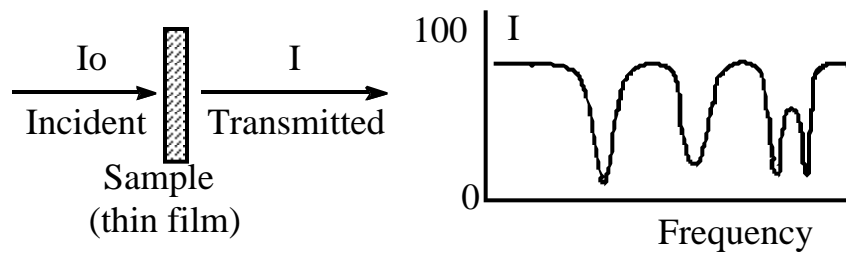


## Infra-Red methods

- In theory a most powerful technique, providing information on:-
  - chemical structure and composition
  - percentage crystallinity
  - orientation of crystal and amorphous regions



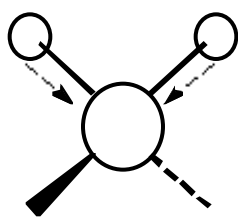
- At certain frequencies the sample absorbs energy.
- These frequencies correspond to energies required to cause the molecule to vibrate.

- **Think of molecules as a series of masses (atoms) connected by springs (bonds). Free to vibrate and absorbs energy in the IR region if :-**

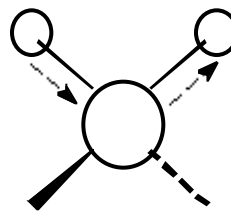
- a) the frequency of the vibration is equal to the frequency of the incident light.**
- b) on vibration the molecules dipole changes.**

### **Fundamental molecular vibrations**

#### **STRETCH**



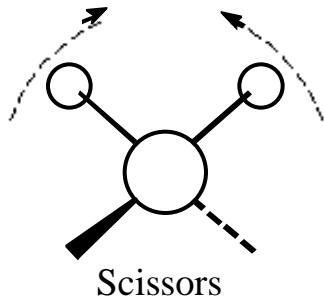
**Symmetric**



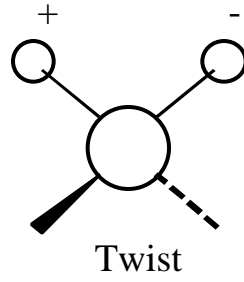
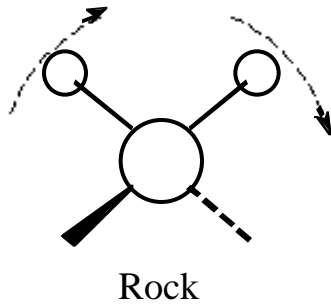
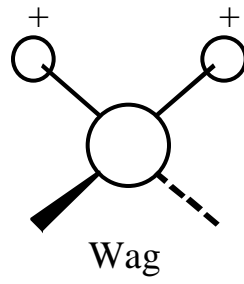
**Asymmetric**

BENDING

IN - PLANE

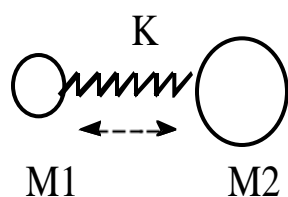


OUT - OF - PLANE



### Theoretical concerns

Vibrational frequency for coupled masses given by :-



$$= \frac{1}{2} c. \{K.(1/M1 + 1/M2)\}$$

**K is spring constant of the bond  
not bond strength.**

**As M increases  
 $\nu$  decreases**

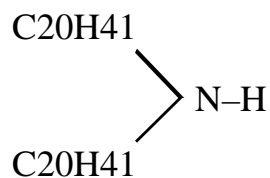
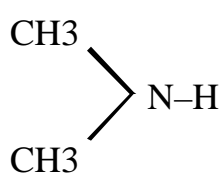
**C-H 3,000cm<sup>-1</sup>  
C-C 1,000cm<sup>-1</sup>  
C-I 500cm<sup>-1</sup>**

**As K increases  
 $\nu$  increases**

**C-N 1050cm<sup>-1</sup>  
C=N 1650cm<sup>-1</sup>  
C≡N 2250cm<sup>-1</sup>**

- If  $M_1$  is large compared to  $M_2$  in the previous equation then  $1/M_1 \rightarrow 0$

then :-  $= \frac{1}{2} c. \{K.1/M_2\}$



- N-H stretch is  $\approx$  same characteristic frequency in both molecules, it's a fingerprint for N-H moiety. Identifies presence or absence of N-H in an unknown material.

