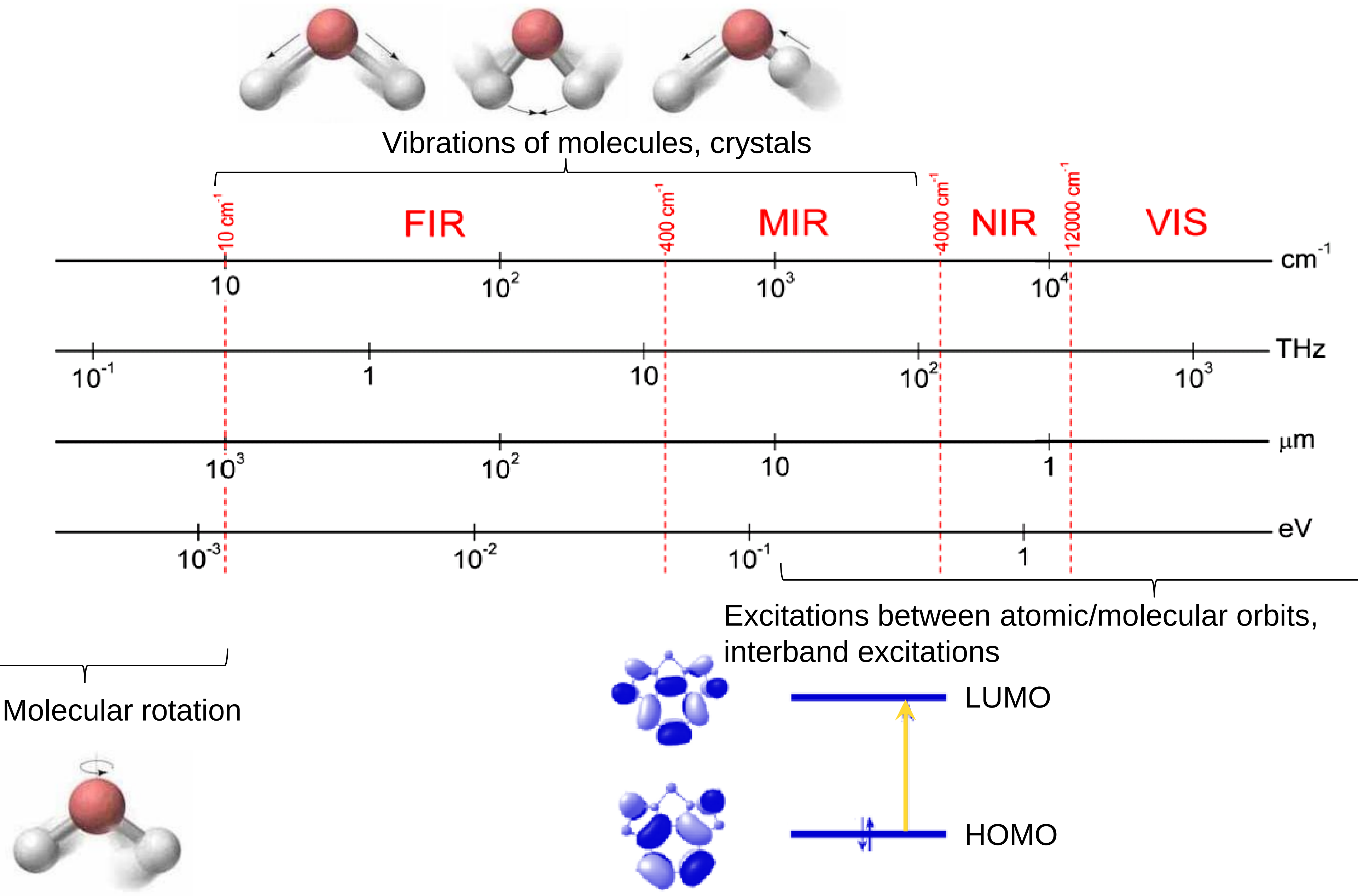
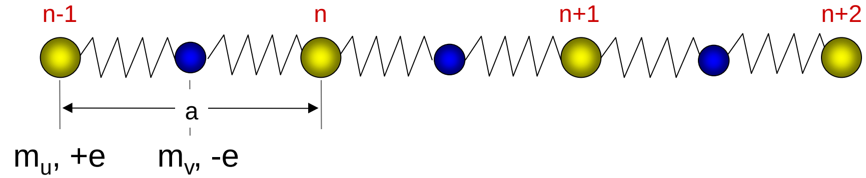
Spectroscopy of electronic excitations



Spectroscopy of electronic excitations

$$m_u \frac{d^2 u_n}{dt^2} = D(v_n + v_{n-1} - 2u_n) - \gamma m_u \frac{du_n}{dt} + eE(t)$$

$$m_v \frac{d^2 v_n}{dt^2} = D(u_n + u_{n-1} - 2v_n) - \gamma m_v \frac{dv_n}{dt} - eE(t)$$



$$\lambda >> a \Rightarrow q << \frac{\pi}{a} \Rightarrow \begin{cases} E(r,t) \approx E_\omega e^{i\omega t} \\ u_n(t) \approx u e^{-i\omega t} \\ v_n(t) \approx v e^{-i\omega t} \end{cases}$$

$$\mu = \frac{m_u m_v}{m_u + m_v} \qquad \omega_{TO} = \sqrt{\frac{2D}{\mu}} \qquad \Omega_{pl}^2 = \frac{ne^2}{\mu}$$

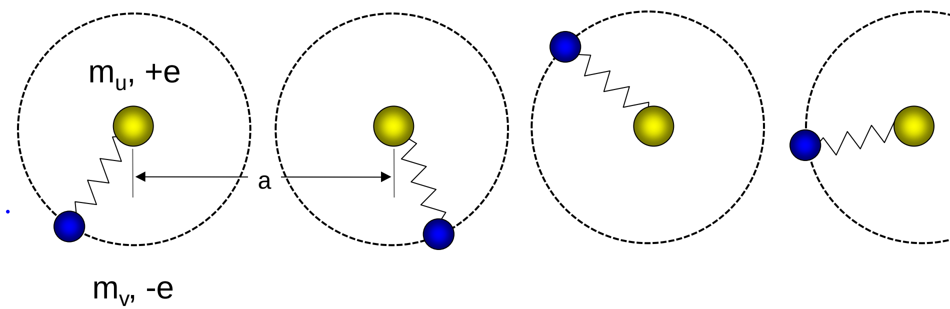
$$P_\omega = en(u_\omega - v_\omega) = \frac{ne^2}{\mu} \frac{1}{\omega_{TO}^2 - \omega^2 - i\gamma\omega} E_\omega$$

$$\varepsilon(\omega) = 1 + \chi(\omega) = 1 + \frac{\Omega_{pl}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega}$$

Bound charges in atoms

$m_u >> m_v$ $\rightarrow$ $$\omega_0 = \sqrt{D\frac{m_u + m_v}{m_u m_v}} \approx \sqrt{\frac{D}{m_v}}$$

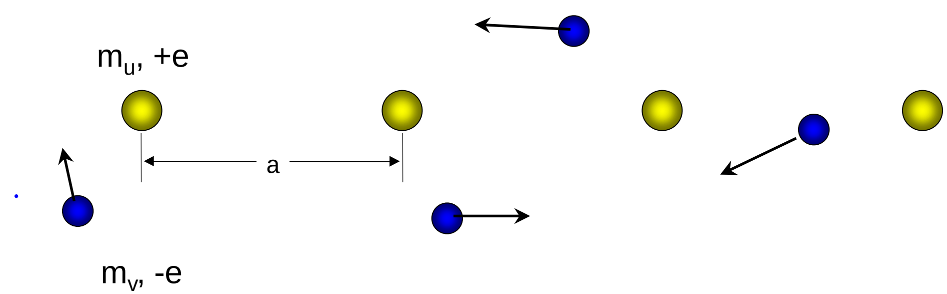
$$\varepsilon(\omega) = 1 + \frac{\Omega_{pl}^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$



Itinerant (metallic) electrons

$m_u >> m_v$ & D=0 $\rightarrow$ $$\begin{cases} \omega_0 = 0 \\ \Omega_{pl}^2 = \frac{ne^2}{m_v} \end{cases}$$

$$\varepsilon(\omega) = 1 - \frac{\Omega_{pl}^2}{\omega^2 + i\gamma\omega}$$



Spectroscopy of electronic excitations

Itinerant (metallic) electrons: Drude model

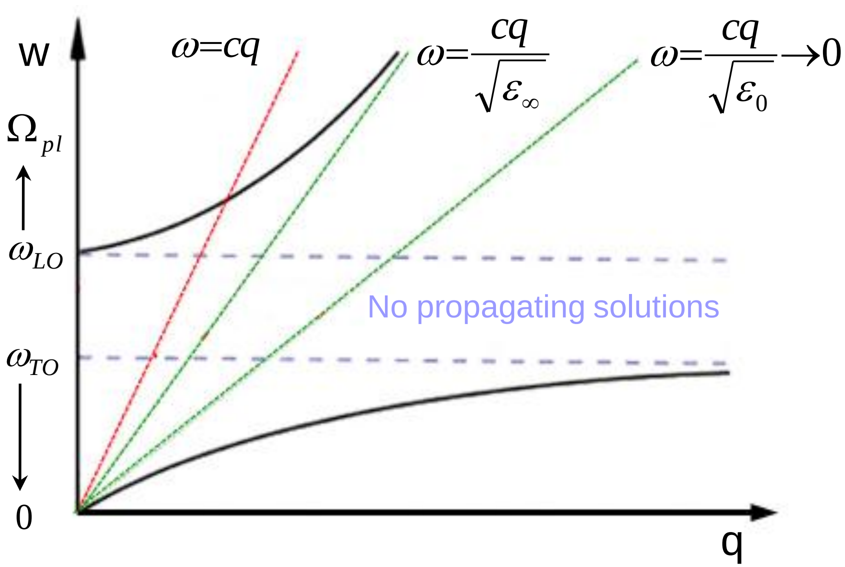
$$\varepsilon(\omega)=1-\frac{ne^2}{m_v}\frac{1}{\omega^2+i\gamma\omega}=1-\frac{\Omega_{pl}^2}{\omega^2+i\gamma\omega}$$

