Lecture 1	Perturbation Theory
Lecture 2	Time-Dependent Perturbation Theory
Lecture 3	Absorption and Emission of Radiation
Lecture 4	Raman Scattering
Workshop	Band Shapes and Convolution

Lecture 1 Perturbation Theory

(1) $$\hat{H}^0\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)}$$

(2) $$\hat{H} = \hat{H}^0 + \hat{H}'$$

(3) $$\hat{H} = \hat{H}^0 + \lambda\hat{H}'$$

(4) $$\hat{H}\,\psi_0 = E_0\psi_0$$

(5) $$\psi_0 = \psi_0(s,\lambda) \qquad E_0 = E_0(\lambda)$$

(6) $$\psi_0 = \psi_0^{(0)} + \lambda\psi_0^{(1)} + \lambda^2\psi_0^{(2)} + \dots$$

(7) $$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \dots$$

(8) $$\left\langle \psi_0^{(0)} \middle| \psi_0 \right\rangle = 1$$

(9) $$\left\langle \psi_0^{(0)} \middle| \psi_0 \right\rangle = 1 = \underbrace{\left\langle \psi_0^{(0)} \middle| \psi_0^{(0)} \right\rangle}_{1} + \lambda \underbrace{\left\langle \psi_0^{(0)} \middle| \psi_0^{(1)} \right\rangle}_{0} + \lambda^2 \underbrace{\left\langle \psi_0^{(0)} \middle| \psi_0^{(2)} \right\rangle}_{0} + \dots$$

(3) $$\hat{H} = \hat{H}^0 + \lambda \hat{H}'$$

(6) $$\psi_0 = \psi_0^{(0)} + \lambda \psi_0^{(1)} + \lambda^2 \psi_0^{(2)} + \ldots$$

(7) $$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \ldots$$

(4) $$\hat{H}\,\psi_0 = E_0 \psi_0$$

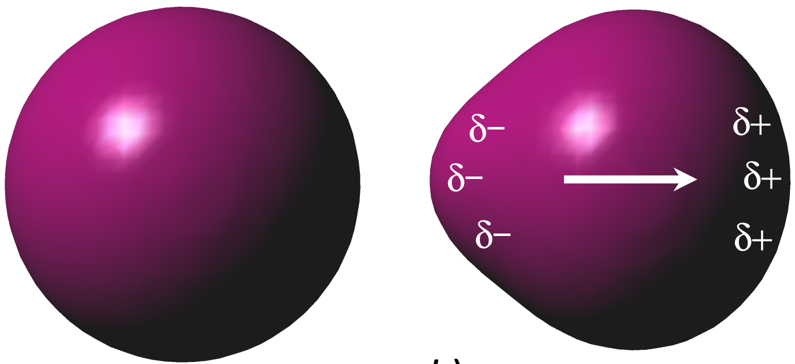
(10) $$\psi_0 = \psi_0^{(0)} \underbrace{- \sum_{k \neq 0} \frac{\left\langle \psi_k^{(0)} \middle| \hat{H}' \middle| \psi_0^{(0)} \right\rangle}{E_k^{(0)} - E_0^{(0)}} \psi_k^{(0)}}_{\psi_0^{(1)}} + \ldots$$

(11) $$E_0 = E_0^{(0)} + \underbrace{\left\langle \psi_0^{(0)} \middle| \hat{H}' \middle| \psi_0^{(0)} \right\rangle}_{E_0^{(1)}} \underbrace{- \sum_{k \neq 0} \frac{\left\langle \psi_k^{(0)} \middle| \hat{H}' \middle| \psi_0^{(0)} \right\rangle}{E_k^{(0)} - E_0^{(0)}} \left\langle \psi_0^{(0)} \middle| \hat{H}' \middle| \psi_k^{(0)} \right\rangle}_{E_0^{(2)}} + \ldots$$

$$J[\phi] = \langle \phi | \hat{H}^0 - E_0^{(0)} | \phi \rangle + \langle \phi | \hat{H}' - E_0^{(1)} | \psi_0^{(0)} \rangle + \langle \psi_0^{(0)} | \hat{H}' - E_0^{(1)} | \phi \rangle \geq E_0^{(2)}$$

To work at home after the EMTCCM-2016:

Consider H atom in an uniform electric field in the z direction
Represent a polarization function by a $2p_z$ STO
Optimize the $2p_z$ ζ-exponent



a) *b*)

$$\phi = 2p_z(\zeta) \qquad \therefore \qquad J[\phi] = J[2p_z(\zeta)] = J(\zeta)$$

$$J\left[\phi\right] = \left\langle \phi \middle| \hat{H}^0 - E_0^{(0)} \middle| \phi \right\rangle + \left\langle \phi \middle| \hat{H}' - E_0^{(1)} \middle| \psi_0^{(0)} \right\rangle + \left\langle \psi_0^{(0)} \middle| \hat{H}' - E_0^{(1)} \middle| \phi \right\rangle \geq E_0^{(2)}$$

$$J\left[2p_z\right] = \left\langle 2p_z \middle| \hat{H}^0 \middle| 2p_z \right\rangle - E_0^{(0)} + 2\left\langle 2p_z \middle| \hat{H}' \middle| 1s \right\rangle$$

$$\hat{H}^0 = -\frac{\nabla^2}{2} - \frac{1}{r} \qquad \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\hat{L}^2 \qquad \hat{L}^2 Y_{\ell,m} = \ell\left(\ell+1\right) Y_{\ell,m}$$

$$\hat{H}' = -z = -r\,\cos\theta$$

$$1s = R_{1s} Y_{0,0} = \left(2\ e^{-r}\right)\left(\frac{1}{2\sqrt{\pi}}\right) = \frac{1}{\sqrt{\pi}} e^{-r}$$

$$2p_z\left(\text{STO}\right) = R_{2\zeta} Y_{1,0} = \left(\frac{2\zeta^{5/2}}{\sqrt{3}} r\ e^{-\zeta r}\right)\left(\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta\right) = \frac{1}{\sqrt{\pi}}\zeta^{5/2} r\ e^{-\zeta r}\cos\theta$$

$$E_0^{(0)} = \left\langle 1s \middle| -\frac{\nabla^2}{2} - \frac{1}{r} \middle| 1s \right\rangle = -0.5 \qquad E_0^{(1)} = \left\langle 1s \middle| -z \middle| 1s \right\rangle = 0$$

$$\left\langle 1s\left|-z\right|2p_z\right\rangle = -\frac{\zeta^{5/2}}{\pi}\int_0^\infty e^{-(\zeta+1)r}r^4dr\int_0^\pi \cos^2\theta\ \sin\theta\ d\theta\int_0^{2\pi}d\phi = -\frac{4}{3}\zeta^{5/2}\int_0^\infty e^{-(\zeta+1)r}r^4dr = -\frac{32\sqrt{\zeta^5}}{(1+\zeta)^5}$$

$$\left\langle R_{2\zeta}\left|-\frac{\nabla^2}{2}-\frac{1}{r}\right|R_{2\zeta}\right\rangle = -\frac{2\zeta^5}{3}\int_0^\infty e^{-2\zeta r}\left(\zeta^2r^2-4\zeta r+2r\right)dr = -\frac{1}{6}(2-3\zeta)\zeta^3$$

$$J[2p_z] = \left\langle R_{2\zeta}\left|\hat{H}^0\right|R_{2\zeta}\right\rangle - \left\langle 1s\left|\hat{H}^0\right|1s\right\rangle + 2\left\langle 1s\left|-z\right|2p_z\right\rangle \geq E_0^{(2)}$$

$$J(\zeta) = -\frac{1}{6}(2-3\zeta)\zeta^3 + 0.5 - 2\frac{32\sqrt{\zeta^5}}{(1+\zeta)^5}$$

$$\min J(\zeta = 0.844)$$

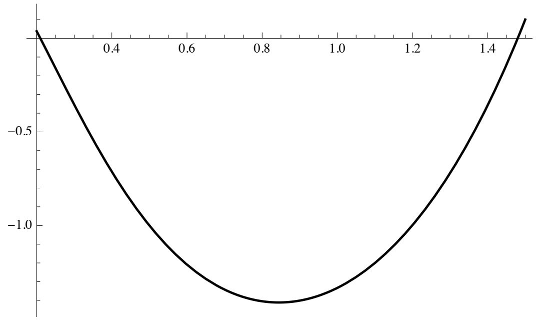
Mathematica code and results:


```
h11 = -0.5;
h22 =
 -(2/3) ζ^5 Integrate[Exp[-2 ζ r] (ζ^2 r^2 - 4 ζ r + 2 r) ,
   {r, 0, Infinity}, Assumptions → ζ > 0]
h12 = -(4/3) Sqrt[ζ^5]
  Integrate[r^4 Exp[-(1 + ζ) r] , {r, 0, Infinity},
   Assumptions → ζ > 0]
ζ /. SetPrecision[
  FindMinimum[h22 - h11 + 2 h12, {ζ, 0.6}][[2]], 3]
Plot[h22 - h11 + 2 h12, {ζ, 0.2, 1.5}, PlotStyle → Black]
```

$$-\frac{1}{6}(2-3\zeta)\zeta^3$$

$$-\frac{32\sqrt{\zeta^5}}{(1+\zeta)^5}$$

0.844



Lecture 2 Time-Dependent Perturbation Theory

(1) $$-\frac{\hbar}{i}\frac{\partial\Psi^0}{\partial t}=H^0\Psi^0$$

(2) $$\hat{H}^0\Psi^0=E^0\Psi^0$$

(3) $$-\frac{\hbar}{i}\frac{\partial\Psi^0}{\partial t}=E^0\Psi^0$$

(4) $$\Psi^0(s,t)=\exp\left(-iE^0t/\hbar\right)\ \psi^0(s)$$

(5) $$\Psi^0(s,0)=\psi^0(s)$$

$$\hat{H}^0\psi_k^0=E_k^0\psi_k^0$$

(6) $$\left(-\frac{\hbar}{i}\frac{\partial}{\partial t}-\hat{H}^0\right)\Psi^0=0$$

