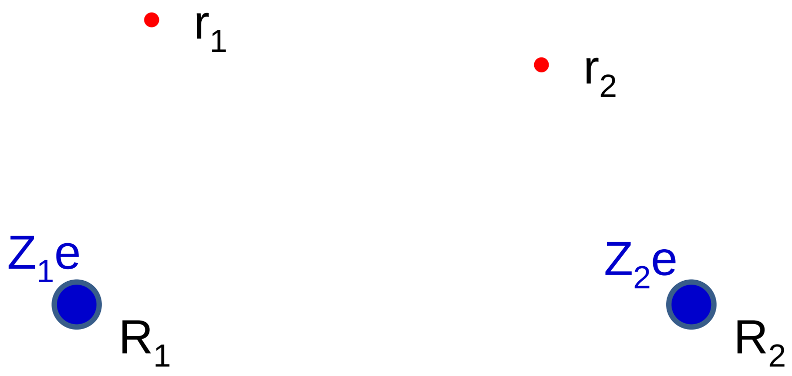
Lattice Dynamics

A complete, non-relativistic, description of a system of N atoms having the positions $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_K, \ldots, \mathbf{R}_N)$ with n electrons located at $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_K, \ldots, \mathbf{r}_n)$ is provided by the time-dependent Schrödinger equation

$$\mathcal{H}\Xi(\mathbf{r},\mathbf{R};t) = i\hbar\frac{\partial}{\partial t}\Xi(\mathbf{r},\mathbf{R};t) \quad , \tag{1}$$

$$\mathcal{H}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{T}(\mathbf{r}) + \mathcal{V}(\mathbf{R}) + \mathcal{V}(\mathbf{r},\mathbf{R}) + \mathcal{V}(\mathbf{r}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})$$



$$\underline{\mathcal{H}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})}$$

$$\mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{r}) + \mathcal{V}(\mathbf{R}) + \mathcal{V}(\mathbf{r},\mathbf{R}) + \mathcal{V}(\mathbf{r})$$

$$\boxed{\begin{aligned}
\mathcal{T}(\mathbf{R}) &= -\frac{\hbar^2}{2}\sum_{K=1}^{N}\frac{\boldsymbol{\nabla}_K^2}{M_K} \\
\mathcal{T}(\mathbf{r}) &= -\frac{\hbar^2}{2m_e}\sum_{k=1}^{n}\boldsymbol{\nabla}_k^2 \\
\mathcal{V}(\mathbf{R}) &= \frac{e^2}{4\pi\epsilon_0}\sum_{K=1}^{N-1}\sum_{L>K}^{N}\frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|} \\
\mathcal{V}(\mathbf{r},\mathbf{R}) &= -\frac{e^2}{4\pi\epsilon_0}\sum_{K=1}^{N}\sum_{k=1}^{n}\frac{Z_K}{|\mathbf{r}_k - \mathbf{R}_K|} \\
\mathcal{V}(\mathbf{r}) &= \frac{e^2}{4\pi\epsilon_0}\sum_{k=1}^{n-1}\sum_{l>k}^{n}\frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}
\end{aligned}}$$

$$\mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})\phi_i(\mathbf{r},\mathbf{R}) = E_i(\mathbf{R})\phi_i(\mathbf{r},\mathbf{R})$$

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$$\mathcal{H}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\mathrm{el}}(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}\Xi(\mathbf{r},\mathbf{R};t) = i\hbar\frac{\partial}{\partial t}\Xi(\mathbf{r},\mathbf{R};t)$$

$$\left[\mathcal{T}(\mathbf{R}) + E_i(\mathbf{R})\right]\chi_i = i\hbar\frac{\partial}{\partial t}\chi_i$$

$$\Xi(\mathbf{r},\mathbf{R};t) \approx \phi_i(\mathbf{r},\mathbf{R})\chi_i(\mathbf{R},t)$$