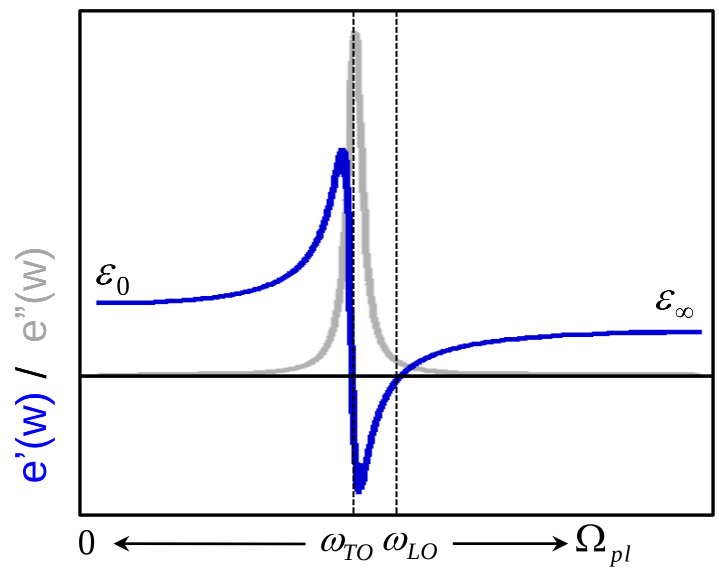
Wave equation:

$$0=\mathbf{q}\times(\mathbf{q}\times\mathbf{E}_{\mathbf{q},\omega})+\frac{\omega^2}{c^2}\varepsilon(\omega)\mathbf{E}_{\mathbf{q},\omega}=\mathbf{q}\times(\mathbf{q}\times\mathbf{E}_{\mathbf{q},\omega})+\frac{\omega^2}{c^2}\left(1-\frac{\Omega_{pl}^2}{\omega^2}\right)\mathbf{E}_{\mathbf{q},\omega} \qquad \Omega_{pl}^2>>\gamma$$

Longitudinal solution $\quad 0=\mathbf{q}\times\mathbf{E}_{\mathbf{q},\omega}\Leftrightarrow\varepsilon(\omega)=0\Rightarrow\omega=\Omega_{pl}$

Dispersion relation: $\quad q^2=\frac{\omega^2}{c^2}\varepsilon(\omega)=\frac{\omega^2}{c^2}\left(1-\frac{\Omega_{pl}^2}{\omega^2}\right)\Rightarrow\omega(q)=\sqrt{\frac{c^2q^2+\Omega_{pl}^2}{1}}$





Spectroscopy of electronic excitations

Itinerant (metallic) electrons: Drude model

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Wave equation:

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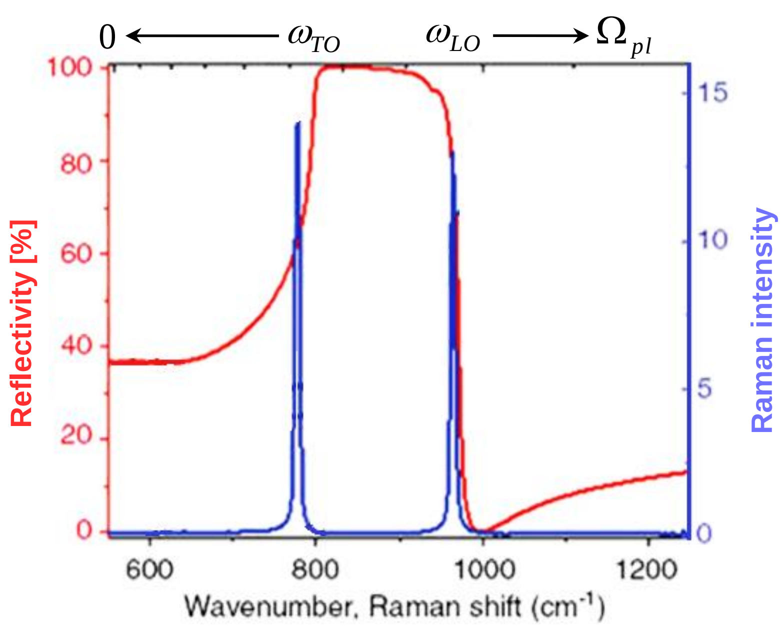
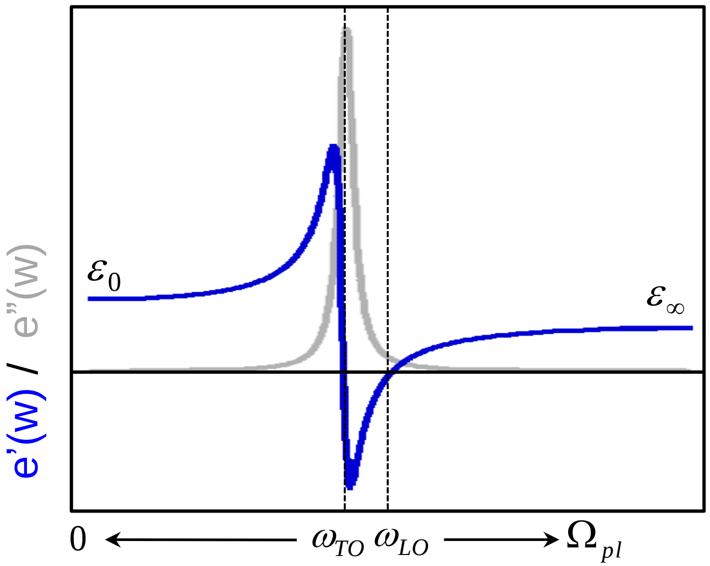




Spectroscopy of electronic excitations

Itinerant (metallic) electrons: Drude model

$$\varepsilon(\omega)=\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2+i\gamma\omega}=\left[\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2+\gamma^2}\right]+i\left[\frac{\Omega_{pl}^2}{\omega}\frac{\gamma}{\omega^2+\gamma^2}\right]=\varepsilon'+i\varepsilon''\qquad \omega_{pl}=\frac{\Omega_{pl}}{\sqrt{\varepsilon_\infty}}$$

$\omega<<\gamma,\omega_{pl}$

$$\varepsilon(\omega)\approx i\left[\frac{\Omega_{pl}^2}{\gamma\omega}\right]\qquad \text{n≈k}$$

$$R(\omega)\approx 1-2\sqrt{\frac{2\gamma\omega}{\Omega_{pl}^2}}=1-2\sqrt{\frac{2\varepsilon_0\omega}{\sigma_0}}$$

$\gamma<<\omega<<\omega_{pl}$

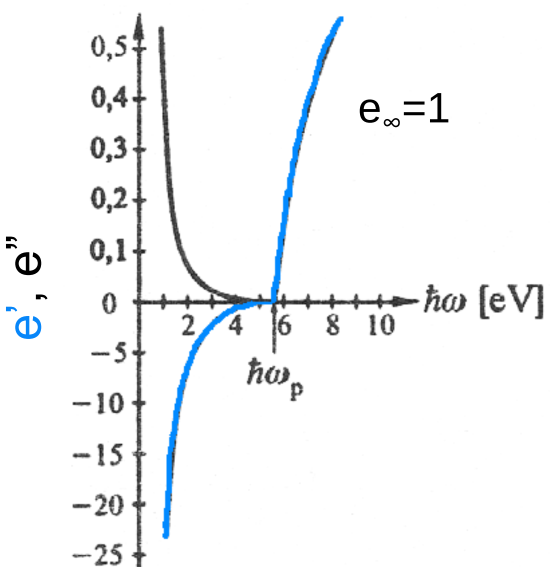
$$\varepsilon(\omega)\approx\left[\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2}\right]+i\left[\frac{\gamma\Omega_{pl}^2}{\omega^3}\right]\qquad \text{n«k}$$

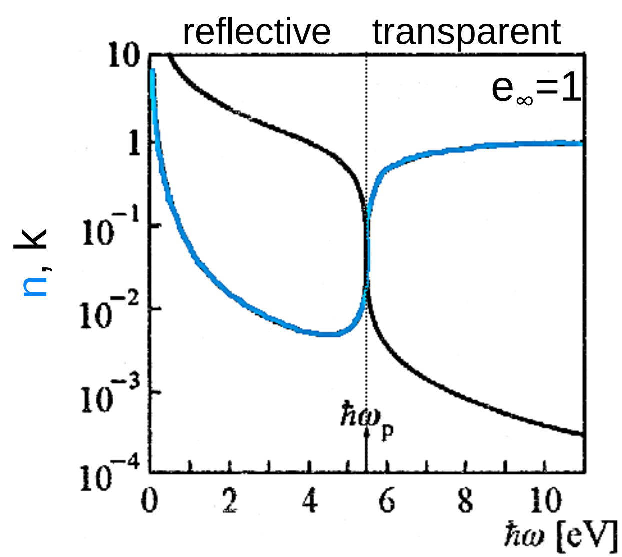
$$R(\omega)\approx 1-\frac{4n}{k^2}\approx 1-\frac{2\gamma}{\Omega_{pl}}$$

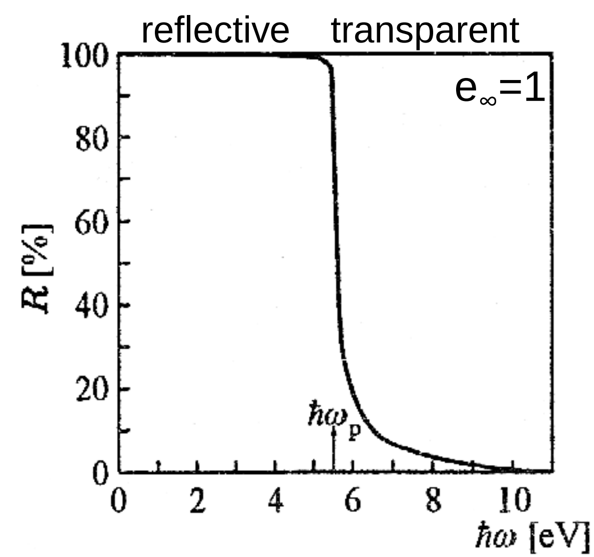
$\gamma,\omega_{pl}<<\omega$

$$\varepsilon(\omega)\approx\left[\varepsilon_\infty-\frac{\omega_{pl}^2}{\omega^2}\right]+i\cdot 0\qquad \text{k ≈0}$$

$$R(\omega)\approx\left|\frac{1-\sqrt{\varepsilon_\infty}}{1+\sqrt{\varepsilon_\infty}}\right|^2,\quad T(\omega)\approx 1$$







