Optical spectroscopy II.

Nanotechnology and Material Science
Lecture XII.
Department of Physics, BME
2024.

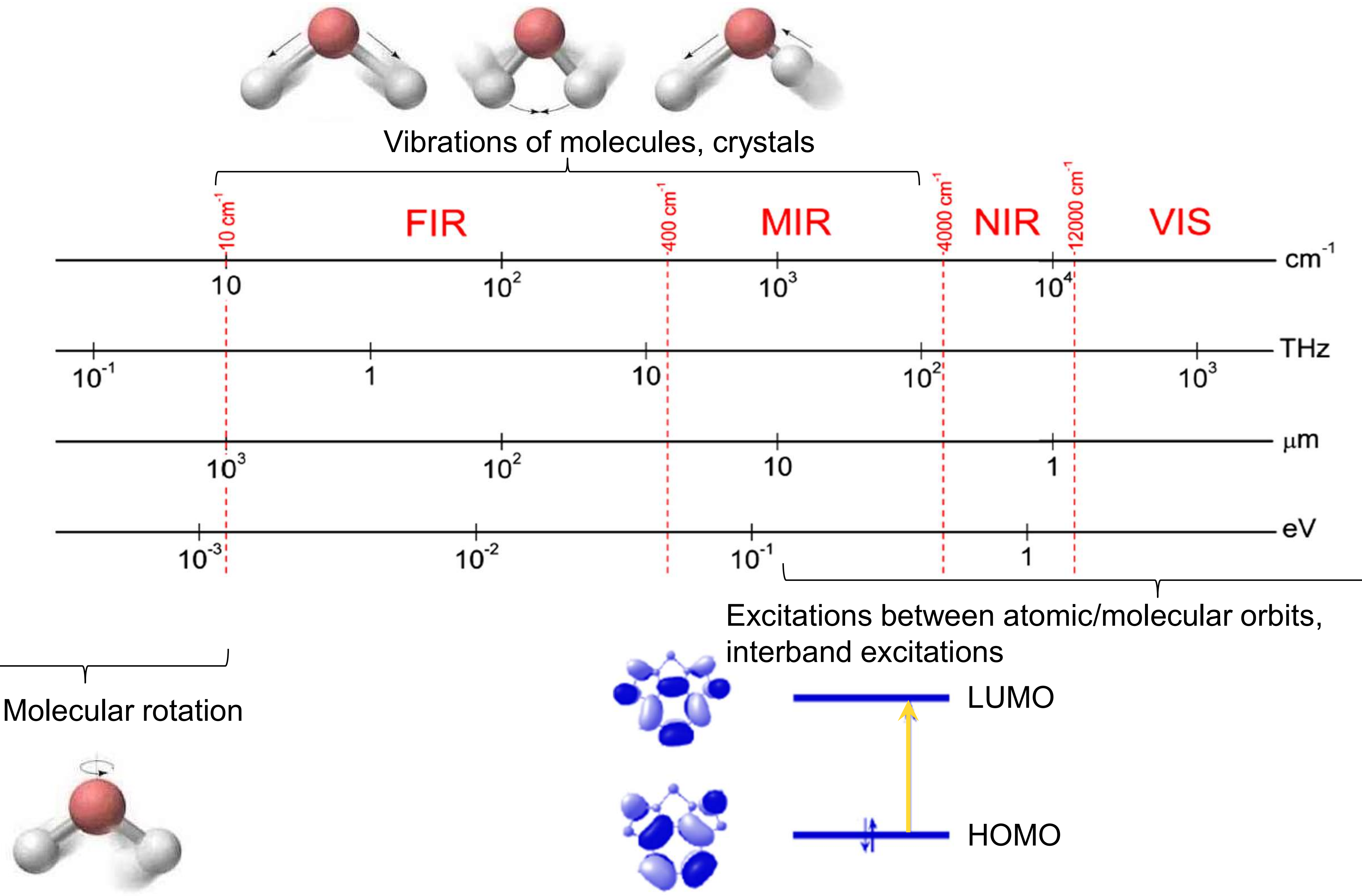
BMETE11MF58

Sándor Bordács

website: https://physics.bme.hu/BMETE11MF58_kov?language=en

Email: bordacs.sandor@ttk.bme.hu

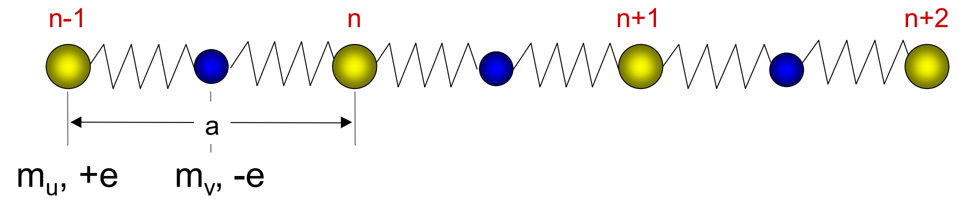
Spectroscopy of electronic excitations



Spectroscopy of electronic excitations

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

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



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

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

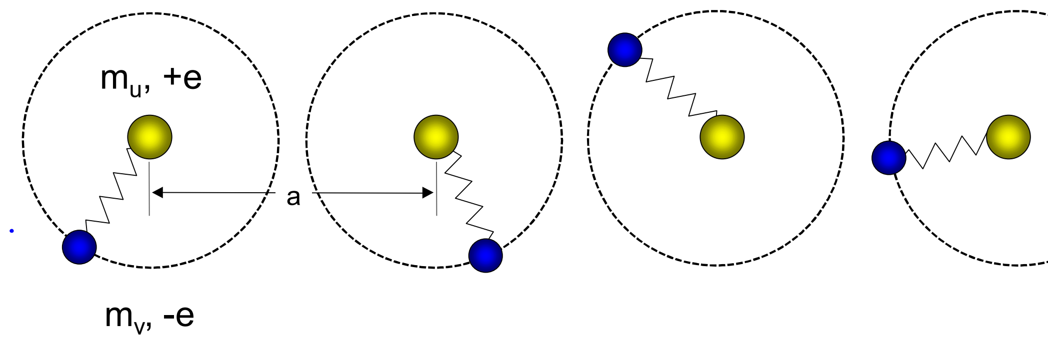
$$P_\omega = en(u_\omega - v_\omega) = \frac{ne^2}{\mu} \frac{1}{\omega_{TO}^2 - \omega^2 - i\gamma\omega} E_\omega$$

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

Bound charges in atoms

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

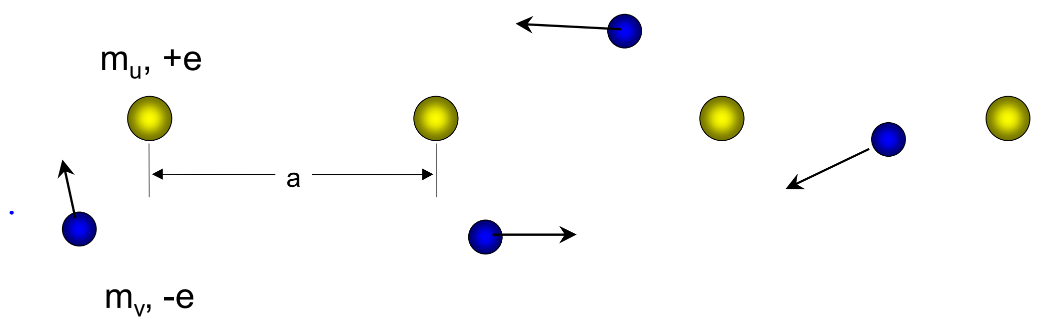
$$\varepsilon(\omega) = 1 + \frac{\Omega_{pl}^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$



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

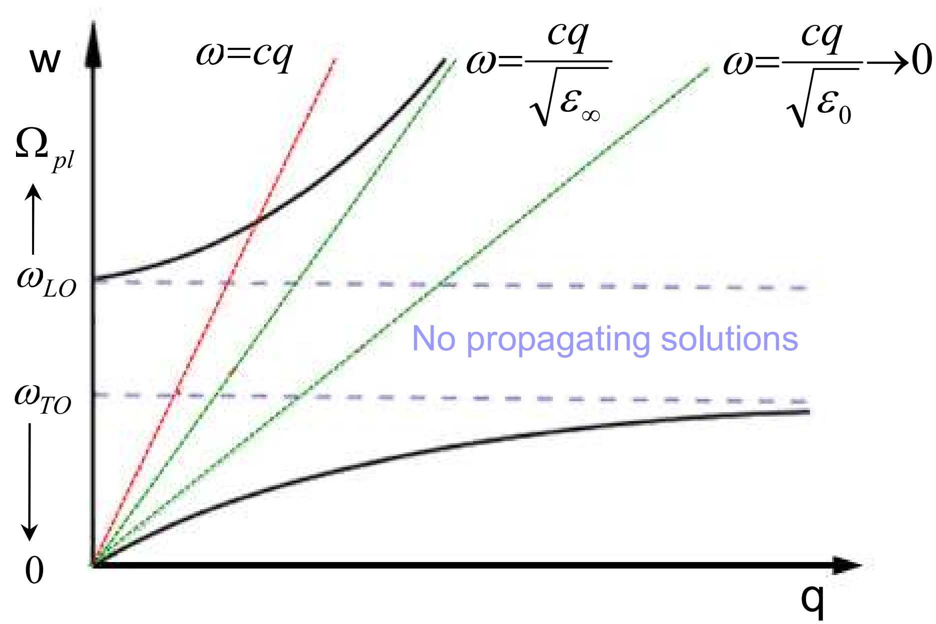
$$\varepsilon(\omega)=1-\frac{ne^2}{m_v}\frac{1}{\omega^2+i\gamma\omega}=1-\frac{\Omega_{pl}^2}{\omega^2+i\gamma\omega}$$

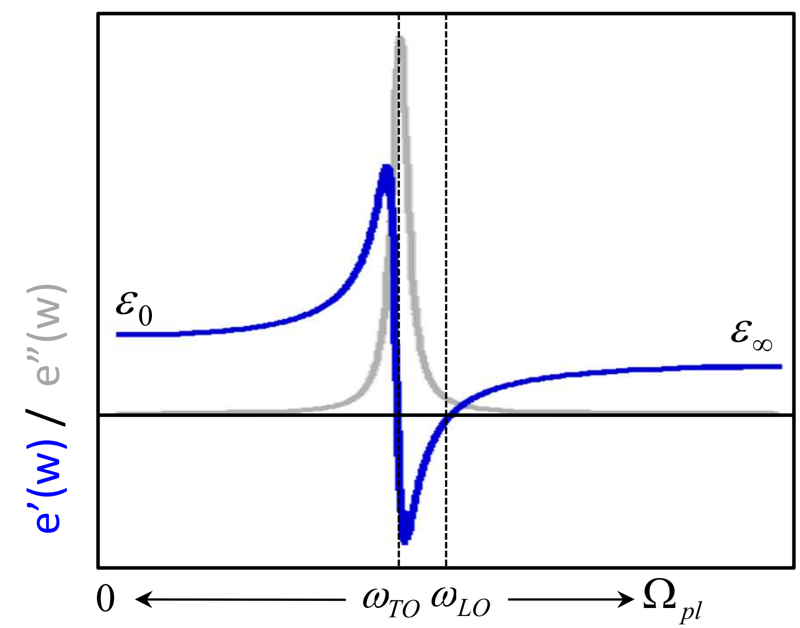
Wave equation:

