Applied Spectroscopy

The Franck-Condon Factor

NC State University

Separation of electronic and nuclear parts of the transition moment

The transition dipole moment,

$$M_{12} = e\langle \Psi_1 | q | \Psi_2 \rangle$$

can be separated into the electronic wavefunction ψ that depends on q and the nuclear wave-function χ that does not.

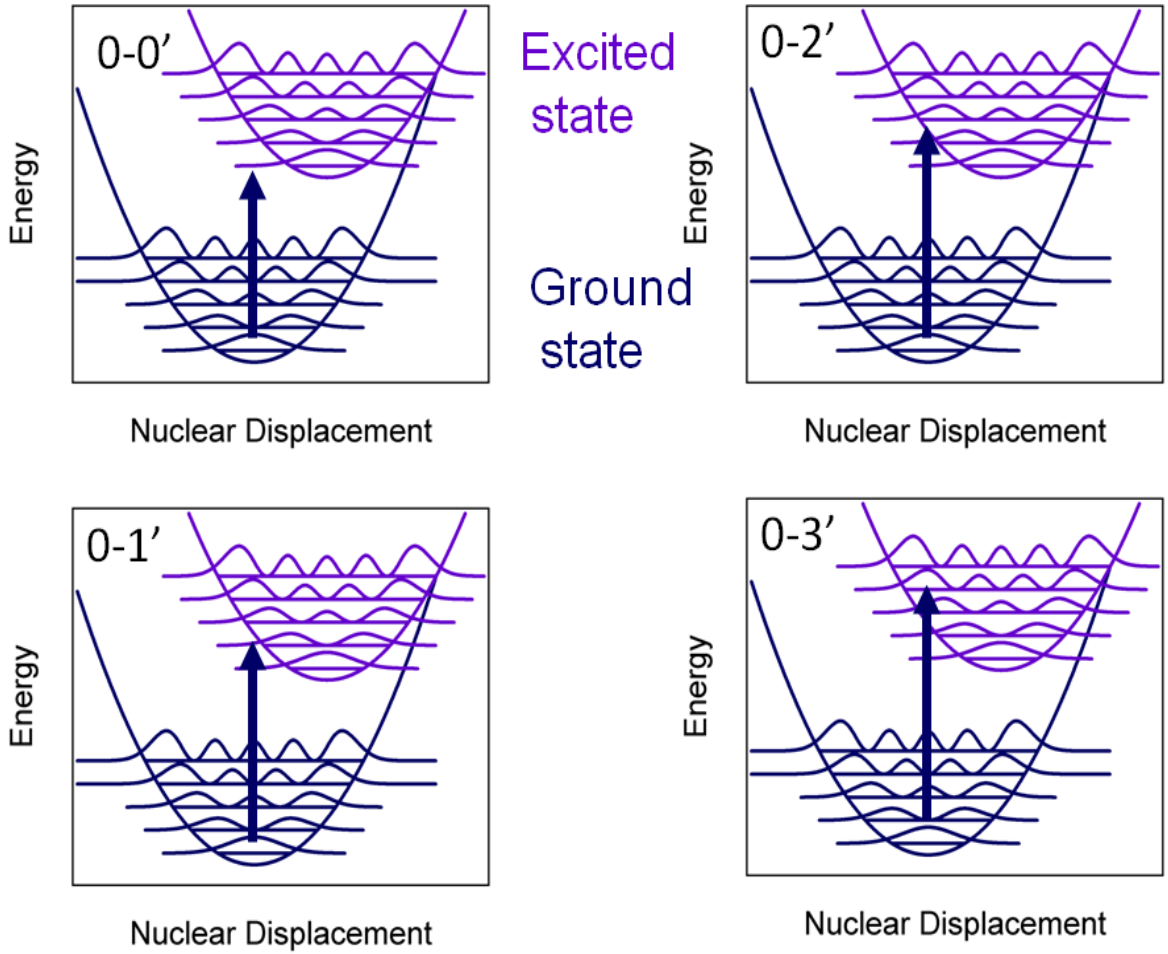
$$e\langle \Psi_1 | q | \Psi_2 \rangle = e\langle \psi_1 | q | \psi_2 \rangle \sum_{v\prime} \langle \chi_{10} | \chi_{2v\prime} \rangle$$