Born-Oppenheimer Approximation

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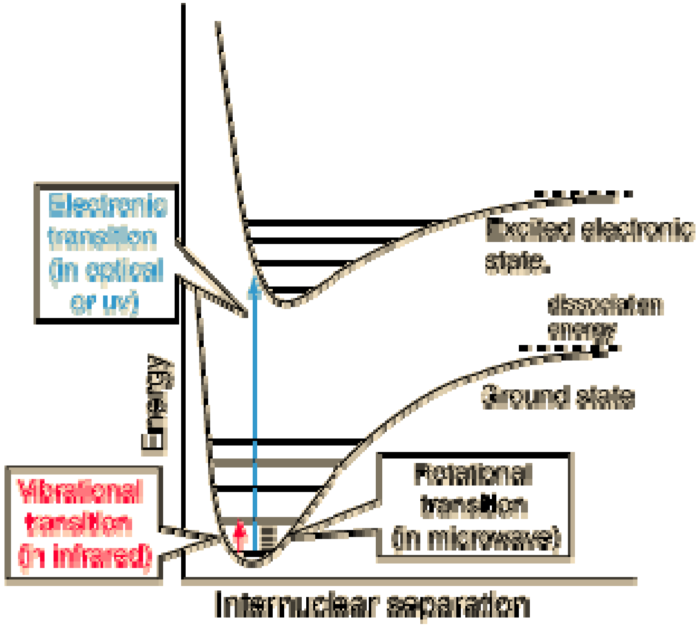
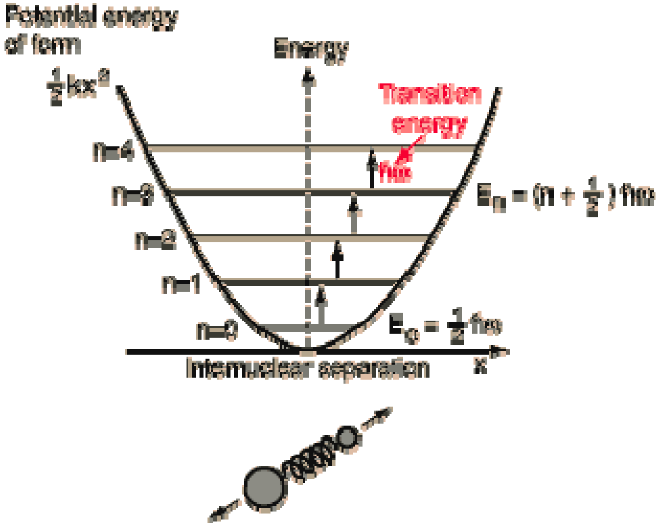
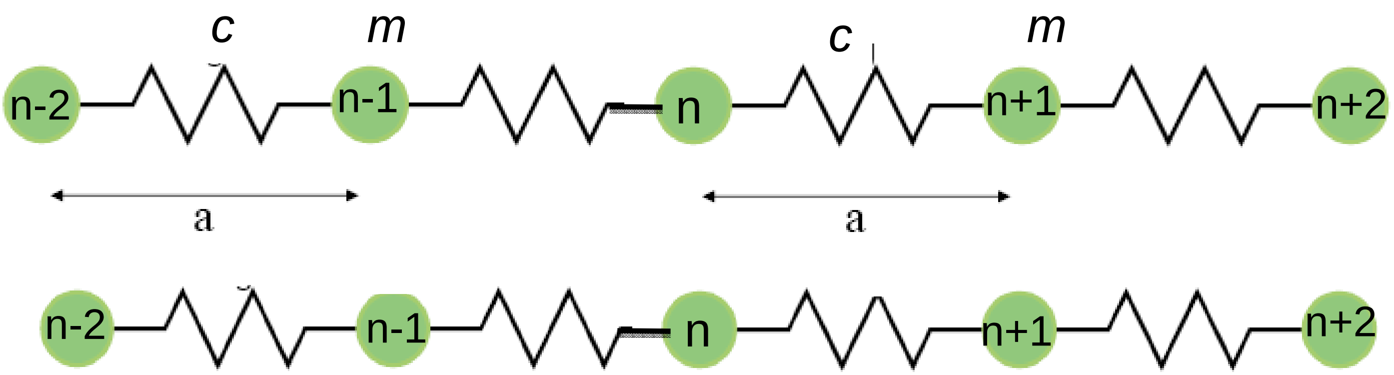
$$\psi_{\text{molecule}}(\vec{r}_i, \vec{R}_j) = \psi_{\text{electrons}}(\vec{r}_i, \vec{R}_j)\,\psi_{\text{nuclei}}(\vec{R}_j)$$

$V(r) = ½\ k\ (r-r_0)^2$





x=0 represents the equilibrium separation between the nuclei.