(7) $$\Psi^0(s,t)=\sum_k c_k\exp\left(-iE_k^0t/\hbar\right)\ \psi_k^0(s)$$

(8) $$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}=\left[\hat{H}^0+\hat{H}'(t)\right]\Psi$$

(9) $$\Psi(s,t)=\sum_k b_k(t)\ \exp\left(-iE_k^0t/\hbar\right)\ \psi_k^0(s)$$

(10) $$-\frac{\hbar}{i}\frac{\partial\Psi(s,t)}{\partial t}=\left[\hat{H}^0+\hat{H}'(t)\right]\Psi(s,t) \qquad \Psi(s,t)=\sum_k b_k(t)\ \exp\left(-iE_k^0 t/\hbar\right)\ \psi_k^0(s)$$

(11) $$-\frac{\hbar}{i}\frac{\partial\overbrace{\left[\sum_k b_k(t)\ \exp\left(-iE_k^0 t/\hbar\right)\ \psi_k^0\right]}^{\Psi(s,t)}}{\partial t}=\left(\hat{H}^0+\hat{H}'\right)\left[\overbrace{\sum_k b_k(t)\ \exp\left(-iE_k^0 t/\hbar\right)\ \psi_k^0}^{\Psi(s,t)}\right]$$

(12) $$-\frac{\hbar}{i}\sum_k\frac{db_k(t)}{dt}\ \exp\left(-iE_k^0 t/\hbar\right)\ \psi_k^0=\sum_k b_k(t)\ \exp\left(-iE_k^0 t/\hbar\right)\ \hat{H}'\psi_k^0$$

(13) $$\frac{db_n(t)}{dt}=-\frac{i}{\hbar}\sum_k b_k(t)\ \exp\left(i\omega_{nk}t\right)\ \left\langle\psi_n^0\middle|\lambda\hat{H}'\middle|\psi_k^0\right\rangle \qquad \omega_{nk}=\frac{E_n^0-E_k^0}{\hbar}$$

(14) $$b_k(t)=b_k^{(0)}+\lambda\ b_k^{(1)}(t)+\lambda^2 b_k^{(2)}(t)+\ldots$$

(15) $$\frac{db_n^{(1)}(t)}{dt}=-\frac{i}{\hbar}\sum_k b_k^{(0)}\exp\left(i\omega_{nk}t\right)\ \left\langle\psi_n^0\middle|\hat{H}'\middle|\psi_k^0\right\rangle$$

(16) $$\frac{db_n^{(2)}(t)}{dt}=-\frac{i}{\hbar}\sum_k b_k^{(1)}(t)\ \exp\left(i\omega_{nk}t\right)\ \left\langle\psi_n^0\middle|\hat{H}'\middle|\psi_k^0\right\rangle$$

$$(17)\qquad \frac{db_n^{(1)}(t)}{dt} = -\frac{i}{\hbar}\sum_k b_k^{(0)} \exp(i\omega_{nk}t)\ \left\langle \psi_n^0 \middle| \hat{H}' \middle| \psi_k^0 \right\rangle$$

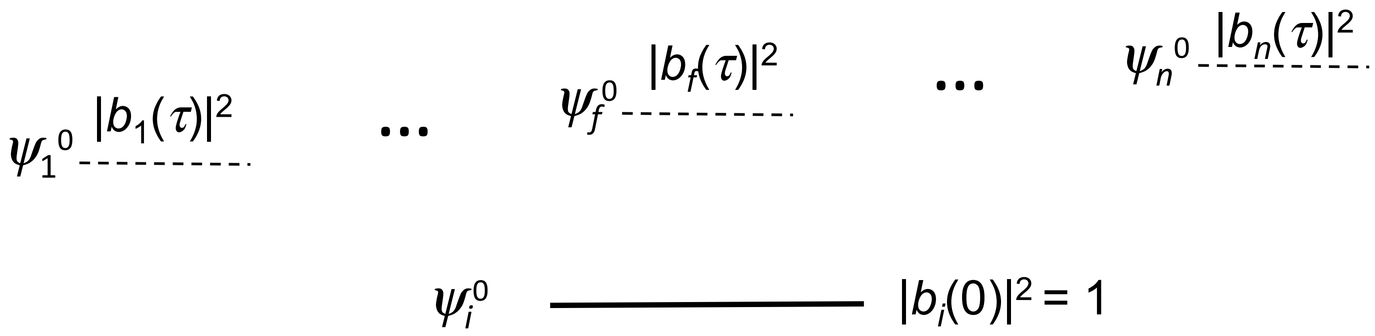
$$(18)\qquad \Psi_i^0 = \exp\left(-iE_i^0 t/\hbar\right)\ \psi_i^0$$

$$(19)\qquad \hat{H}'\ on: \qquad 0 < t < \tau \qquad t \geq \tau\ \Rightarrow\ b_k(t > \tau) = b_k(\tau)$$

$$(20)\qquad \left(b_k^{(0)} = \delta_{ki}\right) \qquad \frac{db_f^{(1)}(t)}{dt} = -\frac{i}{\hbar}\exp(i\omega_{fi}t)\left\langle \psi_f^0 \middle| \hat{H}' \middle| \psi_i^0 \right\rangle$$

$$(21)\qquad b_f(\tau) \approx b_f^{(1)}(\tau) = -\frac{i}{\hbar}\int_0^\tau \left\langle \psi_f^0 \middle| \hat{H}' \middle| \psi_i^0 \right\rangle\ \exp(i\omega_{fi}t)\ dt$$

$$(22)\qquad \boxed{\left|b_f(\tau)\right|^2 \approx \frac{1}{\hbar^2}\left|\int_0^\tau \left\langle \psi_f^0 \middle| \hat{H}' \middle| \psi_i^0 \right\rangle\ \exp(i\omega_{fi}t)\ dt\right|^2}$$



Lecture 3 Absorption and Emission of Radiation

(1) $$\mathcal{E}_x(z,t) = \mathcal{E}_0 \sin(\omega\, t - k\, z) \qquad \omega = \frac{2\pi}{\tau} = 2\pi\nu \qquad k = \frac{2\pi}{\lambda} = 2\pi\tilde{\nu}$$

(2) $$\hat{H}'(t) = -\mathcal{E}_x \hat{\mu}_x = -\mathcal{E}_0 \sin(\omega\, t - k\, z)\hat{\mu}_x \qquad \hat{\mu}_x = \sum_\alpha q_\alpha x_\alpha$$

(3) $$b_f(\tau) \approx -\frac{i}{\hbar} \int_0^\tau \langle \psi_f^0 | \hat{H}' | \psi_i^0 \rangle \ \exp(i\omega_{fi} t)\ dt$$

(4) $$b_f(\tau) \approx \frac{i\mathcal{E}_0}{\hbar} \langle \psi_f^0 | \hat{\mu}_x | \psi_i^0 \rangle \int_0^\tau \sin(\omega\, t - k\, z)\ \exp(i\omega_{fi} t)\ dt$$

(5) $$b_f(\tau) \approx \frac{i\mathcal{E}_0}{\hbar} \langle \psi_f^0 | \hat{\mu}_x | \psi_i^0 \rangle \int_0^\tau \sin(\omega\, t)\ \exp(i\omega_{fi} t)\ dt \qquad \sin(\omega\, t) = \frac{\exp(i\omega t) - \exp(-i\omega t)}{2i}$$

(6) $$b_f(\tau) \approx \frac{\mathcal{E}_0}{2\hbar} \langle \psi_f^0 | \hat{\mu}_x | \psi_i^0 \rangle \int_0^\tau \left\{ \exp\left[i(\omega_{fi} + \omega)t \right] - \exp\left[i(\omega_{fi} - \omega)t \right] \right\} dt \qquad \int_0^\tau \exp(at)\ dt = \frac{\exp(a\tau) - 1}{a}$$

(7) $$b_f(\tau) \approx \frac{\mathcal{E}_0}{2\hbar i} \langle \psi_f^0 | \hat{\mu}_x | \psi_i^0 \rangle \left\{ \frac{\exp\left[i(\omega_{fi} + \omega)\tau \right] - 1}{\omega_{fi} + \omega} - \frac{\exp\left[i(\omega_{fi} - \omega)\tau \right] - 1}{\omega_{fi} - \omega} \right\}$$

