## Rotational-vibrational spectroscopy:

## Rotation and Vibration

- Rotational-vibrational spectroscopy
- Energy states provided by sum of rotational and vibrational energy:
- CO spectrum
- Selection rules



## Rotation and Vibration

Rotational-vibrational spectroscopy
Energy states provided by sum of rotational and vibrational energy:


## Rotation and Vibration

- Simple equation suggests equal spacing on either side of $\tilde{v}=0$.
- Spacing is clearly not equal



## Iclicker: Rotation and Vibration

- Which class of transitions is responsible for the series of lines above 0.3175 ev ?
- A - 1
B-2
C - neither
D - both




## Rotation and Vibration

## Spacing is clearly not equal (1)

## Rotation and Vibration

## Spacing is clearly not equal (2)

## Anharmonicity and Overtones

Harmonic oscillator is only an approximation
Excitations not allowed under approximation.
${ }^{1} \mathrm{H}^{35} \mathrm{Cl}$

## Anharmonicity and Overtones

- Correct harmonic oscillator by retaining higher-order terms in potential.
- $x_{e}$ is anharmonicity constant.
- Divide by hc to get wavenumber
- Fundamental and overtone found at:


## Iclicker: Intensities

- What is the origin of the intensity variation in the P branch?
- A - varying equilibrium bond distances
- B - breakdown of rotational selection rule
- C - breakdown of vibrational selection rule
- D - unequal thermal populations
- E - the photon detection efficiency varies as a function of energy