### **General features of IR**

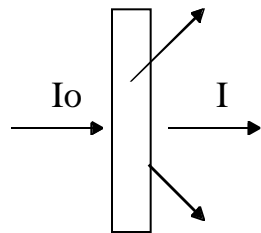
- **IR absorbencies are sensitive to intrachain forces. Exceptions – H bonds and crystal field splitting.**
- **Groups in crystalline polymer chains experience the 'same' environment. The groups in amorphous polymer chains may 'see' slightly different 'forces'.**
- **Crystal bands - narrow; amorphous bands - broader.**
- **Special chain conformations in folds can lead to special absorption frequencies not seen in the amorphous polymer melt or crystal spectrum.**
- **Molecular vibrations combine with and subtract from each other. Harmonics exist at 2x or 3x characteristic frequency. These effects lead to addition 'bands' in the spectra and complexity of analysis.**

### **Procedures to assign origin of bands**

- **Initial selection based on band width**  
Broad – Amorphous      Narrow – Crystalline
- **Melt polymer sample**  
Crystalline and Fold – disappear  
Amorphous – stronger
- **Anneal sample**  
Crystalline – increase slightly  
Fold and Amorphous – decrease slightly
- **Chemical etch (attacks amorphous and fold surface)**  
Crystallinity – approximately constant  
Fold and Amorphous – disappears (greatly reduced)
- **Would like to identify an Internal Thickness Band;**  
intensity is essentially unchanged regardless of  
treatment; solely a function of sample thickness.

## Quantitative studies

- Beer-Lambert law –  $A = \log ( I_0 / I ) = B.t.c$



Thin film

**A = absorbance**

**$I_0$  = incident intensity**

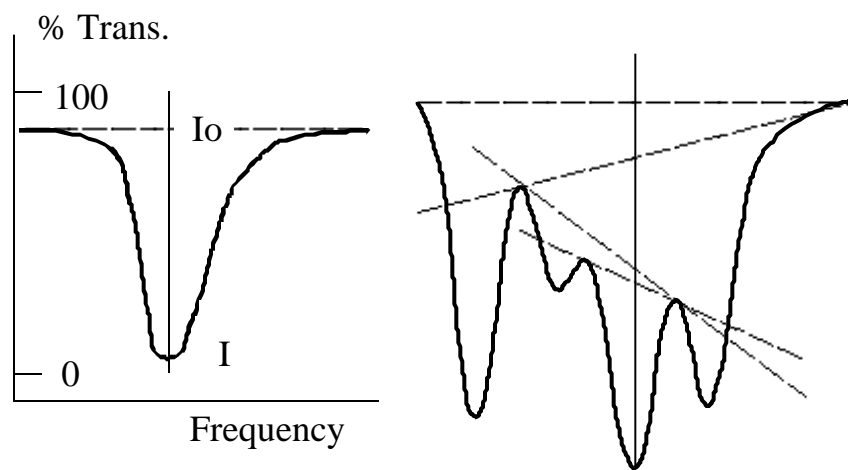
**I = transmitted intensity**

**B = absorption coefficient**

**t = sample thickness**

**c = conc. of absorbing species**

- **Need to draw baselines to allow for non-absorbing losses such as scattering from bulk or surface.**



### To Determine Percentage Crystallinity by IR

- Adsorption by an ITB depends only on the amount of polymer present, not on the concentration of various polymer chain structures (crystal, fold, amorphous).

$$A(\text{itb}) = B(\text{itb}) \cdot t \quad \text{whereas} \quad A(\text{poly}) = B(\text{poly}) \cdot t \cdot c$$

- a) find a crystalline band; disappears on melting.  
b) find an ITB; insensitive to melting, annealing,
- Ratio (cryst) & (itb) bands; eliminate thickness:-

$$A(\text{cryst}) / A(\text{itb}) = B(\text{cryst}) \cdot t \cdot c / B(\text{itb}) \cdot t = K \cdot c$$

- Find K and therefore % crystallinity (c) by calibration with some other technique. IR's a secondary (indirect) method for % crystallinity measurement.
- Why bother using IR; quick and easy for films.
  - a) thin films don't always give good x-ray signals,
  - b) some polymers degrade before melting (DSC).