

## Vibrational Spectra

Now we turn to vibration,  
another mode of molecular  
internal energy.

Vibrational energy is also  
quantized, hence can lead to  
spectroscopic transitions  
(= absorption lines)

# Harmonic Oscillator

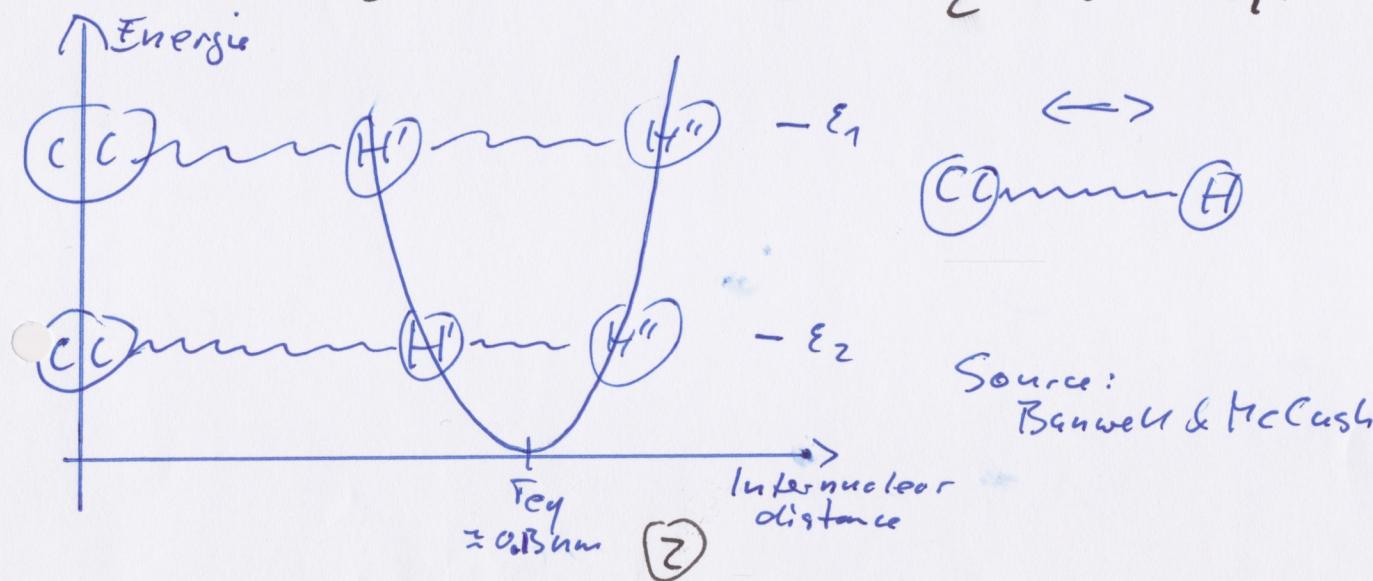
- Assume that there is a restoring force

$$f = -k(r - r_{eq})$$

Then the associated (Hooke's law)

energy is

$$E = \frac{1}{2} k (r - r_{eq})^2$$



# Quantum Mechanical Harmonic Oscillator

A classical Q.M. problem.

Energy levels turn out to be:

$$E_v = (v + \frac{1}{2})\hbar\tilde{\omega} \quad (v = 0, 1, 2, \dots)$$

In spectroscopic units of Kaiser ( $\frac{1}{\text{cm}}$ )

$$\epsilon_v = \frac{E_v}{hc} = (v + \frac{1}{2})\tilde{\nu}$$

What is  $\omega$ ? If  $f$  is really ~~proportional~~ proportional to  $\omega$ , then it is a constant:

$$\tilde{\omega} = \sqrt{\frac{k}{\mu}}$$

## Lowest Vibrational Level

$$E_0 = \frac{1}{2} k \tilde{\omega}$$

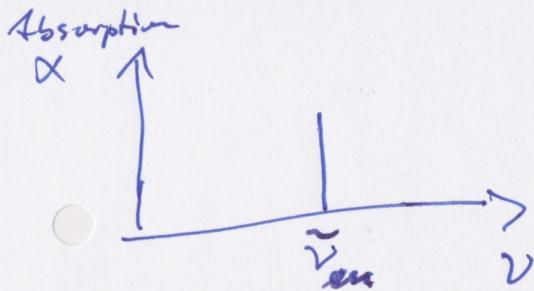
So a molecule can never have zero vibrational energy!

