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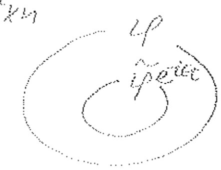
① Time-dependent and independent SE

Time-independent : $\hat{H}\tilde{\psi} = E\tilde{\psi}$ ······ special case of time-dep. (spatial fxn)

Time-dependent : $\hat{H}\psi = i\frac{\partial\psi}{\partial t}$ ······ every physically valid wfn must satisfy this. (spatial + temporal fxn)

$\psi_{\text{independent}} = \tilde{\psi}e^{-iEt}$ hidden time-dependence or "phase"

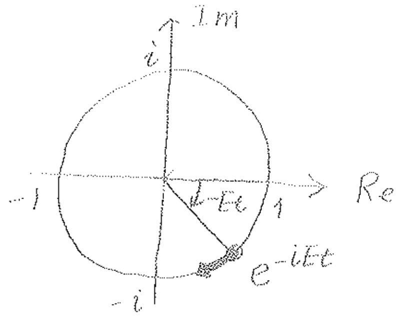


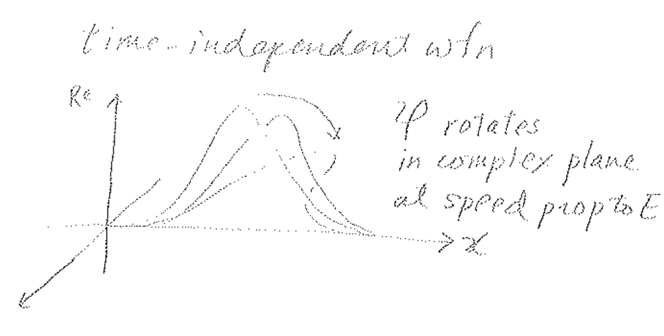
$$\hat{H}\left(\tilde{\psi}e^{-iEt}\right) = i\frac{\partial}{\partial t}\left(\tilde{\psi}e^{-iEt}\right) = E\left(\tilde{\psi}e^{-iEt}\right)$$

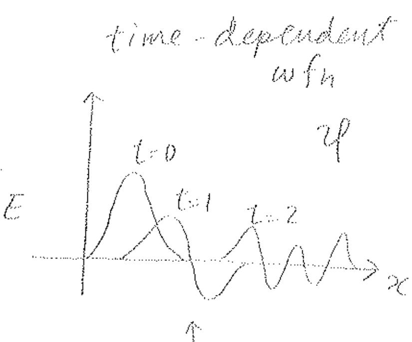
We can recover time-independent SE from time-dependent SE using time-independent $\psi = \tilde{\psi}e^{-iEt}$. In this sense $\psi = \tilde{\psi}e^{-iEt}$ does not depend on time.

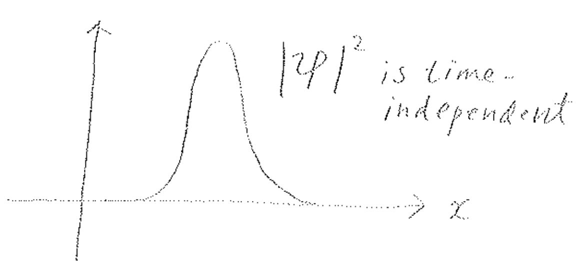
An expectation value $\langle\tilde{\psi}e^{-iEt}|\hat{\Omega}|\tilde{\psi}e^{-iEt}\rangle = \langle\tilde{\psi}|\hat{\Omega}|\tilde{\psi}\rangle$ of any time-independent operator $\hat{\Omega}$ is independent of time and depends only on the spatial part.

