Lecture B4
Vibrational Spectroscopy, Part 2

Quantum Mechanical SHO.

$$\hat{H}\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

WHEN we solve the Schrödinger equation, we always obtain two things:

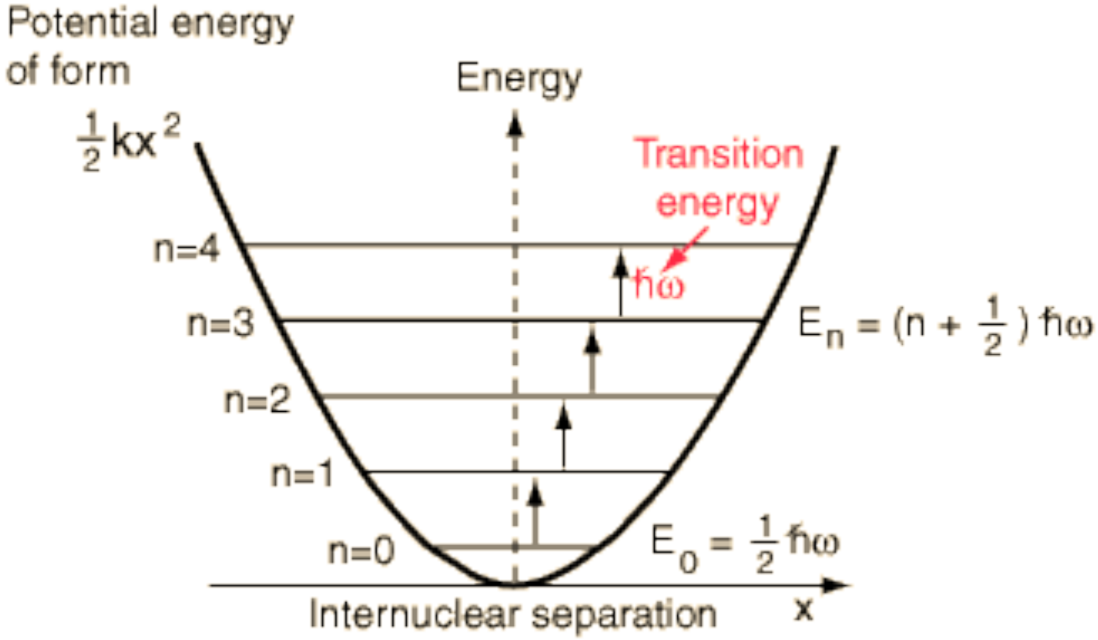
1. a set of eigenstates, $|\psi_n>$.
2. a set of eigenstate energies, E_n

$$\left|\psi_n\right\rangle$$

$$n = 0,1,2\ldots$$

$$E_n = h\nu(n + \tfrac{1}{2})$$

QM predicts the existence of discrete, evenly spaced, vibrational energy levels for the SHO.



$$E_n = h\nu(n + \tfrac{1}{2})$$

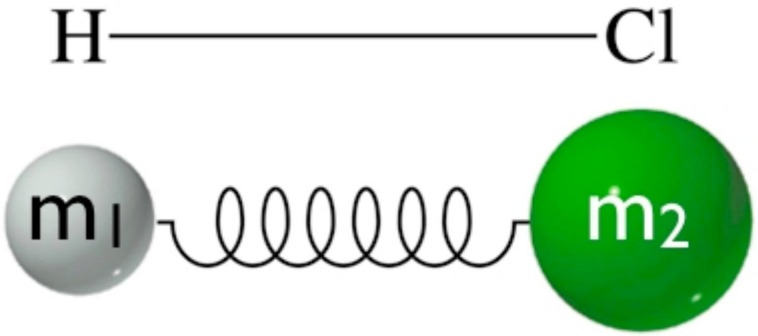
n = 0,1,2,3...

Notes:

- For the ground state (n=0), E = ½hν. This is called the zero point energy.
- Optical selection rule -- SHO can absorb or emit light with a $\Delta n = \pm 1$

The IR absorption spectrum for a diatomic molecule, such as HCl:

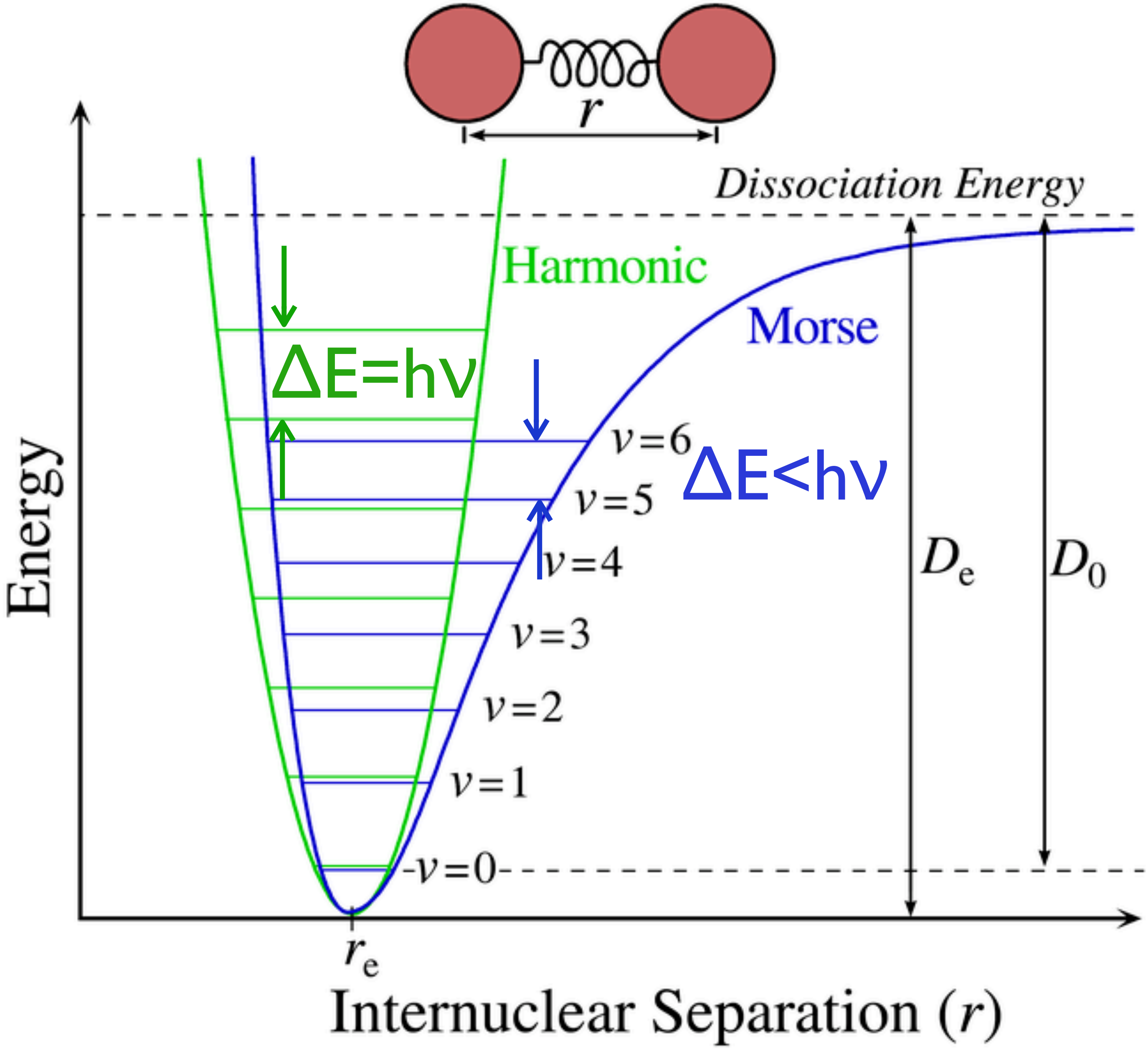
diatomic



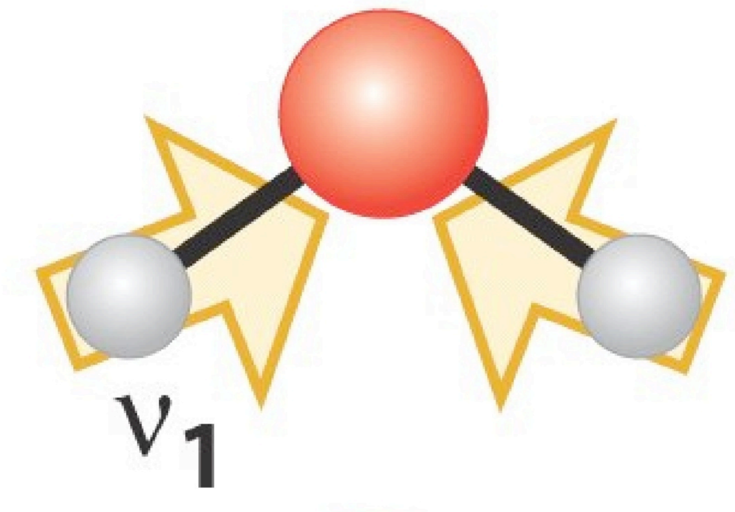
- Optical selection rule 1 -- SHO can absorb or emit light with a $\Delta n = \pm 1$
- Optical selection rule 2 -- a change in molecular dipole moment ($\Delta\mu/\Delta x$) must occur with the vibrational motion.

(Note: μ here means dipole moment).

If a more realistic Morse potential is used in the Schrödinger Equation, these energy levels get scrunched together...



The vibrational spectroscopy of polyatomic molecules gets more interesting...



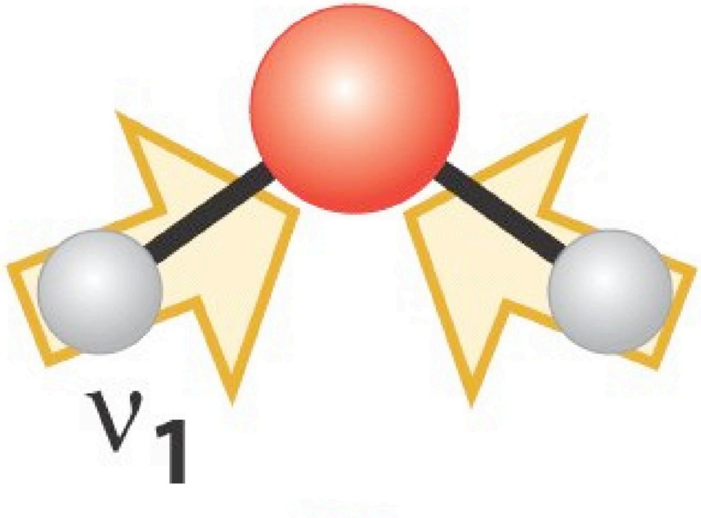
For diatomic or linear molecules: 3N-5 modes

For nonlinear molecules: 3N-6 modes

↑

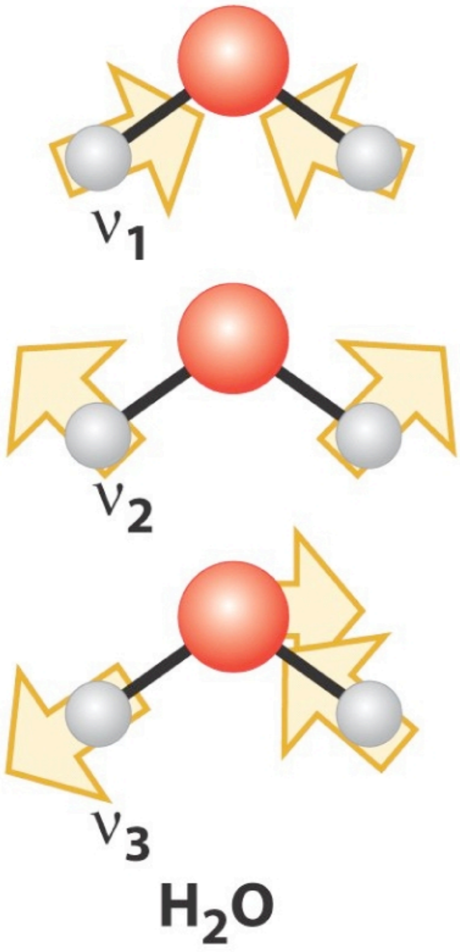
N = number of atoms in molecule

The vibrational spectroscopy of polyatomic molecules gets more interesting...



- Optical selection rule 1 -- SHO can absorb or emit light with a $\Delta n = \pm 1$
- Optical selection rule 2 -- a change in molecular dipole moment ($\Delta\mu/\Delta x$) must occur with the vibrational motion of a mode.

Consider H_2O (a nonlinear molecule):



$$3N-6 = 3(3)-6 = 3$$

- Optical selection rule 2 -- a change in molecular dipole moment ($\Delta\mu/\Delta x$) must occur with the vibrational motion of a mode.

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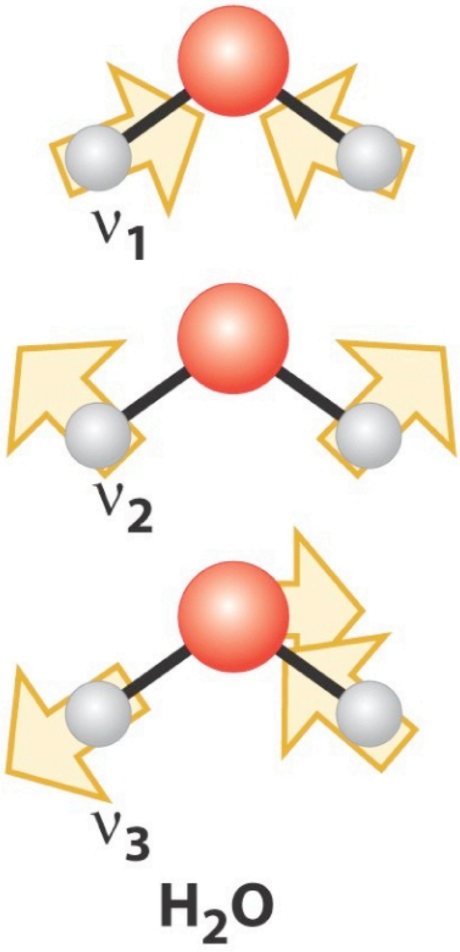
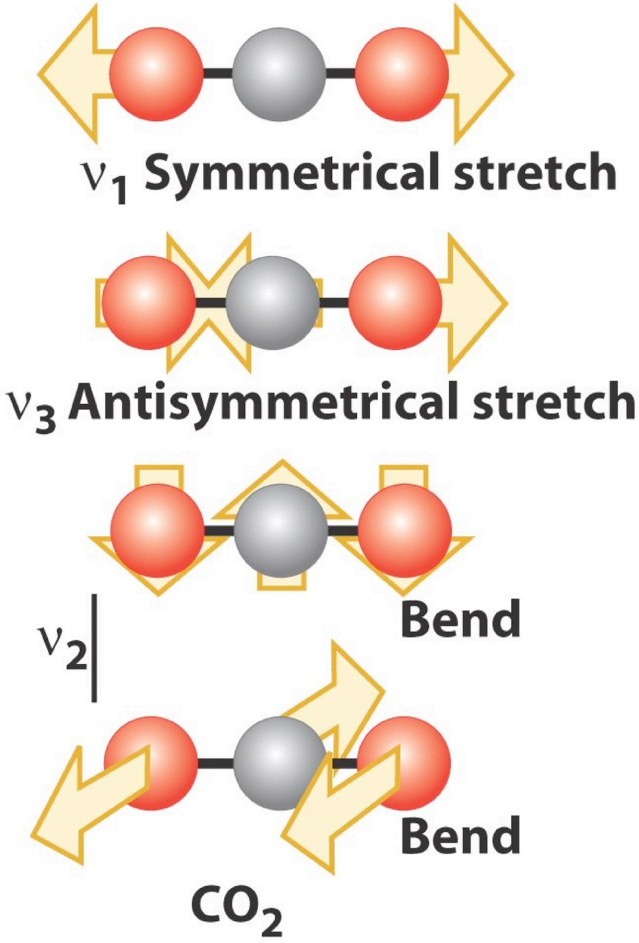