This is different from rotation, where the lowest state had energy zero.

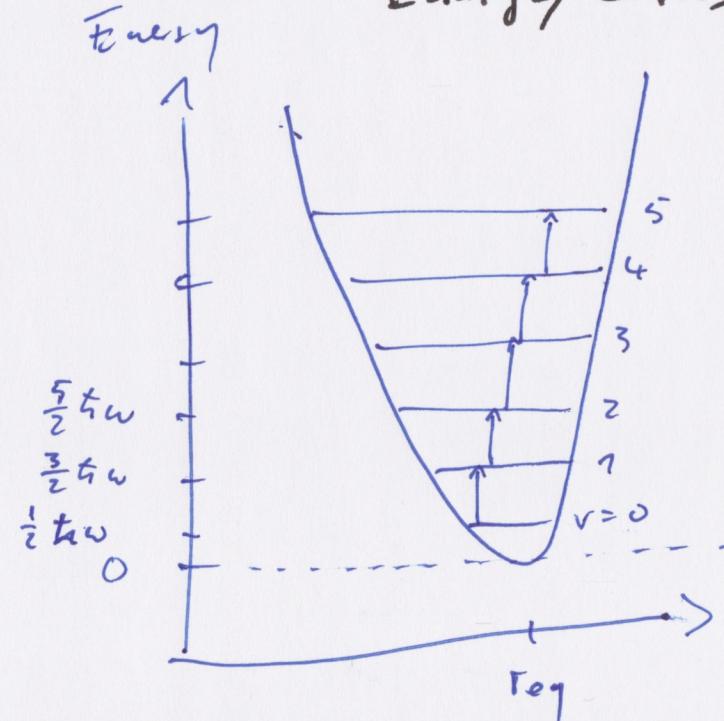
# Selection Rule for Vibrational Transitions

$$\Delta v = \pm 1$$

Spectrum



Energy Levels



$$\begin{aligned} \cancel{\hbar\tilde{\omega}} &= \hbar\tilde{\nu} \\ \Rightarrow \tilde{\nu}_{max} &= \frac{\hbar}{\hbar}\tilde{\omega} = \frac{\tilde{\omega}}{2\pi} \end{aligned}$$

(5)

## In Frequency Space

- Frequency  $\nu$  of the observed line corresponds to the energy difference  $\tilde{\nu}$  between adjacent levels.  
(Which corresponds to the classical frequency at which the molecule would vibrate.)

## Vibration + Rotation

Rotation : Energy separation  $1-10 \text{ cm}^{-1}$

Vibration : "  $100-10000 \text{ cm}^{-1}$

Large difference in characteristic energy

$\Rightarrow$  We can assume that the two motions occur independently.

(This is a case of the Born - Oppenheimer approximation, which strictly also includes vibration)