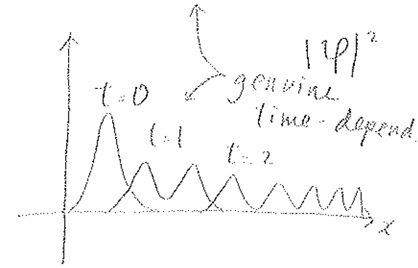
$$e^{-iEt} = \cos(Et) - i\sin(Et)$$











② Time-dependent perturbation theory

[aka linear (and nonlinear) response theory or Fermi's Golden Rule]

Purpose: to explain a single-photon spectroscopic transition such as microwave, infrared, UV/vis absorption and emission, Franck-Condon principle

A photon $\hbar\omega$ = electro$\underbrace{\text{magnetic}}_{\text{negligible effect}}$ wave = oscillating electric field at ω (weak enough to allow perturbation treatment)

i) Zero-th order state = stationary state (e.g. ground state) described perfectly by time-independent SE

0th order

$$\hat{H}^{(0)} \tilde{\Psi}_0^{(0)} e^{-iE_0^{(0)}t} = E_0^{(0)} \tilde{\Psi}_0^{(0)} e^{-iE_0^{(0)}t}$$

we should be explicit about hidden t-dependence

spatial wfn (~ dropped hereafter)

ground state

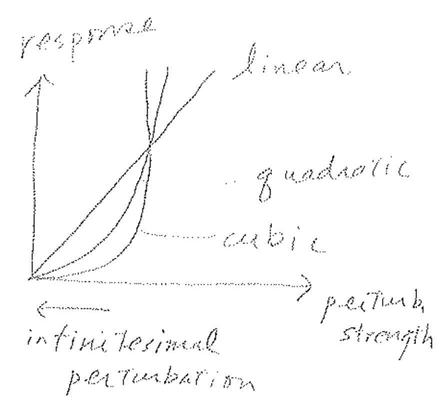
ii) Perturbation

polarization of light

real oscillating electric field in z direction

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}(t) = \hat{H}^{(0)} + \hat{z} \underbrace{E}_{\text{field strength}} \left(e^{i\omega t} + e^{-i\omega t}\right)$$

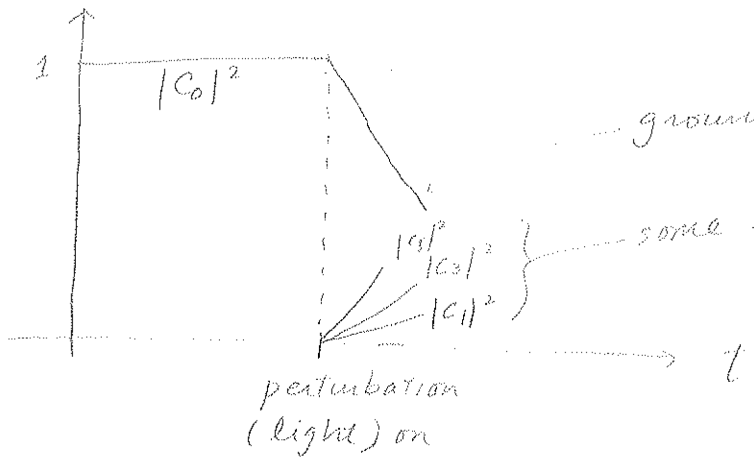
iii) Response (linear response dominates)



$$\Psi_0^{(1)}(t) = \sum_{k=0}^{\infty} c_k(t) \underbrace{\Psi_k^{(0)} e^{-iE_k^{(0)}t}}_{\text{form complete set}}$$

finding $\Psi_0^{(1)}(t)$ is the same as finding $\{c_k(t)\}$

What do we expect $\{C_k(t)\}$ to behave?



ground state population depleted

some excited state pop. increase at rate $\frac{d|C_n|^2}{dt}$

This rate is proportional to transition probability or spectral band intensity we are after.