$$F_n = c(u_{n+1} - u_n) + c(u_{n-1} - u_n)$$

$$m(d^2u_n/dt^2) = c(u_{n+1} + u_{n-1} - 2u_n)$$

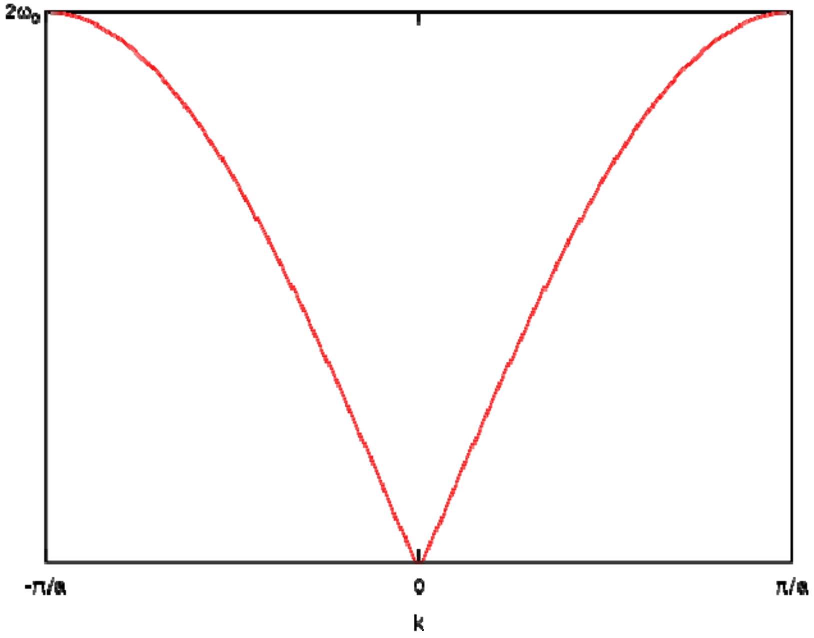
$$u_n = u\, e^{\pm inKa}\, e^{-i\omega t} \Rightarrow -m\omega^2 u_n = c(u_{n+1} + u_{n-1} - 2u_n)$$