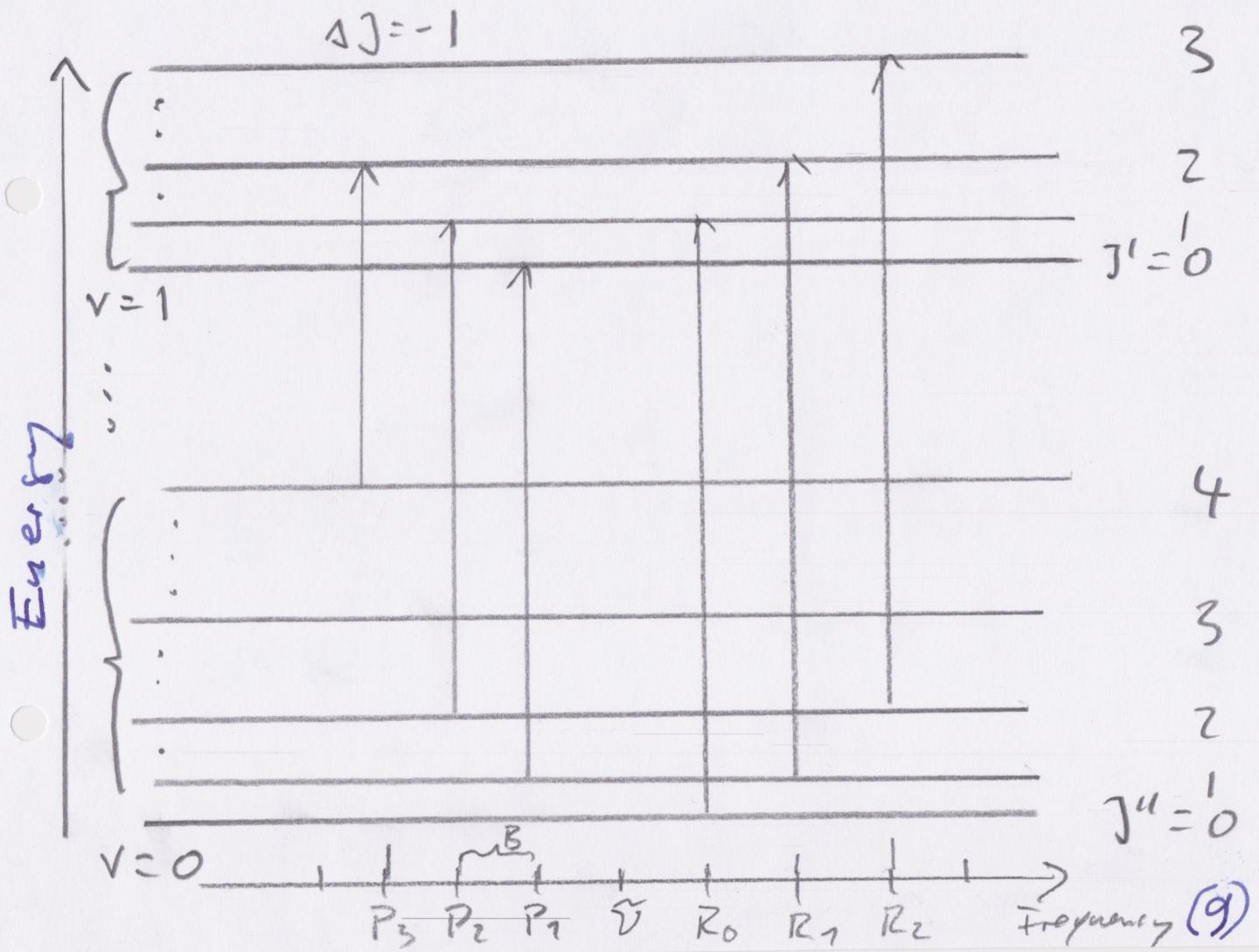
$$\bar{E}_{\text{total}} = \bar{E}_{\text{rot}} + \bar{E}_{\text{vib}} \quad (\text{J})$$

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Considering the discrete energy levels:

$$E_{J,v} = E_J + E_v = BJ(J+1) + (v+\frac{1}{2})\tilde{\nu}$$

Note: There are higher order terms in both rotation (centrifugal stretching) and vibration (non-constant restoring force) that I am ignoring here.



## Selection Rule

$$\Delta V = \pm 1 \text{ and } \Delta J = \pm 1$$

That means, we normally cannot observe the vibrational fundamental directly.

Rotational levels will be filled to varying degrees in a population of molecules  $\Rightarrow$  Different line intensities.

## Transition Frequencies

$$J_J = +1 \quad (\text{R-Branch})$$

$$\Delta E_{J,v} = \tilde{\nu} + 2B(J''+1) \quad J'' = 0, 1, 2$$

$$J_J = -1 \quad (\text{P-Branch})$$

$$\Delta E_{J,v} = \tilde{\nu} - 2B(J'+1) \quad J' = 0, 1, 2$$

Can be combined into:

$$\Delta E_{J,v} = \tilde{\nu} + 2Bm \quad m = \pm 1, \pm 2, \dots$$

These are the frequencies of the observed lines.

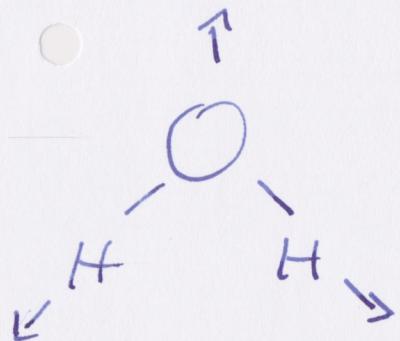
Why are the branches called  
"P" and "R"?