iv) Time-dep. SE

$$\lambda = 1$$

$$\left(\hat{H}^{(0)} + \lambda \hat{H}^{(1)}\right)\left(\psi_0^{(0)} e^{-iE_0^{(0)}t} + \lambda \sum_{k=0}^{\infty} C_k(t)\, \psi_k^{(0)} e^{-iE_k^{(0)}t}\right)$$

$$= i \frac{\partial}{\partial t}\left(\psi_0^{(0)} e^{-iE_0^{(0)}t} + \lambda \sum_{k=0}^{\infty} C_k(t)\, \psi_k^{(0)} e^{-iE_k^{(0)}t}\right)$$

v) First order in λ

$$\hat{H}^{(1)} \psi_0^{(0)} e^{-iE_0^{(0)}t} + \underbrace{\hat{H}^{(0)} \sum_{k=0}^{\infty} C_k \psi_k^{(0)} e^{-iE_k^{(0)}t}}_{\sum_{k=0}^{\infty} C_k E_k^{(0)} \psi_k^{(0)} e^{-iE_k^{(0)}t}} = i \frac{\partial}{\partial t} \sum_{k=0}^{\infty} C_k \psi_k^{(0)} e^{-iE_k^{(0)}t}$$

spatial = time-indep.

$$i \sum_{k=0}^{\infty} \frac{\partial C_k}{\partial t} \psi_k^{(0)} e^{-iE_k^{(0)}t}$$

$$+ \sum_{k=0}^{\infty} C_k E_k^{(0)} \psi_k^{(0)} e^{-iE_k^{(0)}t}$$

cancellation

$$\hat{H}^{(1)} \psi_0^{(0)} e^{-iE_0^{(0)}t} = i \sum_{k=0}^{\infty} \frac{\partial C_k}{\partial t} \psi_k^{(0)} e^{-iE_k^{(0)}t}$$

vi) Multiply $\varphi_n^{(0)*}$ and integrate in the whole space

$$\underbrace{\int \varphi_n^{(0)*}\,\hat{H}^{(1)}\,\varphi_0^{(0)}\,\underbrace{d\mathbf{r}}_{\text{spatial}}}_{H_{n0}^{(1)}}\; e^{-iE_0^{(0)}t} = i\sum_{k=0}^{\infty}\frac{\partial c_k}{\partial t}\underbrace{\int \varphi_n^{(0)*}\varphi_k^{(0)}\,d\mathbf{r}}_{\delta_{nk}}\; e^{-iE_k^{(0)}t}$$

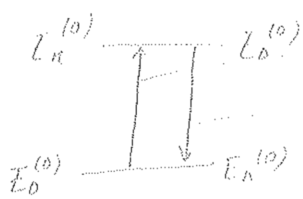
$$E\left(e^{i\omega t}+e^{-i\omega t}\right)\int \varphi_n^{(0)*}\,\hat{z}\,\varphi_0^{(0)}\,d\mathbf{r} = i\frac{\partial c_n}{\partial t}\,e^{-i\left(E_n^{(0)}-E_0^{(0)}\right)t}$$

Though $\frac{\partial c_n}{\partial t}$ is time-dep, it's not oscillatory. The oscillating parts must agree for this equation to be satisfied:

$$E_n^{(0)}-E_0^{(0)}=\pm\omega$$

(remember $\hbar = 1$ a.u.)
$E_n^{(0)}-E_0^{(0)}=\pm\hbar\omega$

Energy conservation law



$E_n^{(0)}-E_n^{(0)}=+\hbar\omega$ (absorption)
$E_n^{(0)}-E_0^{(0)}=-\hbar\omega$ (emission)

(In quantum world, promotion and demotion occurs at an equal probability and Peter Principle does not apply!)

$$\frac{\partial c_n}{\partial t} = -iE\int \varphi_n^{(0)*}\,\hat{z}\,\varphi_0^{(1)}\,d\mathbf{r}$$