$$\Rightarrow -m\omega^2 = c(e^{+iKa} + e^{-iKa} - 2)$$

$$\Rightarrow \omega^2 = (2c/m)(1 - \cos Ka)$$

Dispersion relation for 1D acoustic phonons

$$\omega(K) = (2c/m)^{1/2}(1 - \cos Ka)^{1/2} = 2(c/m)^{1/2}|\sin(Ka/2)|$$

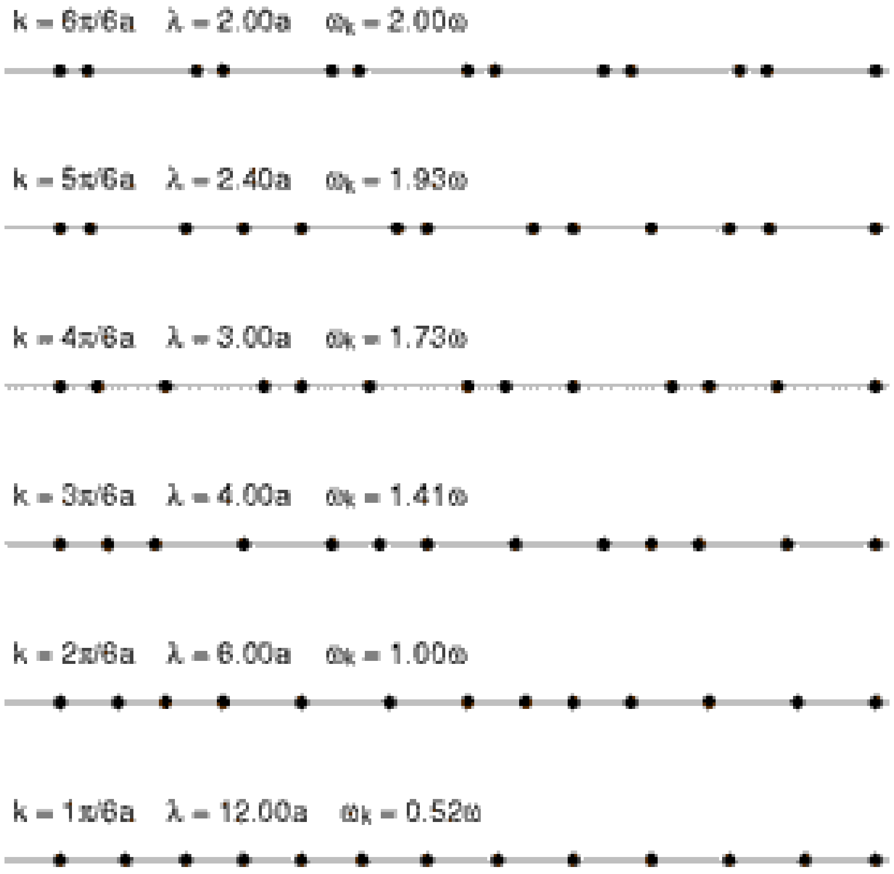


Phase velocity: $v_p = \omega/K$

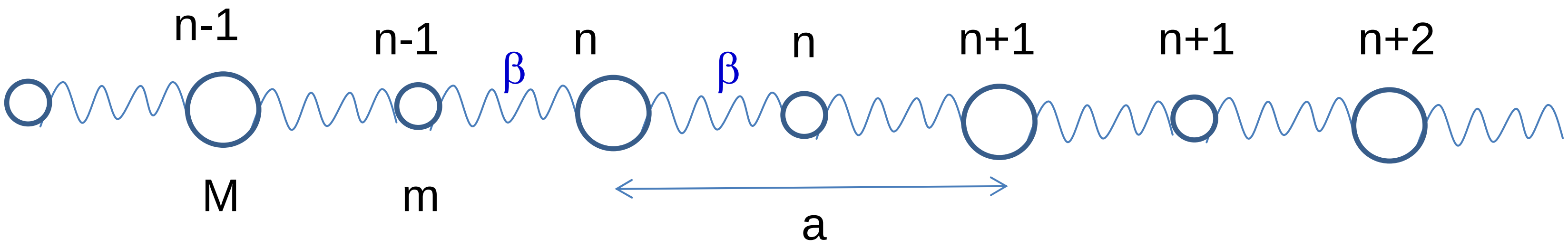
Group velocity: $v_g = \partial\omega/\partial K = a(c/m)^{1/2}\cos(Ka/2)$

For small K: $v_g = v_p$

Phonon


k = 6π/6a λ = 2.00a ω_k = 2.00ω
k = 5π/6a λ = 2.40a ω_k = 1.93ω
k = 4π/6a λ = 3.00a ω_k = 1.73ω
k = 3π/6a λ = 4.00a ω_k = 1.41ω
k = 2π/6a λ = 6.00a ω_k = 1.00ω
k = 1π/6a λ = 12.00a ω_k = 0.52ω

Diatomic linear chain



$$M(d^2u_n/dt^2) = \beta(s_{n+1} + s_{n-1} - 2u_n)$$

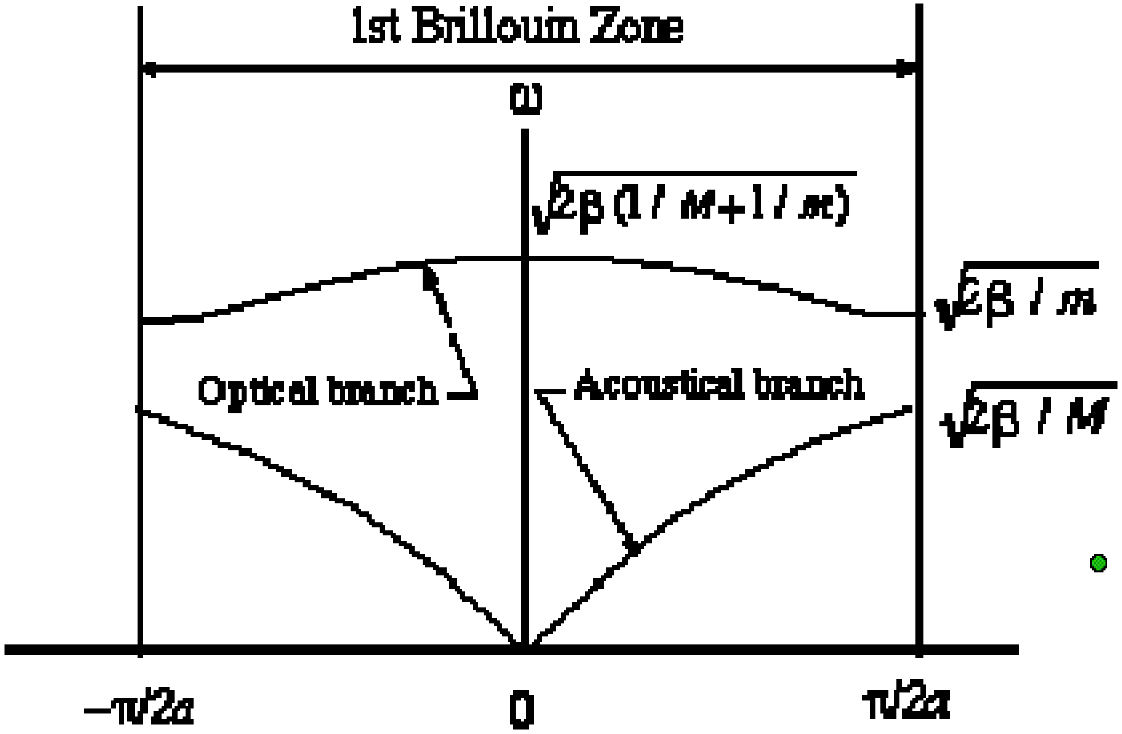
$$m(d^2s_n/dt^2) = \beta(u_{n+1} + u_{n-1} - 2s_n)$$

$u_n = u\,e^{\pm inKa}\,e^{-i\omega t}$ and $s_n = s\,e^{\pm inKa}\,e^{-i\omega t}$