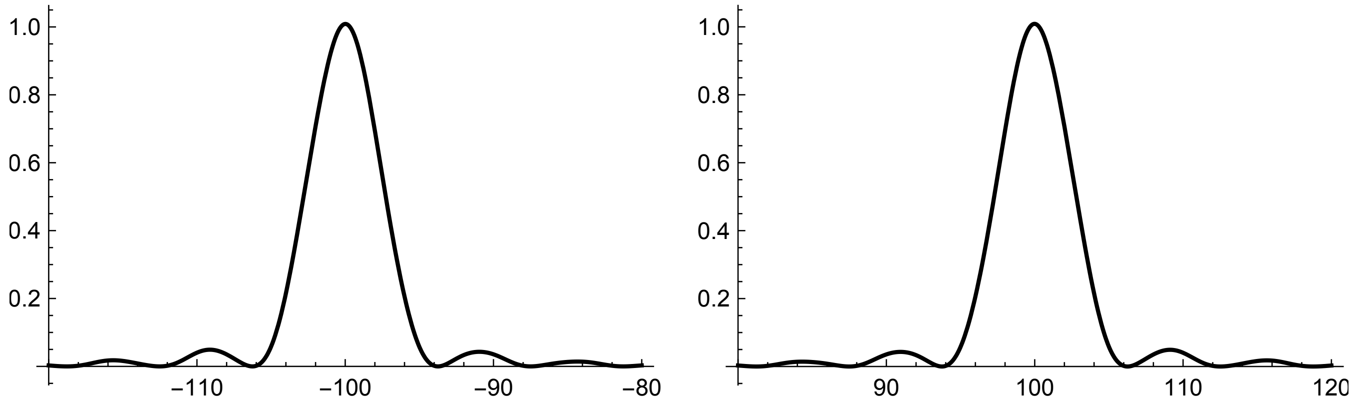
(8) $$s = \omega_{nm} \pm \omega \qquad \lim_{s\to 0} \frac{e^{is\tau} - 1}{s} = \frac{d\left(e^{is\tau} - 1\right)/ds}{ds/ds} = i\,\tau \qquad \lim_{\omega_{fi} \pm \omega \to 0} \frac{\exp\left[i(\omega_{fi} \pm \omega)\tau \right] - 1}{\omega_{fi} \pm \omega} = i\,\tau$$

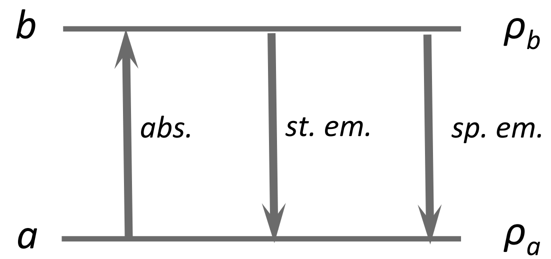
(9) $$\boxed{\left| b_f(\tau) \right|^2 \approx \frac{\mathcal{E}_0^2}{4\hbar^2} \left| \langle \psi_f^0 | \hat{\mu}_x | \psi_i^0 \rangle \right|^2 \left| \left\{ \frac{\exp\left[i(\omega_{fi} + \omega)\tau \right] - 1}{\omega_{fi} + \omega} - \frac{\exp\left[i(\omega_{fi} - \omega)\tau \right] - 1}{\omega_{fi} - \omega} \right\} \right|^2}$$

(10) $$\boxed{\langle \psi_f^0 | x | \psi_i^0 \rangle \quad \langle \psi_f^0 | y | \psi_i^0 \rangle \quad \langle \psi_f^0 | z | \psi_i^0 \rangle}$$

Mathematica code and results:

```
s = 250;
a = 1. × 10 ^ 2;
t = 1.;
emission = Plot[
  (Abs[(Exp[I t (a + x)] - 1) / (a + x) - (Exp[I t (a - x)] - 1) / (a - x)])^2,
  {x, -1.2 a, -0.8 a }, ImageSize → {s, s}, PlotStyle → Black];
absorption = Plot[
  (Abs[(Exp[I t (a + x)] - 1) / (a + x) - (Exp[I t (a - x)] - 1) / (a - x)])^2,
  {x, 0.8 a, 1.2 a }, ImageSize → {s, s}, PlotStyle → Black];
graph = Row[{emission, absorption}, "     "]
Export["absorption_emission.pdf", graph]
```





(1)
$$\overbrace{B\,d\,\rho_a}^{(abs.)}\overbrace{-B\,d\,\rho_b}^{(st.em.)}\overbrace{-A\,\rho_b}^{(sp.em.)}=0$$

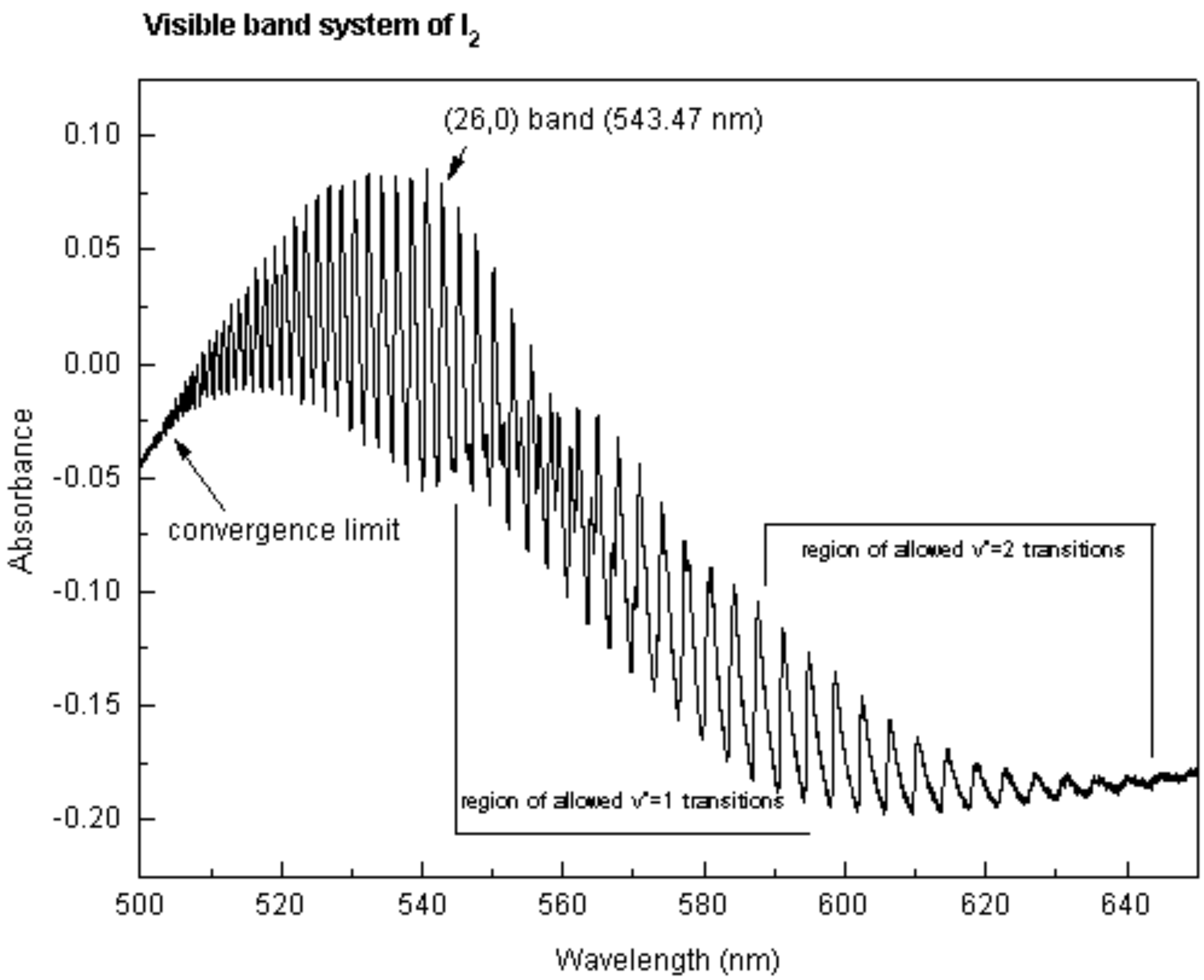
(2)
$$\rho_b=\rho_a\exp\left(-\hbar\omega_{ba}/kT\right)$$

(3)
$$A=B\,d\left[\exp\left(-\hbar\omega_{ab}/kT\right)-1\right]$$

(4)
$$d\propto\omega^3\left[\exp\left(-\hbar\omega/kT\right)-1\right]^{-1}$$

(5)
$$A\propto B\,\omega^3\,\frac{\exp\left(-\hbar\omega_{ab}/kT\right)-1}{\exp\left(-\hbar\omega/kT\right)-1}$$

