

# Raman Spectroscopy

See "Further Information 13.2" of Atkins 8th edition and 19.8 of Thomas Engel, Philip Reid Physical Chemistry

Raman Effect: Scattering of a photon by a molecule.

transfer of some (but not all) energy

all is absorption spectroscopy

Raman complements absorption spectroscopy because the selection rules are different.

- Assume molecule (diatomic) has characteristic vibrational frequency  $\omega_{\text{vib}}$ .  $\rightarrow$  think H<sub>2</sub>O. equally spaced ladder
- Assume the electric field (photon) has frequency  $\omega$ :  $E = E_0 \cos \omega t$

The electric field distorts the molecule slightly because the valence electrons (-ve) and the nuclei/core electrons (+ve) get pulled in opposite directions.

- this induces a time-dependent dipole moment of magnitude  $\mu_{\text{induced}}(t)$  in the molecule of the same frequency as the photon.

The selection rule for Raman comes from:

$$(\alpha)_{12} \equiv \int \psi_2^* \alpha \psi_1 \quad \text{should be non-zero.}$$

where  $\alpha$  is the polarizability of the molecule.

In the linear response approximation, we have

$$\mu_{\text{induced}}(t) = \alpha E = \alpha E_0 \cos \omega t$$

induced dipole is proportional to applied field with  $\alpha$  the proportionality constant.

$\alpha$  depends on the bond length, do Taylor expansion around the equilibrium position:

$$\alpha(r) = \alpha(r_{\text{eq}}) + (r - r_{\text{eq}}) \left. \frac{d\alpha}{dr} \right|_{r_{\text{eq}}} + \dots$$

Could proceed as for absorption case, but we will take a different approach

Due to vibration,  $r \equiv r(t) = r_0 \cos \omega_{\text{vib}} t + r_{\text{eq}}$

Combine and use trig. identities:

$$\mu_{\text{induced}}(t) = \alpha E = \alpha(r_{\text{eq}}) E_0 \cos \omega t + \left. \frac{d\alpha}{dr} \right|_{r_{\text{eq}}} \cdot r_0 E_0 \left[ \cos(\omega + \omega_{\text{vib}}) t + \cos(\omega - \omega_{\text{vib}}) t \right]$$

$$\left. \frac{d\alpha}{dr} \right|_{r_{\text{eq}}} \cdot r_0 E_0 \left[ \underbrace{\cos(\omega + \omega_{\text{vib}}) t}_{\text{anti-Stokes}} + \underbrace{\cos(\omega - \omega_{\text{vib}}) t}_{\text{Stokes}} \right]$$

Recall H.O. only has one frequency (classically)

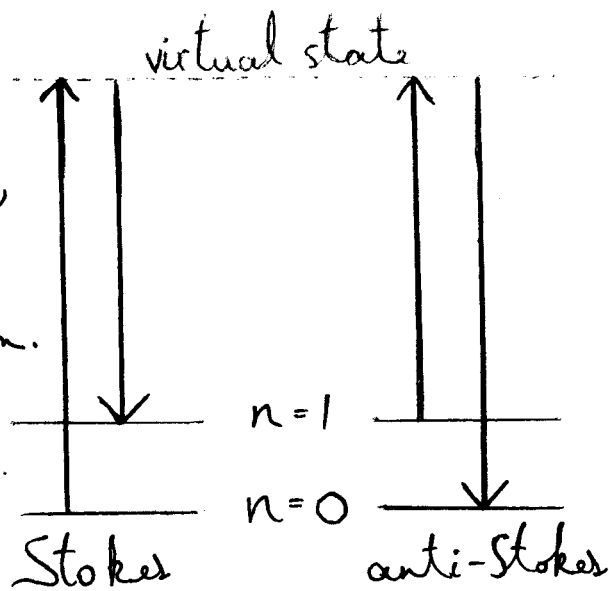
Stokes  $\rightarrow$  light causes a vibrational excitation.

anti-Stokes  $\rightarrow$  light causes a vibrational de-excitation.

Need  $\frac{d\alpha}{dr} \Big|_{r_{eq}} \neq 0$ . Thus for a vibrational mode to be Raman-active, the polarizability of the molecule must change during the vibrational motion.

Homonuclear diatomic is Raman-active.

Absorption and Raman spectroscopy complement each other because active modes for one method may be inactive for the other method.



Peak intensities weaker for anti-Stokes but we will study this later in the course.

Also get rotational Raman spectra. (analysis not shown).