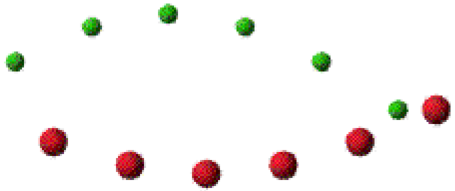
$$\Rightarrow \begin{cases} -M\omega^2 u = \beta s(1 + e^{-iKa}) - 2\beta u \\ -m\omega^2 s = \beta u(1 + e^{iKa}) - 2\beta s \end{cases}$$

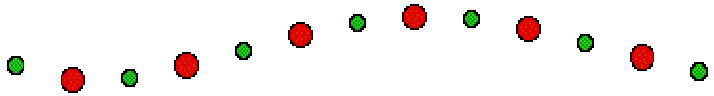
$$\Rightarrow \quad \omega^2 = \beta\left(\frac{1}{m} + \frac{1}{M}\right) \pm \beta\sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4\sin^2 ka}{Mm}}$$

$$\omega^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) \pm \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 ka}{Mm}}$$



Transverse optical mode





Transverse acoustical mode

Scattering by phonons

Phonon is the quantum unit of a crystal vibration.

Incident beam with momentum k interacts with a crystal and comes out with momentum k'.

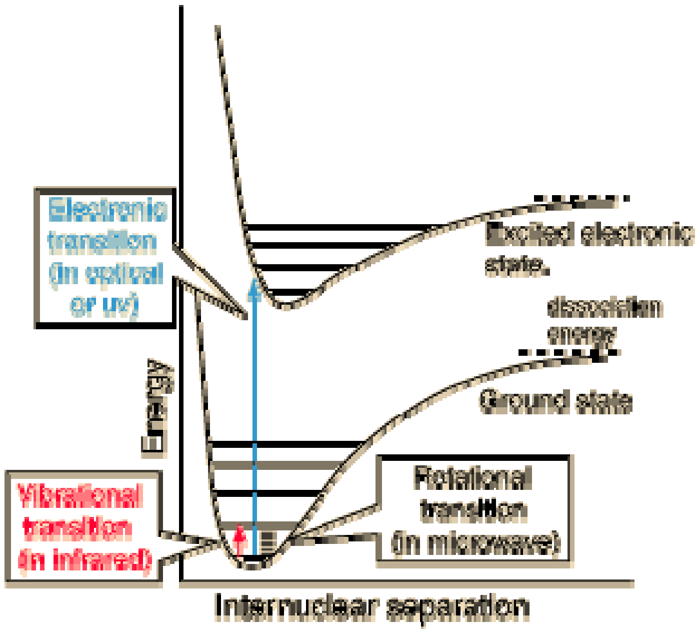
$$k + G = k' \pm K$$

G is a vector in reciprocal lattice.

K lies in the *first brillouin zone*. For 1D, $|K| \leq \pi/a$.