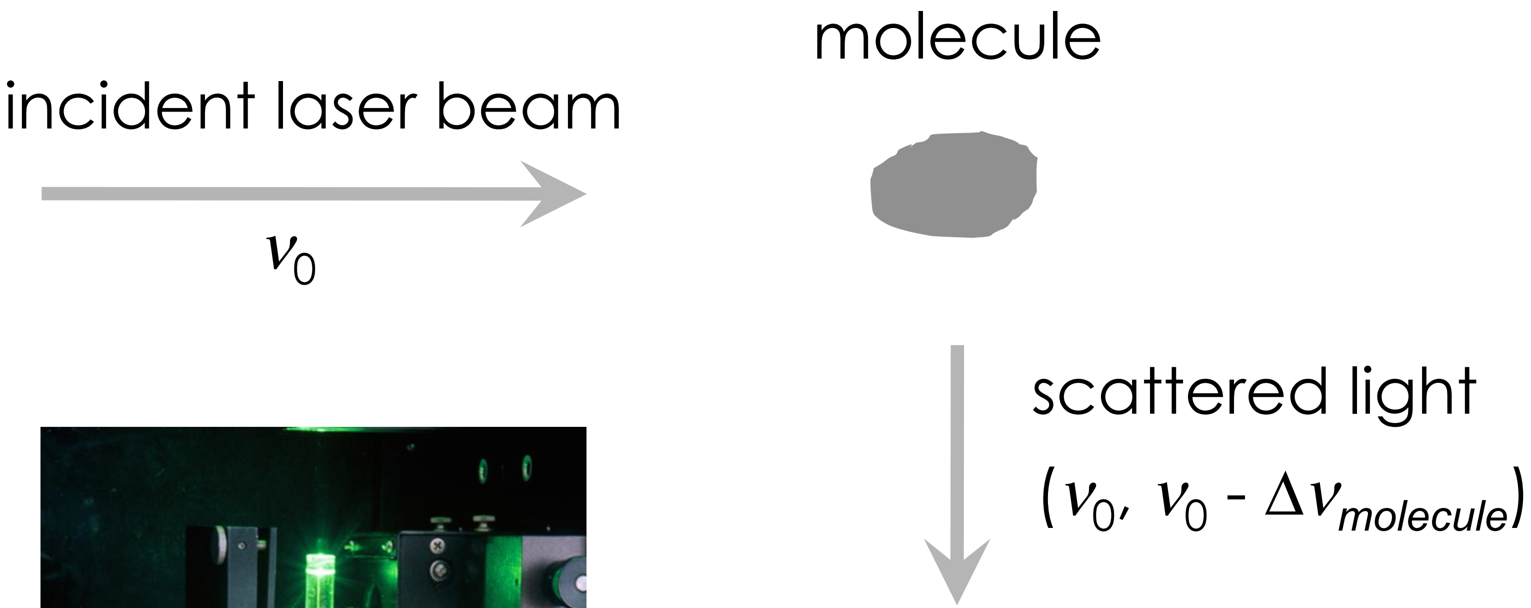
(6)
$$A\propto B\,\omega^3$$

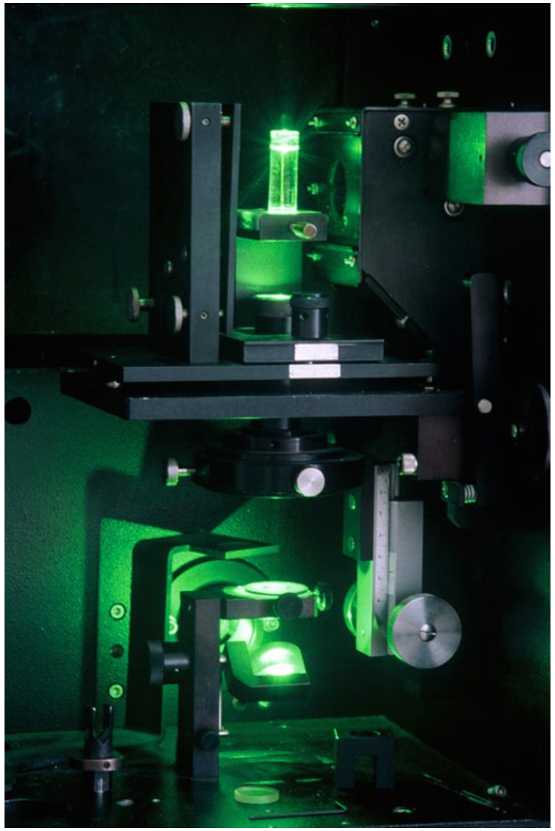


Lab report on the electronic absorption spectrum of iodine:
[www.art-xy.com/2009/10/lab-report-on-**electronic-absorption**.html](www.art-xy.com/2009/10/lab-report-on-electronic-absorption.html)

Electronic absorption spectrum of iodine:
http://www.uni-ulm.de/physchem-praktikum/media/literatur/1987_The_Iodine_Spectrum_Revisited.pdf
ww2.chemistry.gatech.edu/class/pchem/expt6m.pdf

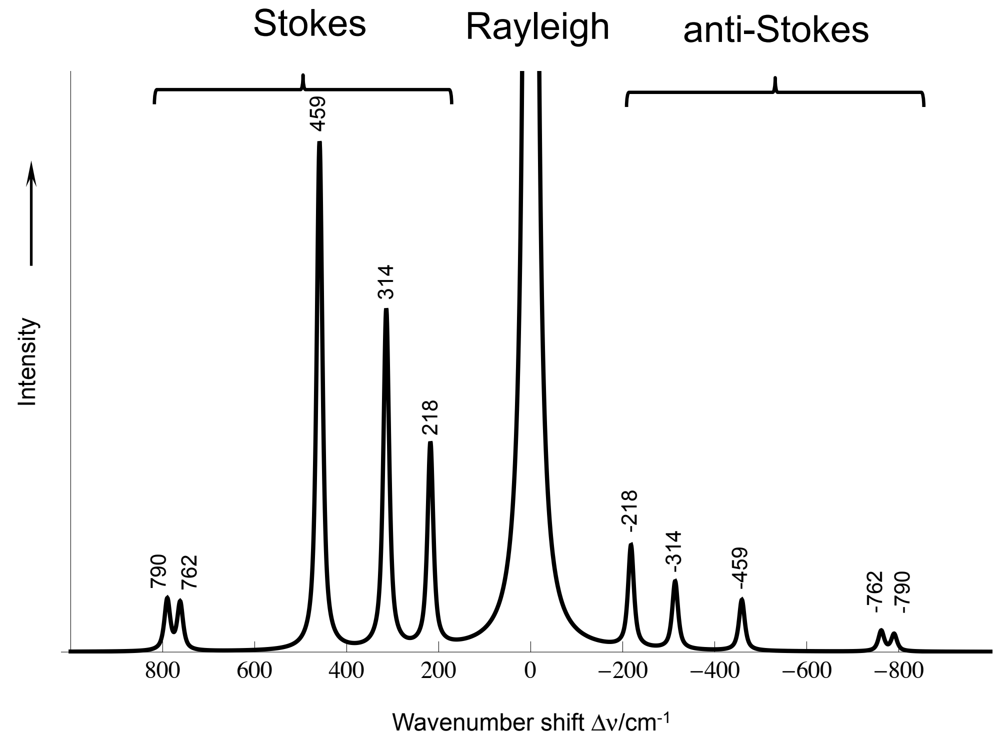
Lecture 4   Raman Scattering





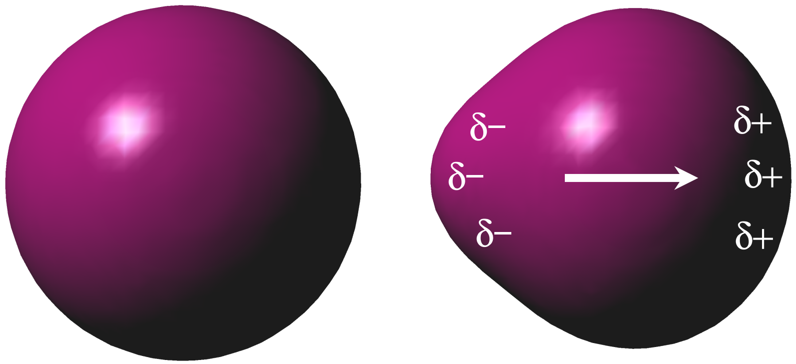
$$\nu_{Raman} = \nu_0 - \Delta\nu_{molecule}$$

$$\Delta\nu_{molecule} = \nu_0 - \nu_{Raman}$$



$$\tilde{\nu}_{Raman} = \tilde{\nu}_0 - \Delta\tilde{\nu}_{vib.trans.}$$

$$\Delta\tilde{\nu}_{vib.trans.} = \tilde{\nu}_0 - \tilde{\nu}_{Raman}$$



(1) $$\mu_{ind} = \alpha\ \mathcal{E}$$

(2) $$\mathcal{E} = \mathcal{E}_0 \cos(2\pi\nu_0 t)$$

(3) $$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial Q}\right)_0 Q + \ldots$$

(4) $$Q = A\ \cos(2\pi\nu t)$$

(5) $$\mu_{ind} = \alpha_0\mathcal{E}_0 \cos(2\pi\nu_0 t) + \left(\frac{\partial\alpha}{\partial Q}\right)_0 A\ \mathcal{E}_0 \cos(2\pi\nu_0 t)\ \cos(2\pi\nu t)$$

(6) $$\mu_{ind} = \alpha_0\mathcal{E}_0 \cos\left(2\pi \overbrace{\nu_0}^{Rayleigh} t\right) + \frac{1}{2}\left(\frac{\partial\alpha}{\partial Q}\right)_0 A\ \mathcal{E}_0 \left\{ \cos\left[2\pi\overbrace{(\nu_0 - \nu)}^{Stokes}t\right] + \cos\left[2\pi\overbrace{(\nu_0 + \nu)}^{anti-Stokes}t\right] \right\}$$