$3N-6 = 3(3)-6 = 3$

All bands are observed in the IR spectrum.

- Optical selection rule 2 -- a change in molecular dipole moment ($\Delta\mu/\Delta x$) must occur with the vibrational motion of a mode.

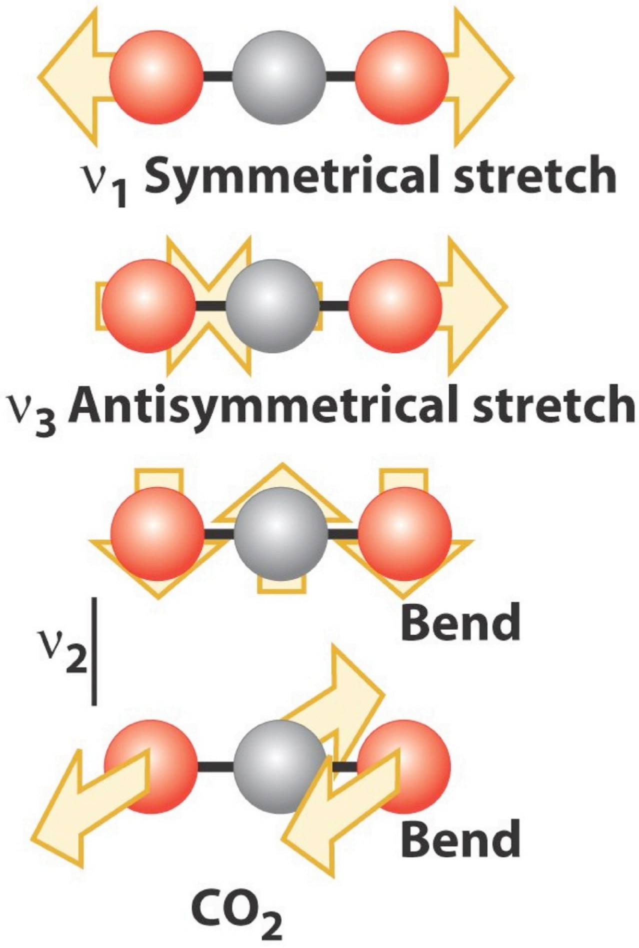
Consider CO_2 (a linear molecule):



$$3N-5 = 3(3)-5 = 4$$

- Optical selection rule 2 -- a change in molecular dipole moment ($\Delta\mu/\Delta x$) must occur with the vibrational motion of a mode.

Consider CO_2 (a linear molecule):

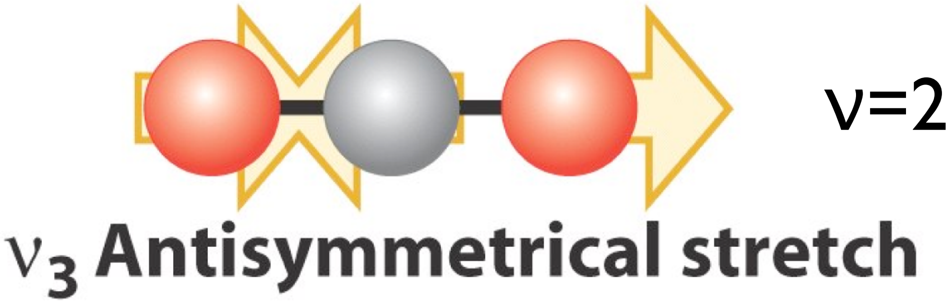


$$3N-5 = 3(3)-5 = 4$$

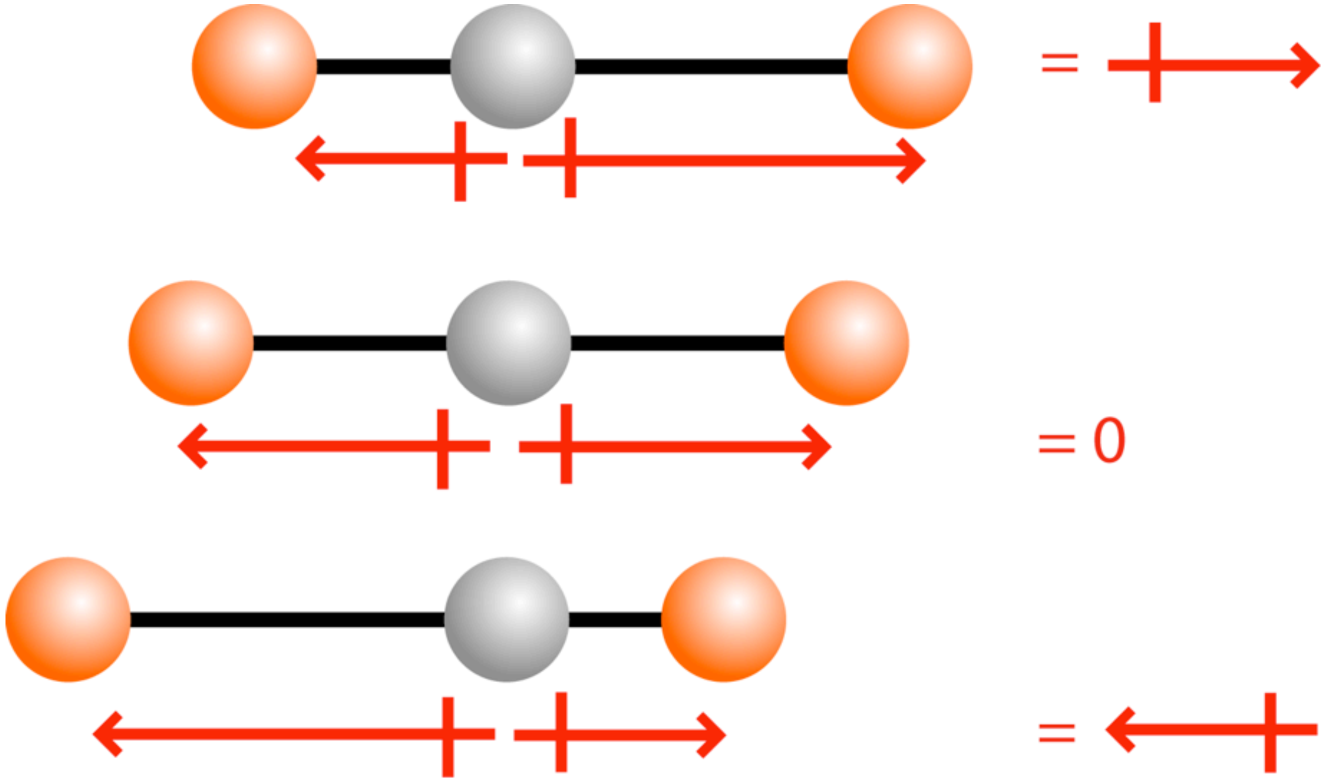
The motion of the symmetrical stretch (ν_1) does not create a new dipole moment, so it is not observed in the IR spectrum.