Spectroscopy of electronic excitations

Itinerant (metallic) electrons: Drude model

$$\varepsilon(\omega)=\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2+i\gamma\omega}=\left[\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2+\gamma^2}\right]+i\left[\frac{\Omega_{pl}^2}{\omega}\frac{\gamma}{\omega^2+\gamma^2}\right]=\varepsilon'+i\varepsilon''$$

$$\omega_{pl}=\frac{\Omega_{pl}}{\sqrt{\varepsilon_\infty}}$$

$\omega<<\gamma,\omega_{pl}$

$$\varepsilon(\omega)\approx i\left[\frac{\Omega_{pl}^2}{\gamma\omega}\right] \quad \text{n≈k}$$

$$R(\omega)\approx1-2\sqrt{\frac{2\gamma\omega}{\Omega_{pl}^2}}=1-2\sqrt{\frac{2\varepsilon_0\omega}{\sigma_0}}$$

$\gamma<<\omega<<\omega_{pl}$

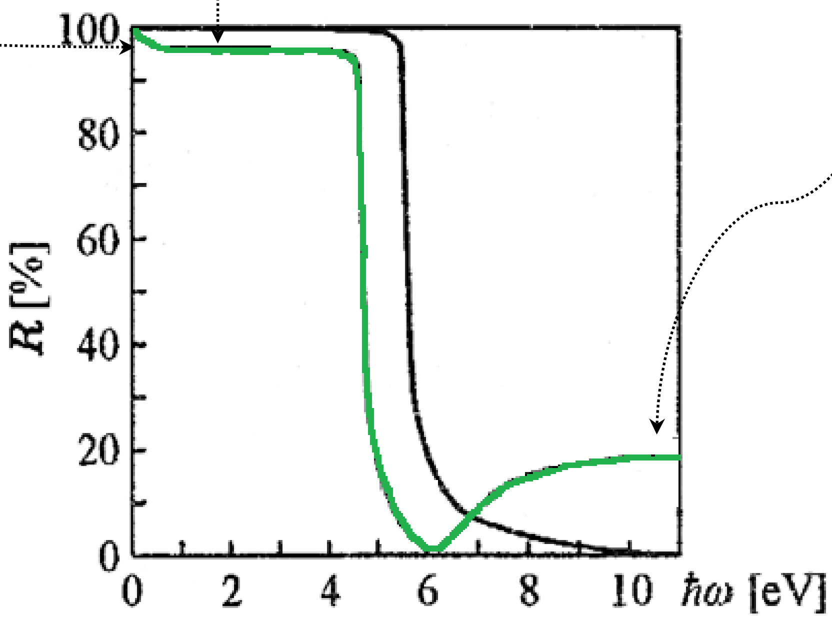
$$\varepsilon(\omega)\approx\left[\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2}\right]+i\left[\frac{\gamma\Omega_{pl}^2}{\omega^3}\right] \quad \text{n«k}$$

$$R(\omega)\approx1-\frac{4n}{k^2}\approx1-\frac{2\gamma}{\Omega_{pl}}$$

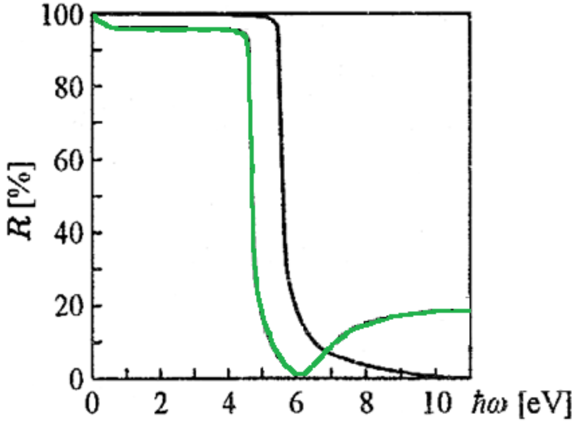
$\gamma,\omega_{pl}<<\omega$

$$\varepsilon(\omega)\approx\left[\varepsilon_\infty-\frac{\omega_{pl}^2}{\omega^2}\right]+i\cdot0 \quad \text{k ≈0}$$

$$R(\omega)\approx\left|\frac{1-\sqrt{\varepsilon_\infty}}{1+\sqrt{\varepsilon_\infty}}\right|^2, \quad T(\omega)\approx1$$



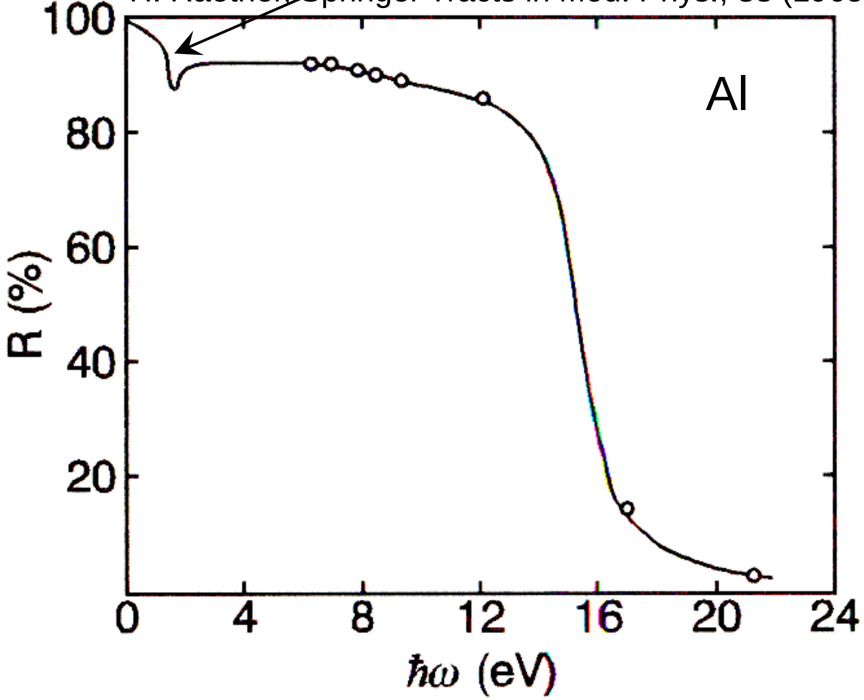
Spectroscopy of electronic excitations



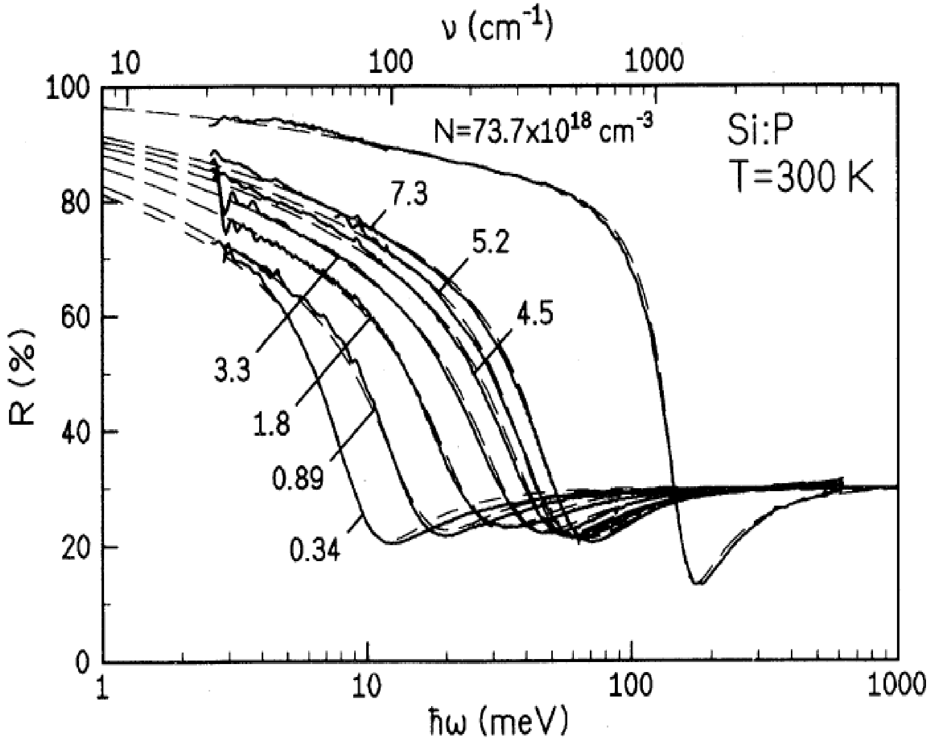
Plasmaedge touches the continuum of the interband excitations, the reflectivity does not drop