(7) $$\left(\frac{\partial\alpha}{\partial Q}\right)_0 \neq 0$$

$$\cos(A+B) = \cos(A)\cos(B) - \sin(A)\sin(B)$$

$$\cos(A-B) = \cos(A)\cos(B) + \sin(A)\sin(B)$$

$$\frac{1}{2}\left[\cos(A+B) + \cos(A-B)\right] = \cos(A)\cos(B)$$

(1) $$\boldsymbol{\mu}_{ind} = \boldsymbol{\alpha}\ \boldsymbol{\mathcal{E}}$$

(2) $$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} \mathcal{E}_x \\ \mathcal{E}_y \\ \mathcal{E}_z \end{pmatrix} \qquad \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx}\mathcal{E}_x + \alpha_{xy}\mathcal{E}_y + \alpha_{xz}\mathcal{E}_z \\ \alpha_{yx}\mathcal{E}_x + \alpha_{yy}\mathcal{E}_y + \alpha_{yz}\mathcal{E}_z \\ \alpha_{zx}\mathcal{E}_x + \alpha_{zy}\mathcal{E}_y + \alpha_{zz}\mathcal{E}_z \end{pmatrix}$$

(3) $$\Psi_i = \psi_i \exp(-\mathrm{i}\omega_i t) \qquad \Psi_f = \psi_f \exp(-\mathrm{i}\omega_f t)$$

(4) $$\Psi_r = \psi_r \exp\left[-\mathrm{i}(\omega_r - \mathrm{i}\Gamma_r)t\right]$$

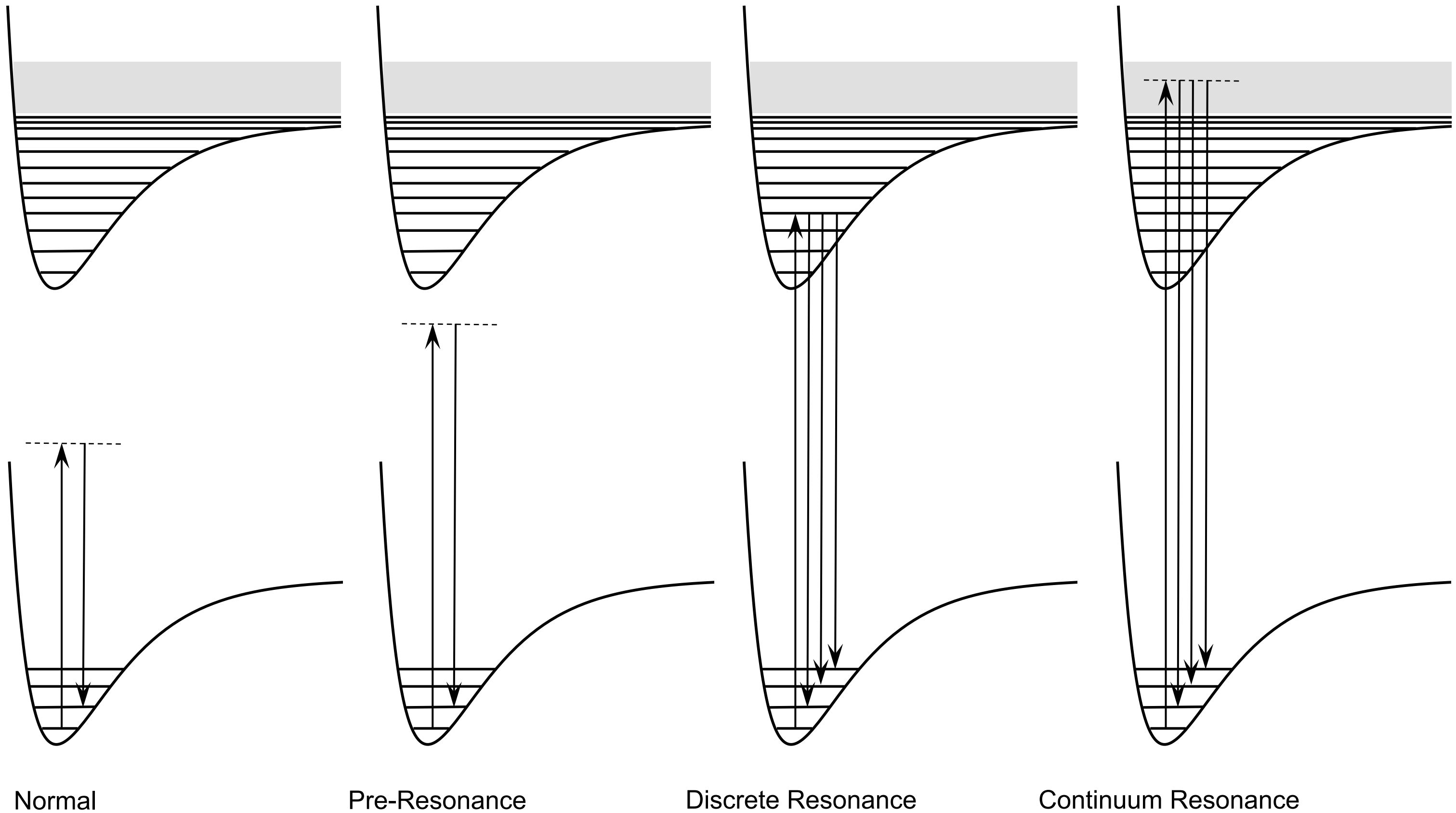
(5) $$\Delta E\ \Delta t \sim \hbar \ \Rightarrow\ (E = \hbar\omega)\ \Rightarrow\ \Delta\omega\ \Delta t \sim 1 \ \Rightarrow\ 2\Gamma_r\tau_r \sim 1 \ \Rightarrow\ \boxed{\Gamma_r \sim \frac{1}{2\tau_r}}$$

(6) $$\omega_{ri} = \omega_r - \omega_i$$

(7) $$\mathcal{E}_\sigma = \mathcal{E}_{\sigma 0} \exp\left[-\mathrm{i}(\omega_0 - \omega_{fi})\right] \qquad \omega_0 = E_0/\hbar \qquad \sigma = x,\ y,\ z$$

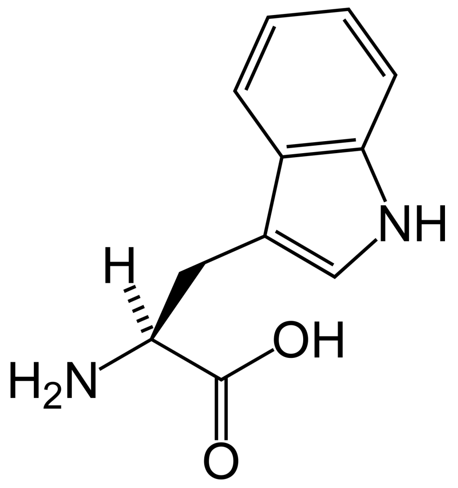
(8) $$\boxed{(\alpha_{\rho\sigma})_{fi} = \left\langle \psi_f^0 \middle| \alpha_{\rho\sigma} \middle| \psi_i^0 \right\rangle = \frac{1}{\hbar}\sum_{r\neq i,f}\left(\frac{\left\langle \psi_f^0 \middle| \hat{\mu}_\rho \middle| \psi_r^0 \right\rangle \left\langle \psi_r^0 \middle| \hat{\mu}_\sigma \middle| \psi_i^0 \right\rangle}{\omega_{ri} - \omega_0 - \mathrm{i}\Gamma_r} + \frac{\left\langle \psi_f^0 \middle| \hat{\mu}_\sigma \middle| \psi_r^0 \right\rangle \left\langle \psi_r^0 \middle| \hat{\mu}_\rho \middle| \psi_i^0 \right\rangle}{\omega_{rf} + \omega_0 + \mathrm{i}\Gamma_r} \right)}$$

$$\left(\alpha_{\rho\sigma}\right)_{fi} = \left\langle \psi_f^0 \middle| \alpha_{\rho\sigma} \middle| \psi_i^0 \right\rangle = \frac{1}{\hbar}\sum_{r\neq i,f}\left(\frac{\left\langle \psi_f^0 \middle| \hat{\mu}_\rho \middle| \psi_r^0 \right\rangle \left\langle \psi_r^0 \middle| \hat{\mu}_\sigma \middle| \psi_i^0 \right\rangle}{\omega_{ri} - \omega_0 - \mathrm{i}\Gamma_r} + \frac{\left\langle \psi_f^0 \middle| \hat{\mu}_\sigma \middle| \psi_r^0 \right\rangle \left\langle \psi_r^0 \middle| \hat{\mu}_\rho \middle| \psi_i^0 \right\rangle}{\omega_{rf} + \omega_0 + \mathrm{i}\Gamma_r} \right)$$