- Optical selection rule 2 -- a change in molecular dipole moment ($\Delta\mu/\Delta x$) must occur with the vibrational motion of a mode.

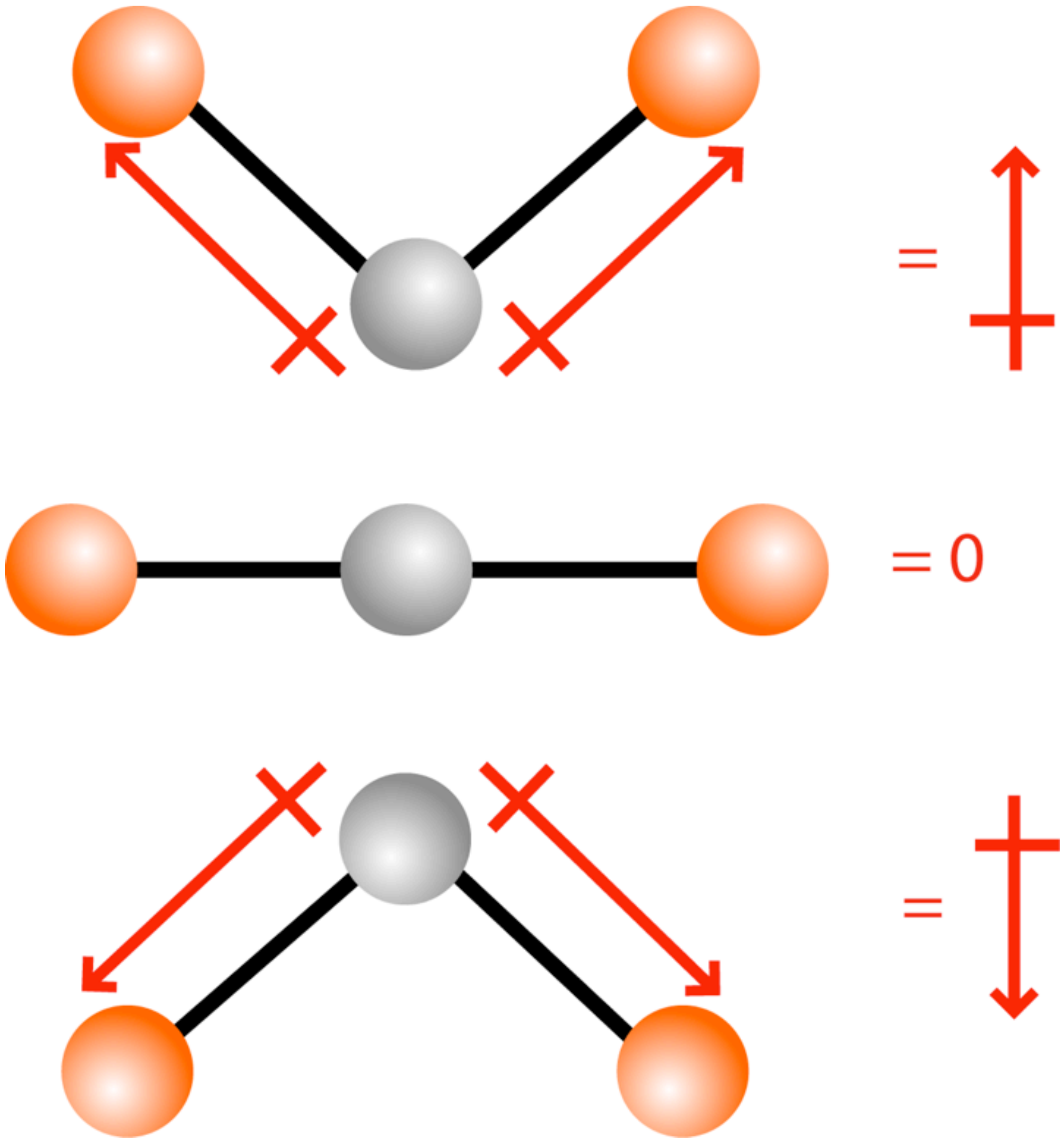
Let's break down the antisymmetric CO_2 stretch to see if the molecular dipole moment varies during this vibration.



ν=2349 cm^{-1}



...what about the bend?



ν=667 cm^{-1}

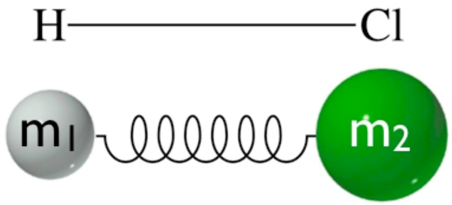
Summary:

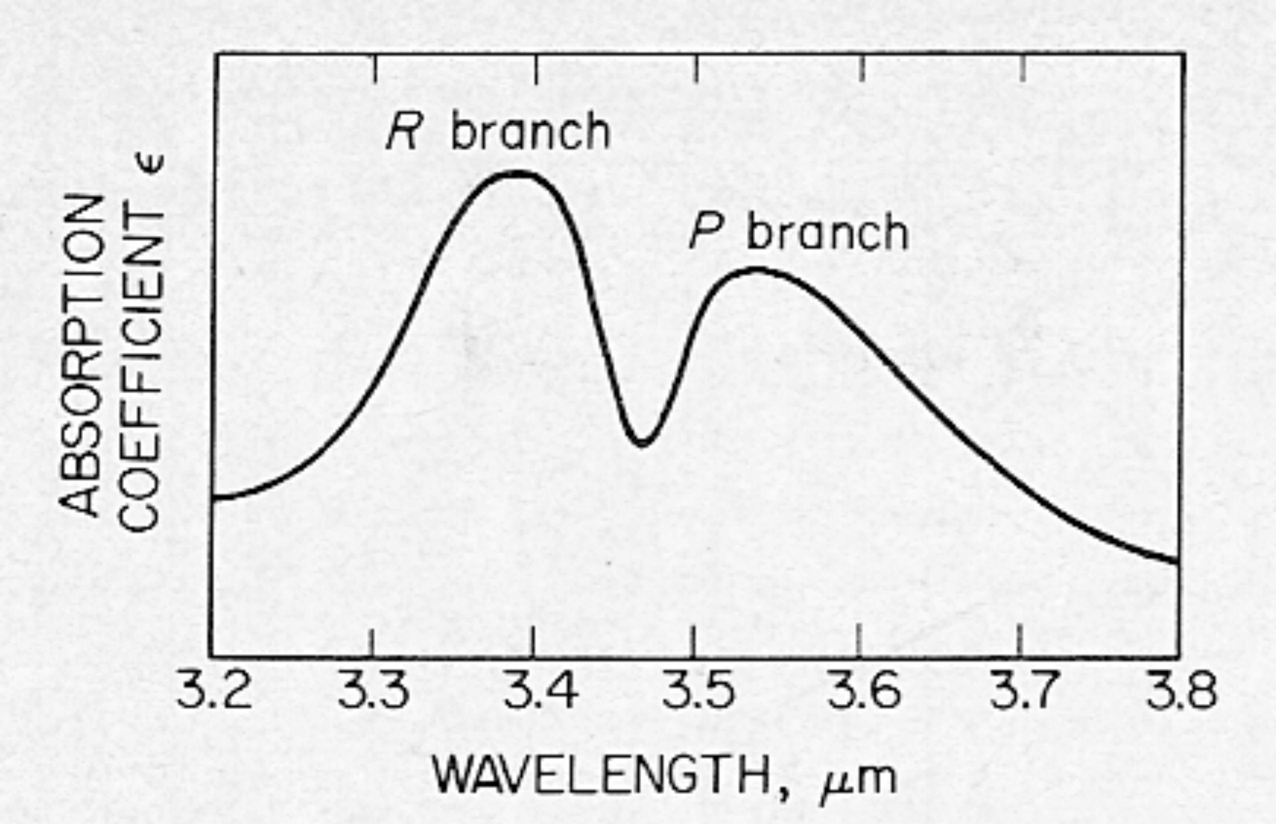
- ... CO_2 has 3N-5 = **4** vibrational modes:
  2 "degenerate" bends (ν = 667 cm^{-1})
  1 asymmetric stretch. (ν = 2349 cm^{-1})
  1 symmetric stretch. (ν = 1380 cm^{-1})