Al

H. Raether, Springer Tracts in Mod. Phys., **38** (1965)

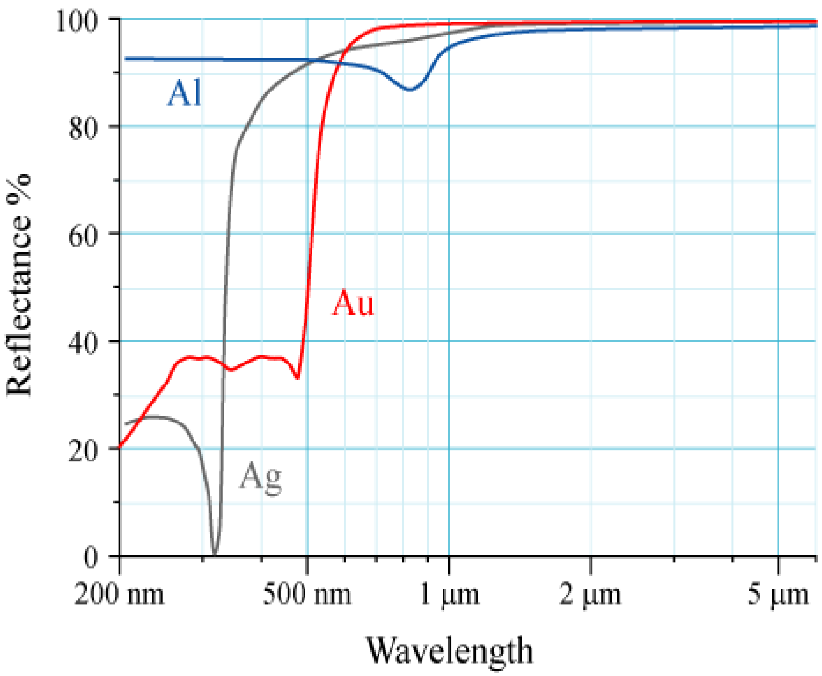


Si:P A. Gaymann, Phys. Rev. B **52**, 16486 (1995)

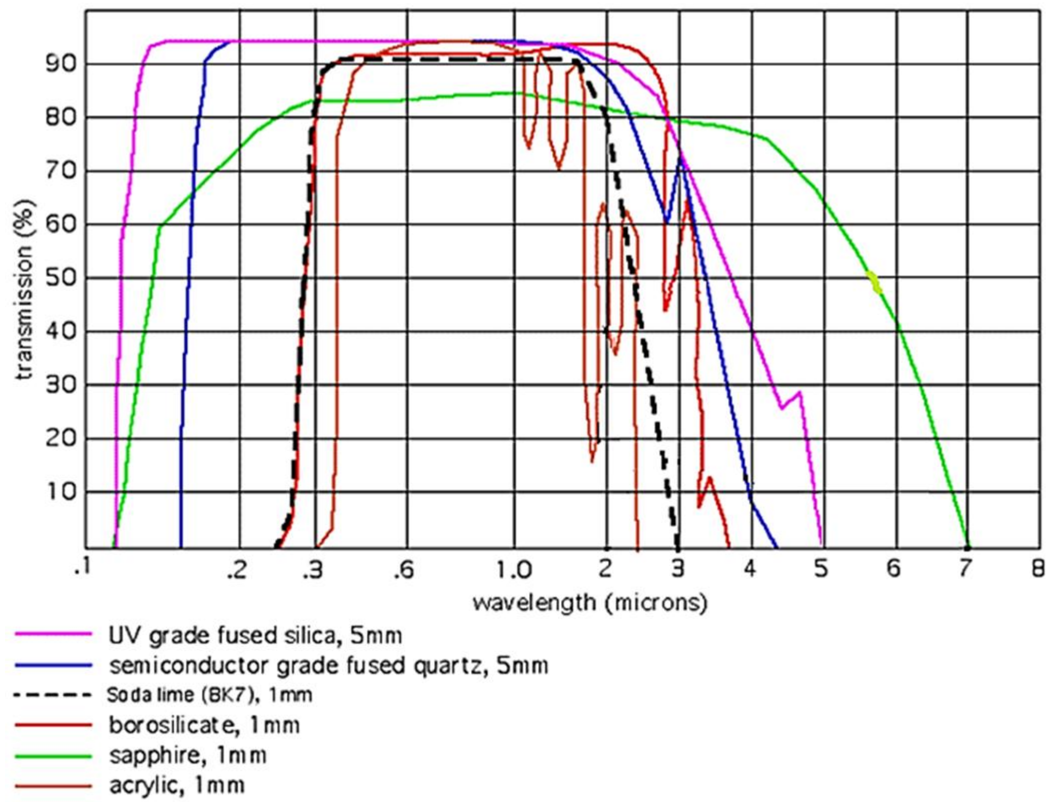


Spectroscopy of electronic excitations

Metals used on reference mirrors



Insulators, semiconductors often used in lenses, windows, cuvette



Spectroscopy of electronic excitations

An electron in electromagnetic fields: $H = \frac{(\mathbf{p}+e\mathbf{A})^2}{2m} - e\Phi + \frac{e}{m}\mathbf{BS} + \zeta\mathbf{LS}$

Hydrogen (like) atom: $H = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r} + \zeta\mathbf{LS}$

H_0 $\qquad$ H_{LS}

$$H_0 = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] + \frac{\hbar^2 \mathbf{l}^2}{2mr^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$[l_i, l_j] = i\varepsilon_{ijk} l_k$$

$$[l_i, \mathbf{l}^2] = 0$$

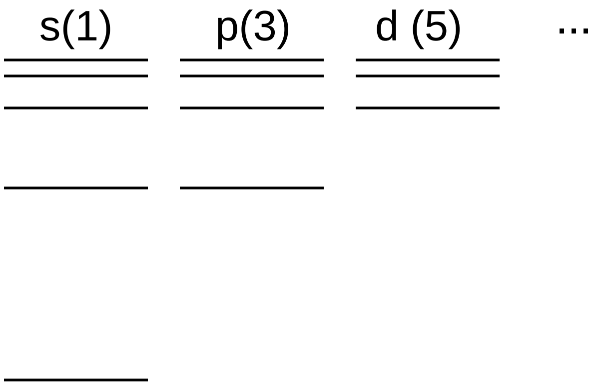
$$[l_i, H_0] = [\mathbf{l}^2, H_0] = 0$$

$$|nlm\rangle = R_{nl}(r) Y_l^m(\theta, \varphi)$$

$$\mathbf{l}^2 Y_l^m = l(l+1) Y_l^m$$

$$l_z Y_l^m = m Y_l^m$$

$$E_{nlm} = E_n = -R\frac{1}{n^2}$$



Spectroscopy of electronic excitations

Electromagnetic radiation: $V = -\mathbf{E}\boldsymbol{\mu}$

$$\boldsymbol{\mu} = e\mathbf{r}$$

Time dependent perturbation: $\langle f|V|i\rangle = \langle s_f|\langle n_f l_f m_f| -\mathbf{E}\boldsymbol{\mu} |n_i l_i m_i\rangle|s_i\rangle$

$$\langle f|V|i\rangle \propto \delta_{s_f s_i} \int Y_{l_f}^{m_f} Y_1^{0,\pm 1} Y_{l_i}^{m_i}\, d\Omega$$

Spherical harmonics [edit]

l = 0[1] [edit]

$$Y_0^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$$

l = 1[1] [edit]

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot e^{-i\varphi} \cdot \sin\theta = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \frac{(x-iy)}{r}$$

$$Y_1^{0}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \cos\theta = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \frac{z}{r}$$

$$Y_1^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot e^{i\varphi} \cdot \sin\theta = -\frac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \frac{(x+iy)}{r}$$

l = 2[1] [edit]

$$Y_2^{-2}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \cdot e^{-2i\varphi} \cdot \sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \cdot \frac{(x-iy)^2}{r^2}$$

$$Y_2^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot e^{-i\varphi} \cdot \sin\theta \cdot \cos\theta = \frac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot \frac{(x-iy)z}{r^2}$$

$$Y_2^{0}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}} \cdot (3\cos^2\theta - 1) = \frac{1}{4}\sqrt{\frac{5}{\pi}} \cdot \frac{(2z^2-x^2-y^2)}{r^2}$$

$$Y_2^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot e^{i\varphi} \cdot \sin\theta \cdot \cos\theta = -\frac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot \frac{(x+iy)z}{r^2}$$

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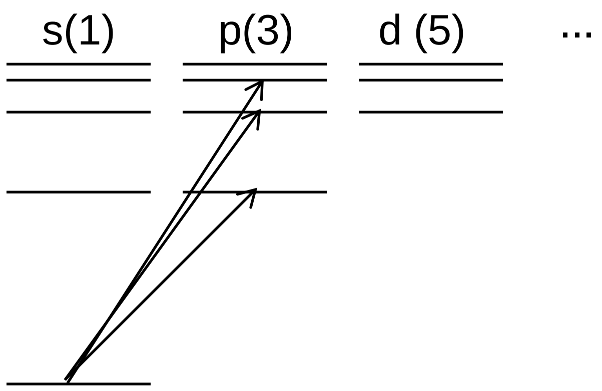
Selection rules:

I. $m_f = m_i + 0, \pm 1$

II. $|l_f - l_i| = \pm 1$



Spectroscopy of electronic excitations

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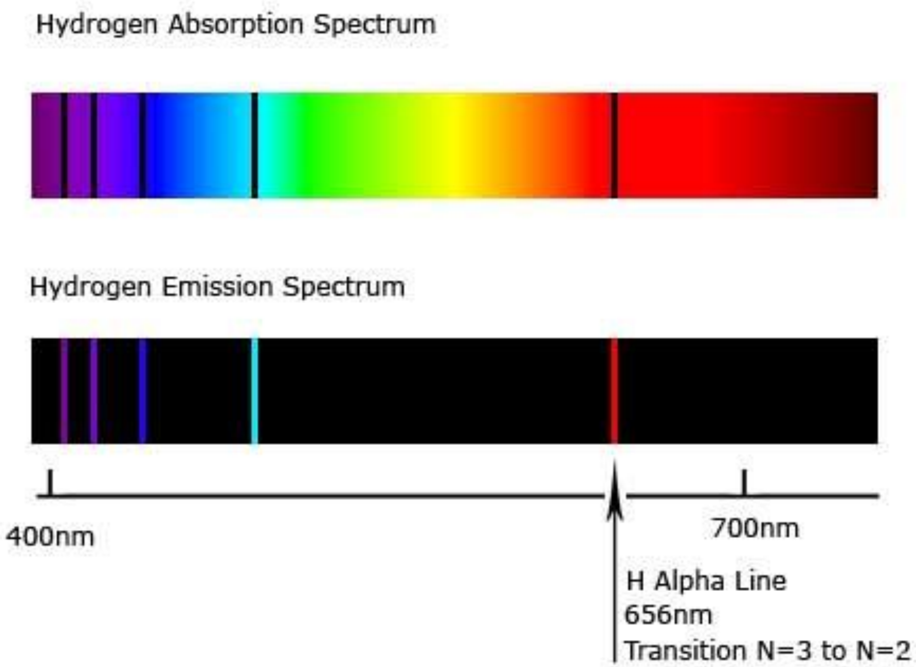
$$\langle f|V|i\rangle \propto \delta_{s_f s_i} \int Y_{l_f}^{m_f} Y_1^{0,\pm 1} Y_{l_i}^{m_i}\, d\Omega$$