Summary of Raman selection rules:

vibration  $\Delta n = \pm 1$

rotation  $\Delta l = \pm 2$

Advantages of Raman: can use any  $\omega$  you want. If you use visible light,

① can avoid absorption of light by  $H_2O$ ,  $CO_2$ , etc.

② can use optical microscopy to focus with a spatial resolution better than  $0.01 \text{ mm} = 10 \mu\text{m}$ .

"Raman microscope" or "microRaman"

## Infrared Spectroscopy on larger molecules

Infrared radiation from  $300\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  (which we sense as warmth) is absorbed primarily by molecular vibrations. The vibrations determine the peak positions, and rotational motion adds fine structure to the peaks. But this fine structure is lost for larger molecules or even for small molecules in the liquid phase.

The vibrational-rotational spectrum of HCl is simple to understand and we can calculate the bond length directly from the measurement of the spacing of the absorption lines.

For polyatomic molecules things are more complicated.

Each fundamental type of vibration of a polyatomic molecule is called a normal mode. A normal mode is a collective motion of all the atoms in the molecule where each atom moves in phase with each other at a particular frequency.

A linear molecule like  $\text{CO}_2$  containing  $N$  atoms has  $3N - 5$  normal modes of vibration. So  $\text{CO}_2$  has 4 normal modes and HCl has 1 normal mode

## More on Normal Modes (from Engel/Reid)

63 1/2

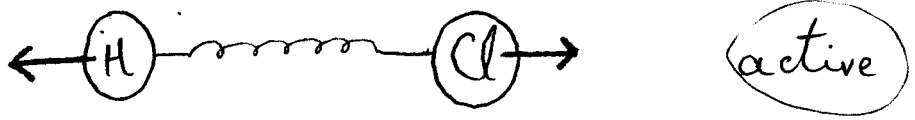
- ① During a vibrational period, the center of mass remains fixed and all the atoms undergo in-phase periodic motion about their equilibrium positions.
- ② All atoms reach their minimum and maximum amplitudes at the same time.
- ③ These collective motions are called normal modes and the frequencies are called normal mode frequencies.
- ④ The frequencies measured in vibrational spectroscopy are the normal mode frequencies.
- ⑤ All normal modes are independent in the harmonic approximation, meaning that excitation of one normal mode does not result in any energy transfer into the other modes.
- ⑥ Any seemingly random motion of the atoms in a molecule can be expressed as a linear combination of the normal modes of that molecule.

A non linear molecule like  $\text{CH}_2\text{Cl}_2$  containing  $N$  atoms has  $3N-6$  fundamental modes of vibration, so methylene dichloride has 9 normal modes.

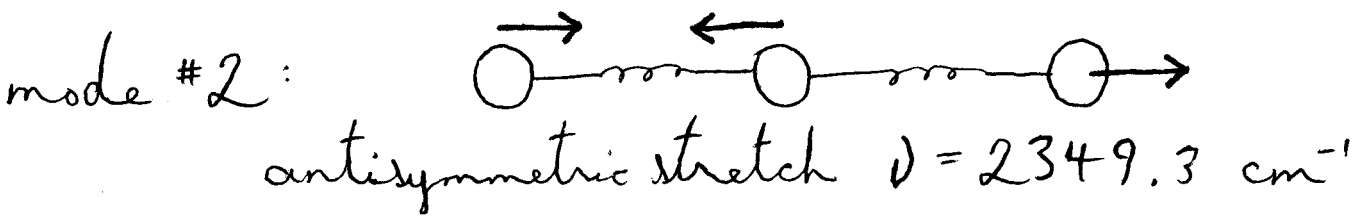
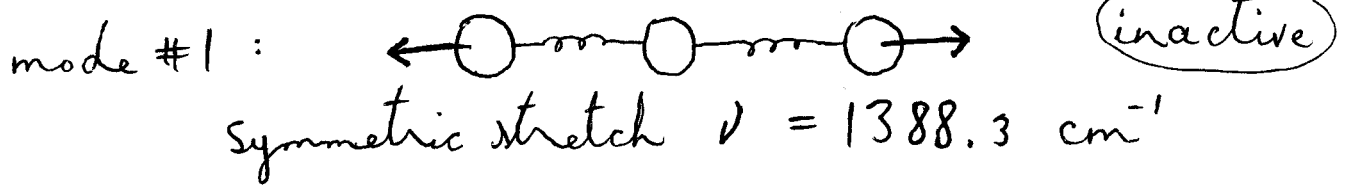
Normal modes can be stretching or bending motions