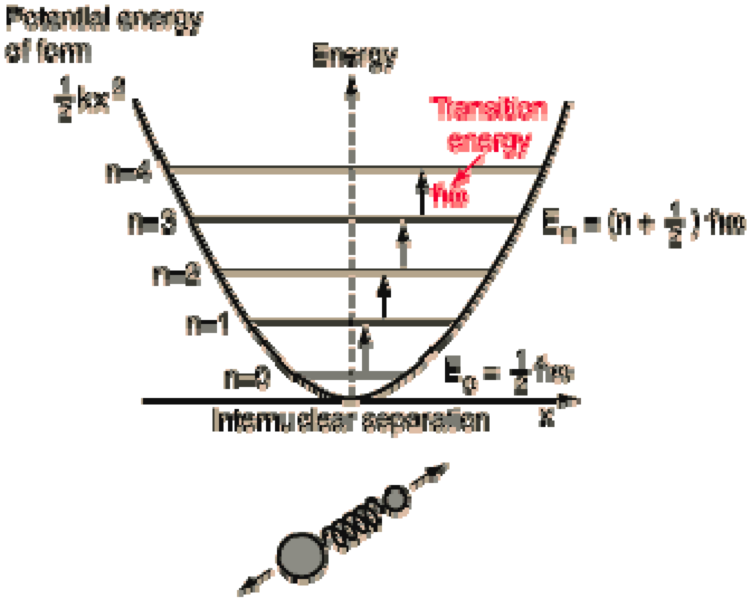
Electronic Spectroscopy

1. Photons in, photons out – PL
2. Photons in, electrons out – UPS, XPS
3. Electrons in, electrons out – EELS



Vibrational Spectroscopy

1. Photons in, photons out – IR, Raman
2. Electrons in, electrons out – EELS



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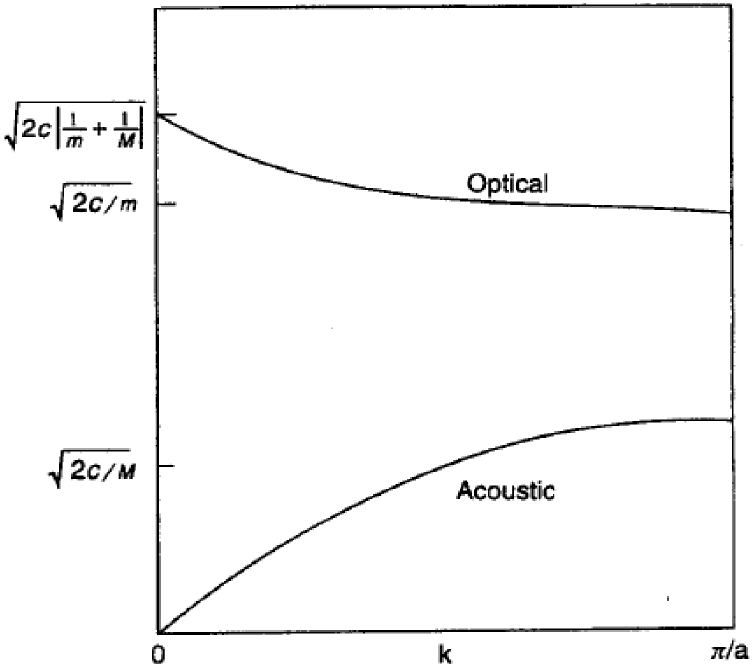
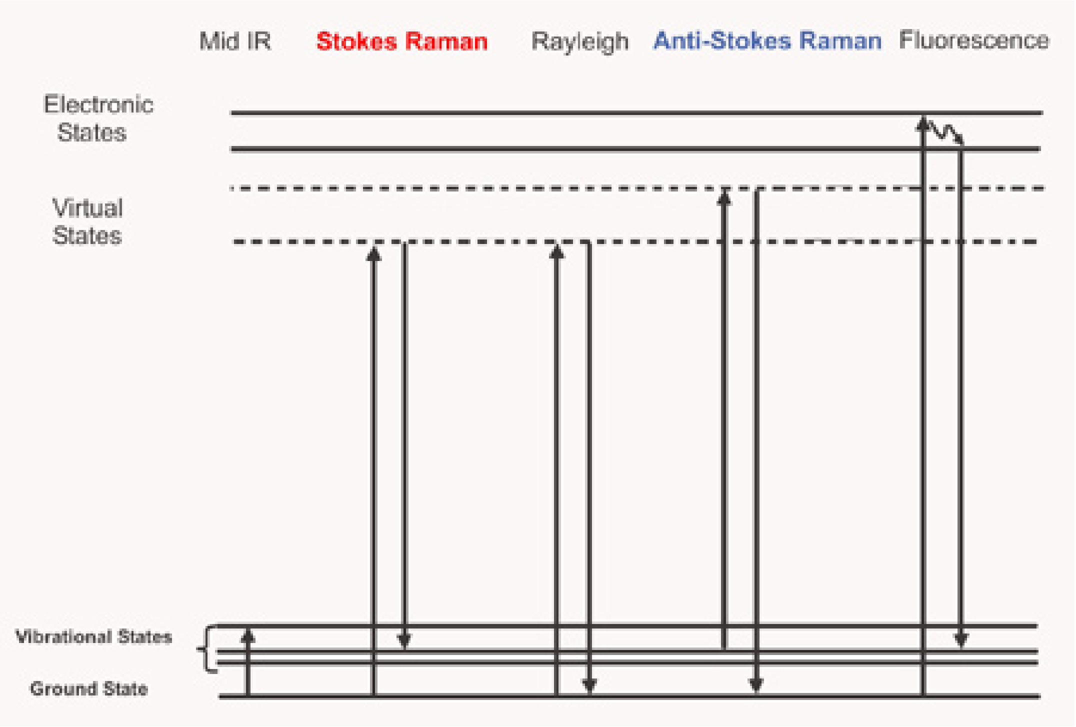
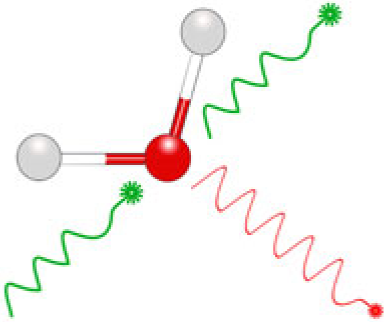
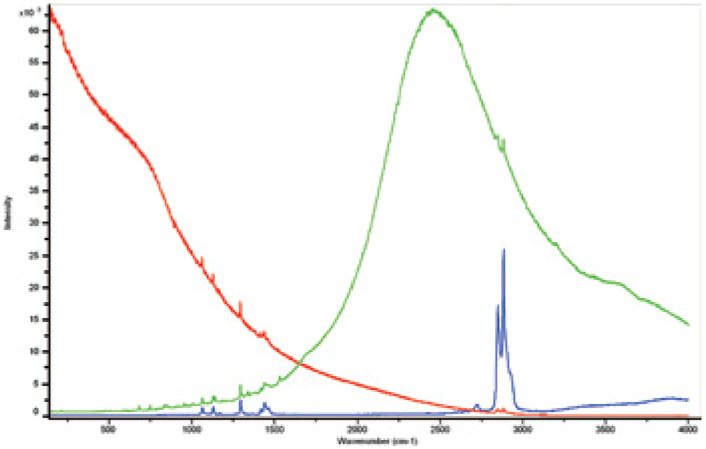


