

# Towards Spectroscopy:

## Born-Oppenheimer Picture (approximation)

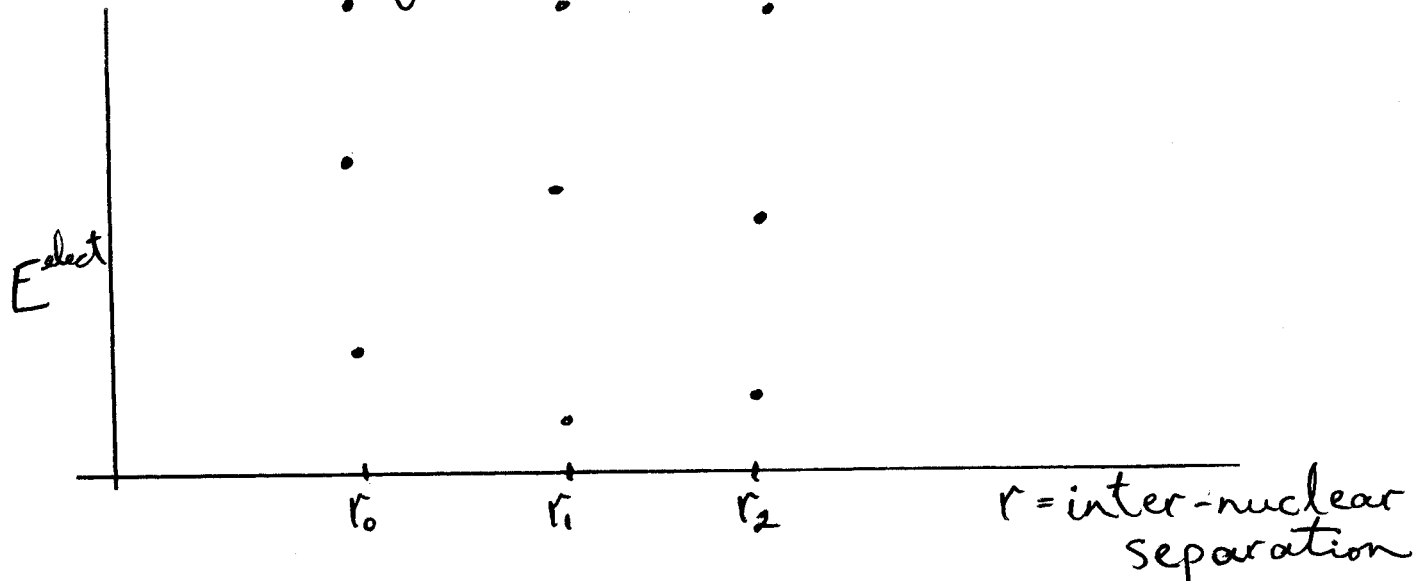
Atoms and molecules consist of nuclei and electrons.