- stretching (symmetric and antisymmetric)
- bending (scissoring, rocking, wagging, twisting)

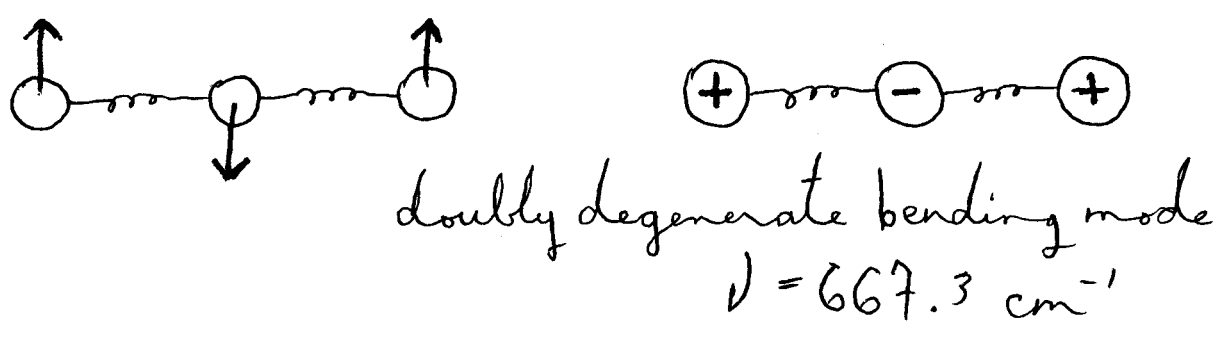
**HCl** linear :  $3(2)-5=1$  normal mode



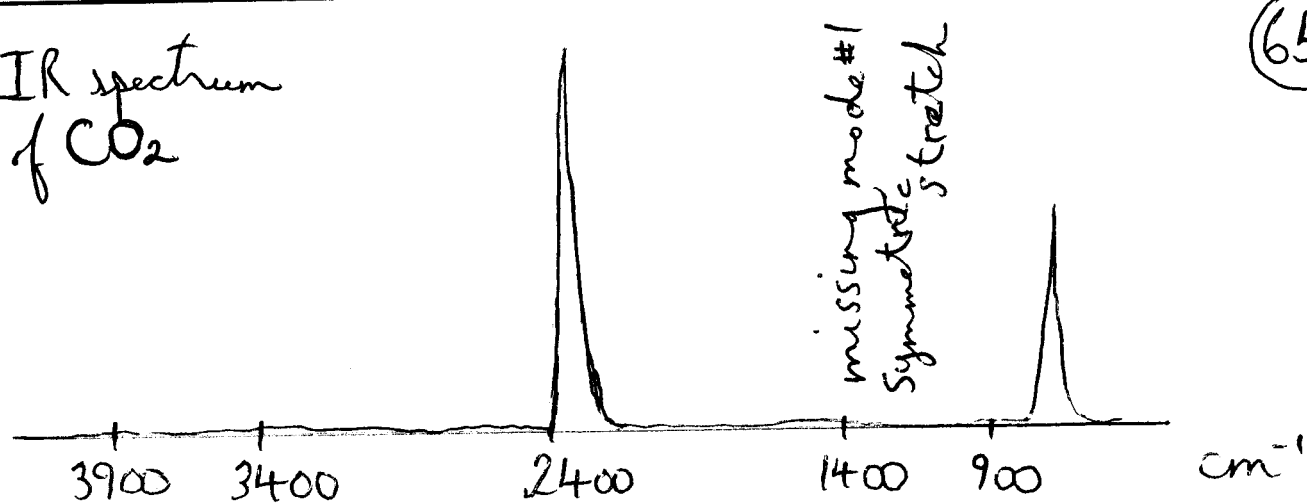
**CO<sub>2</sub>** linear :  $3(3)-5=4$  normal modes



modes #3 and 4



IR spectrum  
of  $\text{CO}_2$



$\text{CH}_2\text{Cl}_2$  non-linear  $5 \cdot 3 - 6 = 9$  normal modes

see animations of these modes + spectrum at  
<http://cat.middlebury.edu/~chem/chemistry/ch2cl2/vib.html#2>  
(need a special plugin)

Why is the spectrum so complicated? In addition to the peaks centered on the fundamental (normal mode) frequencies, other peaks appear in the spectra of polyatomic molecules.

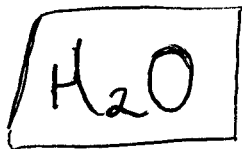
Some of these can be because of violations of the  $\Delta n = \pm 1$  selection rule due to anharmonicity.