The Theory of Raman Spectroscopy







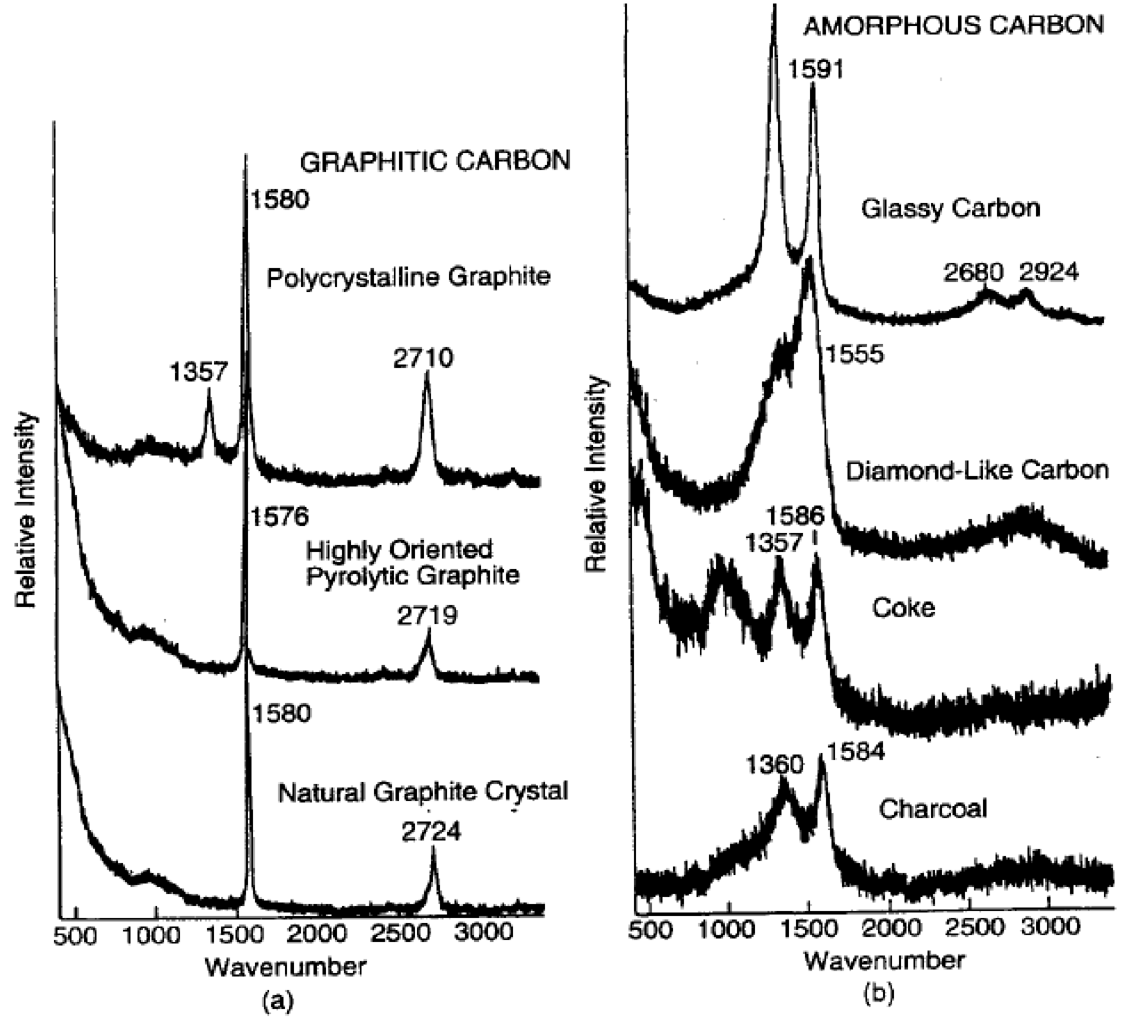


Figure 8.19. Raman spectra of (a) crystalline graphites and (b) noncrystalline, mainly graphitic, carbons. The *D* band appears near 1355 cm^{-1} and the *G* band, near 1580 cm^{-1}. [From D. S. Knight and W. B. White, *J. Mater, Sci.* **4**, 385 (1989).]