↓ heavy                      ↓ light

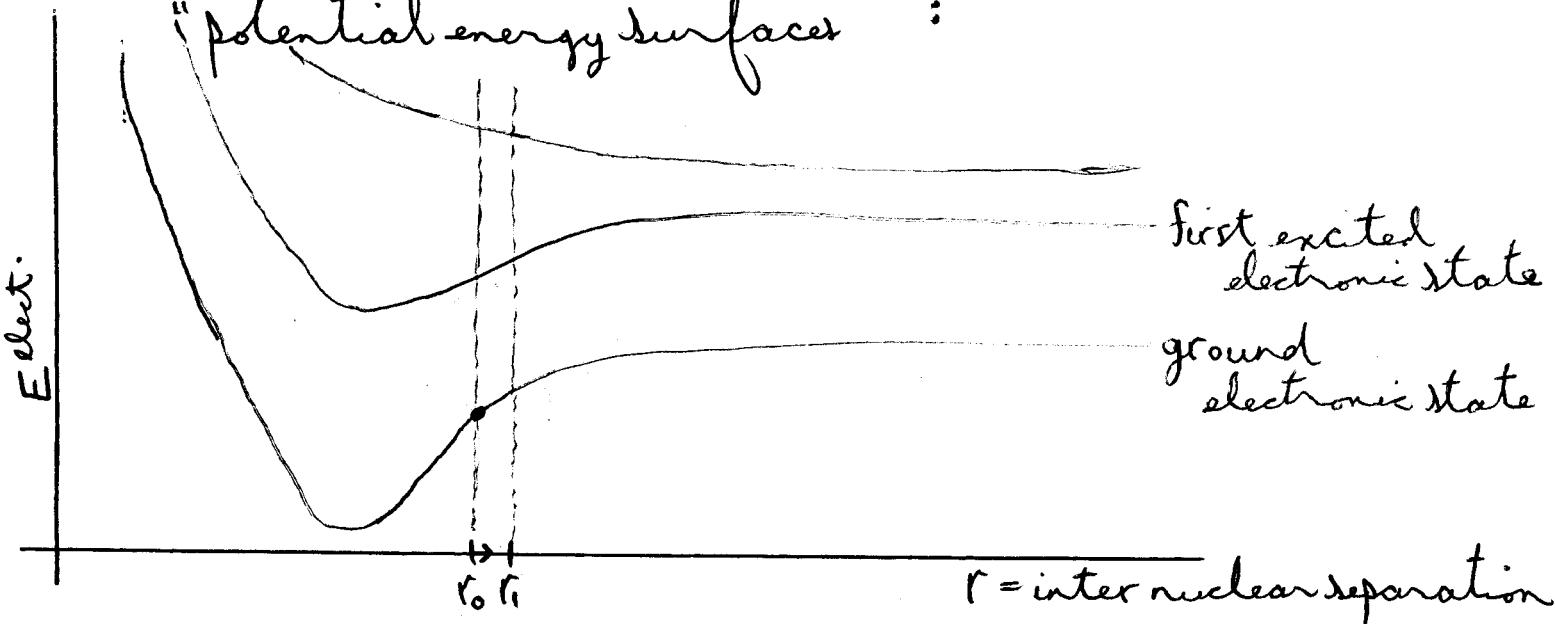
Born-Oppenheimer approximation. Also called the adiabatic approximation

Consider (for simplicity) a diatomic molecule (eg HCl).  
 Clamp / freeze the nuclei in space, a distance  $r_0$  apart.  
 For this case (nuclei clamped a distance  $r_0$  apart), solve the Schrodinger equation for the stationary electronic states.  
 Get the energy of the ground electronic state  $E_0^{elect.}(r_0)$ , the first excited electronic state  $E_1^{elect.}(r_0)$ , etc.

Repeat for a distance  $r_1, r_2, \dots$



"connect the dots" to obtain the  
"potential energy surfaces":



Consider being at  $r_0$  with clamped / frozen nuclei, and being in the ground electronic state.

Unclamp / unfreeze the nuclei, and suppose  $r$  begins to increase and is now  $r = r_1$ . What is the energy of the electrons (which interact, of course, with the nuclei)?

The Born-Oppenheimer, or adiabatic, approximation says that at  $r = r_1$ , the electrons behave as if the nuclei were always at  $r = r_0$  (frozen). In other words, the electrons respond instantaneously (adapt immediately) to changes in  $r$ .

The electrons "shadow" the nuclei.

think of one player guarding another player from driving to the basket in basketball.

Since the electrons "track" the nuclei, we only need to figure out how the nuclei behave, and then we'll know where the electrons are (in the Born-Oppenheimer picture).

$E^{\text{elect}}$  also includes the potential energy between the (clamped) nuclei.

Hence  $E^{\text{elect}}$  is the potential energy function under which the nuclei move.

Whence to find the stationary nuclear states and energies, we should solve

$$\sum_{i=1}^N -\frac{\hbar^2}{2m_i} \nabla_i^2 \psi + E^{\text{elect}} \psi = E \psi \quad \text{for } N \text{ nuclei}$$

↑ kinetic energy
↑ potential energy
↑ eigenvalues

eigenfunctions

For a diatomic this equation becomes a central force problem! Why? because  $E^{\text{elect}} = E^{\text{elect}}(r)$  where  $r =$  internuclear separation.