(= constant in time)

$$c_n = -i\int_0^t H_{n0}^{(1)}\,dt \;\propto\; -iE\int \varphi_n^{(0)*}\,\hat{z}\,\varphi_0^{(0)}\,d\mathbf{r}$$

vii) Fermi's Golden Rule

$$W_{n\leftarrow 0} \propto \frac{\partial |C_n|^2}{\partial t} \propto |E|^2 \left| \underbrace{\int \psi_n^{(0)*}\, \hat{z}\, \psi_0^{(0)}\, d\mathbf{r}}_{\text{TDM}} \right|^2$$

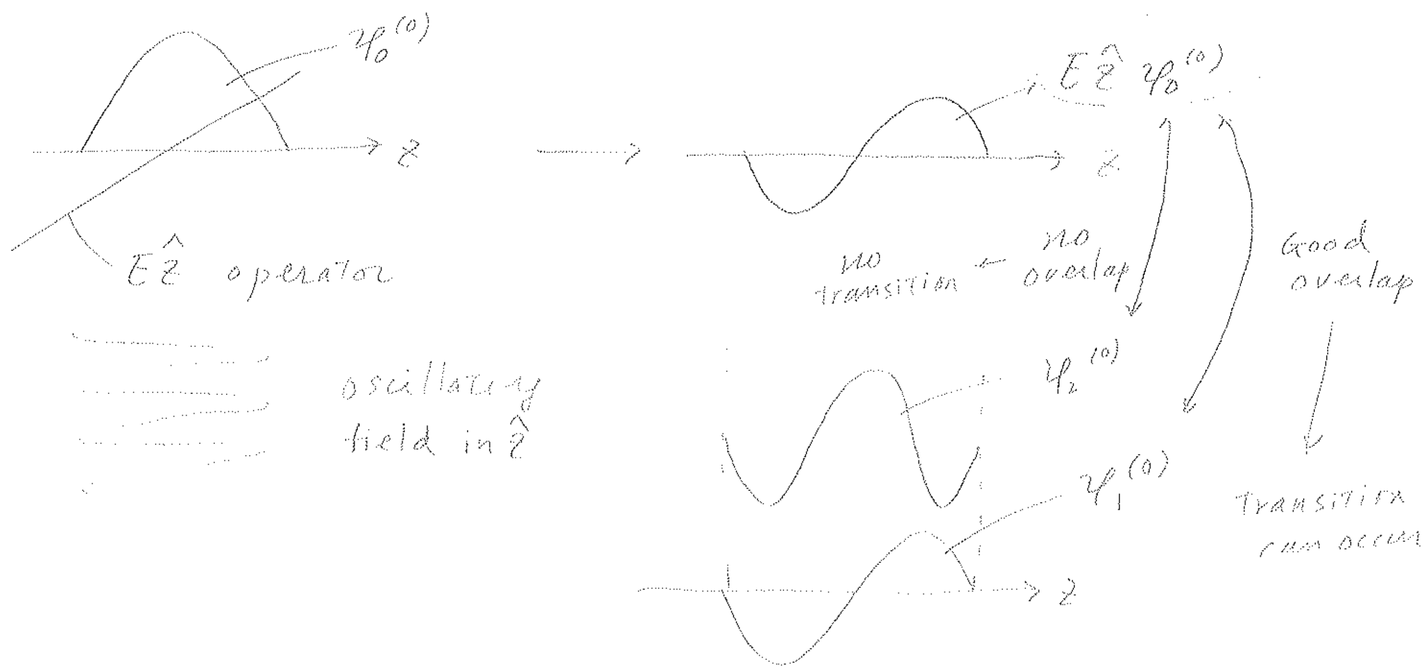
transition rate or probability

if $E_n^{(0)} - E_0^{(0)} = \pm \hbar\omega$

TDM

transition dipole moment

Physical interpretation

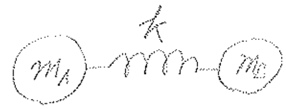


(3) IR absorption

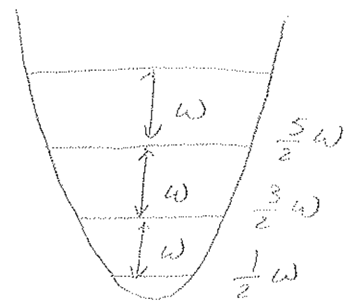
i) Diatomic vibration Schrödinger eq.