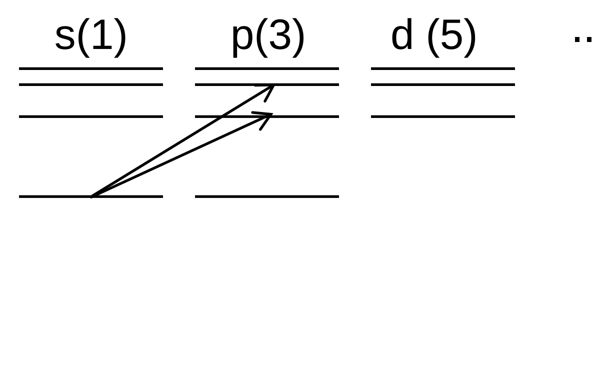
Balmer series (n=2): $\Delta E = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$

Selection rules:

I. $m_f = m_i + 0, \pm 1$

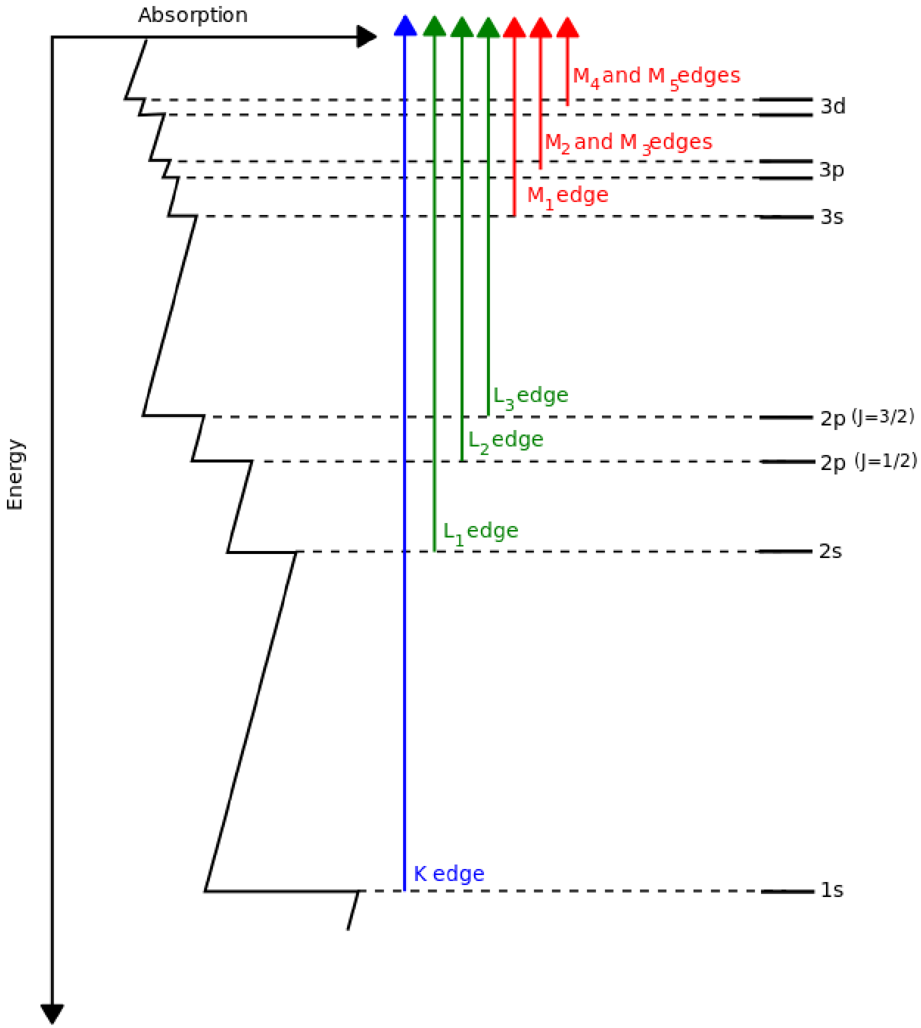
II. $|l_f - l_i| = \pm 1$



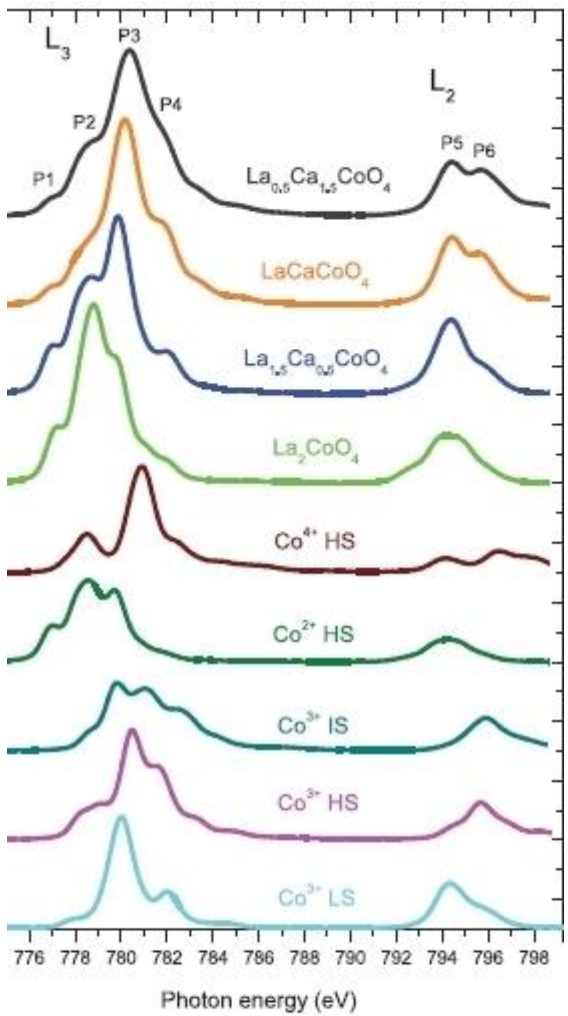


Spectroscopy of electronic excitations

X-ray absorption spectroscopy (XAS)