But in polyatomic molecules, combination bands also appear.

For example, normal mode 1 can go from  $n_1 = 0 \rightarrow 1$   
and simultaneously normal mode 2 can go from  $n_2 = 0 \rightarrow 1$ .

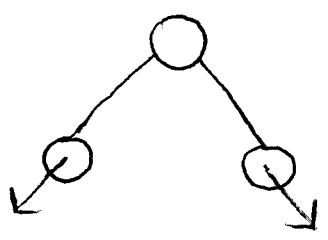
This will give an absorption peak centered at  $\nu_1 + \nu_2$ .

In particular, water shows strong combination bands.



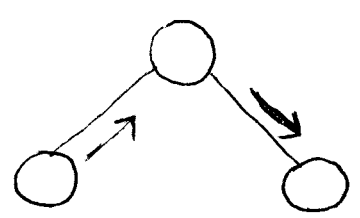
non-linear  $3 \cdot 3 - 6 = 3$  normal modes

mode #1



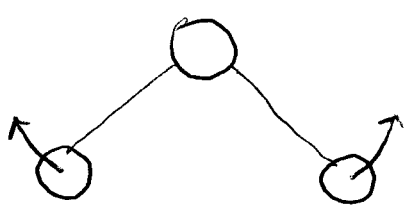
Symmetric stretch  
 $\nu = 3657.05 \text{ cm}^{-1}$

mode #2



asymmetric stretch  
 $\nu = 3755.93 \text{ cm}^{-1}$

mode #3



bend  
 $\nu = 1594.75 \text{ cm}^{-1}$

For animations see <http://www.lsbu.ac.uk/water/vibrat.html>

This is for an isolated molecule (gas phase). What about liquid water? have hydrogen bonding

Variations in the environment around each liquid water molecule gives rise to significant broadening and shifting of the peaks.

In addition, combinations of vibrations with librations give many additional peaks. Librations are restricted rotations i.e. rocking motions

See web site given above.



# Applications of Infrared Spectroscopy

IR is commonly used to identify and determine quantitatively the amount of various substances present in mixtures.

The identification of a compound is based on the existence of characteristic group frequencies that have roughly the same value regardless of the compound in which the group appears. Typical of such groups are those with multiple bonds such as



Chart of characteristic vibrations: see Fig. 5 at <http://www.wag.caltech.edu/home/jang/genchem/infrared.htm>

# Anharmonicity

Ans

Recall the harmonic oscillator approximation is a Taylor series expansion, to 2<sup>nd</sup> order, of  $E^{\text{elect}}(r)$  around the equilibrium bond length, called  $r_0$  or  $r_{\text{eq}}$ .

This approx. does not allow the molecule to dissociate (why?)

For a molecule in a highly excited vibrational state, the harmonic approx. is poor (the restoring force is no longer proportional to the displacement) and additional terms should be included in the Taylor series.

• We say the motion is anharmonic.