For more complicated molecules,  
 $\Delta J = 0$  and  $\pm 2$  may also be  
allowed. All possible branches are:

$\Delta J = -2 \quad -1 \quad 0 \quad +1 \quad +2$

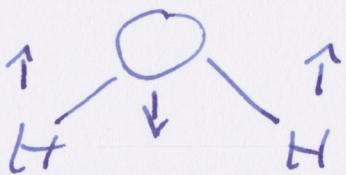
Name : O P Q R S

# Fundamental Vibrations of H<sub>2</sub>O



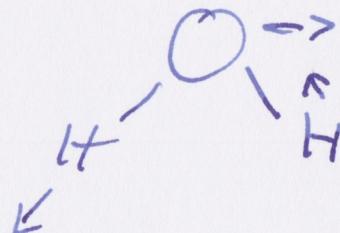
Symmetric  
stretch

$$\tilde{\nu}_1 = 3651.7 \text{ cm}^{-1}$$



Symmetric  
bend

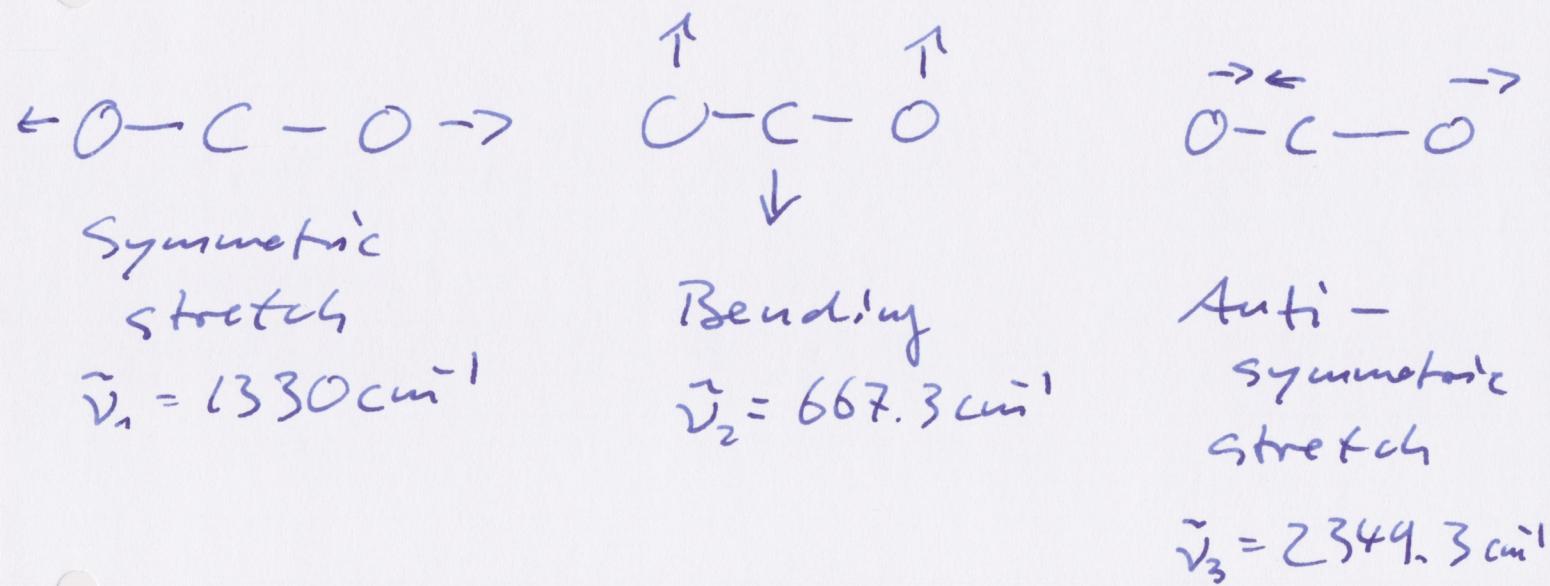
$$\tilde{\nu}_2 = 1515.0 \text{ cm}^{-1}$$



Anti-symmetric  
stretch

$$\tilde{\nu}_3 = 3755.8 \text{ cm}^{-1}$$

# Fundamental Vibrations of CO<sub>2</sub>



(1K)