$$\left(-\frac{1}{2\mu} \frac{\partial^2}{\partial x^2} + \underbrace{\frac{1}{2} k x^2}_{\text{harmonic}} \right) \varphi(x) = E\, \varphi(x)$$

reduced mass $\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$



$$\psi_v(x) = N_v \underbrace{H_v(x)}_{\substack{\text{Hermite} \\ \text{polynomial}}} \underbrace{e^{-\sqrt{\mu k}\, x^2/2}}_{\text{Gaussian}}$$



$E_v = (v + \frac{1}{2})\,\omega\,, \quad \omega = \sqrt{\frac{k}{\mu}}$ (same as classical)

ii) IR abs.

$$\langle e_0 v_n | \hat{z} | e_0 v_m \rangle = \langle v_n | \langle e_0 | \hat{z} | e_0 \rangle | v_m \rangle \quad \text{BO approx.}$$

e_0: same electronic

v_n: different final vib. state

v_m: ground electronic state, initial vibrational state

$\langle e_0 | \hat{z} | e_0 \rangle$ → proportional to perm. dipole μ_z

$$\propto \langle v_n | \mu_z | v_m \rangle = \mu_z \underbrace{\langle v_n | v_m \rangle}_{\text{orthogonal}} = 0 \; ???$$

No IR abs. occurs?

The fallacy is that μ_0 is assumed to be constant w/ x.
$|e\rangle$ and μ_0 is parametrically dependent on x.

$$\langle e_0 v_n | \hat{z} | e_0 v_m \rangle = \langle v_n | \mu_z^0 + \left(\frac{\partial \mu_z}{\partial x}\right) \hat{x} + \cdots | v_m \rangle \overset{\text{double harmonic approx.}}{\sim} \left(\frac{\partial \mu_z}{\partial x}\right) \langle v_n | \hat{x} | v_m \rangle$$

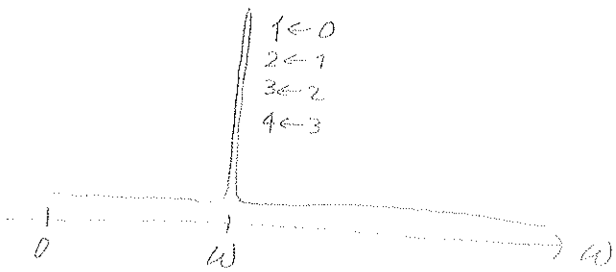
iii) Hermite polynomial

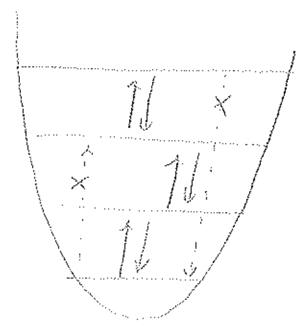
$$x H_v(x) = v H_{v-1}(x) + \frac{1}{2} H_{v+1}(x) \qquad \text{recursion}$$

$$\langle v_n | \hat{x} | v_m \rangle \propto \int_{-\infty}^{\infty} H_n \, x \, H_m \, e^{-x^2/2\alpha^2} dx$$

$$= \underbrace{m \int_{-\infty}^{\infty} H_n H_{m-1} e^{-x^2/2\alpha^2} dx}_{\sim 0,\ n \neq m-1} + \underbrace{\frac{1}{2} \int_{-\infty}^{\infty} H_n H_{m+1} e^{-x^2/2\alpha^2} dx}_{\sim 0,\ n \neq m+1}$$