- ...Three of these modes alter the dipole moment of the molecule (both bends and the asym stretch); one does not (the sym stretch).

- ...This means that CO_2 can absorb and radiate IR light at energies corresponding to 667 cm^{-1} and 2349 cm^{-1}, **even though it has no permanent dipole moment.**

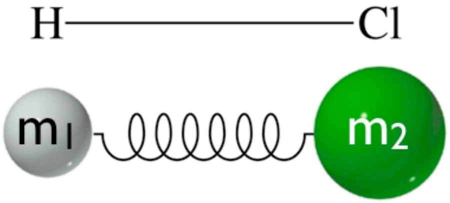
HCl IR absorption spectrum in the gas phase:

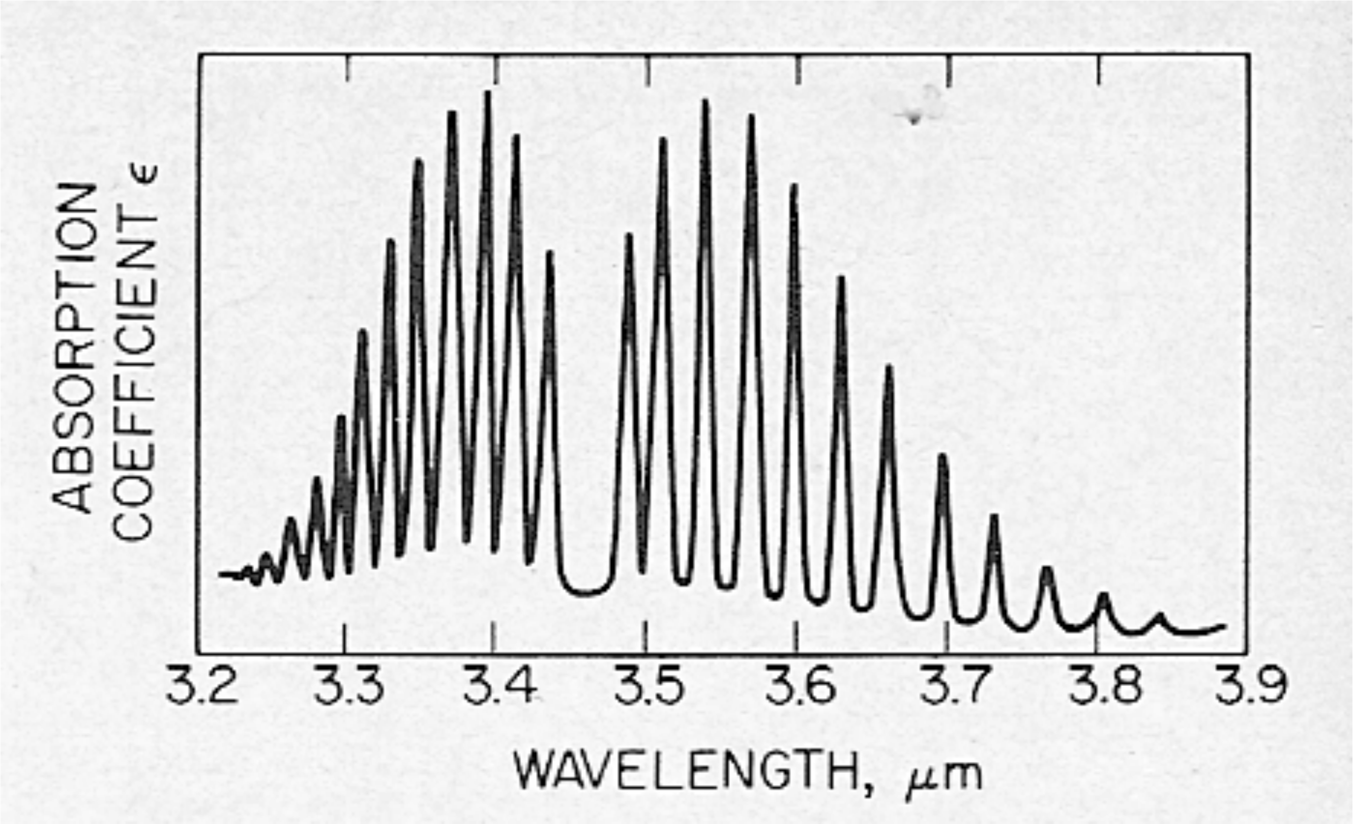




In the gas phase, the lineshape of the IR absorption bands molecules becomes broad.

