.8
first difference, cm^{-1}	19.6	41.2*	21.4	22.1	22.6	23.2	23.7	--

2. Calculation of the average difference between adjacent peaks

R-branch:

$$2925.6 - 2906.0 = 19.6 \text{ cm}^{-1}$$

$$2944.7 - 2925.6 = 19.1 \text{ cm}^{-1}$$

$$2963.1 - 2944.7 = 18.4 \text{ cm}^{-1}$$

P-branch:

$$2864.8 - 2843.4 = 21.4 \text{ cm}^{-1}$$

$$2843.4 - 2821.3 = 22.1 \text{ cm}^{-1}$$

$$2821.3 - 2798.7 = 22.6 \text{ cm}^{-1}$$

$$\widetilde{\Delta\nu} = \frac{19.6 + 19.1 + 18.4 + 21.4 + 22.1 + 22.6}{6} = 20.5 \text{ cm}^{-1} = 2B \quad \Rightarrow \quad B = 10.3 \text{ cm}^{-1}$$

3. Obtaining the bond length

$$B = \frac{h}{8\pi^2 Ic} \quad \Rightarrow \quad I = \frac{h}{8\pi^2 Bc} = \frac{h}{4\pi^2 \widetilde{\Delta\nu} c} \quad I = 2.73 \cdot 10^{-47} \text{ Js}^2$$

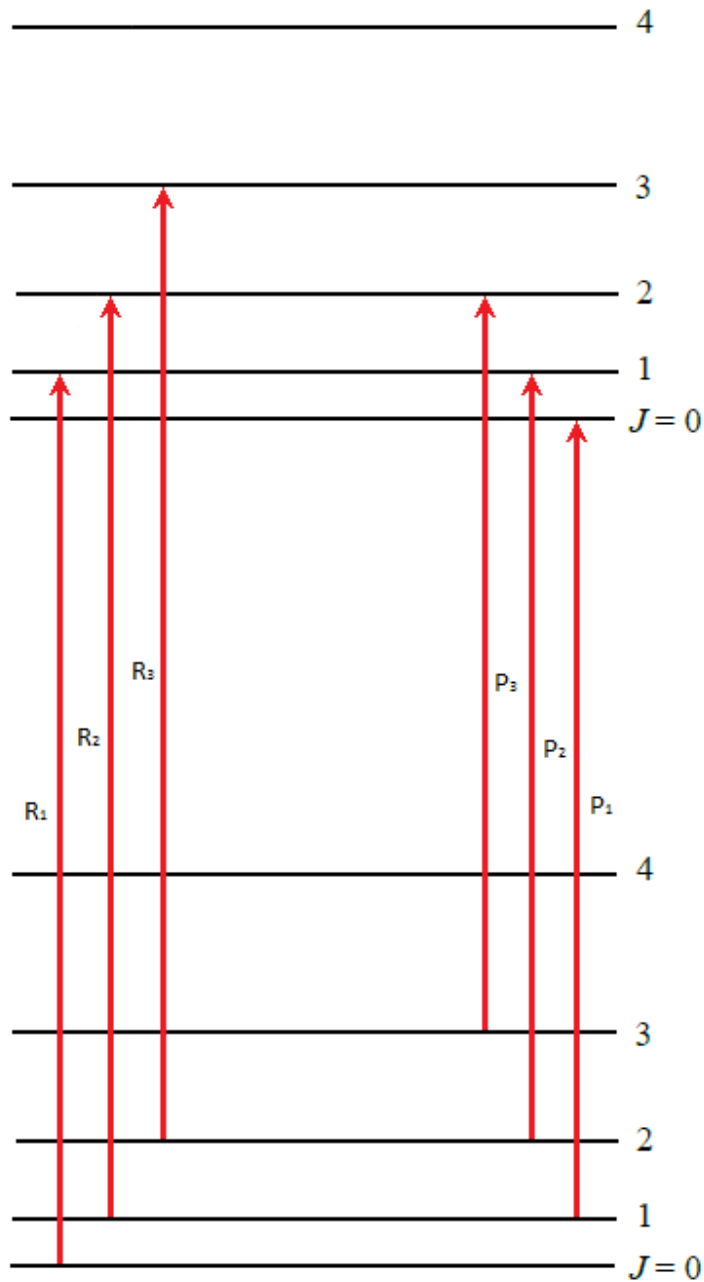
$$\frac{m_1 m_2}{m_1 + m_2} = \frac{M_H M_{Cl}}{(M_H + M_{Cl})L} = 1.627 \cdot 10^{-27} \text{ kg}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 \quad \Rightarrow \quad r = \sqrt{I \frac{m_1 + m_2}{m_1 m_2}} = 1.30 \cdot 10^{-10} \text{ m}$$

Sketch an energy level diagram indicating the rotational quantum numbers of the levels and showing the first three transitions of the P and R branches. Identify these six transitions in your measured spectrum.