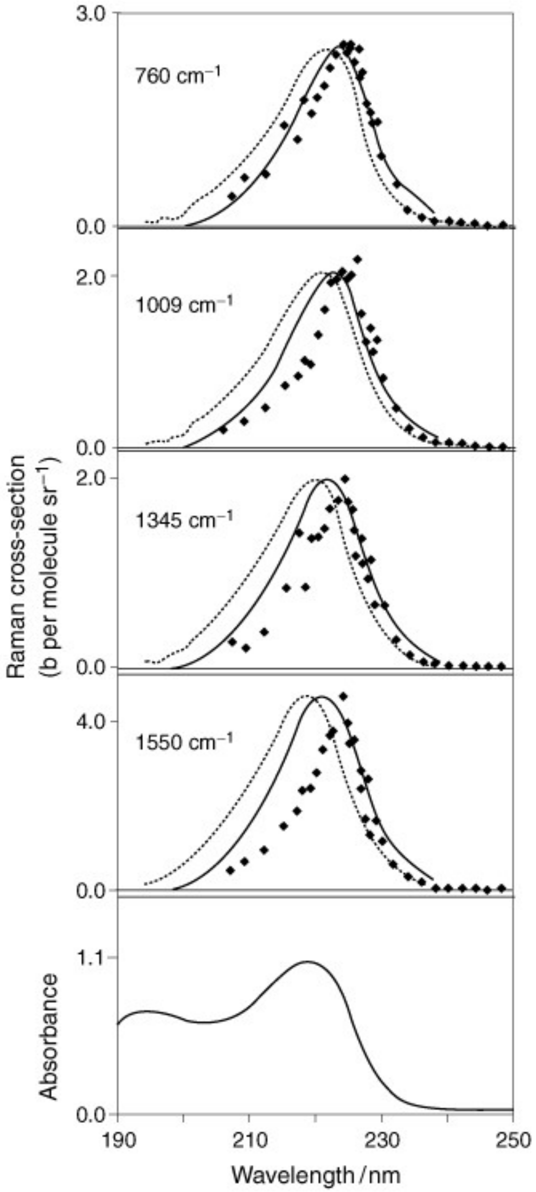


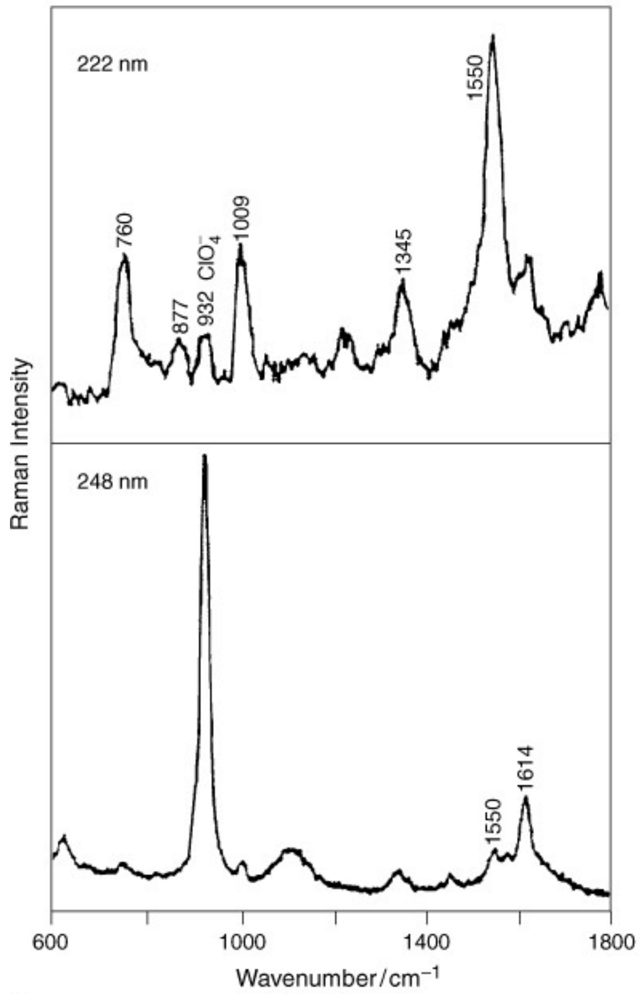
Further Reading: D. Long, *Raman Spectroscopy* and D.L. Rousseau, P.F. Williams, "Resonance Raman scattering of light from a diatomic molecule", *J. Chem. Phys.* , *64*, 3519-3537 (1976).

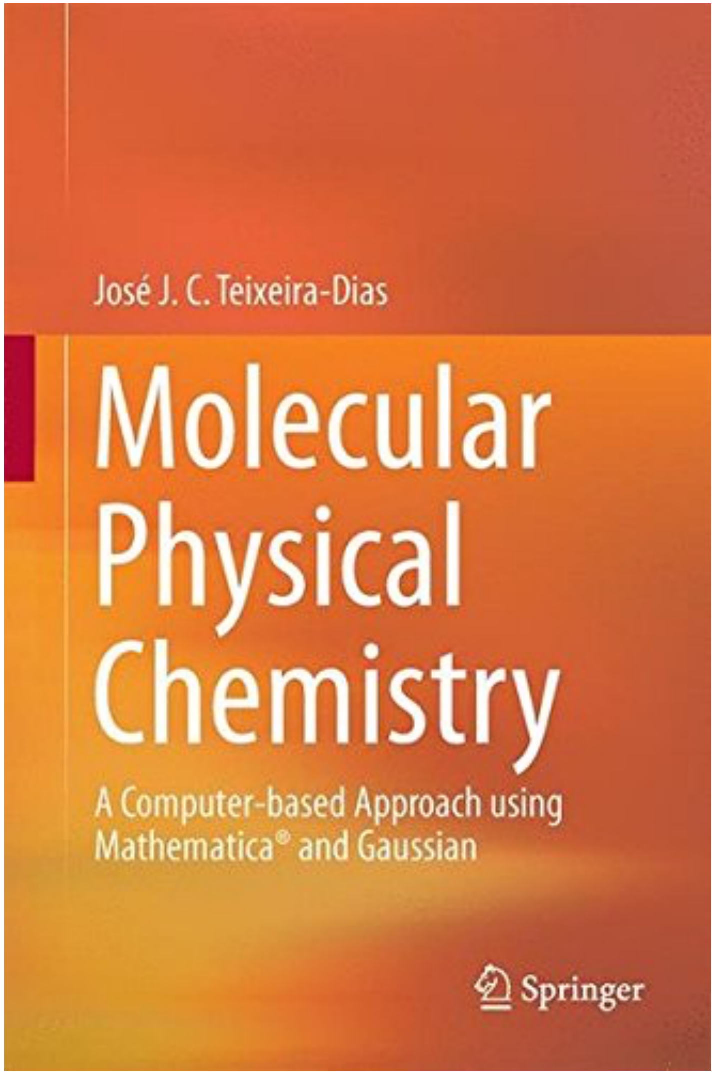
"Tryptophan UV Resonance Raman Excitation Profiles", J.A. Sweeney, S.A. Asher, *J. Phys. Chem*. 1990, *94*, 4784-4791



tryptophan







Available on 22 Nov 2016 (see amazon.co.uk)

Workshop Introduction to Mathematica®

***Mathematica* (www.wolfram.com)**
Author of *Mathematica*: Wolfram Research Inc. Champaign, Illinois, 2010.

Basic Rules

1. Capital letters in all command names

2. [ ] surround function arguments

3. { } are used for lists and ranges

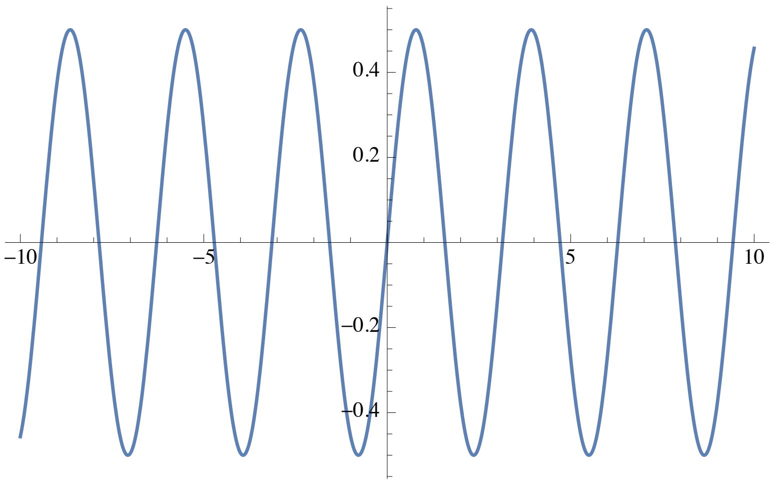
4. Shift+Enter to evaluate input

Examples

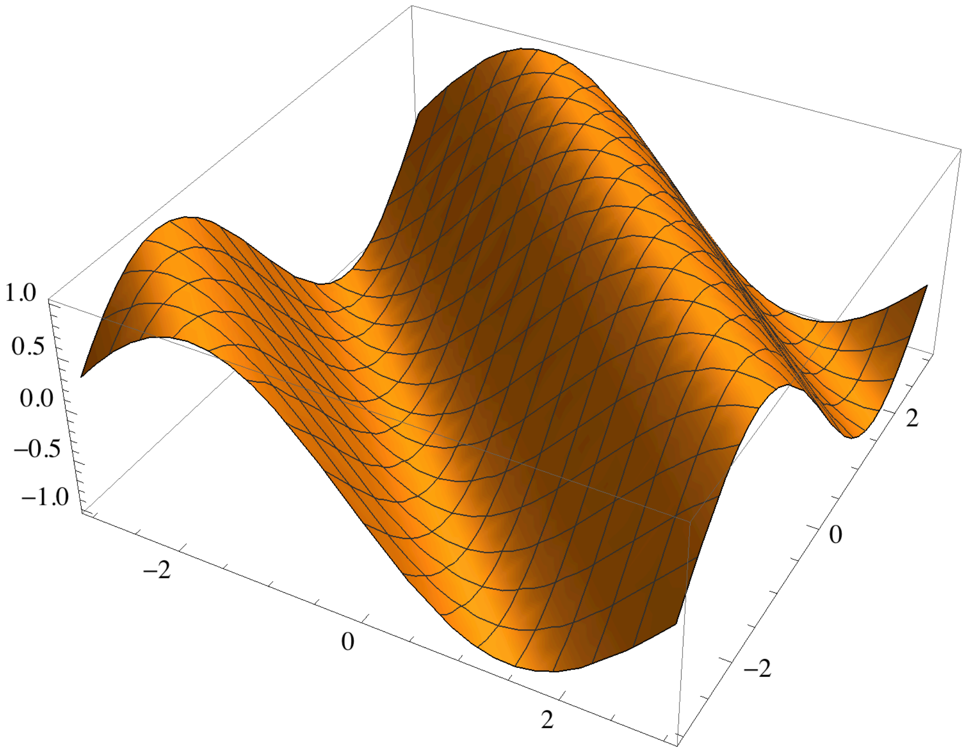
```
Integrate[Cos[2 * x], x]
```

$\frac{1}{2}$ Sin[2 x]