The energy  $E$  for a central force problem is obtained by solving the radial equation after changing to spherical polar coordinates.  $\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$

This looks like  $-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \left[ \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - l(l+1)R \right] + E^{\text{elect}}(r)R = ER.$

To proceed, define  $F(r)$  by  $R(r) = \frac{F(r)}{r}$  ( $\Rightarrow F = rR$ )

Then  $\frac{dR}{dr} = \frac{d}{dr} \left( \frac{F}{r} \right) = \frac{1}{r} \frac{dF}{dr} - \frac{F}{r^2}$  and

~~The~~  $\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) = \frac{d}{dr} \left( r \frac{dF}{dr} - F \right) = r \frac{d^2 F}{dr^2} + \frac{dF}{dr} - \frac{dF}{dr} = r \frac{d^2 F}{dr^2}$

We get

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \left[ r \frac{d^2 F}{dr^2} - l(l+1) \frac{F}{r} \right] + E^{\text{elect}}(r) \frac{F}{r} = E \frac{F}{r}$$

$$\Rightarrow -\frac{\hbar^2}{2\mu} \frac{d^2 F}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} F + E^{\text{elect}}(r) F = E F.$$

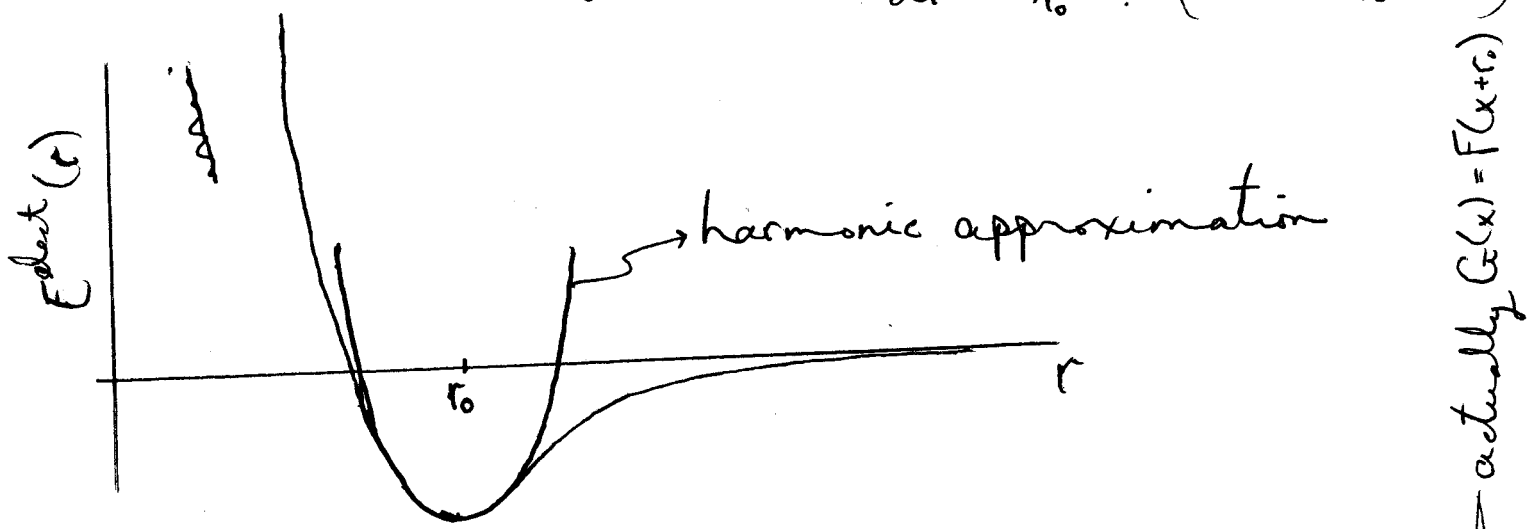
This energy  $E$  is due to vibrational and rotational motion. For no rotation (pure vibration) we have  $l=0$  to give

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + E^{\text{elect}}(r) \right] F(r) = E F(r).$$

We will now perform a Taylor series expansion of  $E^{elect}(r)$  about its minimum and truncate at 2<sup>nd</sup> order.

(see 5-3 of McQuarrie/Simon)

$$E^{elect}(r) \approx E^{elect}(r_0) + \frac{1}{2}(r-r_0)^2 \left. \frac{d^2 E^{elect}}{dr^2} \right|_{r_0} \quad \left( \left. \frac{dE^{elect}}{dr} \right|_{r_0} = 0 \right)$$



Let  $x = r - r_0$  and  $\mu\omega_0^2 = \left. \frac{d^2 E^{elect}}{dr^2} \right|_{r_0}$  to give

$$[E - E^{elect}(r_0)] \textcircled{F(x)} = \left[ \frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu\omega_0^2 x^2 \right] \textcircled{F(x)}$$

This is the harmonic oscillator equation (1d) we solved earlier!

$$E_n = E^{elect}(r_0) + \hbar\omega_0 \left( n + \frac{1}{2} \right) \quad , n \geq 0 \in \mathbb{Z}$$

Pure vibrational energies of a diatomic in the Born-Oppenheimer, harmonic approximation.