One approach is to use an analytic function which

a) is an excellent approx. to a realistic anharmonic potential

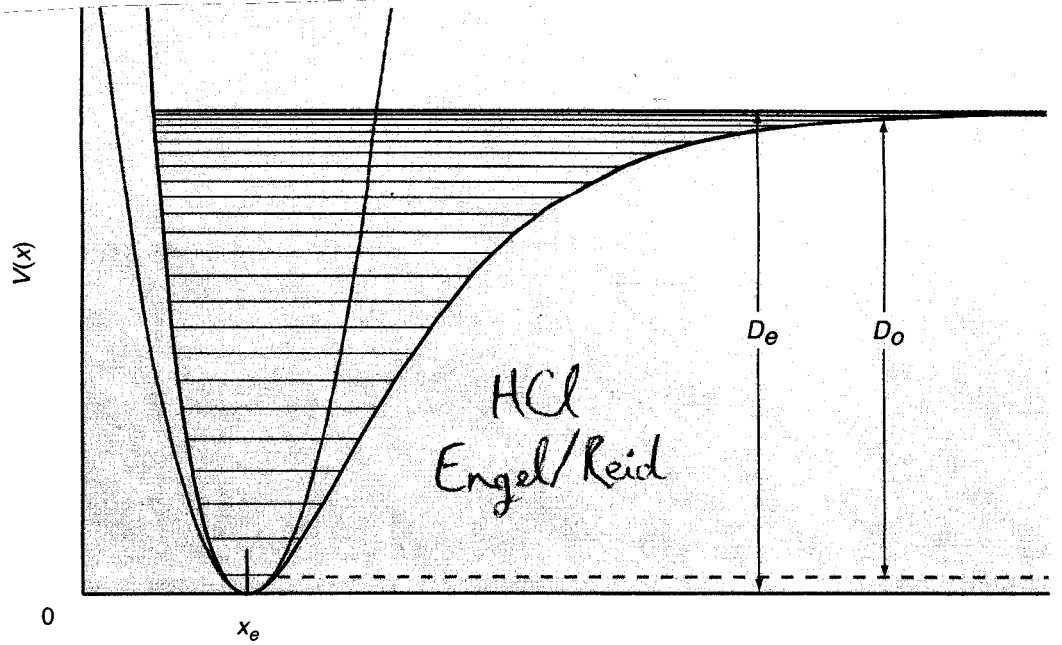
b) can be solved exactly

$$\text{Morse potential: } V(r) = D_e [1 - e^{-\alpha(r-r_0)}]^2$$

$$\text{where } \alpha = \left(\frac{k}{2D_e}\right)^{1/2} = \left(\frac{\mu\omega^2}{2D_e}\right)^{1/2} \text{ where } k = \left.\frac{d^2V}{dr^2}\right|_{r_0}$$

Notice that  $V(r_0) = V'(r_0) = 0$  and  $V''(r_0) = 2\alpha^2 D_e \equiv k$ .

The bond energy is  $D_0$  which differs from  $D_e$  by the zero-point energy.



The energy levels are given by:

$$E_n = \hbar\omega(n + \frac{1}{2}) - \underbrace{\frac{(\hbar\omega)^2}{4D_e}}_{\text{anharmonic correction}} (n + \frac{1}{2})^2$$

anharmonic correction

Selection rules: can see overtones  $\Delta n = 2, 3, \dots$

because we no longer have H.O. wavefunctions.

~~Example problem: the vibrational levels of HgH converge rapidly,~~

~~$n=0 \rightarrow 1$  is  $1203.7 \text{ cm}^{-1}$ ,  $n=1 \rightarrow 2$  is  $965.6 \text{ cm}^{-1}$ ,~~

~~$n=2 \rightarrow 3$  is  $632.4 \text{ cm}^{-1}$ ,  $n=3 \rightarrow 4$  is  $172 \text{ cm}^{-1}$ .~~

↑ Estimate the dissociation energy.

~~the first 5 vibrational energy levels of HCl are at~~  
 ~~$144.83 \text{ cm}^{-1}$ ,  $1481.86 \text{ cm}^{-1}$ ,~~

Example problem: You measure the following vibrational transitions for HCl:

$\Delta n$	
$0 \rightarrow 1$	$2885.64 \text{ cm}^{-1}$
$1 \rightarrow 2$	$2781.54 \text{ cm}^{-1} > 104.10$
$2 \rightarrow 3$	$2677.44 \text{ cm}^{-1} > 104.10$
$3 \rightarrow 4$	$2573.32 \text{ cm}^{-1} > 104.12$

Estimate the dissociation energy.

$$\Delta E = E_{n+1} - E_n = h\nu(n+3/2) - \frac{(h\nu)^2}{4D_e}(n+3/2)^2 - h\nu(n+1/2) + \frac{(h\nu)^2}{4D_e}(n+1/2)^2$$

$$= h\nu - \frac{(h\nu)^2}{4D_e} [n^2 + 3 + 9/4 - n^2 - n - 1/4] = h\nu - \frac{(h\nu)^2}{2D_e}(n+1)$$

$$\text{Hence } \Delta \Delta E = \frac{(h\nu)^2}{2D_e} = 104.10 \text{ cm}^{-1} \Rightarrow 2D_e = \frac{(h\nu)^2}{\Delta \Delta E} = \frac{(h\nu)^2}{104.10 \text{ cm}^{-1}}$$

$$\text{Thus } \Delta E = h\nu - \Delta \Delta E(n+1) \Rightarrow h\nu = \Delta E + \Delta \Delta E(n+1)$$

$$\text{For } n=0 \text{ get } h\nu = 2885.64 + 104.10 \text{ cm}^{-1} = 2989.74 \text{ cm}^{-1}$$

$$\text{Hence } D_0 = D_e - \frac{1}{2}h\nu = \frac{(h\nu)^2}{2\Delta \Delta E} - \frac{h\nu}{2} = 41437.6 \text{ cm}^{-1} = 495.7 \text{ kJ/mol}$$

Actual value is 432 kJ/mol