$= \text{nonzero if } n = m \pm 1$

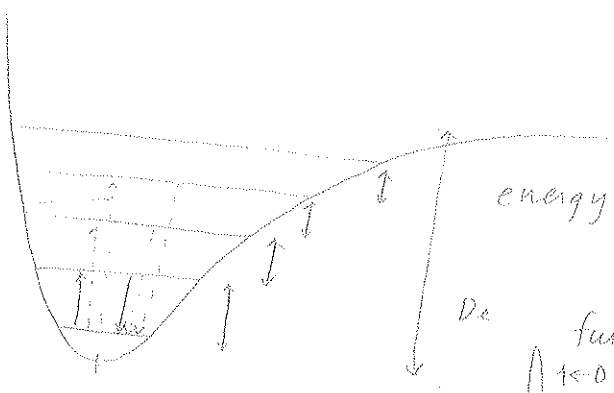


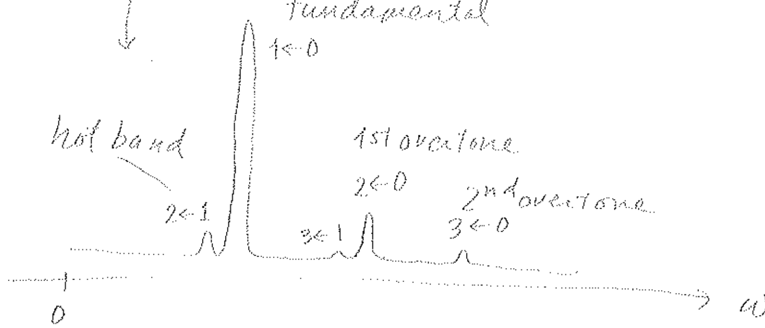


All allowed transitions have freq ω

iv) Anharmonicity

overtones now have small but nonzero transition probability





Morse potential $\quad V(r) = D_e \left\{ 1 - e^{-a(r_e - r)} \right\}^2$

$$E_v = \left(v + \frac{1}{2}\right)\omega - \frac{1}{4D_e} \left\{ \omega \left(v + \frac{1}{2}\right) \right\}^2, \quad \omega = \sqrt{\frac{k}{m}} = a\sqrt{\frac{2D_e}{m}}$$

harmonic force const at r = re

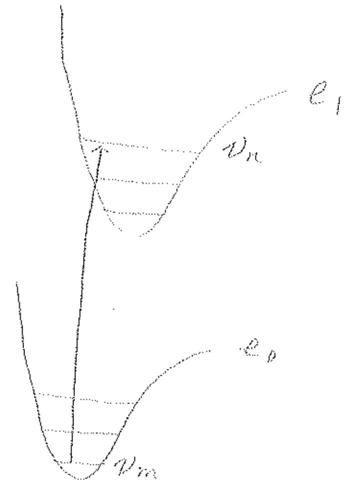
④ UV/vis absorption

$$\langle e_1 v_n | \hat{z} | e_0 v_m \rangle$$

BO approx.

$$= \langle e_1 | \hat{z} | e_0 \rangle \underbrace{\langle v_n | v_m \rangle}_{\substack{\text{orthonormal} \\ \delta_{nm}}}$$

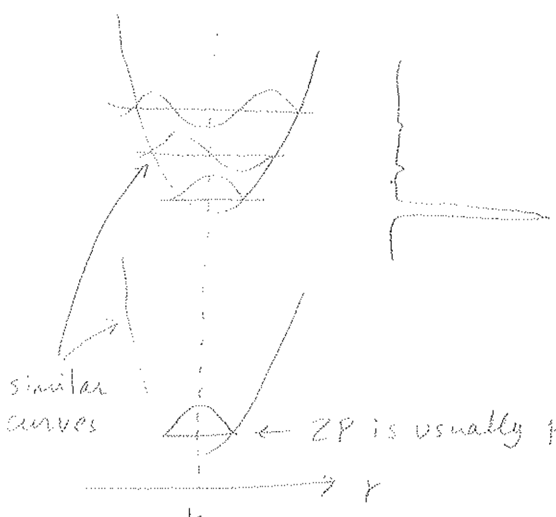
= 0-0 transition only ???