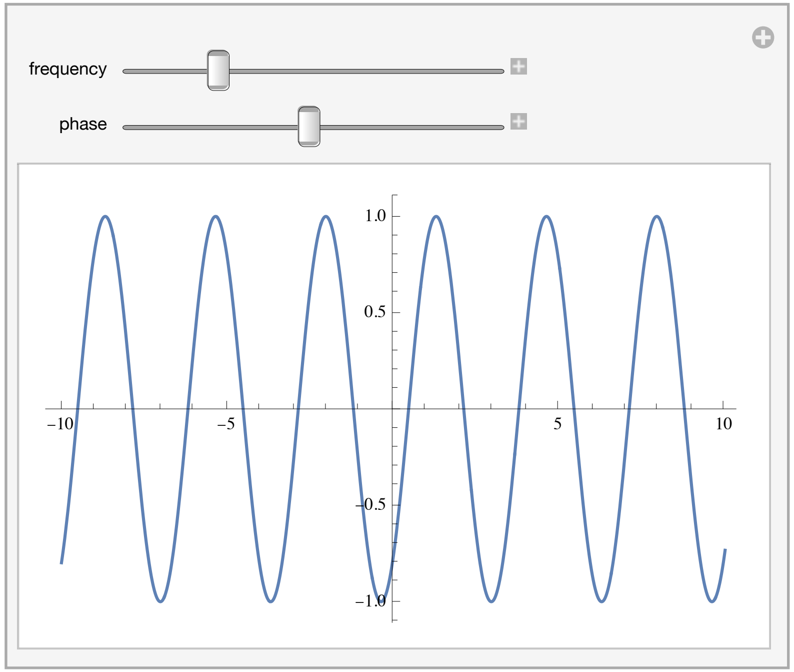
```
Plot[Sin[2 * x] / 2, {x, -1 0, 1 0}]
```



```
Plot3D[Sin[x + y], {x, -3, 3}, {y, -3, 3}]
```



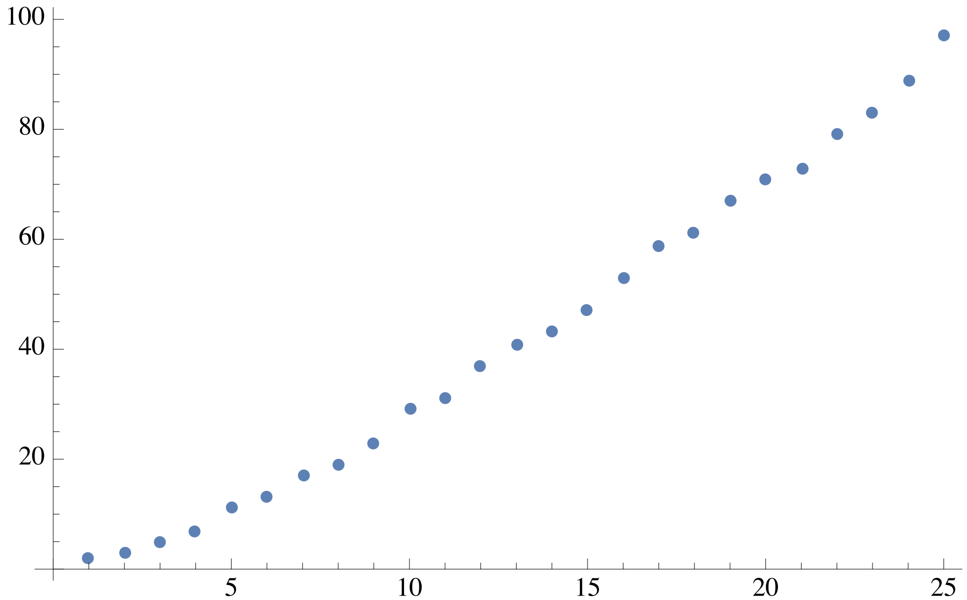
```
Manipulate[
 Plot[Sin[frequency * x + phase], {x, -10, 10}],
 {frequency, 1, 5}, {phase, 1, 10}]
```



```
myPrimes = Prime[Range[1, 25]]
```

{2, 3, 5, 7, 11, 13, 17, 19, 23, 29, 31, 37, 41, 43, 47, 53, 59, 61, 67, 71, 73, 79, 83, 89, 97}

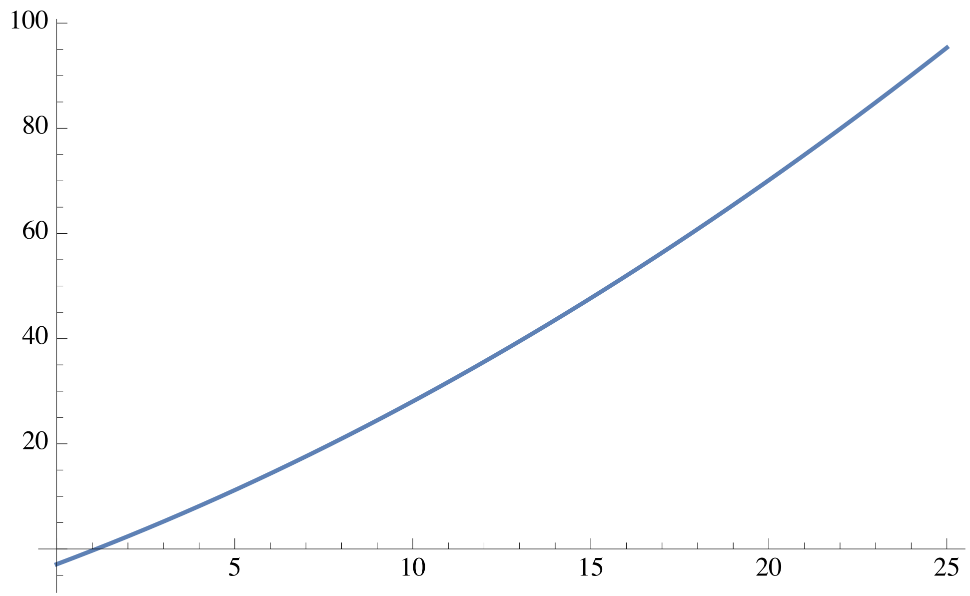
```
myListPlot = ListPlot[myPrimes]
```



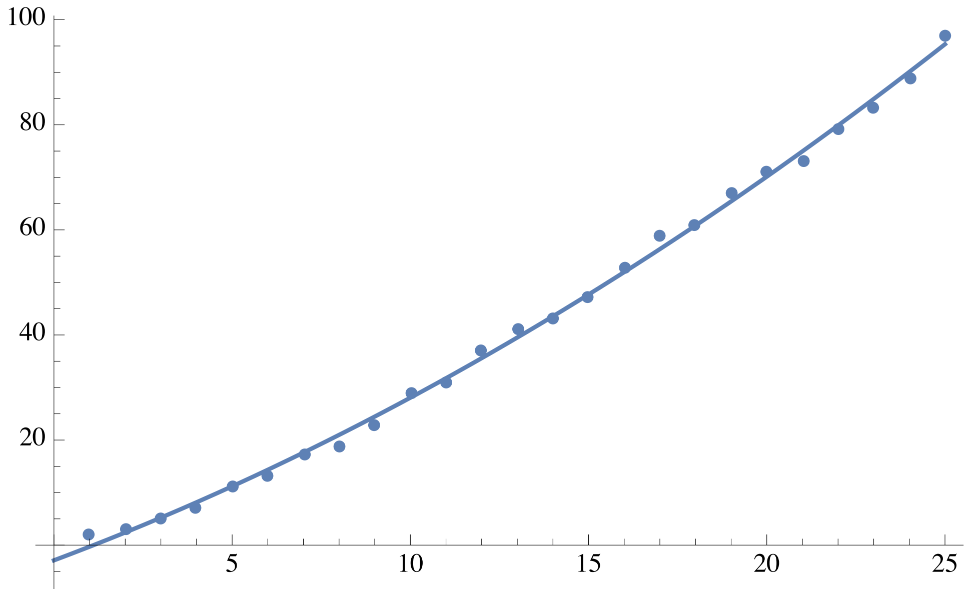
```
myFittedCurve = Fit[myPrimes, {1, x, x^2}, x]
```

$-2.89565 + 2.5392\,x + 0.0555927\,x^2$

```
myFittedPlot = Plot[myFittedCurve, {x, 0, 25}]
```



```
Show[myFittedPlot, myListPlot]
```