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

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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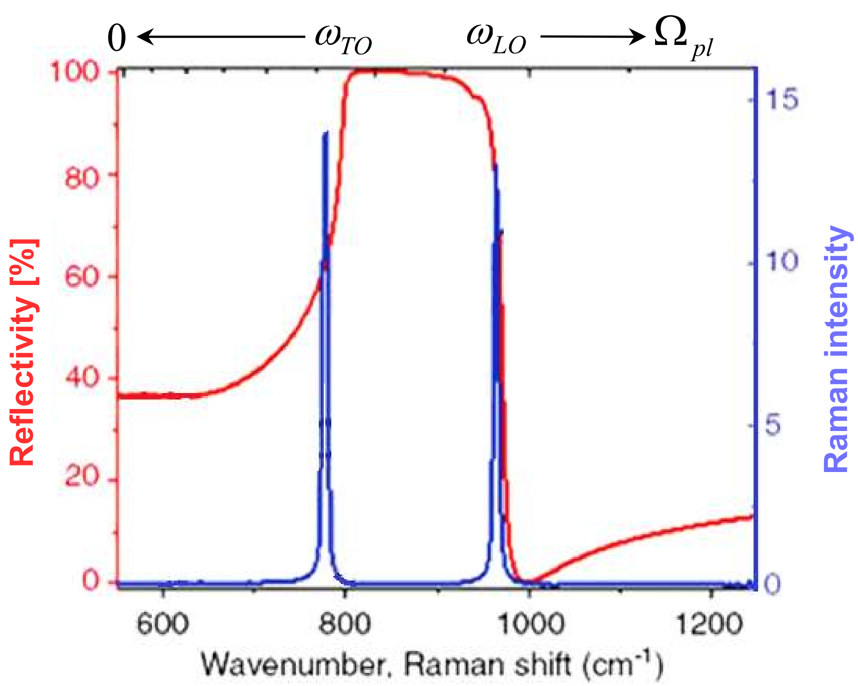
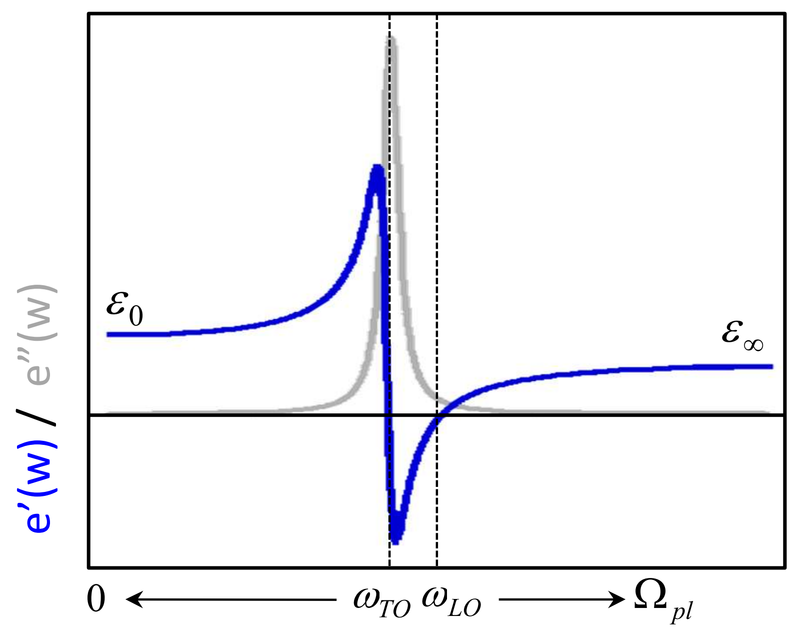




Spectroscopy of electronic excitations

Itinerant (metallic) electrons: Drude model

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

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

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

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

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

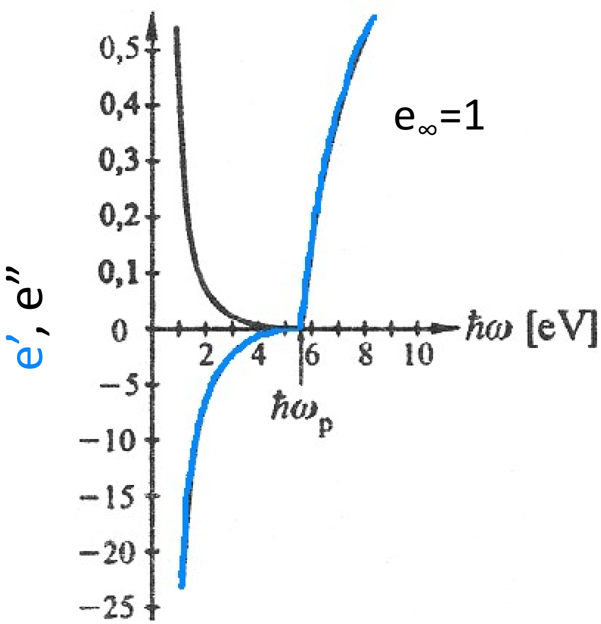
$$\varepsilon(\omega)\approx\left[\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2}\right]+i\left[\frac{\gamma\Omega_{pl}^2}{\omega^3}\right] \qquad n\ll k$$

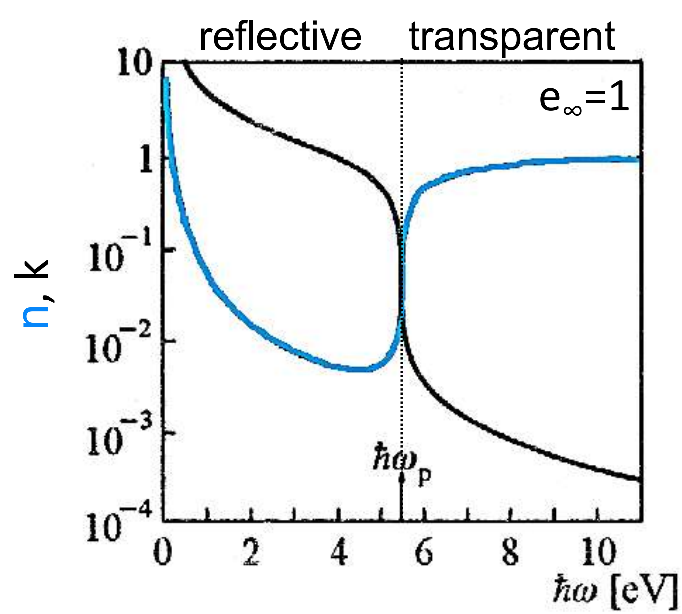
$$R(\omega)\approx 1-\frac{4n}{k^2}\approx 1-\frac{2\gamma}{\Omega_{pl}}$$

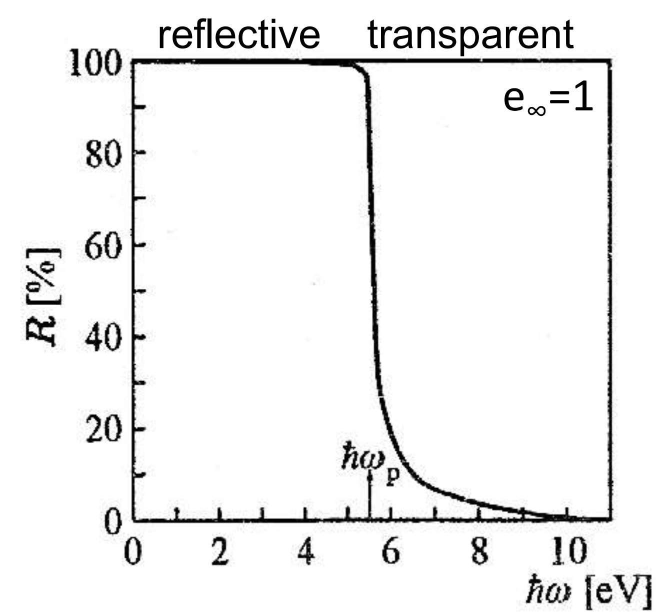
$\gamma,\omega_{pl}<<\omega$

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

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







Spectroscopy of electronic excitations

Itinerant (metallic) electrons: Drude model

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

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

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

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

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

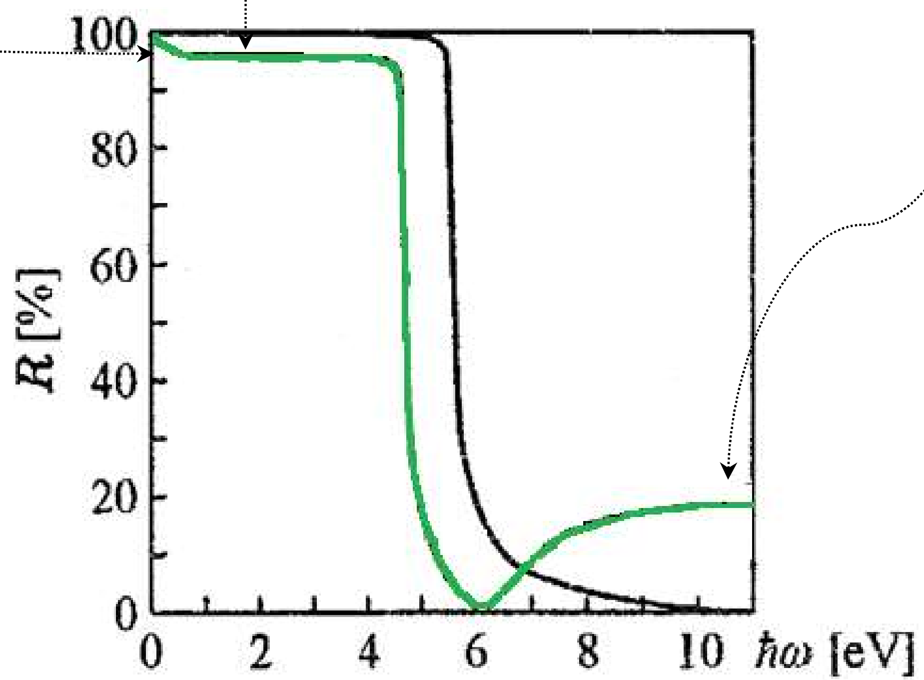
$$\varepsilon(\omega)\approx\left[\varepsilon_\infty-\frac{\Omega_{pl}^2}{\omega^2}\right]+i\left[\frac{\gamma\Omega_{pl}^2}{\omega^3}\right]\qquad \text{n«k}$$