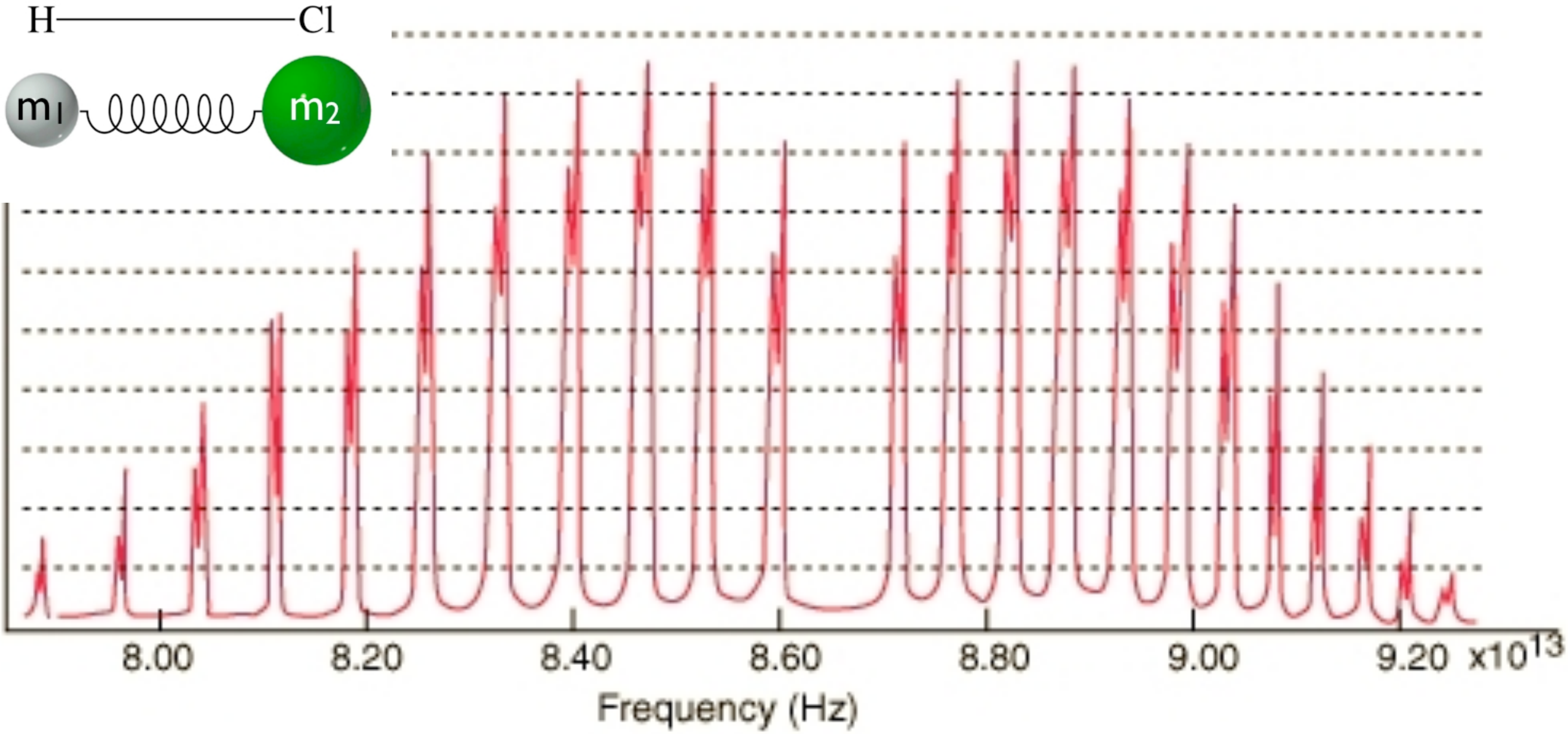
HCl IR absorption spectrum in the gas phase:





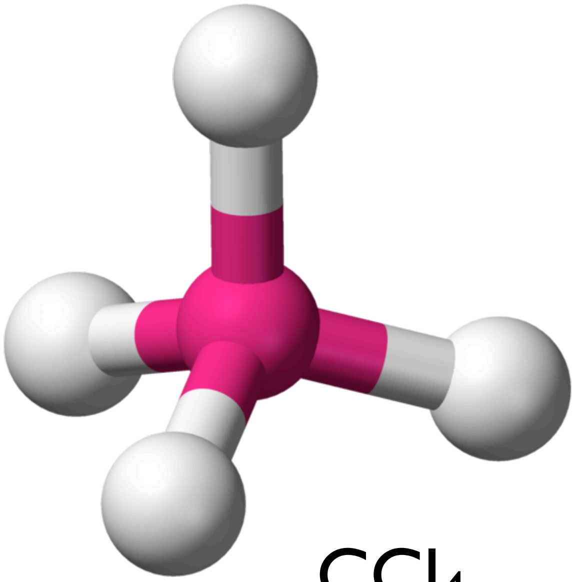
At high resolution, MANY lines are observed. This splitting of the vibrational spectrum is due to the presence of many rotational quantum states.

HCl IR absorption spectrum in the gas phase:

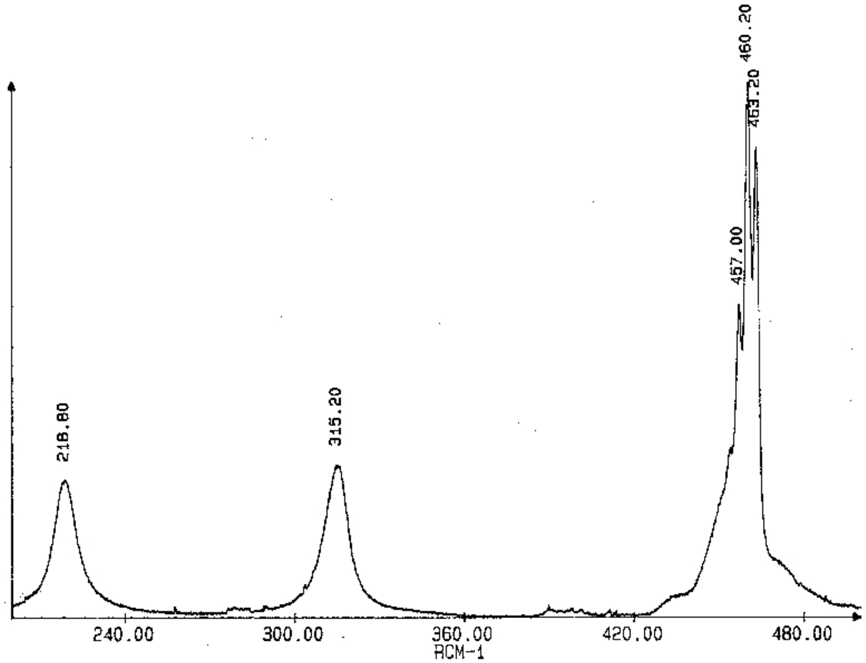


BTW -- a very high resolution spectrum of HCl shows PAIRS of bands due to $H^{35}Cl$ and $H^{37}Cl$.

Symmetric stretches ARE NOT observed in the IR spectrum. But they ARE observed in another type of vibrational spectroscopy: Raman scattering

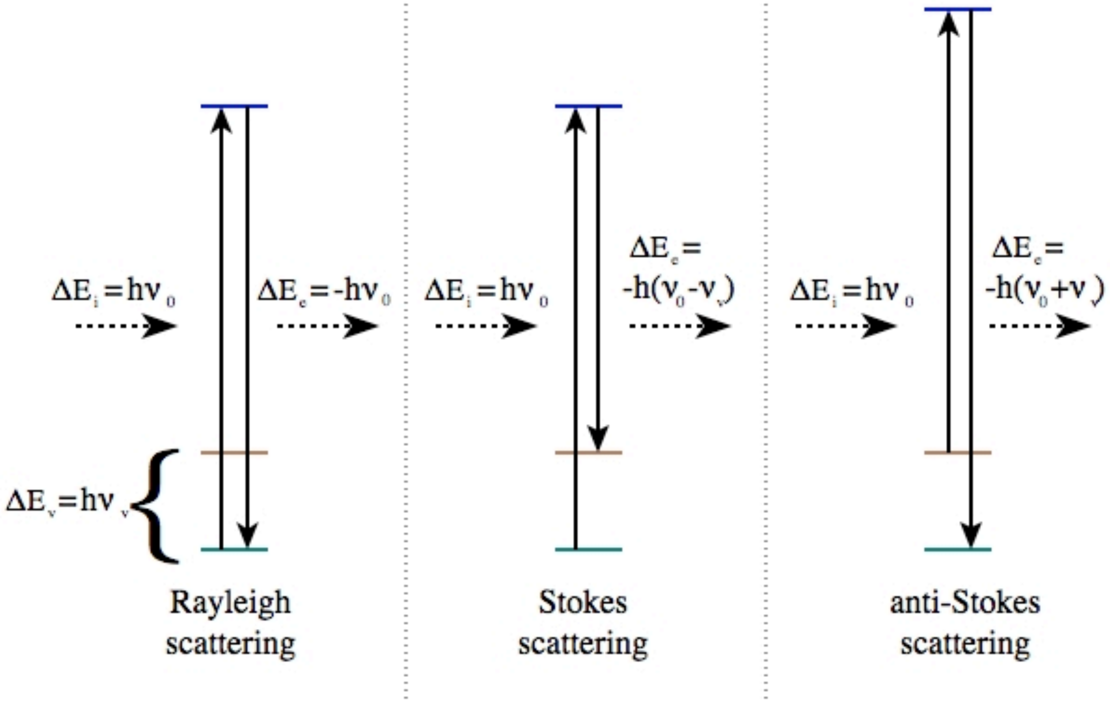


CCl_4



CCl_4 Raman Spectrum

Raman scattering: Inelastic light scattering



C.V. Raman
1888-1970

1930 Nobel Prize in Physics

Raman scattering: Inelastic light scattering

Vibrational Raman scattering occurs when incident light induces a molecular dipole moment via the molecular polarizability. This dipole moment radiates light at a new wavelength, as determined by the energy levels of the molecule.