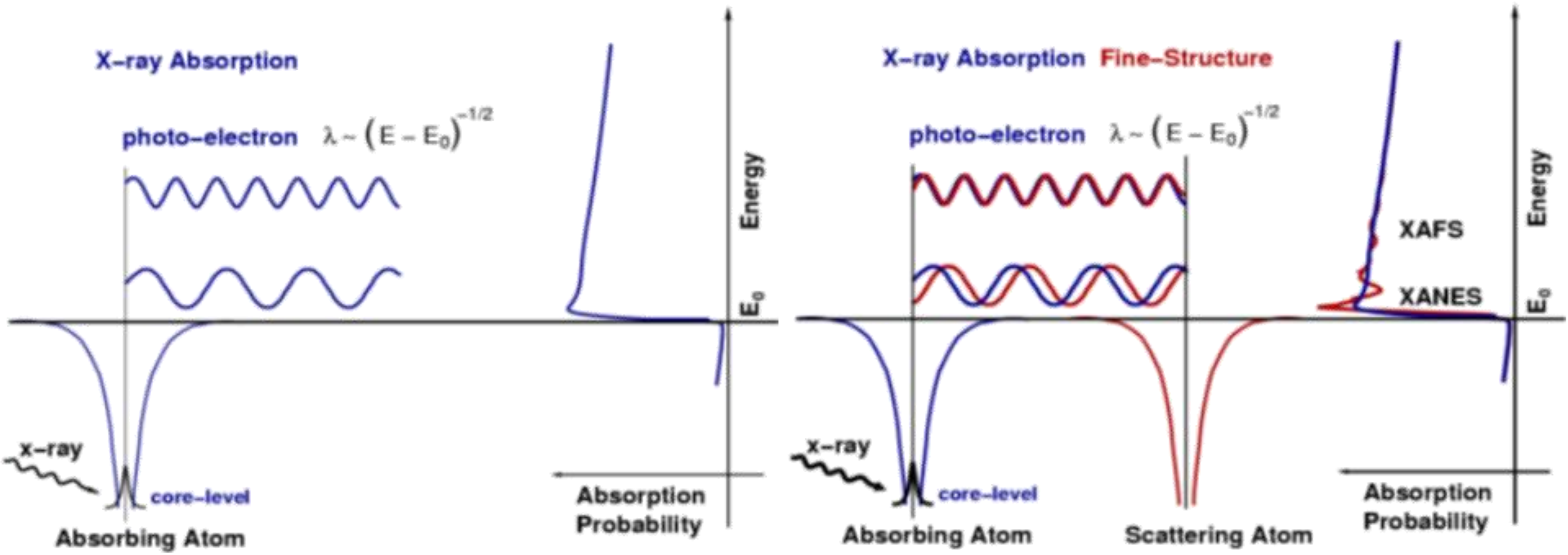


Sensitive:
composition, charge state, environment



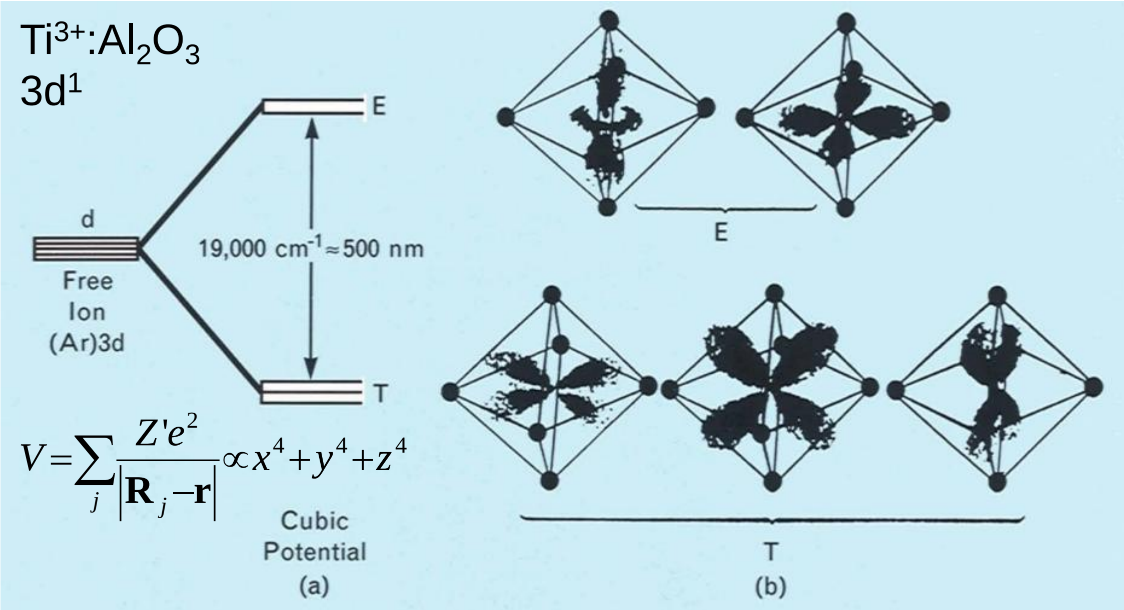
Spectroscopy of electronic excitations

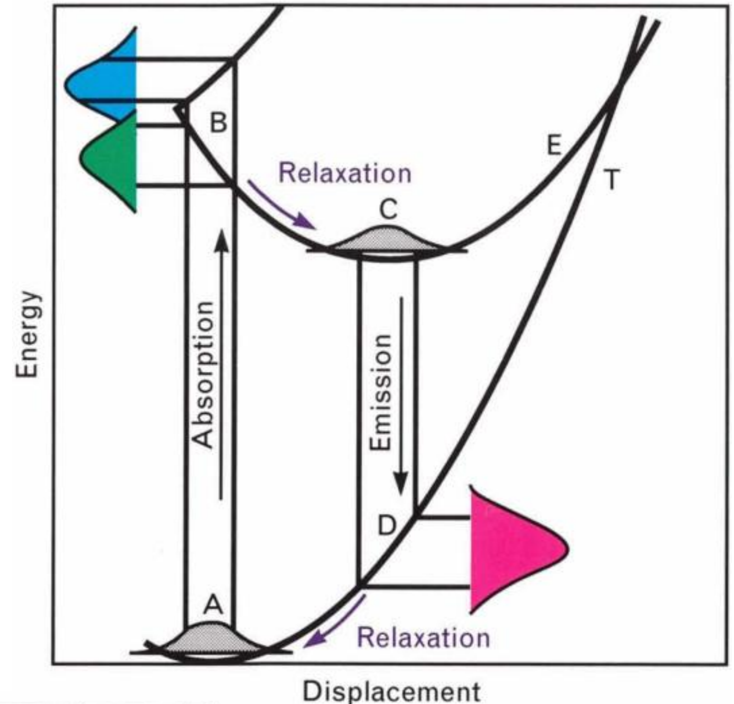
X-ray absorption spectroscopy (XAS)
XANES (**X**-ray **A**bsorption **N**ear **E**dge **S**tructure)
EXAFS (**E**xtended **X**-Ray **A**bsorption **F**ine **S**tructure)

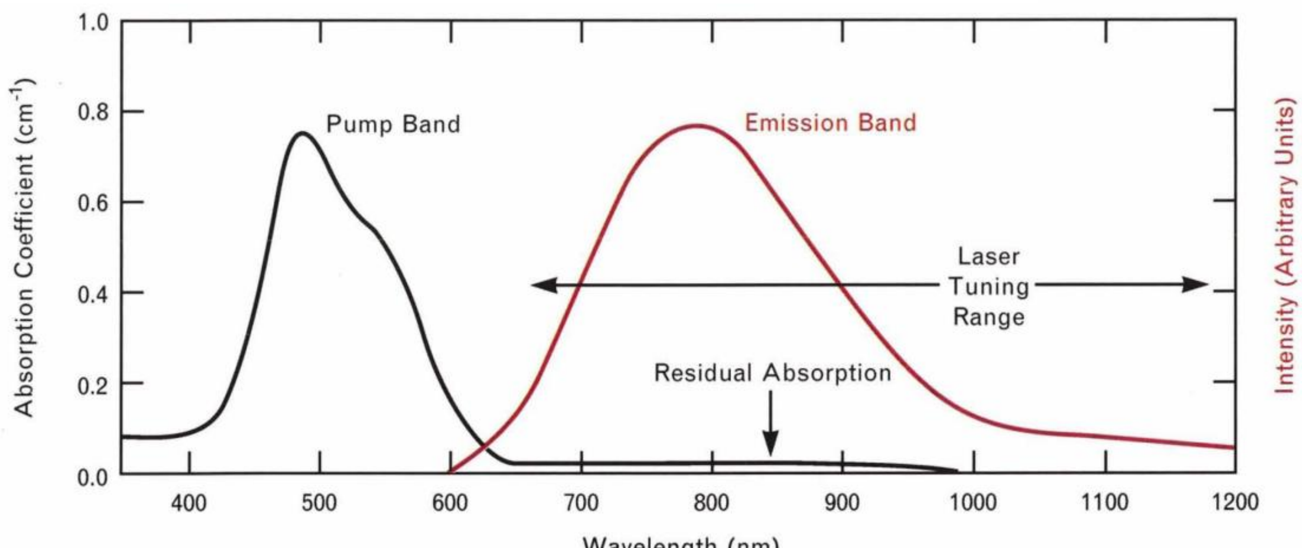


Spectroscopy of electronic excitations

Ti:sapphire LASER





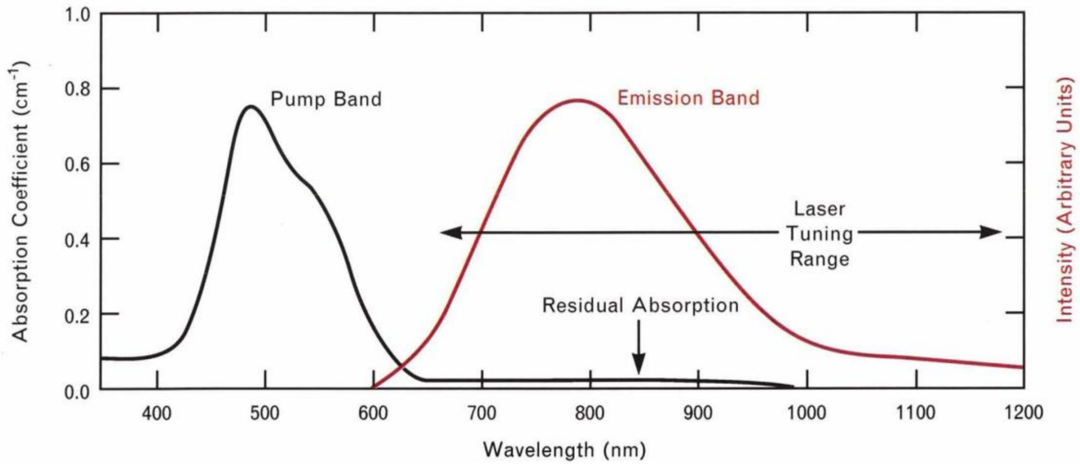


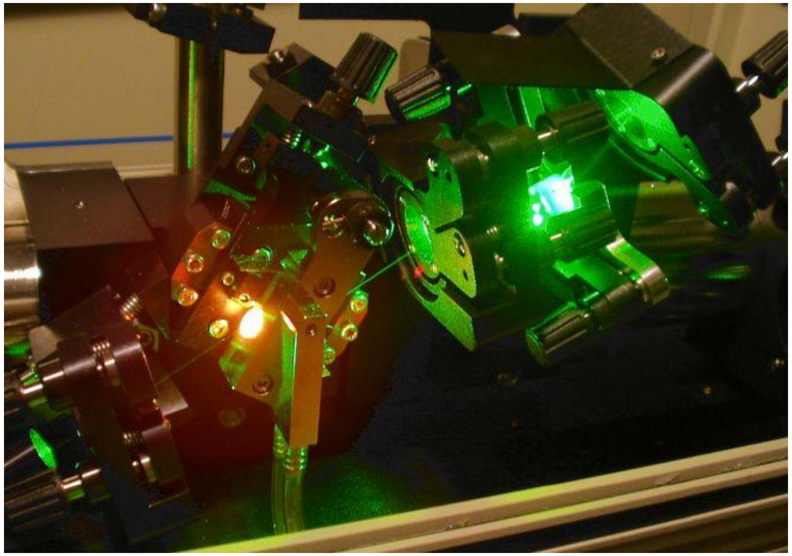
K.F. Wall and A. Sanchez. The Lincoln Laboratory Journal, 2 447 (1990)