Consider now a rigid rotor, namely where  $l \neq 0$  but the vibrational motion produces only small displacements: approx.  $r = r_0$  in the  $\frac{\hbar^2 l(l+1)}{2\mu r^2}$  term

then we are looking to solve

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r_0^2} + E^{\text{elect}}(r_0) + \frac{1}{2}(r-r_0)^2 \frac{d^2 E^{\text{elect}}}{dr^2} \Big|_{r_0} \right) F = E F$$

which yields  $E_{nl} = E_2^{\text{elect}}(r_0) + \hbar\omega_0(n+1/2) + \frac{\hbar^2 l(l+1)}{2\mu r_0^2}$

rigid-rotor / harmonic oscillator approx.

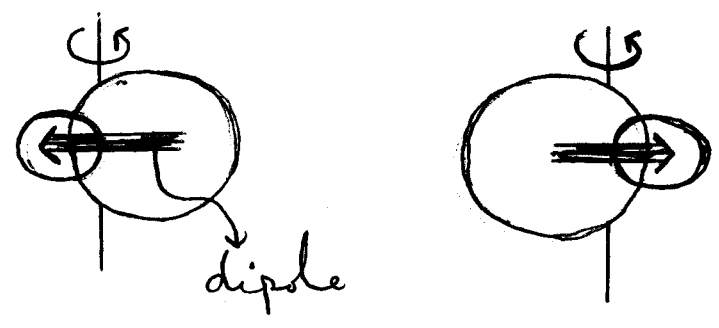
## Selection Rules

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation.

The underlying idea is that, for a molecule to be able to interact with the electromagnetic field and absorb or emit a photon of frequency  $\omega$ , it must possess, at least transiently, a dipole oscillating at that frequency  $\omega$ .

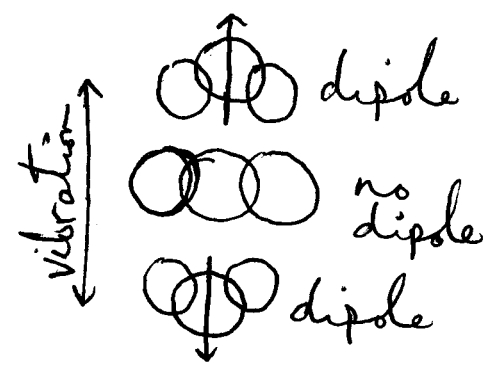
For emission and absorption spectra (Raman is different) we can say that for rotational transitions, there is no spectrum unless the molecule has a permanent dipole moment. That is, the molecule must be polar.

A polar molecule appears to possess a fluctuating dipole when rotating but a nonpolar molecule does not.



For vibrational transitions, there is no emission/absorption unless the dipole moment of the molecule changes during the vibration. The idea is that the molecule can shake the electromagnetic field into oscillation if its dipole changes as it vibrates.

Note 1 The permanent dipole moment of the molecule can be zero as long as it changes during vibration: CO<sub>2</sub>



Note 2 Some vibrational motions do not affect the molecule's dipole moment. Such vibrations are called inactive.



## Specific selection rules for the rigid rotor / harmonic oscillator diatomic molecule.

Consider the electric field to be along the  $z$ -axis (in the laboratory frame). Transitions between states 1 and 2 occur if  $(\mu_z)_{12} \equiv \int \psi_2^* \mu_z \psi_1$  is non-zero

where  $\mu_z$  is the  $z$ -component of the molecular dipole moment.

Rigid rotor selection rule is  $\Delta l = \pm 1$

The rigid-rotor wavefunctions are the spherical harmonics  $Y_{lm}(\theta, \phi)$  since  $r$  is not changing.