C.V. Raman
1888-1970

1930 Nobel Prize in Physics

Vibrational Raman scattering

Induced molecular dipole moment:

$$\mu = \alpha E$$

α is the molecular polarizability.

$$E(t) = E_0 \cos(\omega_0 t)$$

$$\alpha(t) = \alpha_0 + \alpha_{vib} \cos(\omega_{vib} t)$$

$$\mu(t) = \alpha(t) E(t)$$

ω_0 is a visible frequency

ω_{vib} is a vibrational (IR) frequency

Vibrational Raman scattering - Classical description

$$\mu(t) = \alpha_0 E_0 \boxed{\cos(\omega_0 t)}$$

$$+\tfrac{1}{2}\alpha_{vib} E_0 \Big(\big[\cos(\omega_0 + \omega_{vib})t\big] + \big[\cos(\omega_0 - \omega_{vib})t\big] \Big)$$

Three colors are scattered from the molecules:

ω_0 is called Rayleigh Scattering

$\omega_0 - \omega_{vib}$ is called Stokes Raman Scattering

$\omega_0 + \omega_{vib}$ is called Anti-Stokes Raman Scattering

Vibrational Raman scattering - Classical description

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Three colors are scattered from the molecules:

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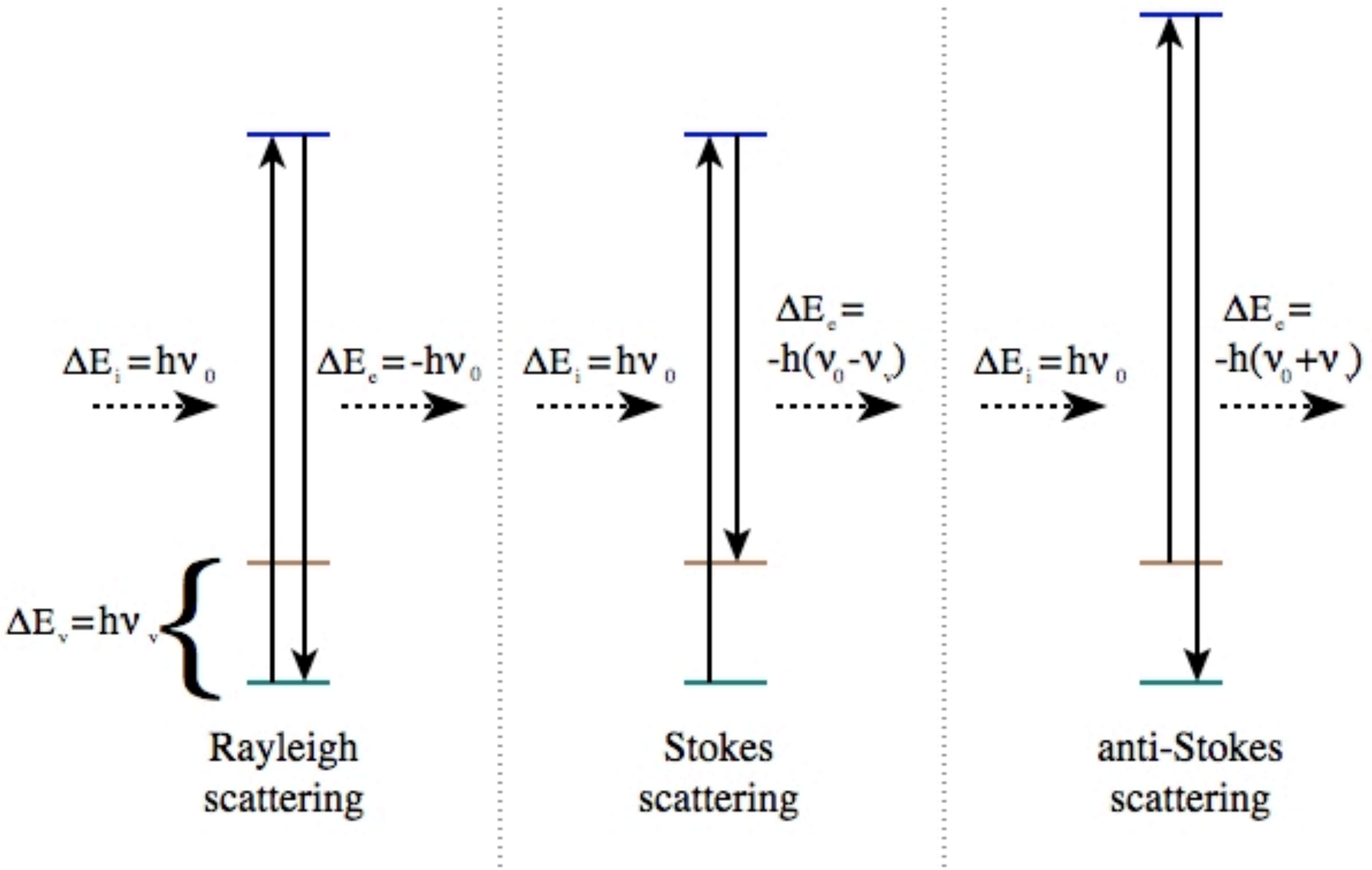
Vibrational Raman scattering - QM description



ω_0 is called Rayleigh Scattering

$\omega_0 - \omega_{vib}$ is called Stokes Raman Scattering

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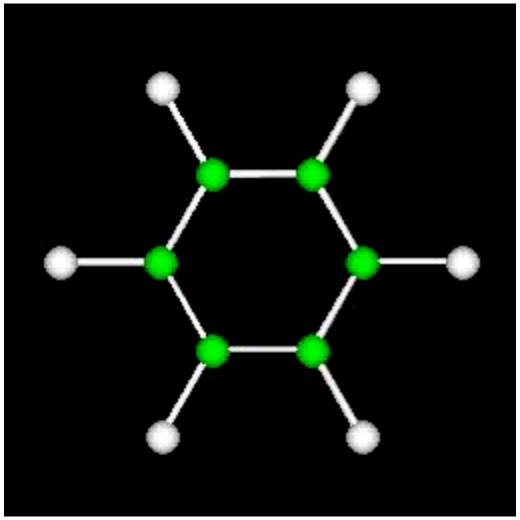
Vibrational Raman scattering selection rules

$$\mu(t) = \alpha_0 E_0 \cos(\omega_0 t)$$
$$+\tfrac{1}{2}\alpha_{vib} E_0\left(\left[\cos\left(\omega_0 + \omega_{vib}\right)t\right] + \left[\cos\left(\omega_0 - \omega_{vib}\right)t\right]\right)$$