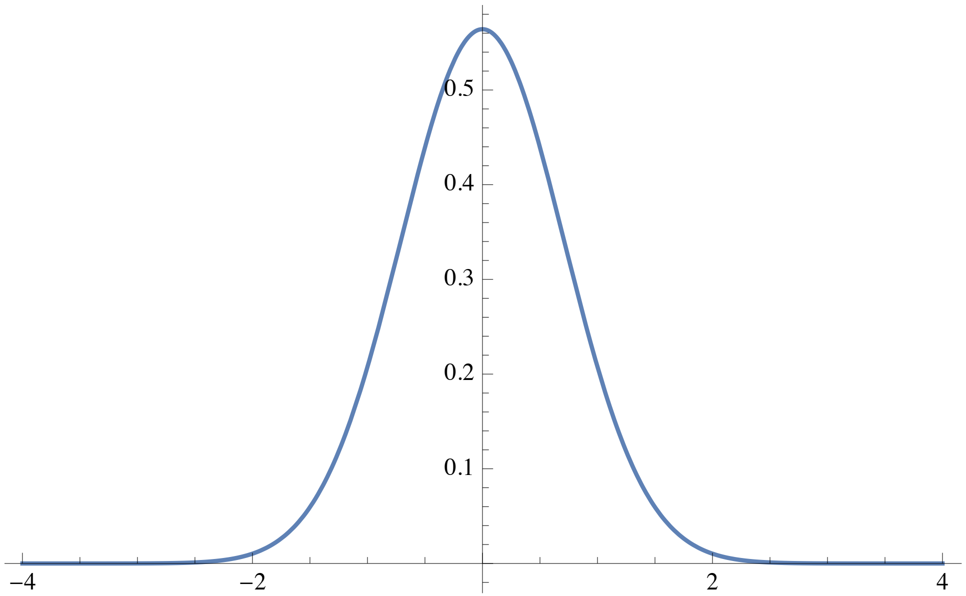


Workshop   Band Shapes and Convolution

Gaussian Band Shape

```
g[x_, x0_, a_] := Exp[-(a (x - x0))^2]
norm = Integrate[g[x, x0, a], {x, -Infinity, Infinity}, Assumptions -> {x0 > 0, a > 0}]
Plot[g[x, 0, 1.] / (norm /. a -> 1), {x, -4, 4}]
```

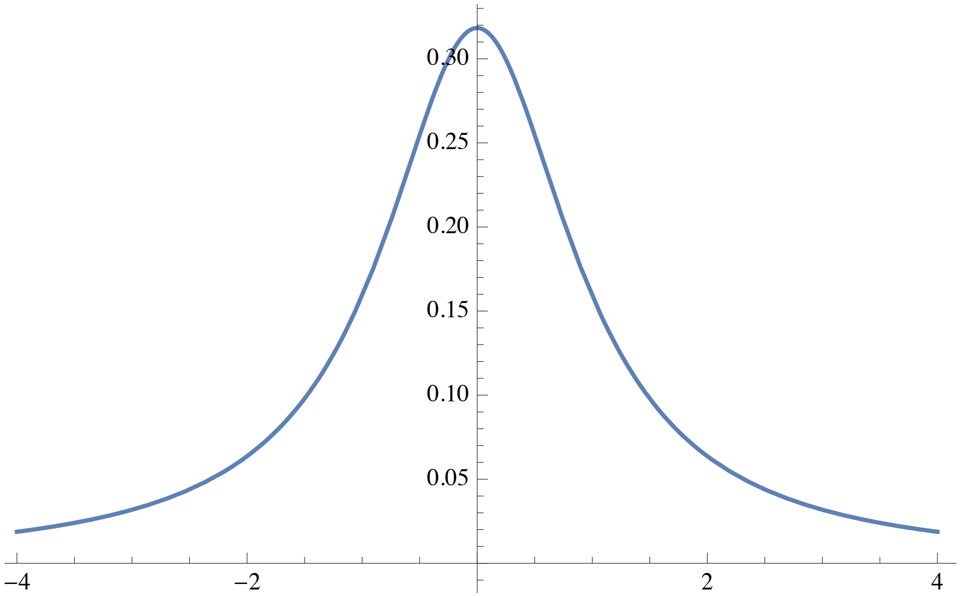
$$\frac{\sqrt{\pi}}{a}$$

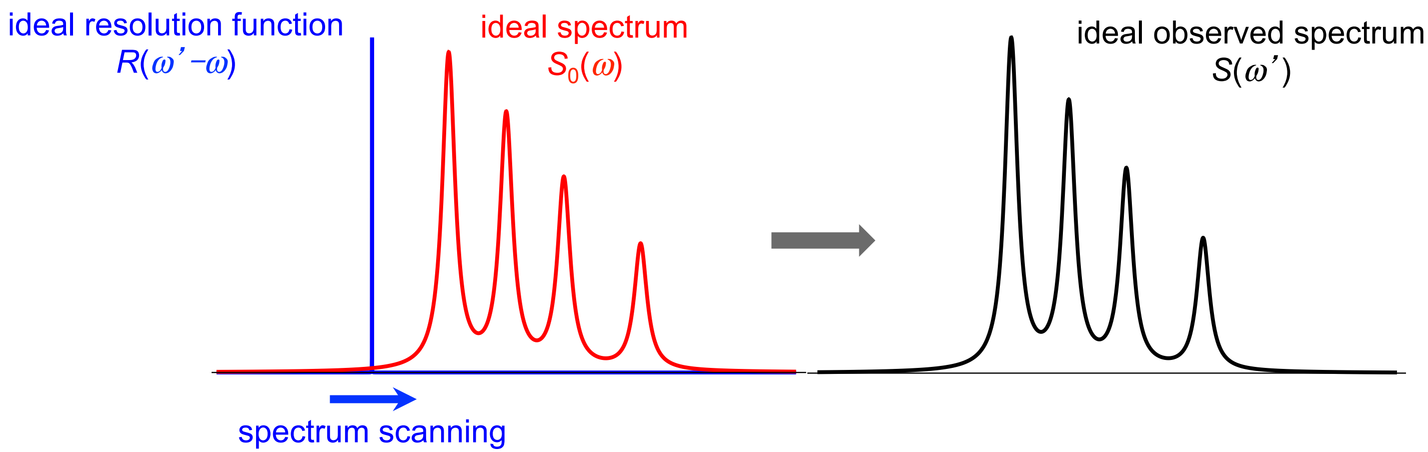


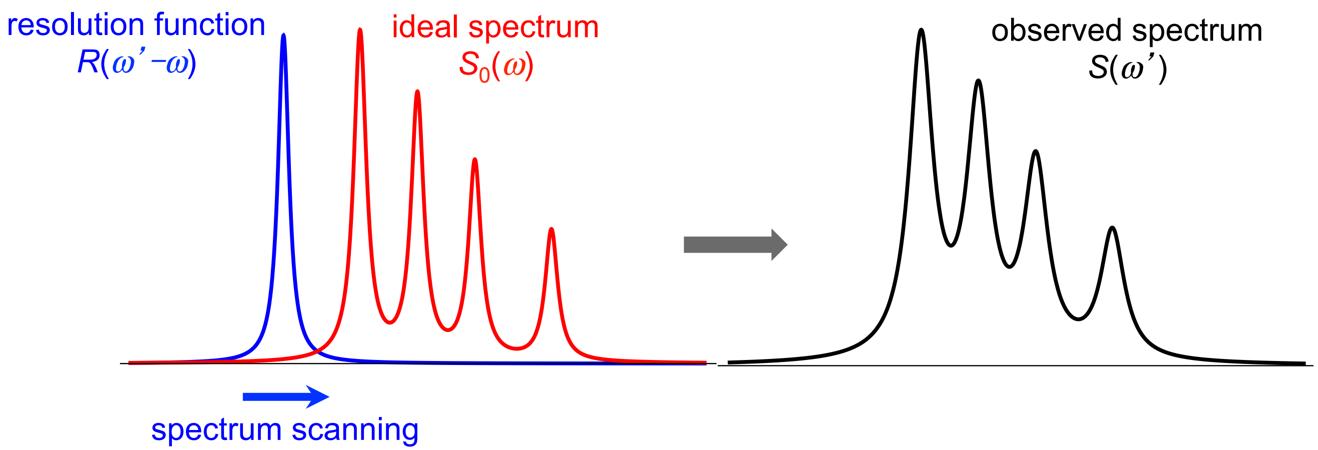
Lorentzian Band Shape

```
f[x_, x0_, a_] := 1 / (a^2 + (x - x0)^2)
norm = Integrate[f[x, x0, a], {x, -Infinity, Infinity}, Assumptions -> {x0 > 0, a > 0}]
Plot[f[x, 0, 1.] / (norm /. a -> 1), {x, -4, 4}]
```

$$\frac{\pi}{a}$$







$$S(\omega') = (S_0 * R)(\omega') \equiv \int_{-\infty}^{\infty} S_0(\omega)\, R(\omega' - \omega)\, d\omega$$

Convolution

```
f[x_,a_]:=a/Pi/(a^2+x^2)
aa=Plot[{f[x,1.]/f[0,1.],f[x,2.]/f[0,2.]},{x,-10,10},PlotRange->All,
PlotStyle->{Red,Blue}];
conv=Convolve[f[x,1.],f[x,2.],x,y];
conv/.y->0;
bb=Plot[conv/%,{y,-10,10},PlotRange->All,PlotStyle->Black];
Show[aa,bb]
```