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

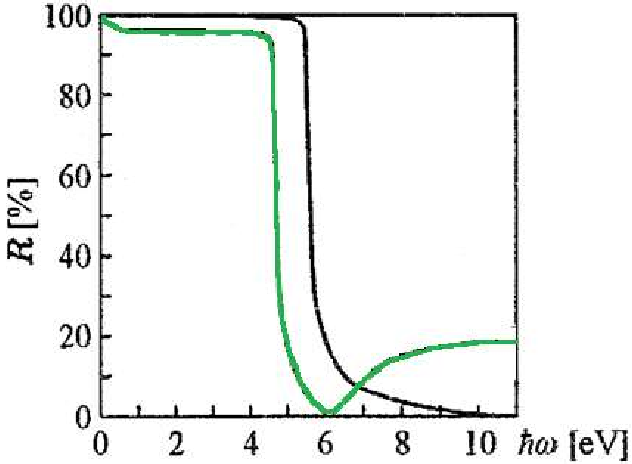
$\gamma,\omega_{pl}<<\omega$

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

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



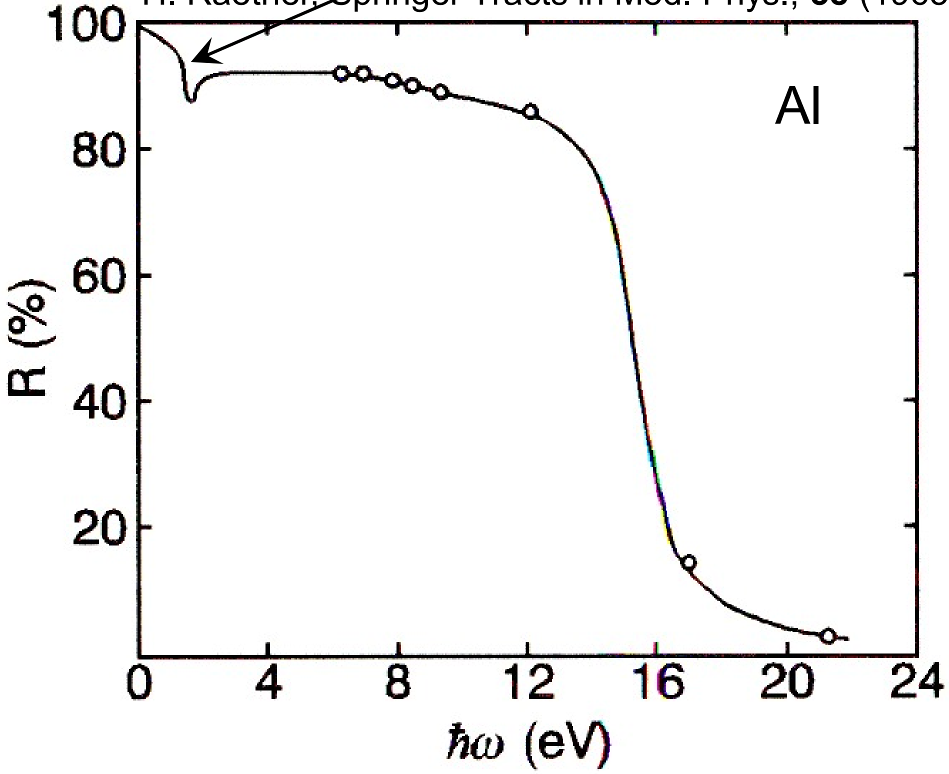
Spectroscopy of electronic excitations



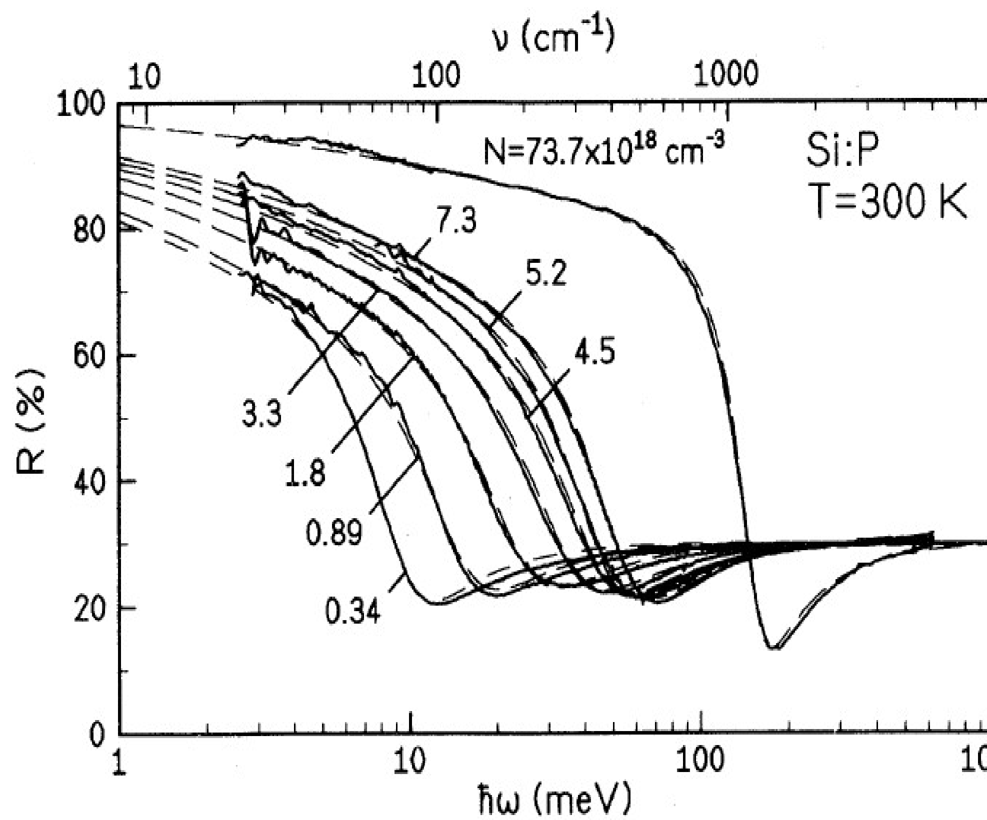
Plasmaedge touches the continuum of the interband excitations, the reflectivity does not drop

Al

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

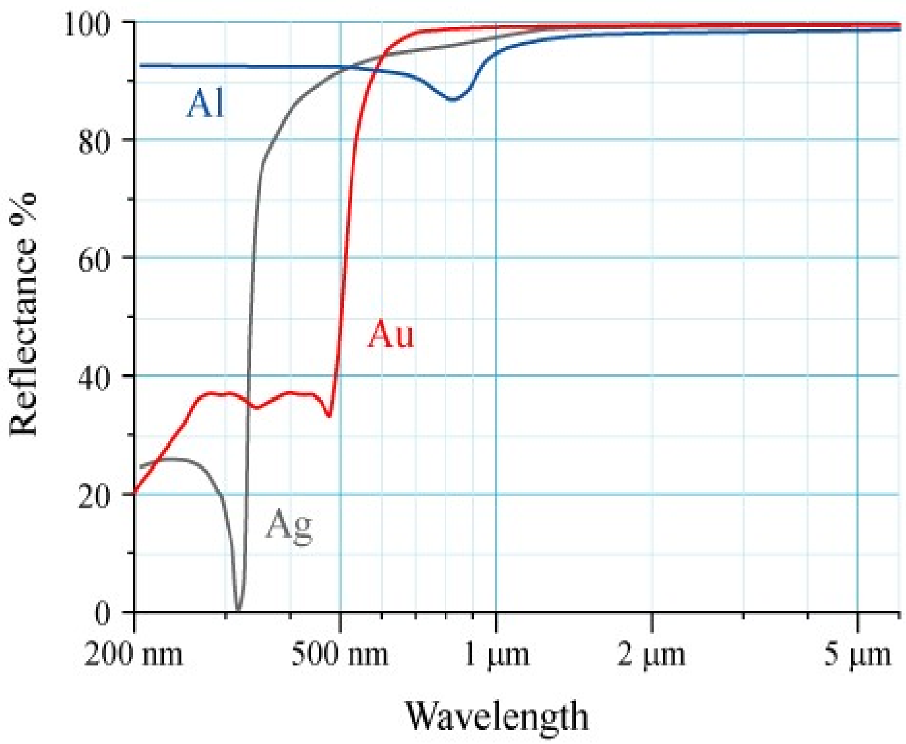


Si:P A. Gaymann, Phys. Rev. B **52**, 16486 (1995)

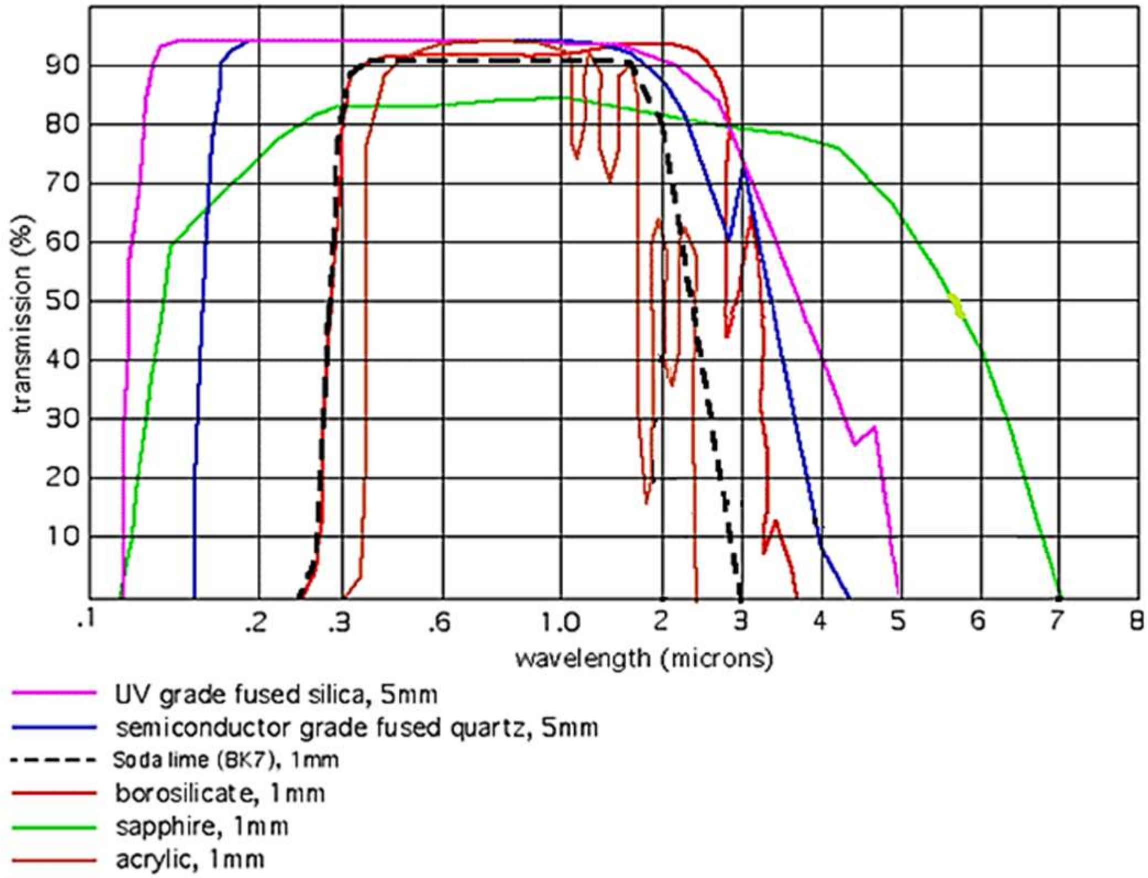


Spectroscopy of electronic excitations

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: $H=\underbrace{\frac{p^2}{2m}-\frac{Ze^2}{4\pi\varepsilon_0 r}}_{H_0}+\underbrace{\zeta\mathbf{LS}}_{H_{LS}}$

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

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

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

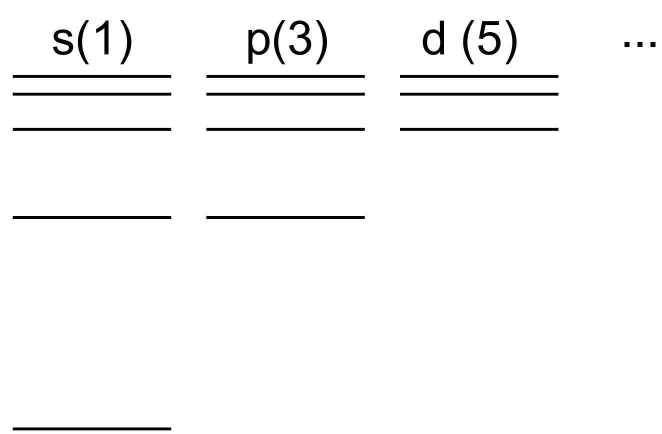
$$[l_i,H_0]=[\mathbf{l}^2,H_0]=0$$

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

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

$$l_zY_l^m=mY_l^m$$

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



Spectroscopy of electronic excitations

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

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

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

$$\langle f|V|i\rangle \propto \delta_{s_f s_i} \int Y_{l_f}^{m_f} Y_1^{0,\pm1} Y_{l_i}^{m_i}\, d\Omega$$

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]

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

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

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

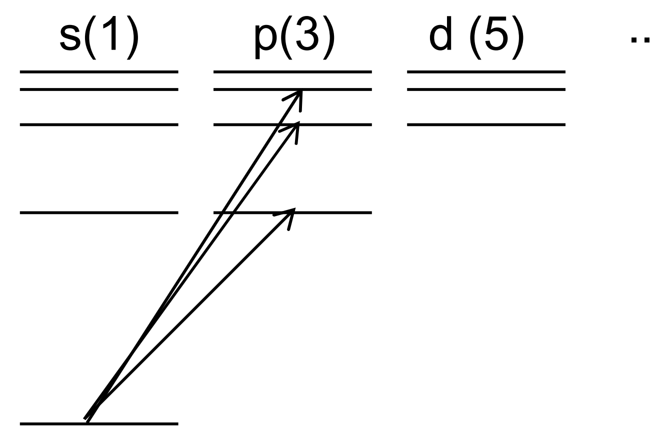
$$Y_2^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta\cdot\cos\theta = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cdot\frac{(x+iy)z}{r^2}$$

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

Selection rules:

I. $m_f = m_i + 0, \pm1$

II. $|l_f - l_i| = \pm1$



Spectroscopy of electronic excitations

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

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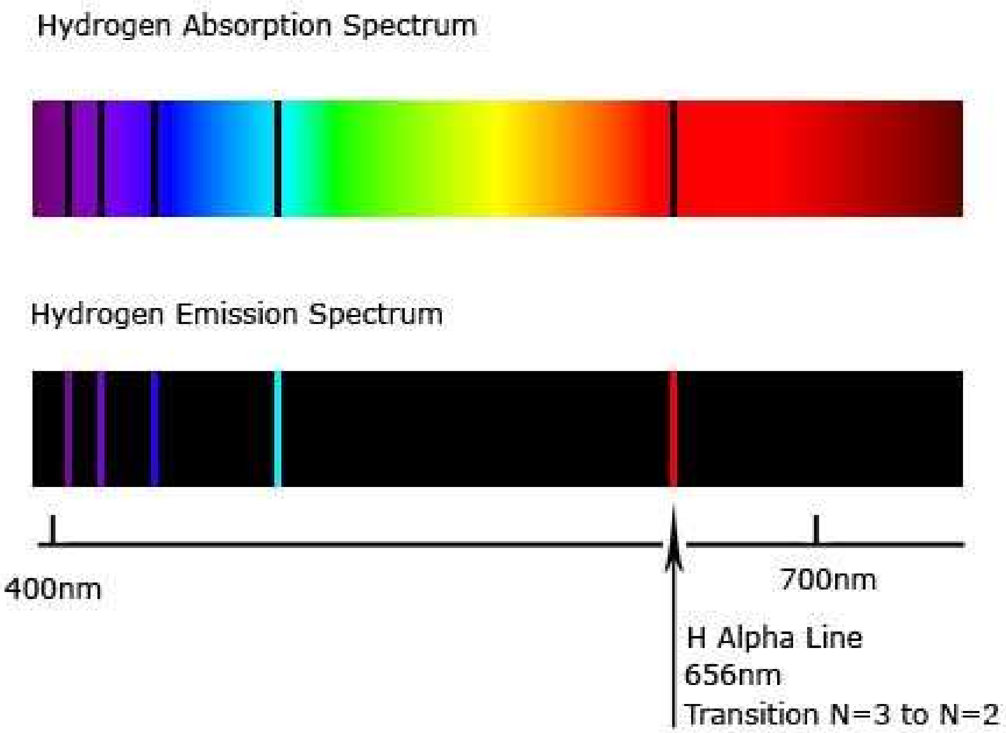
$$\langle f|V|i\rangle \propto \delta_{s_f s_i} \int Y_{l_f}^{m_f} Y_1^{0,\pm1} Y_{l_i}^{m_i} d\Omega$$

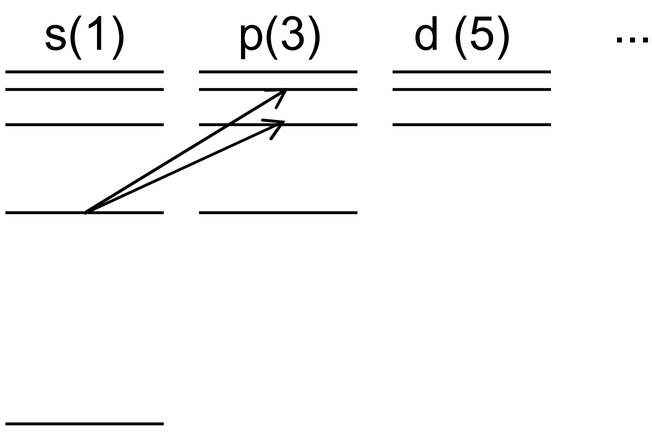
Balmer series (n=2): $\Delta E = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$

Selection rules:

I. $m_f = m_i + 0, \pm1$

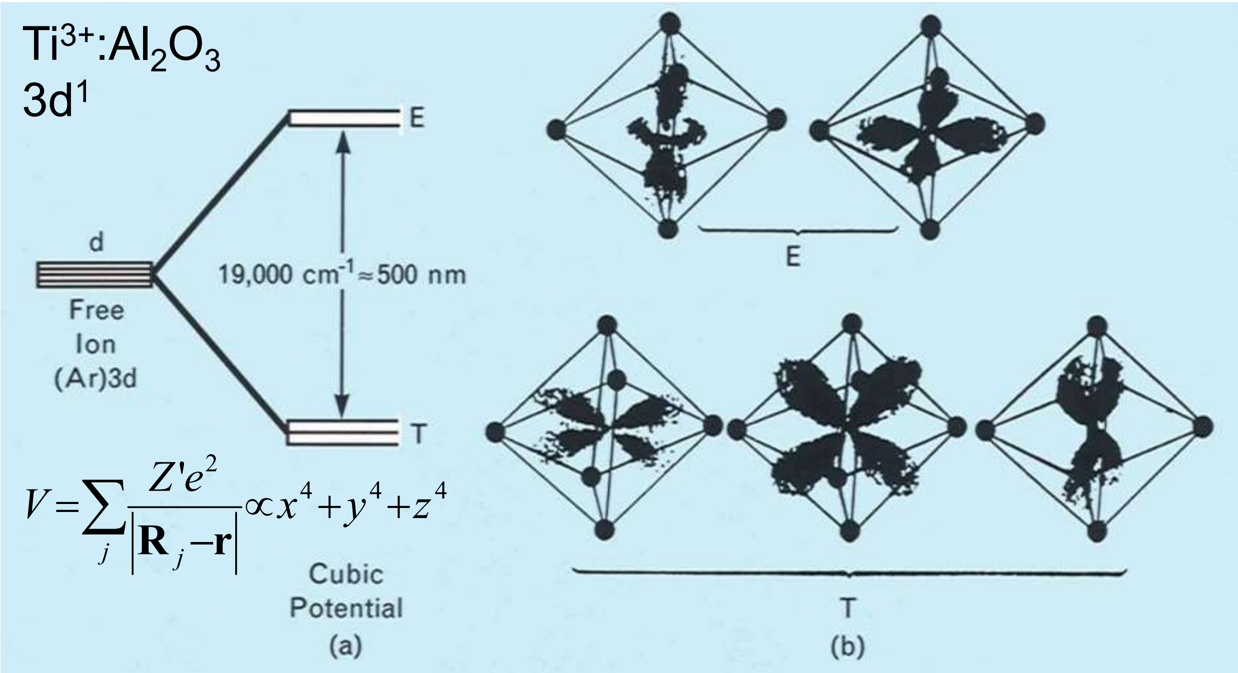
II. $|l_f - l_i| = \pm1$

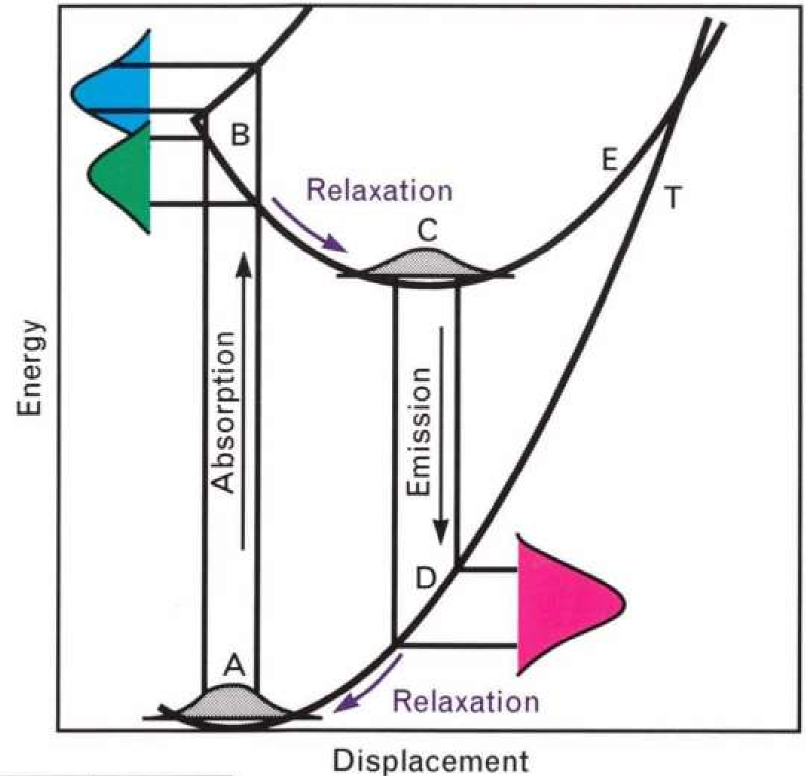


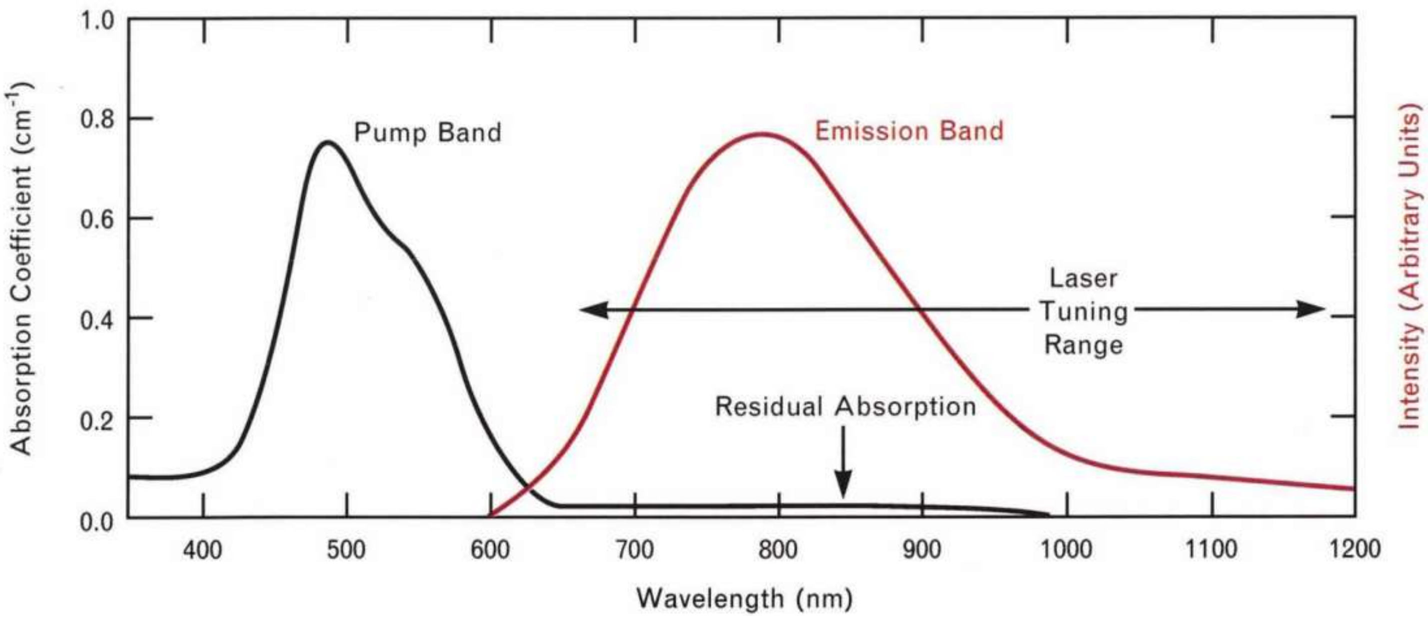


Spectroscopy of electronic excitations

Ti:sapphire LASER



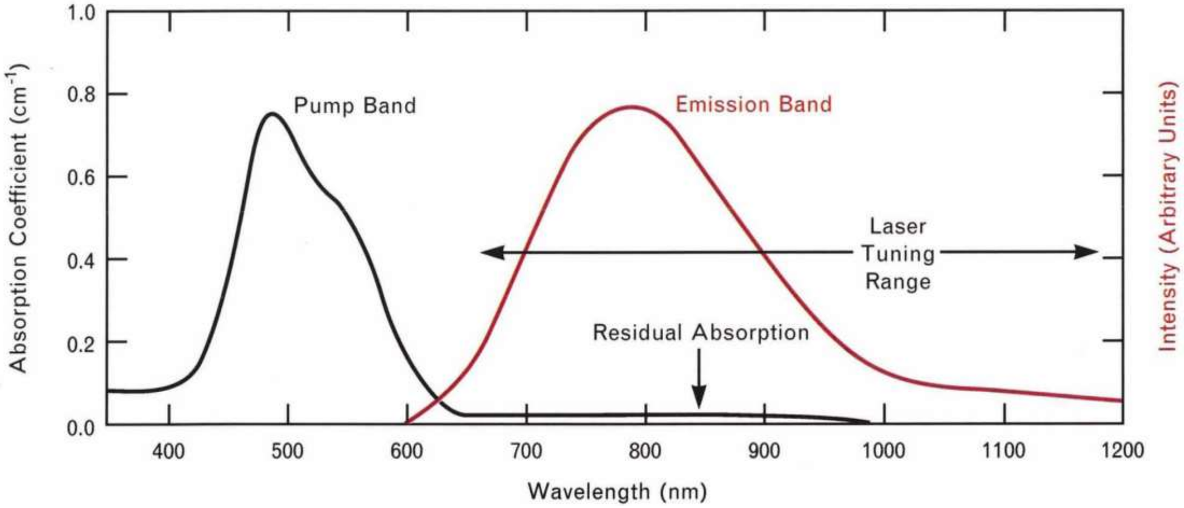




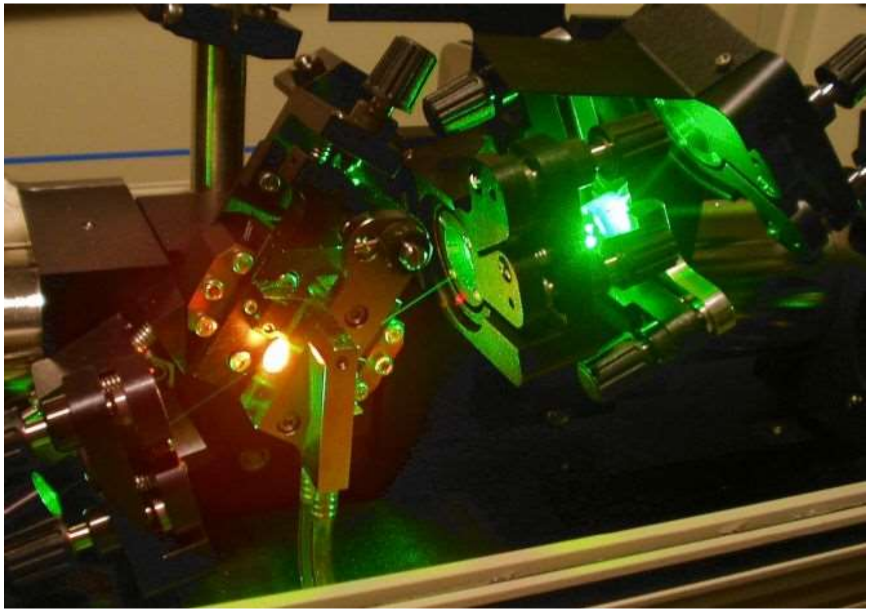
K.F. Wall and A. Sanchez. The Lincoln Laboratory Journal, 2 447 (1990)

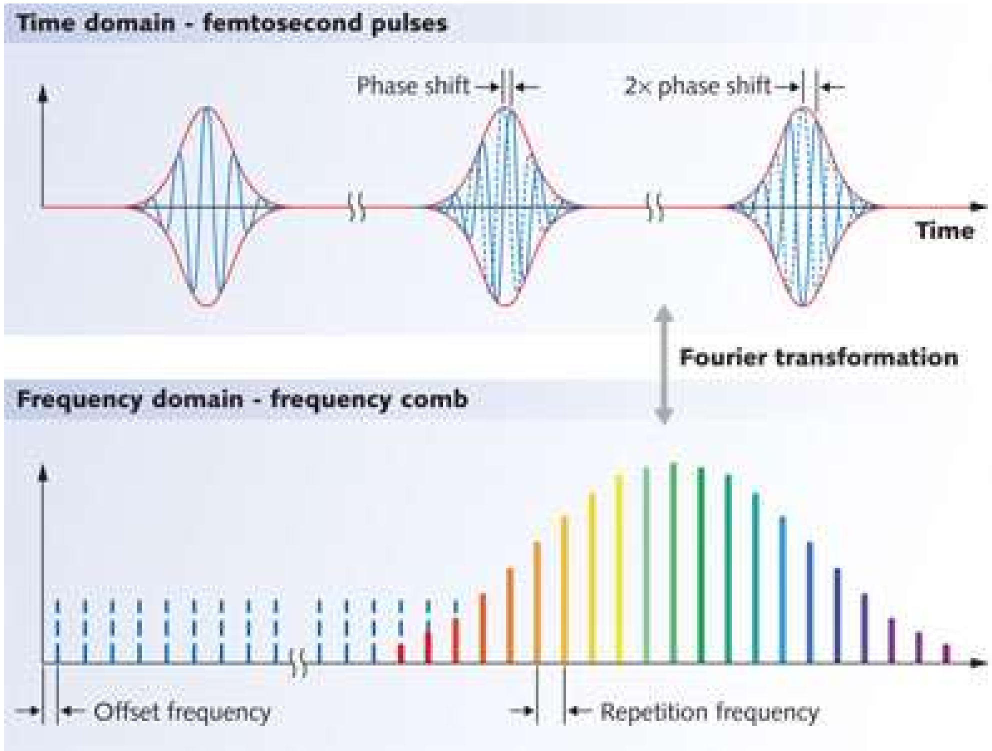
Spectroscopy of electronic excitations

Ti:sapphire LASER



Pump: green, lasing: NIR

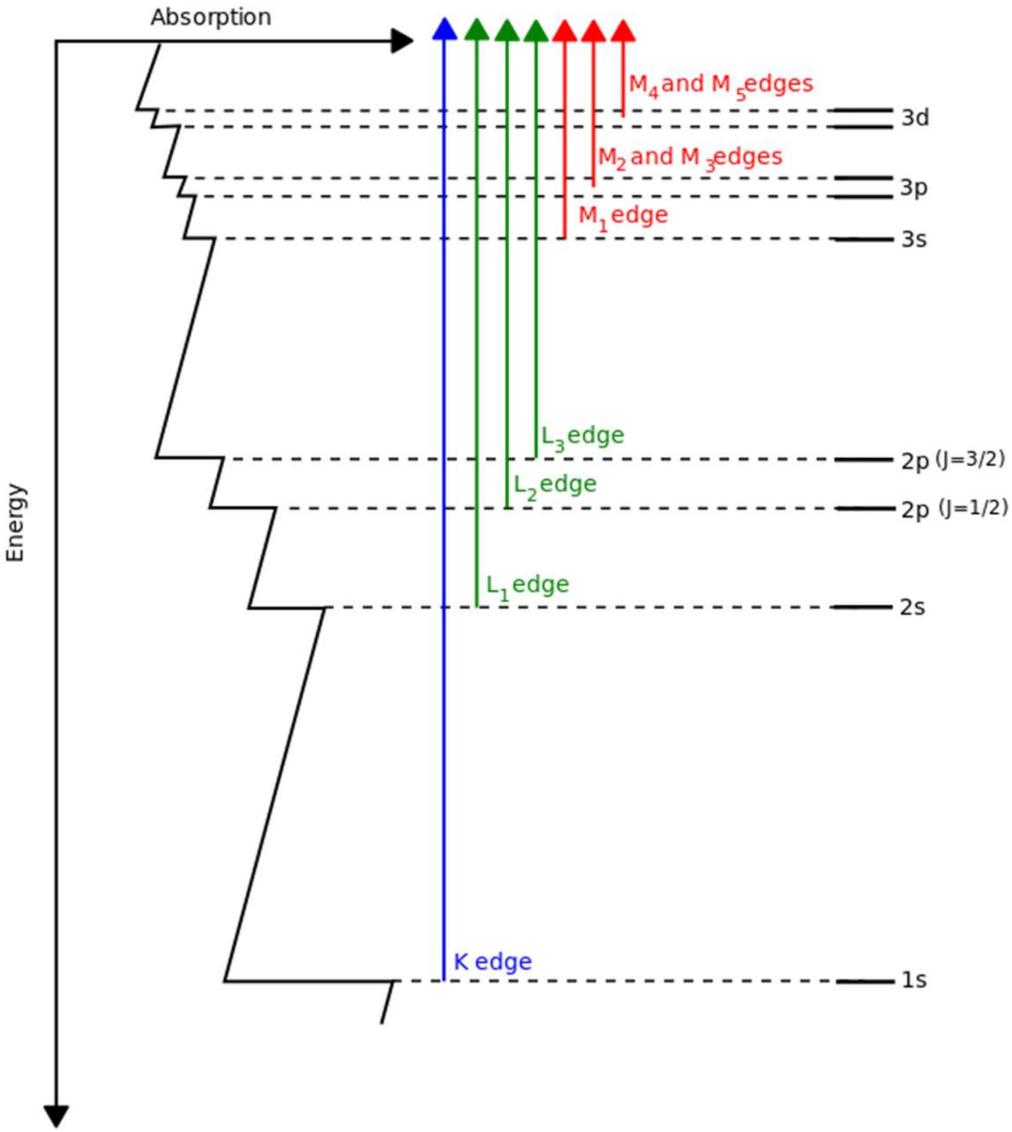




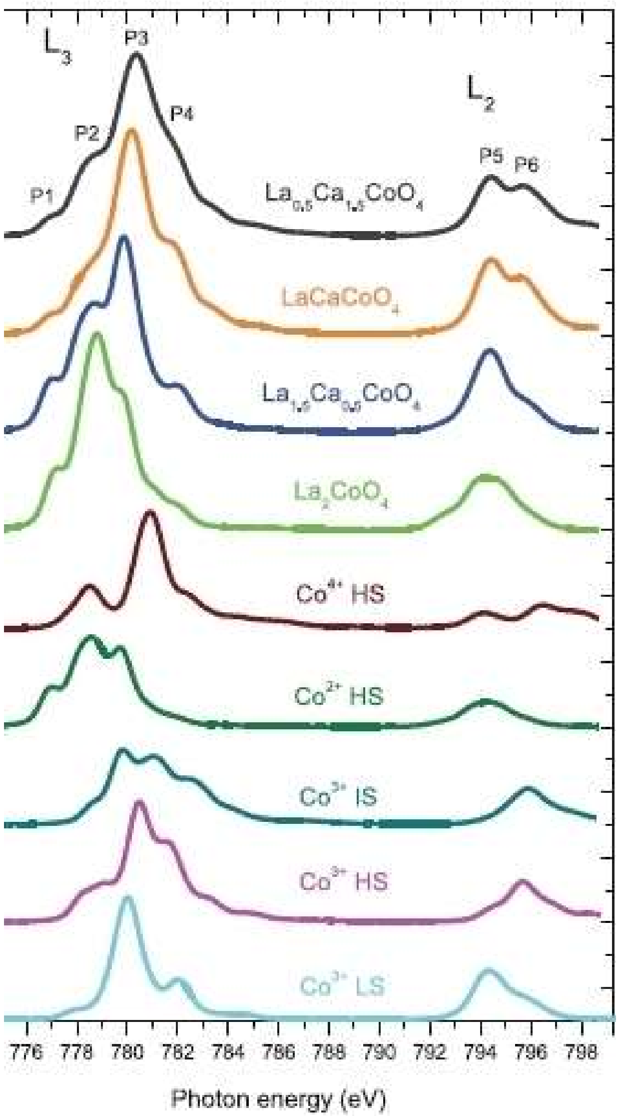
Cental wavelength: 800 nm (375 THz)
Pulse width: 10-100 fs
Repetition rate: 80 MHz ($\frac{c}{2L}$), resonantor: ~2 m

Spectroscopy of electronic excitations

X-ray absorption spectroscopy (XAS)