Transitions between any two states are allowed if

$$(\mu_z)_{l,m,l',m'} = \int_0^{2\pi} \int_0^\pi Y_{l'm'}^*(\theta, \phi) \mu_z Y_{lm}(\theta, \phi) \sin\theta d\theta d\phi$$

is non-zero.  $\mu_z = \mu \cos\theta$ , giving

↪ Jacobian

$$(\mu_z)_{l,m,l',m'} = \mu \int_0^{2\pi} \int_0^\pi Y_{l'm'}^* Y_{lm} \cos\theta \sin\theta d\theta d\phi$$

↑  
It must clearly be non-zero, proving our claim that a molecule must have a permanent dipole moment to have a rotational spectrum.



When is this expression non-zero for  $\mu \neq 0$ ?

We need to use the properties of the spherical harmonics...

The math is straightforward, and gives

$$m = m' \quad \text{and} \quad \begin{cases} l' = l+1 \\ \text{or} \\ l' = l-1 \end{cases}$$

Another way to express this is  $\Delta m = 0$ ,  $\Delta l = \pm 1$

Harmonic Oscillator selection rule is  $\Delta n = \pm 1$

Wavefunctions are  $\Psi_n(x) = (x^n + ?x^{n-2} + ?x^{n-4} + \dots) e^{-\alpha x^2}$ ,  $n \geq 0$   
 $\in \mathbb{Z}$

For a transition between  $n$  and  $n'$  we need to look at

$$(\mu_z)_{nn'} = \int_{-\infty}^{\infty} \Psi_n^*(x) \mu_z \Psi_{n'} dx$$

To proceed, we Taylor-expand  $\mu_z$  about the equilibrium internuclear separation

$$\mu_z \approx \mu_0 + \left. \frac{d\mu_z}{dx} \right|_{x=0} \cdot x + \dots$$

where  $x=0$  is the equilibrium sep.

We truncate at 1<sup>st</sup> order, which is a good approx.

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$$\text{This gives } (\mu_z)_{n'n} = \mu_0 \int_{-\infty}^{\infty} \psi_{n'}^* \psi_n + \left. \frac{d\mu}{dx} \right|_0 \int_{-\infty}^{\infty} \psi_{n'}^* x \psi_n$$

The first term is 0 unless  $n'=n$  (orthogonality)  
but this is NOT a transition (no change).

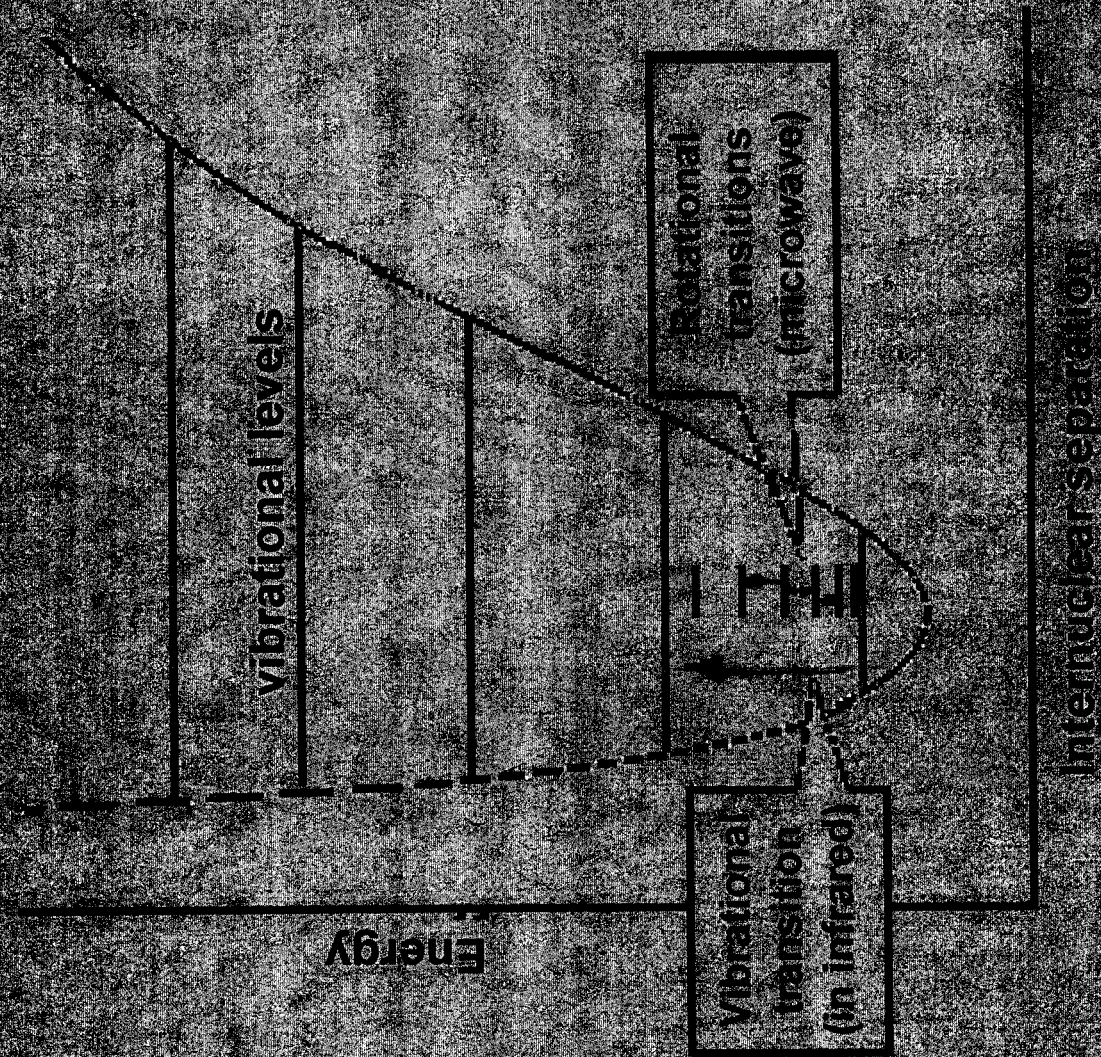
Thus the permanent dipole moment plays no role in vibrational spectroscopy. (except that real molecules are not harmonic oscillators, so we should correct this to read: the permanent dipole moment plays a negligible role in vibrational spectroscopy.)