Reciprocal lattice

In crystallography, the **reciprocal lattice** of a Bravais lattice is the set of all vectors **K** such that

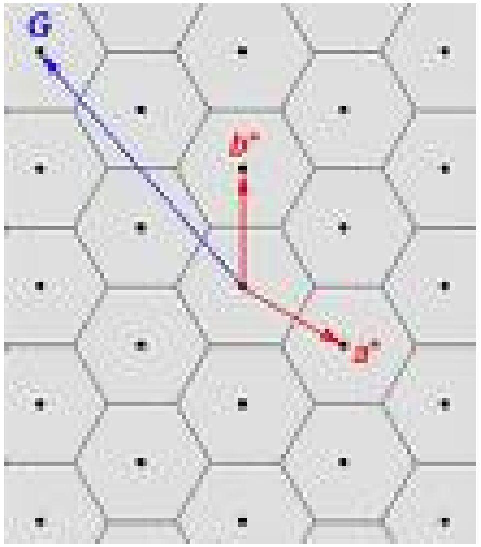
$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1$$

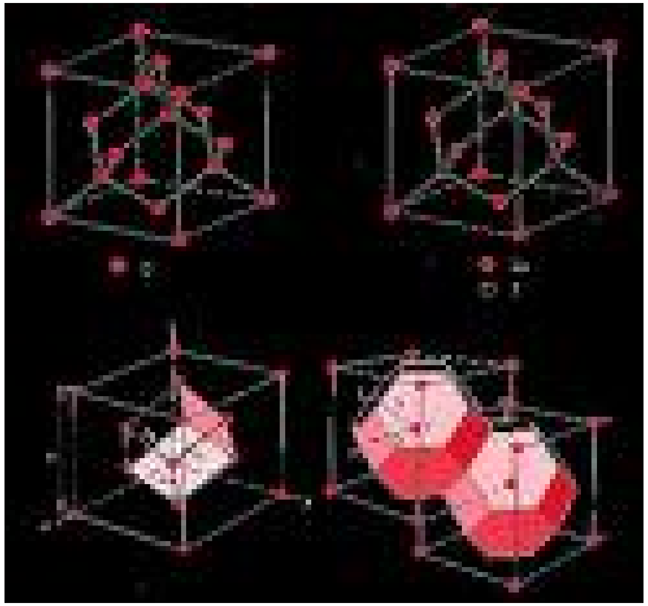
for all lattice point position vectors **R**. This reciprocal lattice is itself a Bravais lattice, and the reciprocal of the reciprocal lattice is the original lattice.
For an infinite three dimensional lattice, defined by its primitive vectors $(\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3})$, its reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through the formulae

$$\mathbf{b_1} = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$

$$\mathbf{b_2} = 2\pi \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_2} \cdot (\mathbf{a_3} \times \mathbf{a_1})}$$

$$\mathbf{b_3} = 2\pi \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_3} \cdot (\mathbf{a_1} \times \mathbf{a_2})}.$$





Reciprocal lattice of FCC is BCC

Reciprocal lattice of BCC is FCC

Density of Phonon States

The phonon density of states gives the number of modes per unit frequency per unit volume of real space.

For 1D: $D(\omega) = (1/\mathrm{L})(d\mathrm{N}/d\omega) = (1/\mathrm{L})(d\mathrm{N}/d\mathrm{K})(d\mathrm{K}/d\omega) = (1/(\pi v_g))$

For 2D: $D(\omega) = (1/\mathrm{L}^2)(d\mathrm{N}/d\omega) = (\mathrm{K}/(2\pi v_g))$

For 3D: $D(\omega) = (1/\mathrm{L}^3)(d\mathrm{N}/d\omega) = (\mathrm{K}^2/(2\pi^2 v_g))$

Phonon heat capacity

Heat capacity at constant volume

$$C_v = (\partial U/\partial T)_v$$

Debye Model

$$\omega = vK$$

$$D(\omega) = (1/L^3)(dN/d\omega) = (K^2/(2\pi^2 v_g)) = (\omega^2/(2\pi^2 v^3))$$

$$U = \int D(\omega)\langle n(\omega)\rangle\hbar\omega \, d\omega$$

$$N = \int^{\omega_D} D(\omega)\, d\omega$$

$$C_v = (\partial U/\partial T)_v = 2.4\pi^4 N k_B (T/\theta)^3$$