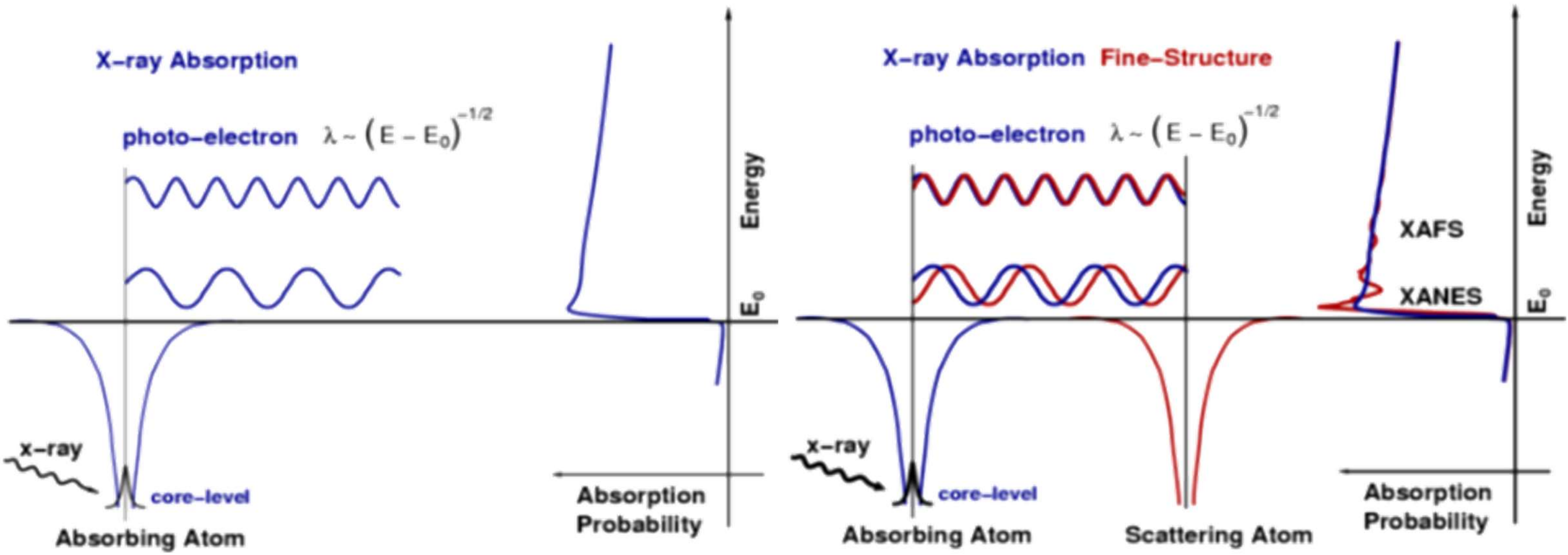


Sensitive:
composition, charge state, environment



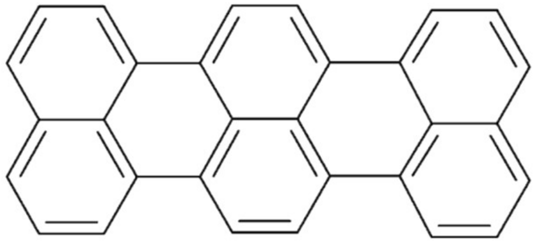
Spectroscopy of electronic excitations

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

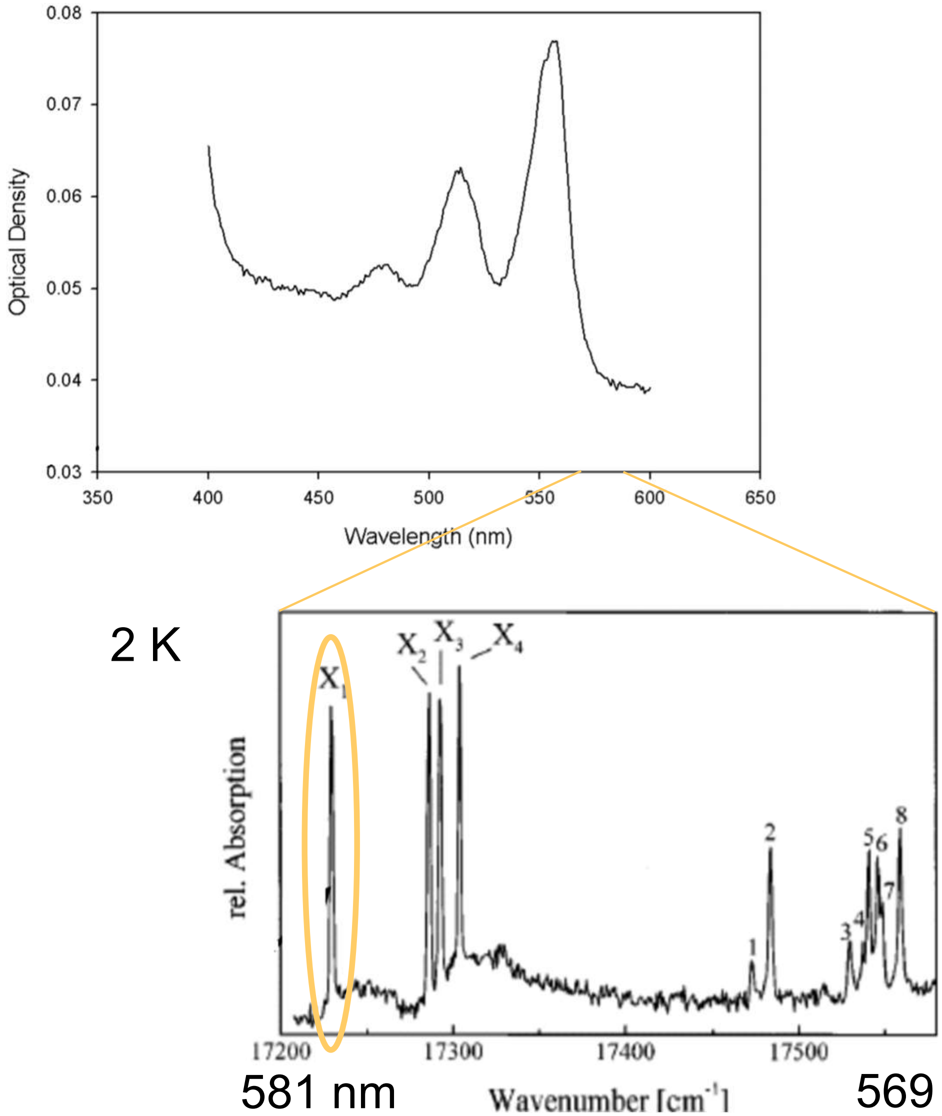
Terrilene



in para-Terphenyl crystals

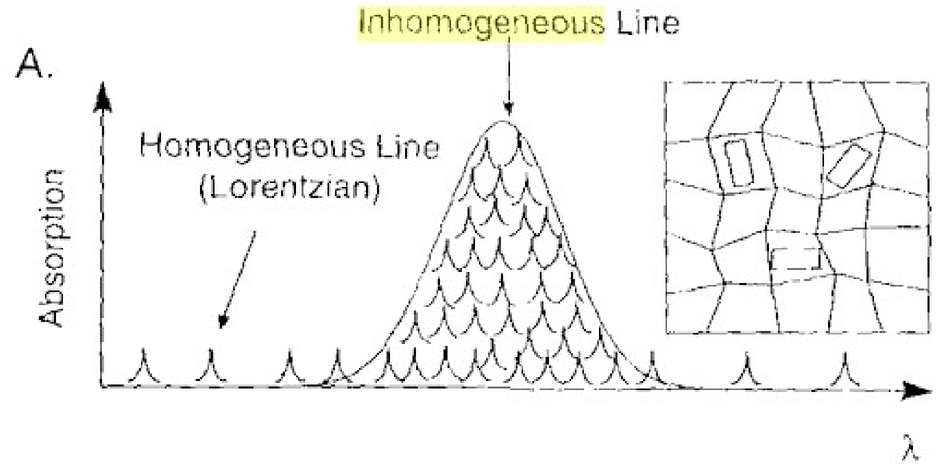
300 K

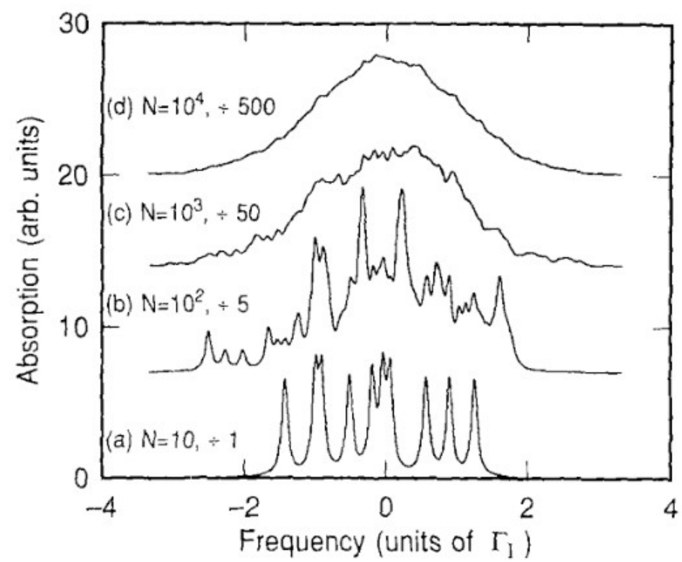
2 K



581 nm

569 nm



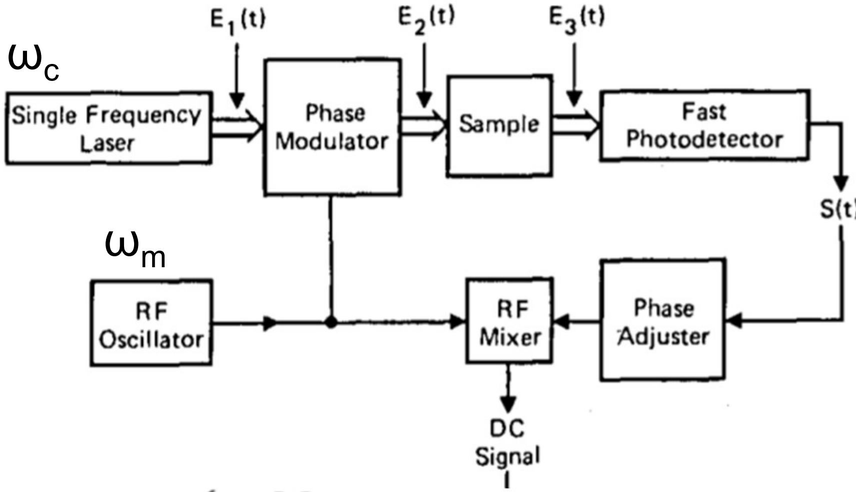


W.E. Moermer Nobel lecture (2014)

S. Kummer, et al., J. Chem. Phys. **107** 7673 (1997).

Spectroscopy of electronic excitations

FM modulation spectroscopy



$$\tilde{E}_2(t) = E_0\left\{-\frac{M}{2}\exp[\mathrm{i}(\omega_c-\omega_m)t] + \exp(\mathrm{i}\omega_c t) + \frac{M}{2}\exp[\mathrm{i}(\omega_c+\omega_m)t]\right\}$$

$$\tilde{E}_3(t) = E_0\left\{-T_{-1}\frac{M}{2}\exp[\mathrm{i}(\omega_c-\omega_m)t] + T_0\exp(\mathrm{i}\omega_c t) + T_1\frac{M}{2}\exp[\mathrm{i}(\omega_c+\omega_m)t]\right\}.$$

Amplitude transmission: $T_j = \exp(-\delta_j - \mathrm{i}\phi_j)$

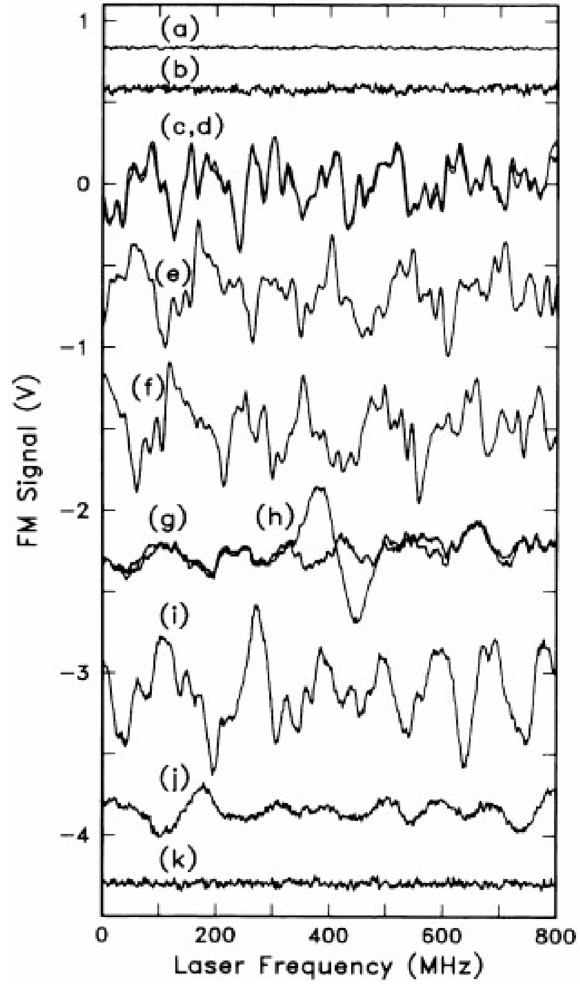


FIG. 1. FM spectra in the cosine phase for a single crystal of pentacene in *p*-terphenyl. Trace *a*, no light on the detector. Trace *b*, 3 μW on the detector at a wavelength not in resonance with the O_1-site absorption. Traces *c* and *d*, FM spectra at 1.4 K near the peak of the O_1 absorption at 592.3 nm with a focused spot. Trace *e*, a new spot on the sample, same spectral range as for trace *c*. Trace *f*, laser center frequency offset by 50 MHz from that for trace *e*. Trace *g*, larger laser spot (0.75 mm diam). Trace *h*, persistent hole burned in the spectral range of trace *g*. Trace *i*, 1.4 K, focused spot. Trace *j*, 5.6 K, same location. Trace *k*, 7 K. The vertical scale is exact for traces *c* and *d*; all the other traces have the same scale but are offset vertically for clarity. 1 V corresponds to a change in αL of 1.1×10^{-3}. The detection bandwidth was 0.1 to 300 Hz and $\nu_m = 58.1$ MHz with $M = 0.16$. The frequency scale was calibrated by optical observation of the rf sideband spacing.