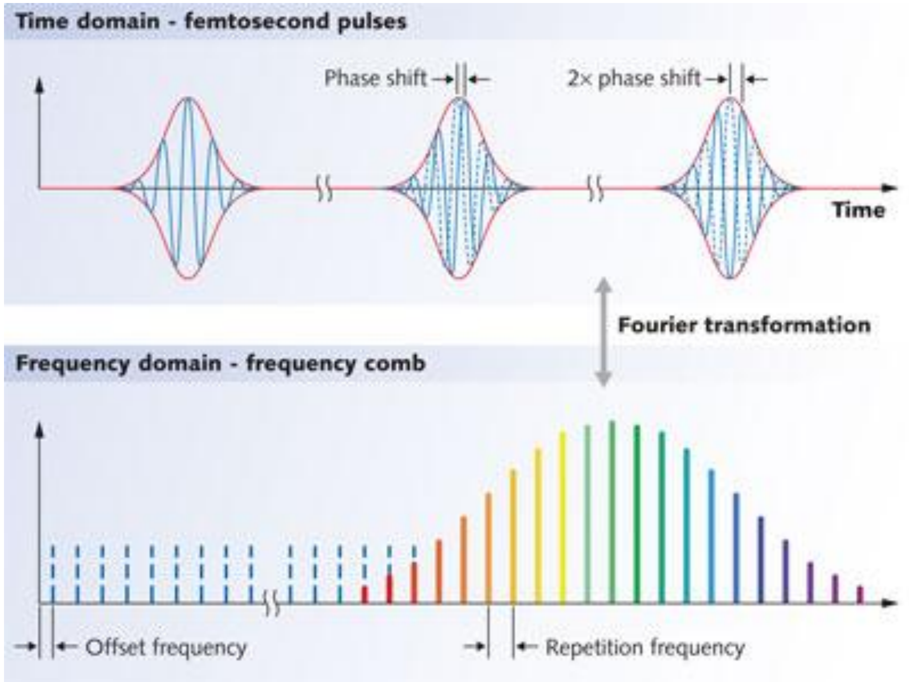
Spectroscopy of electronic excitations

Ti:sapphire LASER

Pump: green, lasing: NIR



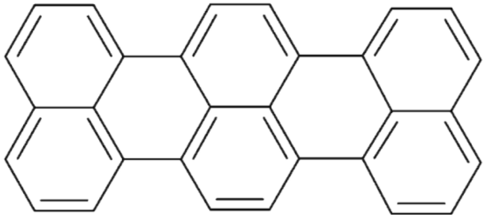




Cental wavelength: 800 nm (375 THz)
Pulse width: 10-100 fs
Repetition rate: 80 MHz ($\frac{c}{2L}$), resonantor: ~2 m

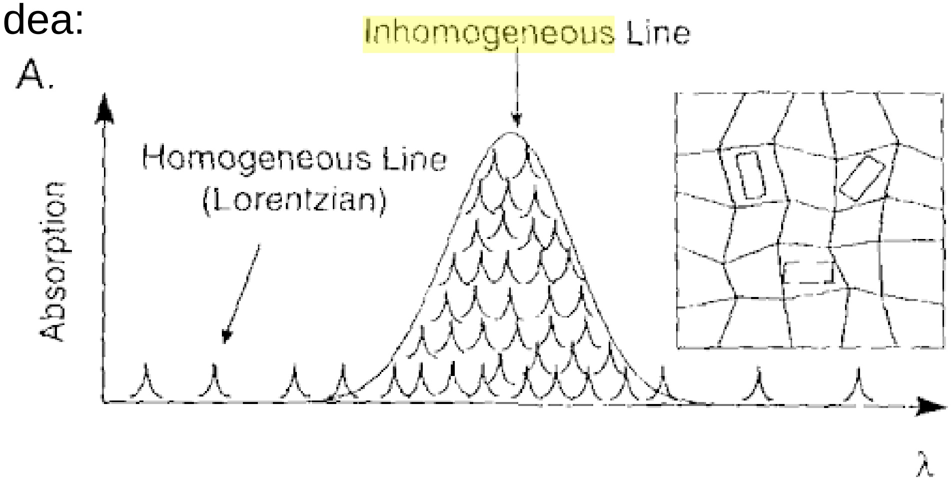
Spectroscopy of electronic excitations

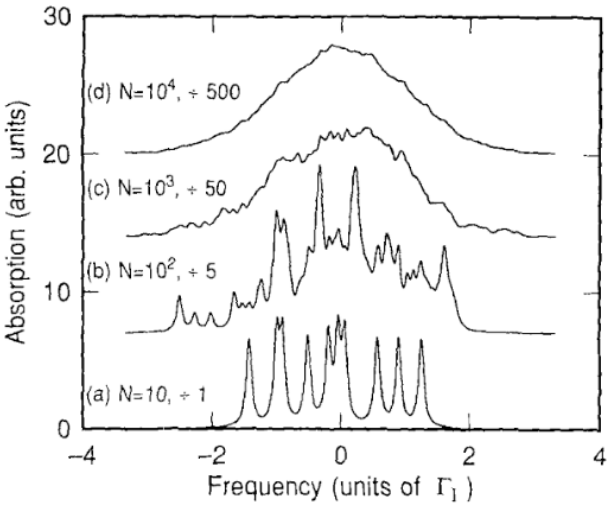
Terrilene



in para-Terphenyl

Idea:





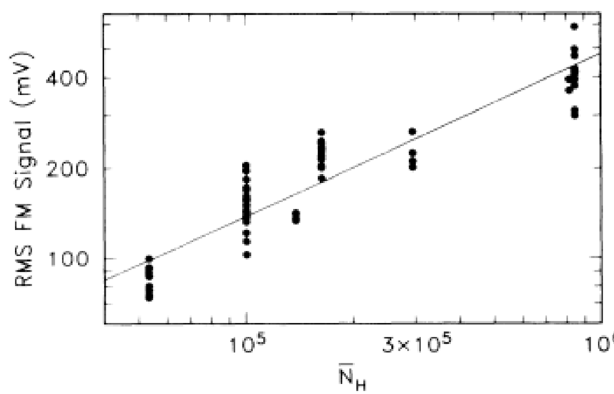
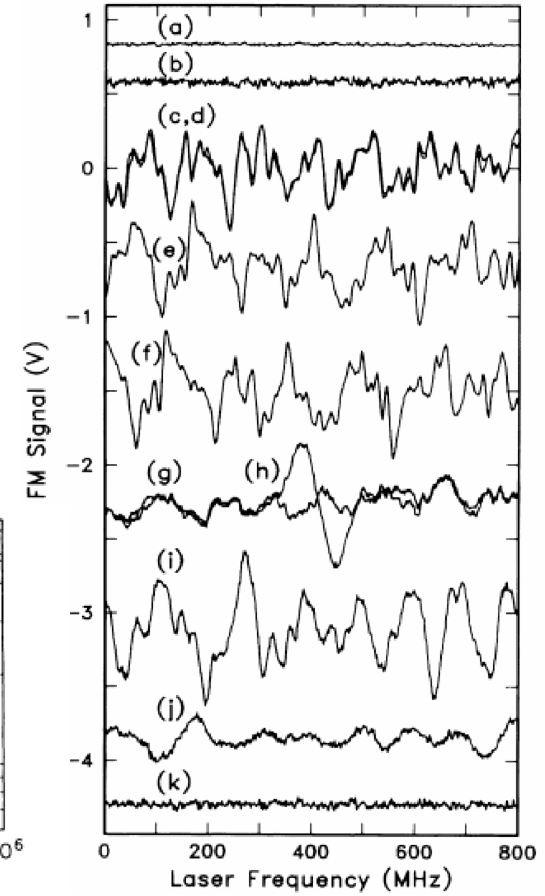


FIG. 2. rms amplitude of FM signal vs $\overline{N}_H$, with use of in-focus spectra similar to trace c in Fig. 1 with $\nu_m = 50$ MHz. The solid line is a least-squares fit with slope 0.54 ± 0.05.

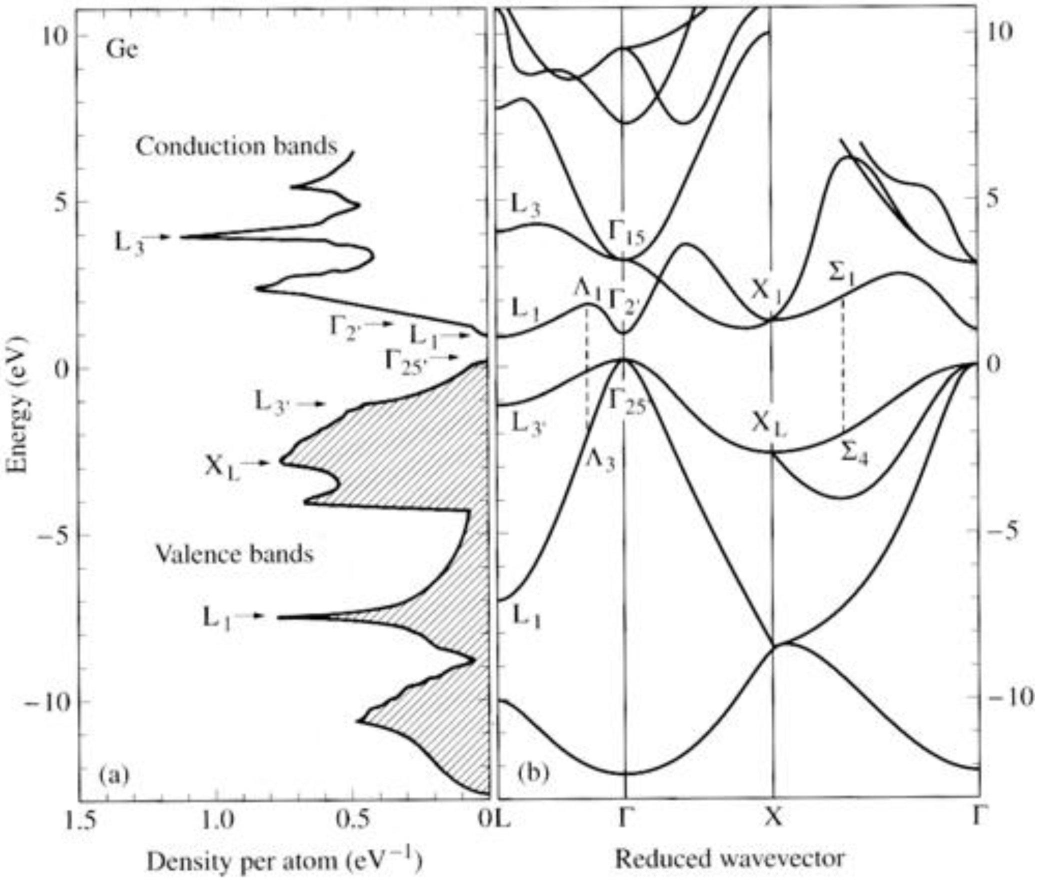
Experiment:

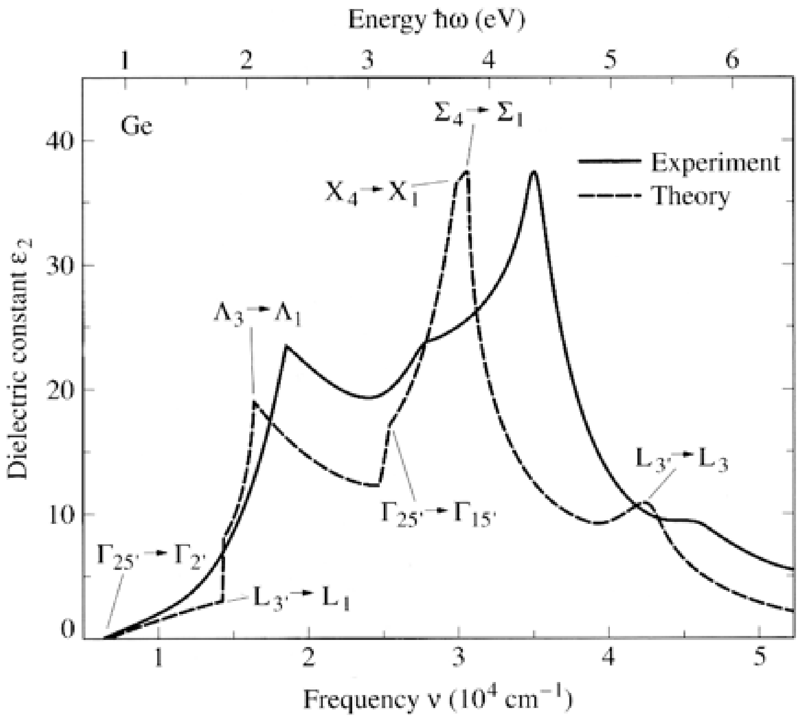


W.E. Moerner Nobel lecture (2014)

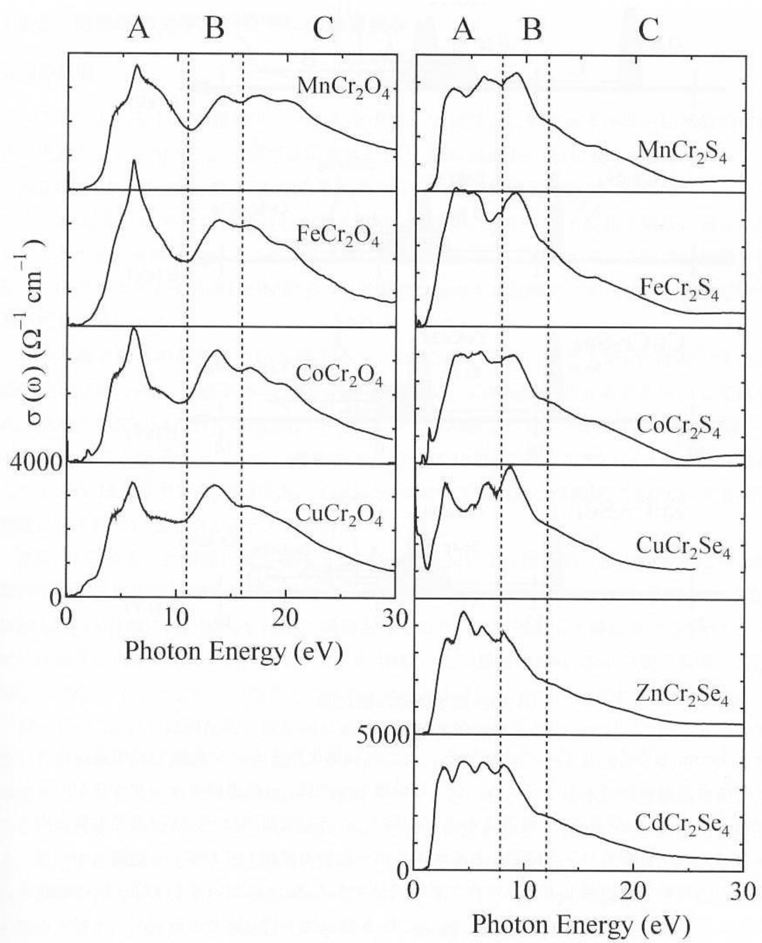
W. E. Moerner and T. P. Carter, Phys. Rev. Lett. 59, 2705 (1987).

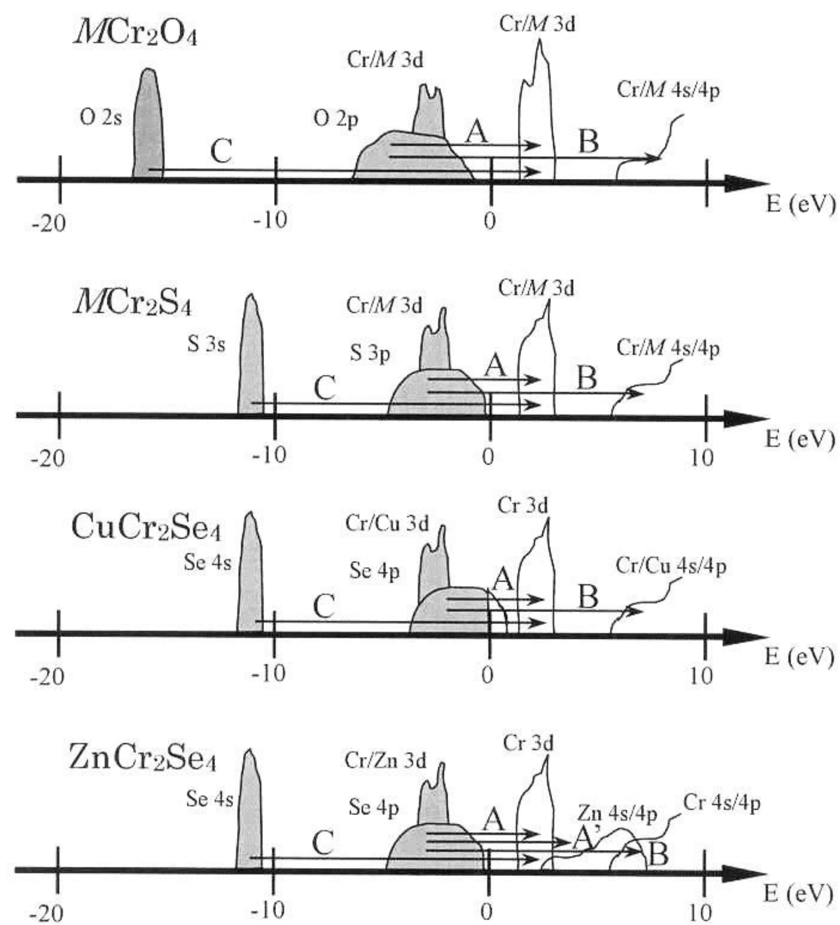
Bandstructure and absorption spectra of germanium





Interband transitions

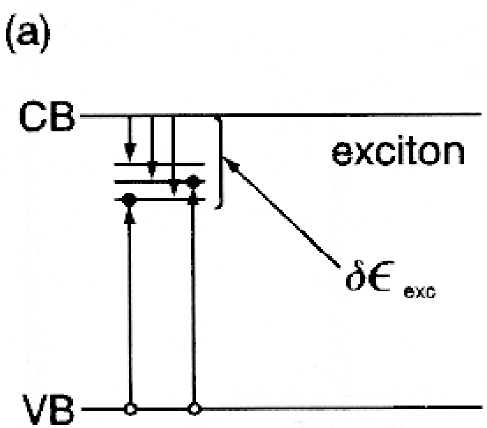




Spectroscopy of electronic excitations

Excitons

Cu_2O: direct transition through the band gap is forbidden
"p" type (l=1) excitons are allowed
P.W. Baumeister, PR **121**, 359 (1957)



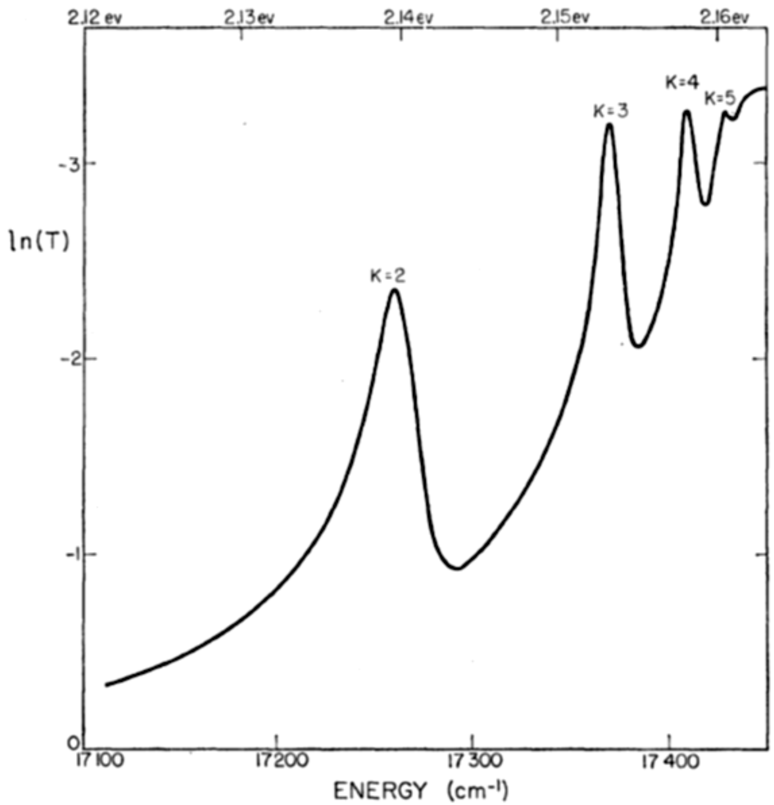


FIG. 6. The logarithm of the transmission as a function of photon energy of a Cu_2O sample at 77°K, showing the details of the yellow series of exciton lines.