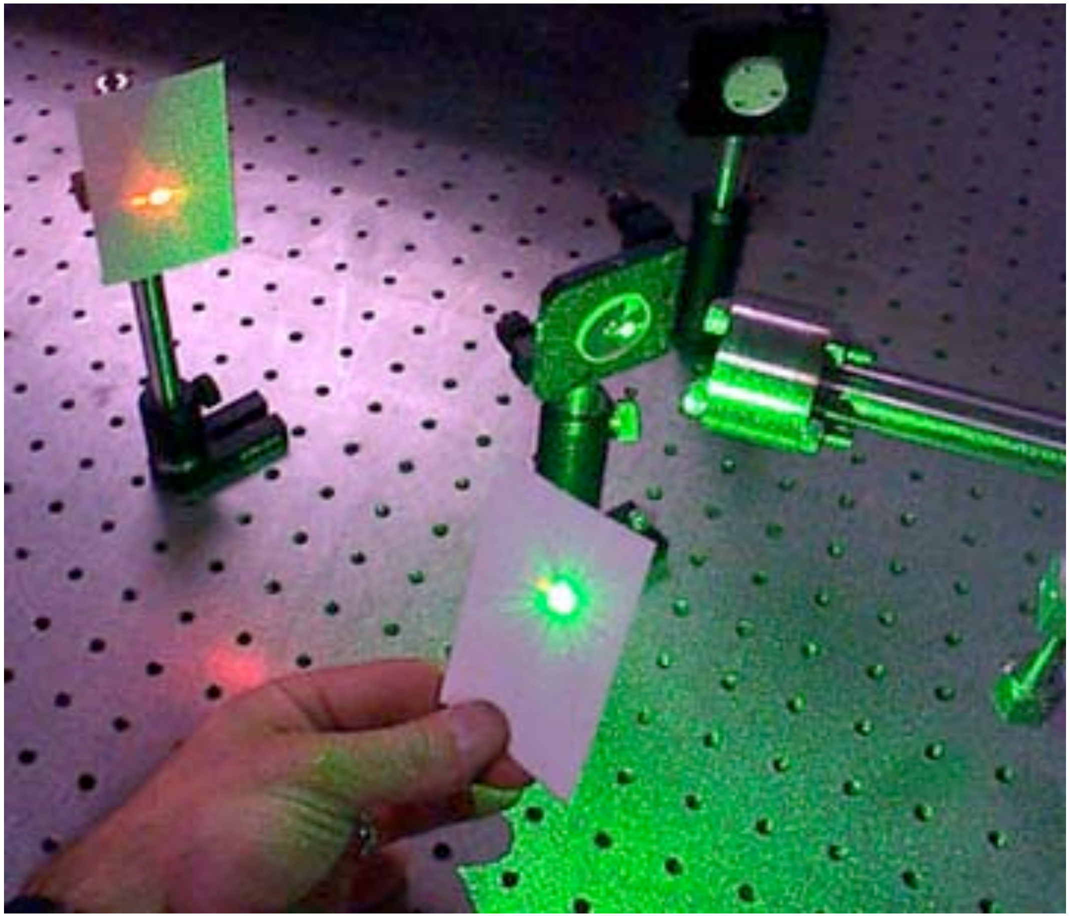
- For a normal mode vibration to be Raman active, $\Delta\alpha/\Delta x$ must be non-zero: the vibration must change the molecular polarizability.

Symmetric modes can have large changes in molecular polarizability.



3000 cm^{-1} CH breathing mode

Vibrational Raman scattering



Benzene

λ_0 = 500 nm

ω_0 = 20,000 cm^{-1}

$\omega_S = \omega_0 - \omega_{vib}$

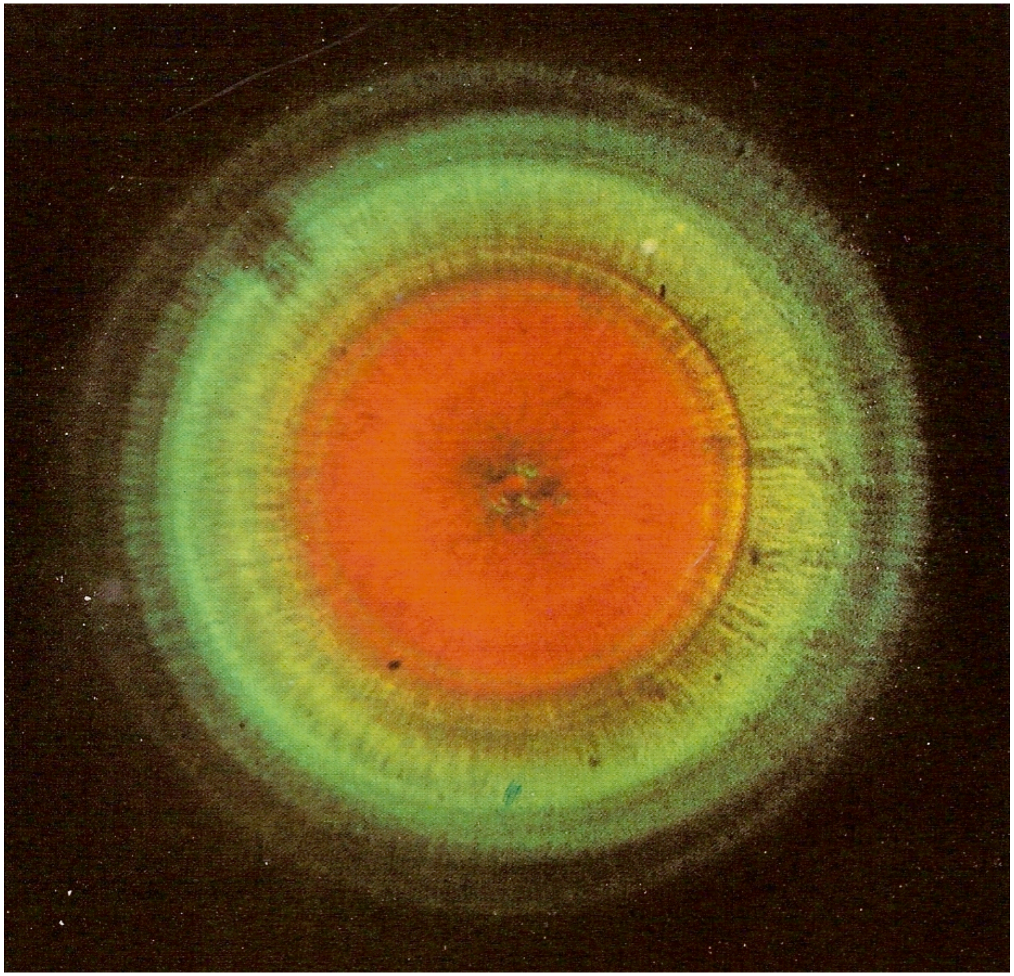
ω_S = 20,000 - 3000 cm^{-1}

ω_S = 16,000 cm^{-1}

λ_S = 625 nm

$\omega_0 - \omega_{vib}$ is called Stokes Raman Scattering

Vibrational Raman scattering



Benzene

λ_0 = 650 nm

ω_0 = 15,385 cm^{-1}

$\omega_{AS} = \omega_0 + \omega_{vib}$

ω_{AS} = 15,385 + 3000 cm^{-1}

ω_{AS} = 18,385 cm^{-1}

λ_{AS} = 544 nm

$\omega_0 + \omega_{vib}$ is called Anti-Stokes Raman Scattering