γ~8 MHz

G. C. Bjorklund, et al., Appl. Phys B **32** 145 (1983).
W. E. Moerner and T. P. Carter, Phys. Rev. Lett. 59, 2705 (1987).

Spectroscopy of electronic excitations

Laser induced fluorescence

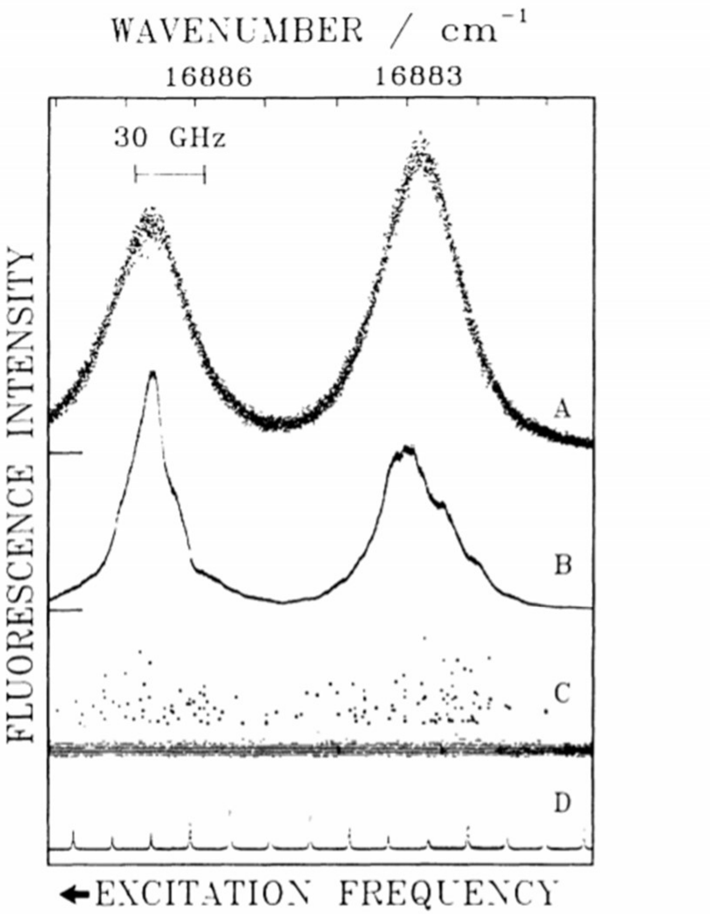
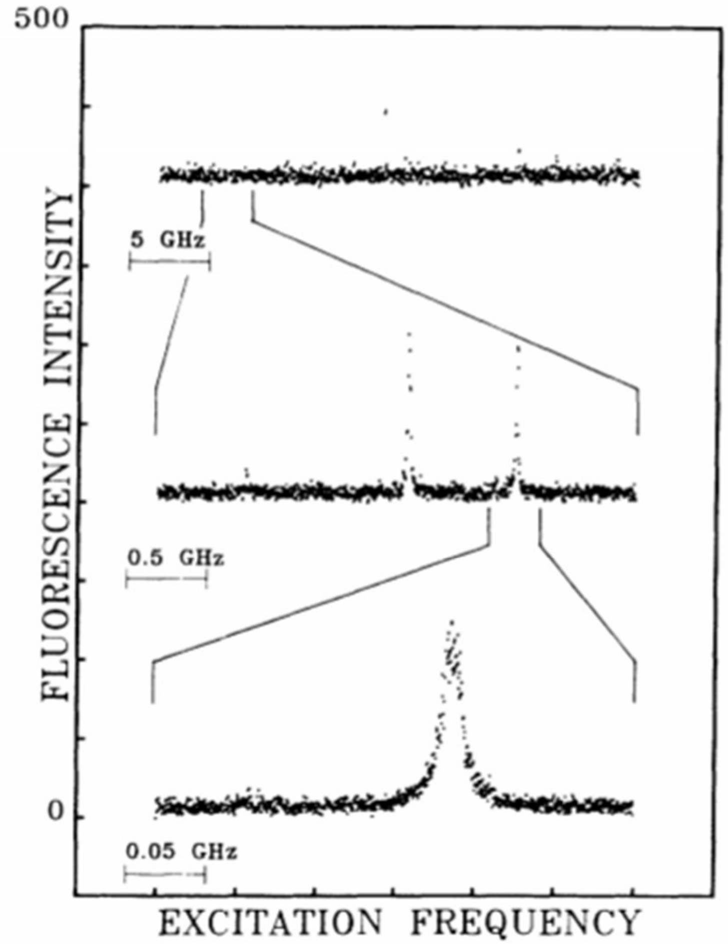


FIG. 1. O_1,O_2 region of the fluorescence excitation spectra of pentacene in different *p*-terphenyl crystals. Curve *A*, thick melt-grown crystal showing the Gaussian inhomogeneous bands. *B*, sublimation flake presenting narrower bands and substructure presumably due to cooling-induced defects. *C*, spectrum of a very small volume of a sublimation flake. The dots are the narrow excitation peaks of individual molecules. *D*, calibration spectrum of an etalon.



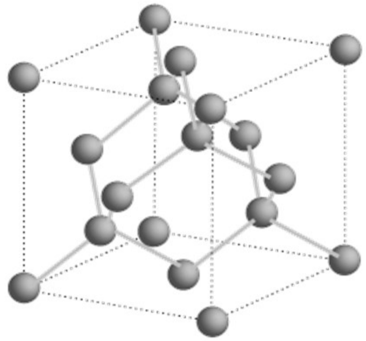
γ~12 MHz

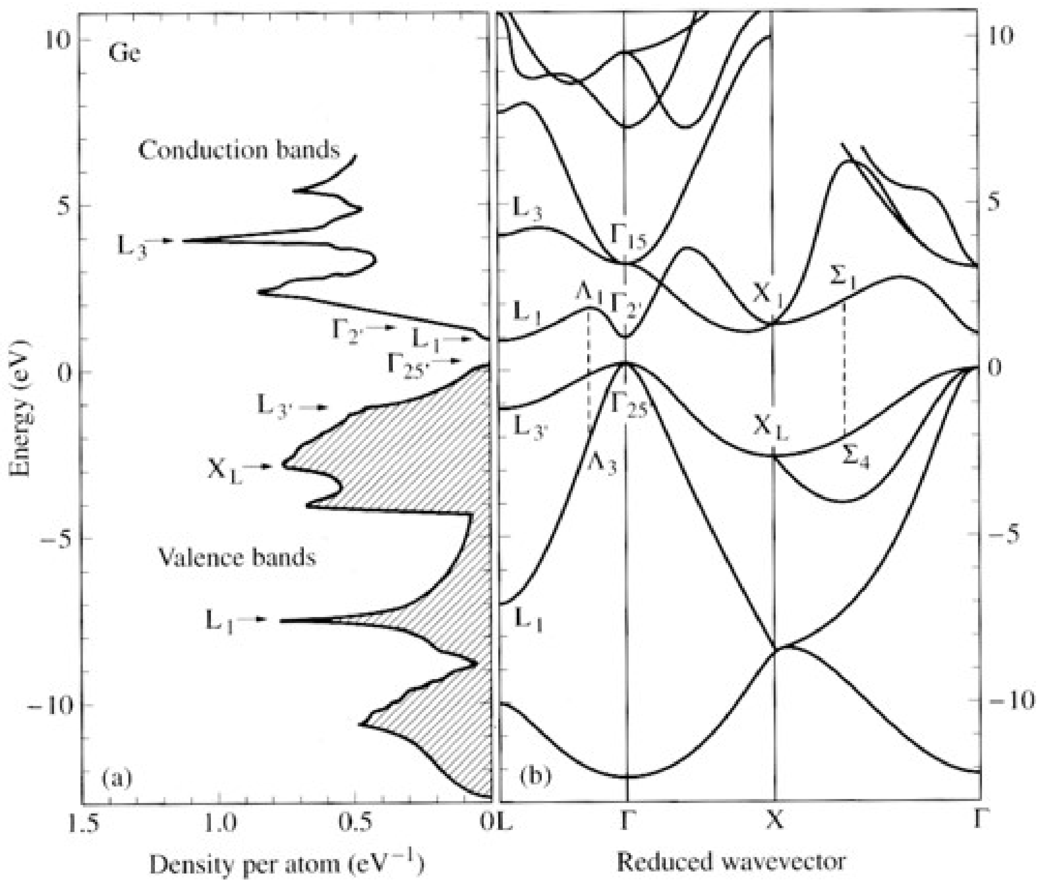
FIG. 2. Shape of a single molecule's excitation peak at different frequency scales. The bottom spectrum is approximately Lorentzian with FWHM about 12 MHz. The vertical scale is in counts/channel.

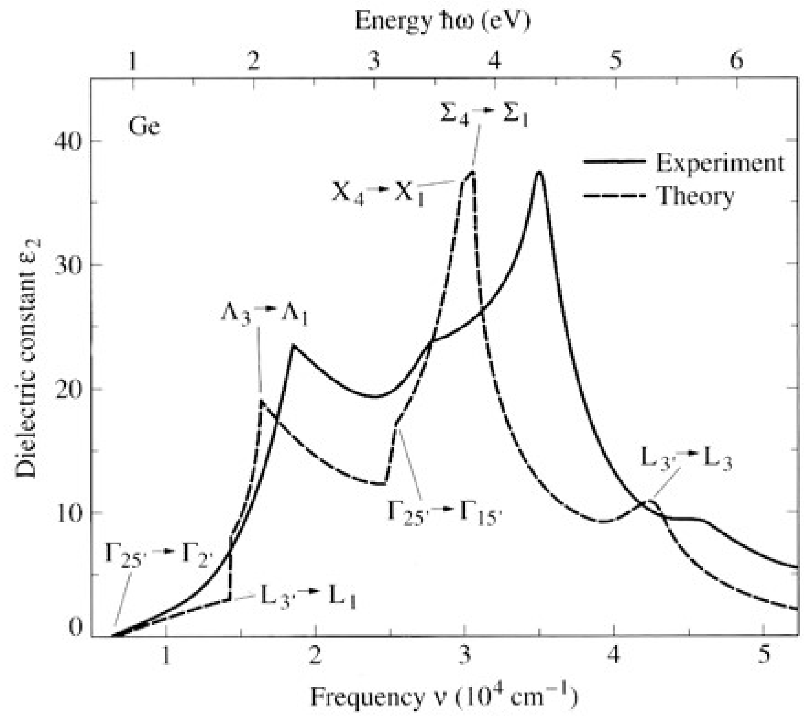
M. Orrit abd J. Bernard, Phys. Rev. Lett. 65, 2716 (1990).