Sample: Physical Chemistry - Vibrational spectrum of HCl



You will notice that the first differences change in a systematic way - ie they get larger as we move out from the centre of the spectrum towards lower wavenumbers, and smaller as we move out from the centre towards higher wavenumbers. Why is this?

Let us consider the nearest frequency of rotational modes with quantum numbers J and $J + 1$:

$$\nu_{rot1} = BJ(J + 1),$$

$$\nu_{rot2} = B(J + 1)(J + 2)$$



Sample: Physical Chemistry - Vibrational spectrum of HCl

The distance between them equals

$$\Delta v_{rot} = v_{rot2} - v_{rot1} = 2B(J + 1). \quad (1)$$

Taking into account the expression for the rotational constant B and the moment of inertia I , Eq. 1 can be written in the following form:

$$\Delta v_{rot} = \frac{2h(m_1 + m_2)(J + 1)}{8\pi^2 c m_1 m_2 r^2},$$

where r is the bond length of the molecule. Single molecule can be imagined as a spring with a large stiffness k . For the high energy terms one needs to take into account that a centrifugal force causes the change of the bond length $F_c = k\delta r$, $\delta r \ll r$, $\delta r > 0$. Thus

$$\Delta v_{rot} = \frac{B_0}{(r_0 + \delta r)^2}, \quad B_0 = \frac{2h(m_1 + m_2)(J + 1)}{8\pi^2 c m_1 m_2},$$

and r_0 is the equilibrium bond length. Due to smallness of δr one can write a Taylor series in the following form:

$$\Delta v_{rot} = \frac{B_0}{r_0^2} - 2\frac{B_0}{r_0^3}\delta r,$$

Therefore we can see that the increasing of the centrifugal force $F_c \sim \delta r$ causes the decreasing of the Δv_{rot} which we see in the experiment.

In simple words at high rotational levels the molecule stretches thus the moment of inertia increases, causing the decrease of Δv .

Under high resolution each transition appears as a doublet. Why is this?

The doublets in the spectrum appear due to presence of molecules H^{37}Cl . A peak of H^{37}Cl is a bit shifted towards low energies due to the lower moment of inertia of molecule:

$$\Delta v = \frac{h}{4\pi^2 I c} = \frac{h}{4\pi^2 c r^2} \cdot \frac{m_1 + m_2}{m_1 m_2}$$

$\frac{h}{4\pi^2 c r^2}$ is a constant. Expression $\frac{m_1 + m_2}{m_1 m_2}$ is slightly larger for H^{35}Cl , so its peak occurs at higher energies,

and the H^{37}Cl peak can be found nearby.

The intensity of the lines in the P and R branch are not all the same. Account for this.

The relative intensity of the P- and R-branch lines depends on the thermal distribution of electrons; more specifically, they depend on the population of the lower J state. If we represent the population of the J th upper level as N_j and the population of the lower state as N_0 , we can find the population of the upper state relative to the lower state using the Boltzmann distribution:

$$\frac{N_j}{N} = (2J + 1)e^{-\frac{E_j}{kT}}, \quad E_j = \frac{h^2}{8\pi^2 I} J(J + 1)$$



Sample: Physical Chemistry - Vibrational spectrum of HCl

$(2J+1)$ gives the degeneracy of the J th upper level arising from the allowed values of M_J ($+J$ to $-J$). As J increases, the degeneracy factor increases and the exponential factor decreases until at high J , the exponential factor wins out and N_J/N_0 approaches zero at a certain level, J_{max} . Thus, when

$$\frac{d}{dJ} \left(\frac{N_J}{N_0} \right) = 0$$

by differentiation, we obtain

$$J_{max} = \left(\frac{kT}{2hB} \right)^{\frac{1}{2}} - \frac{1}{2}$$

This is the reason that rovibrational spectral lines increase in energy to a maximum as J increases, then decrease to zero as J continues to increase.

In simple words the peak intensity depends on occupancy of corresponding rotational level of molecule. The largest 2nd peaks in series mean that the most filled is the 2nd rotational level.