The second term is non-zero for  $n'=n+1$  or  $n'=n-1$ .  
Namely  $\Delta n = \pm 1$ . This can be proved by using the harmonic oscillator wavefunctions.

It is also necessary that  $\left. \frac{d\mu}{dx} \right|_0 \neq 0$ . This derivative is zero for homonuclear diatomics as well as for certain vibrations of polyatomic molecules. (ex: symmetric stretch of  $\text{CO}_2$  or  $\text{CH}_4$ ).

For polyatomics, the selection rules can be derived from group theory, which we will not cover.

Potential curve representing the ground electronic state of HCl



# Vibrational and Rotational Transitions in HCl

Transitions from the ground vibrational state to the first excited state of HCl with a change  $\Delta J = +1$  or  $\Delta J = -1$  in rotational angular momentum.



# Rigid Rotor - Harmonic Oscillator Spectroscopy

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The infrared absorption spectrum of HCl can be analyzed to gain information about both rotations and vibrations of the molecule.

The absorption lines shown involve transitions from the ground state  $n=0$  to the first excited vibrational state of HCl,  $n=1$ . The rotational angular momentum must change by  $l = \pm 1$  during such a vibrational transition according to the RRHO ~~rule~~ selection rules. This is what we observe experimentally.

The "missing" line in the center would correspond to the  $n=0$  to  $n=1$  transition without any change in  $l$ . What is observed is a closely spaced series of lines going upwards and downwards from the missing pure vibrational line.

The splitting of the lines shows the difference in rotational inertia of the two chlorine isotopes  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$ .

# Bond force constant for HCl

Approx. the  $n=0$  to  $n=1$  vibrational transition by the harmonic oscillator model.

$$E_{n=0} = \hbar\omega(1/2), \quad E_{n=1} = \hbar\omega(1+1/2) \implies \Delta E = \hbar\omega$$

$$\text{and } \omega = \sqrt{k/\mu} \quad \text{where } \mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \text{reduced mass.}$$