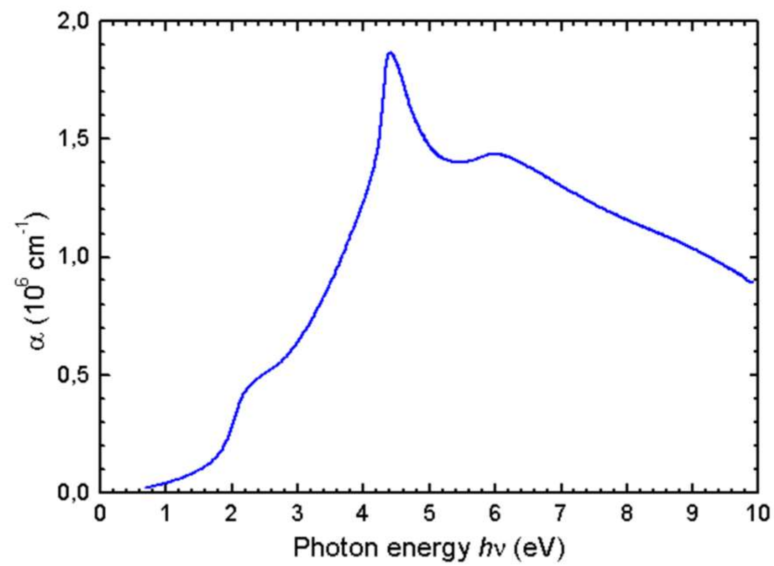
Spectroscopy of electronic excitations

Bandstructure of germanium





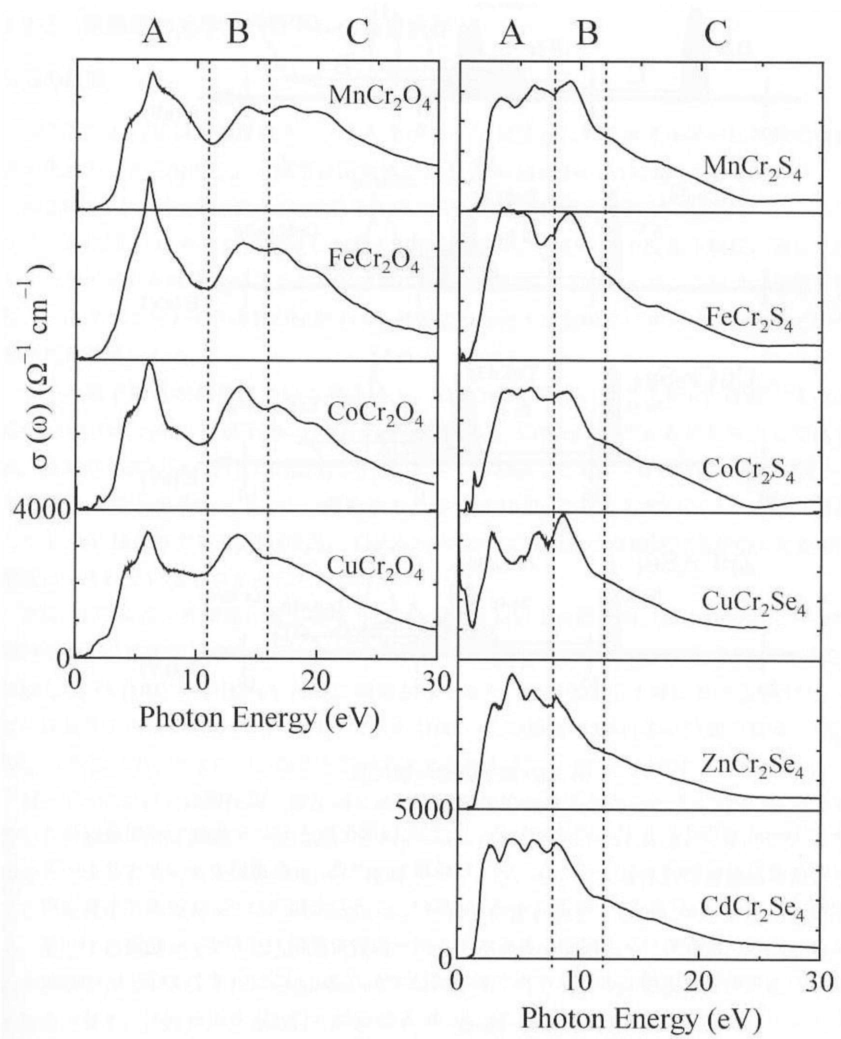


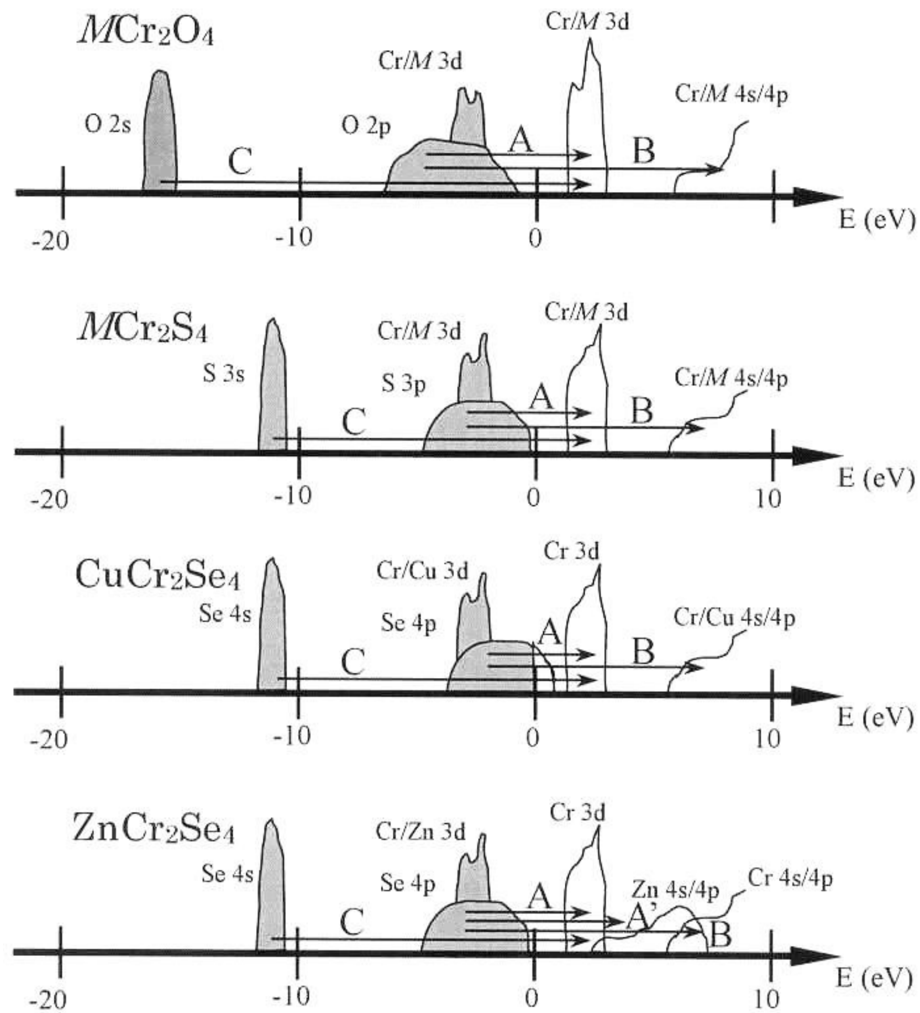


Philipp H. P. and E. A. Taft, Phys. Rev. 113, 4 1002 (1959).

Spectroscopy of electronic excitations

Interband transitions

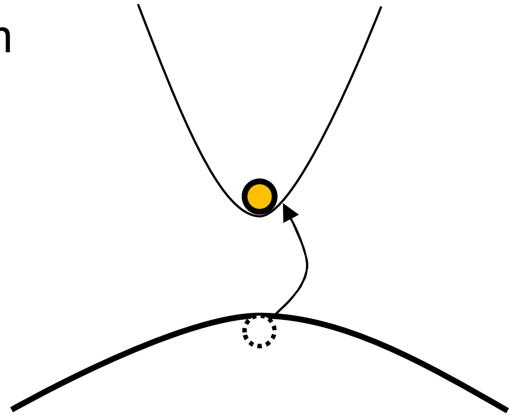


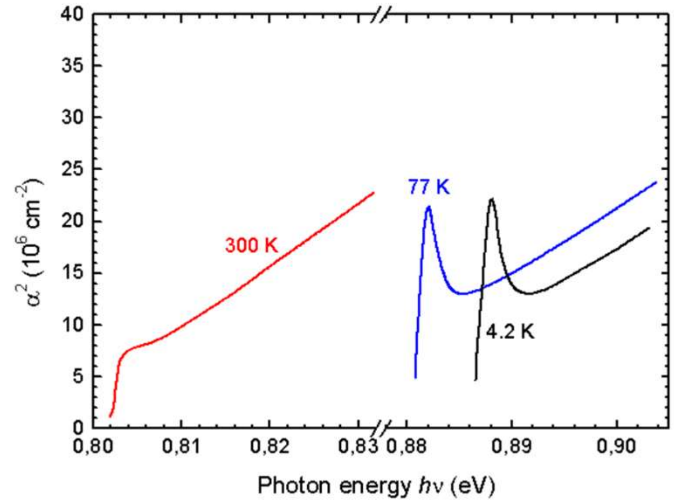


Spectroscopy of electronic excitations

Excitons

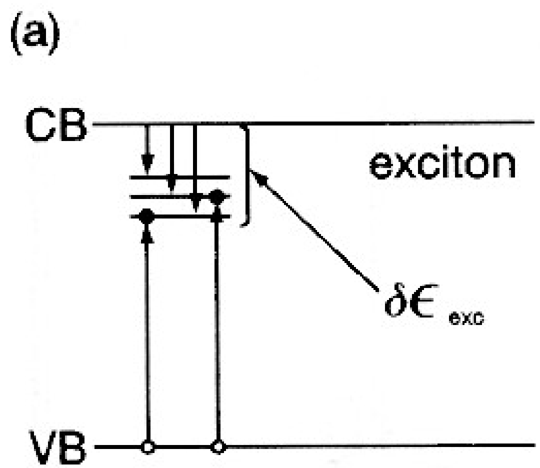
Excitons in germanium





Cu_2O: direct transition through the band gap is forbidden “p” type (l=1) excitons are allowed

P.W. Baumeister, PR **121**, 359 (1957)



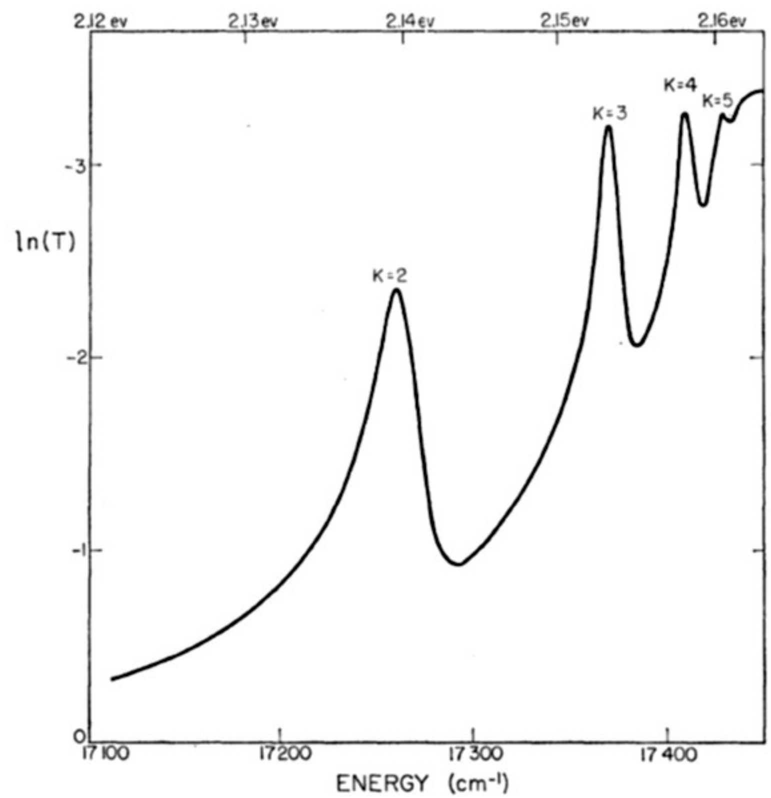


FIG. 6. The logarithm of the transmission as a function of photon energy of a Cu_2O sample at 77°K, showing the details of the yellow series of exciton lines.