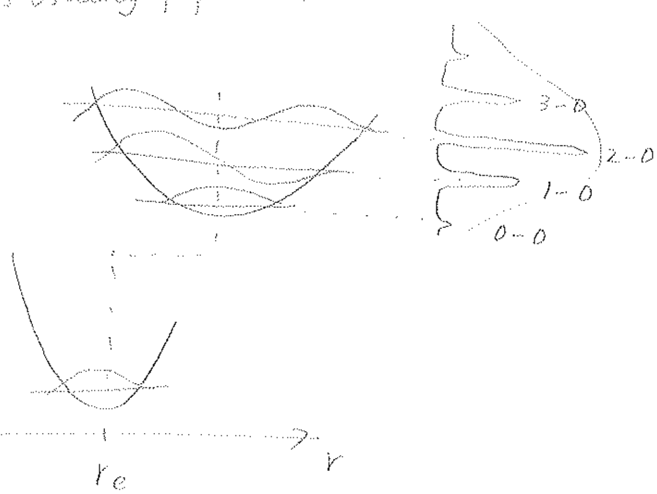
The fallacy is that v_n and v_m are eigenfxn of different vib. Schrödinger eqs. (the former for e_1 state, the latter for e_0) and are not orthogonal

$$\langle e_1 v_n | \hat{z} | e_0 v_m \rangle = \underbrace{\langle e_1 | \hat{z} | e_0 \rangle}_{\substack{\text{electronic} \\ \text{TDM}}} \underbrace{\langle v_n | v_m \rangle}_{\substack{\text{Franck-Condon} \\ \text{factor}}}$$

(Not "Frank")
James Franck is a Nobel Laureate from Johns Hopkins



0-0 dominates = excited electron is non or anti bonding

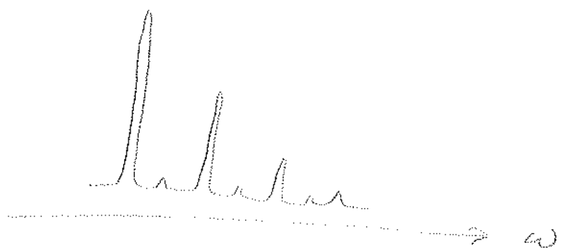


long FC progression = excited electron is bonding; significant weakening of bond and bond elongation.

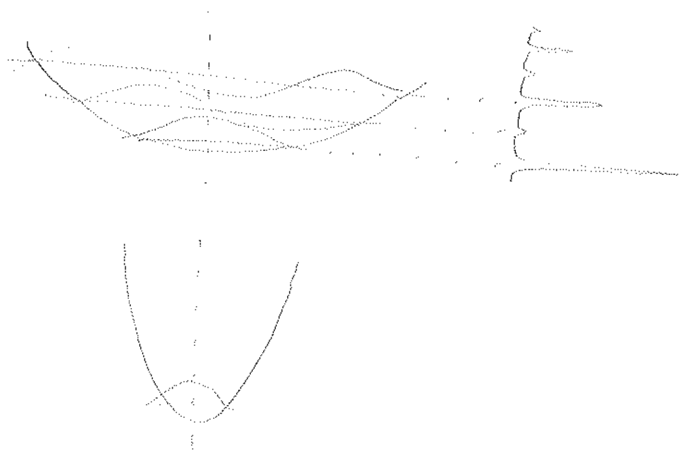
Q: How can one measure vib freqs of molecule in an excited state?
(electronic)

A: Just measure UV/vib abs.

Q: What does this FC progression suggest re. the shape and relative position of two potentials?



A:



r_e