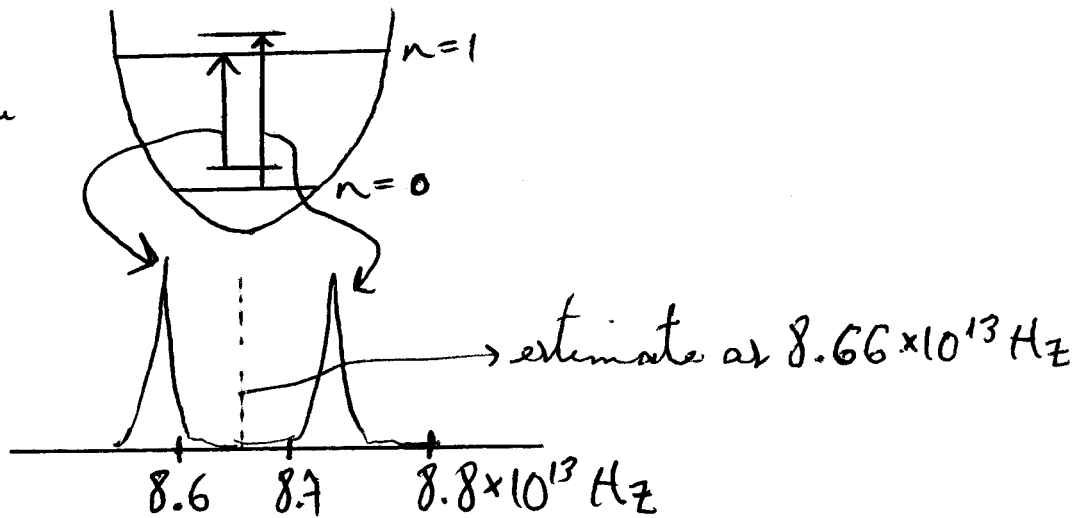
But this is the "missing" line in the infrared absorption spectrum of HCl, so what can we do?

We can use the midpoint between the  $n=0, l=1 \rightarrow n=1, l=0$  and the  $n=0, l=0 \rightarrow n=1, l=1$  transitions.

This assumes that the first excited vibrational state does not stretch the bond.

$$\mu \approx \frac{(1)(35)}{1+35} \approx 1 \text{ amu}$$

very roughly



$$2\pi(8.66 \times 10^{13} \text{ Hz}) = \sqrt{k/\mu}$$

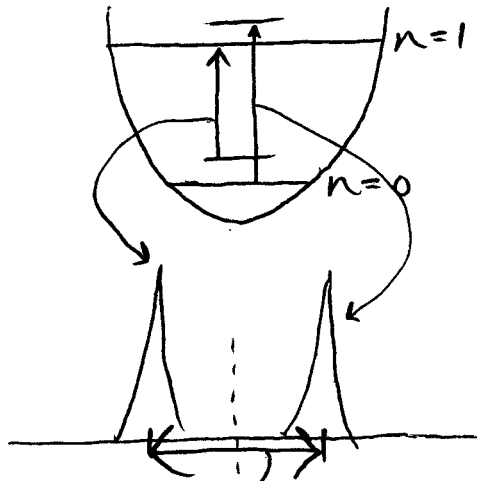
$$\implies k = [2\pi(8.66 \times 10^{13} \text{ Hz})]^2 (0.9796 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})$$

$$k = 481 \text{ N/m}$$

# Bond length of HCl

The rigid rotor energy levels are  $E_l = \frac{l(l+1)\hbar^2}{2I}$

where  $I = \mu r^2$



This difference should be approx. twice the rotational energy from  $l=0$  to  $l=1$ .

$$\Delta E_l = \frac{2\hbar^2}{2I} \Rightarrow \Delta E = \frac{\hbar^2}{\mu r^2}$$

$$\Delta E_{l=1 \text{ to } l=0} = \frac{1(2)\hbar^2}{2I} - \frac{0(1)\hbar^2}{2I} = \frac{2\hbar^2}{2I}$$

$$\text{Twice this is } 2\Delta E = \frac{4\hbar^2}{2I} = h(0.12 \times 10^{13} \text{ Hz})$$

Using  $I = \mu r^2$  this gives  $r = 0.13 \text{ nm} = 1.3 \text{ \AA}$ .

Can do pure rotational spectroscopy of HCl in the microwave region, and in a similar manner can assign bond lengths.

cm <sup>-1</sup>	83.03	103.73	124.3	145.03	165.51	185.86	206.38	226.5
$l \rightarrow l+1$	3-4	4-5	5-6	6-7	7-8	8-9	9-10	10-11
r (nm)	0.1288	0.1288	0.1289	0.1289	0.1290	0.1291	0.1292	0.1293

centrifugal distortion