These enter the rate expression as the square

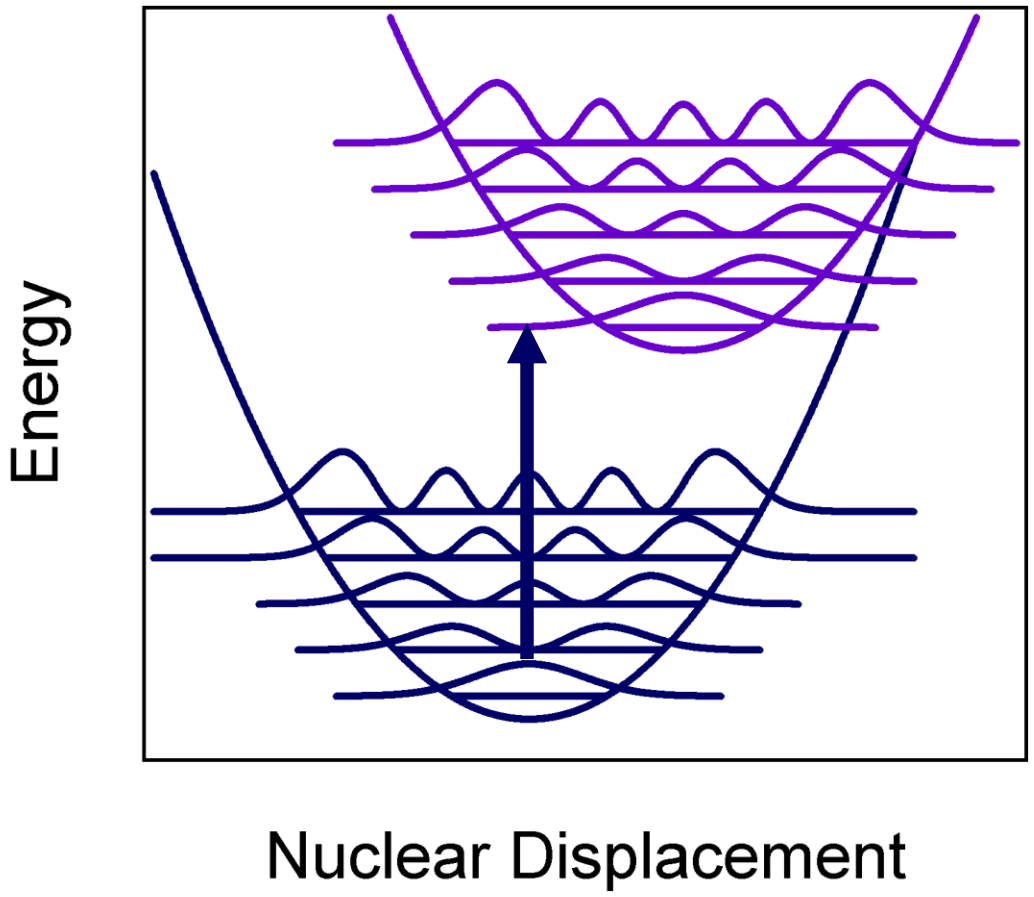
$$|e\langle \psi_1 | q | \psi_2 \rangle|^2 \sum_{v\prime} \langle \chi_{10} | \chi_{2v\prime} \rangle^2 = |M_{12}|^2 FC$$

The nuclear part

Because of the separation of time scales given the Born-Oppenheimer approximation, the transition between electronic states is rapid compared to nuclear motion. Therefore, we say that the transition occurs vertically on the scale of nuclear motion.



The Franck-Condon factor is due to the overlap of ground state v=0 with excited state v'=0', 1', etc.

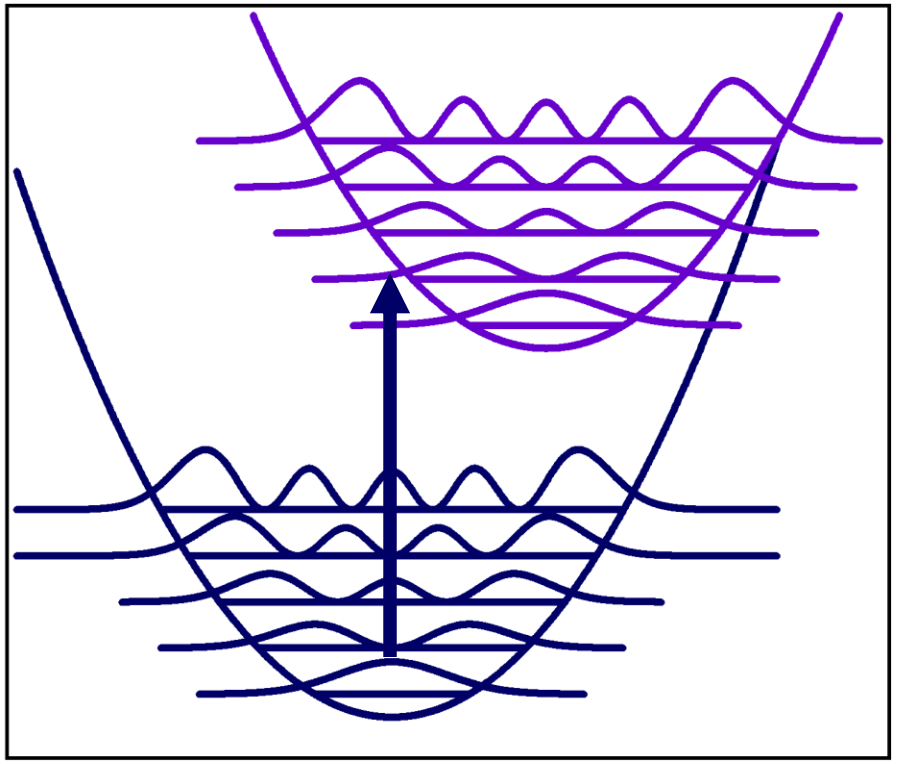


Excited state

0-0'

Ground state

The Franck-Condon factor is due to the overlap of ground state v=0 with excited state v'=0', 1', etc.

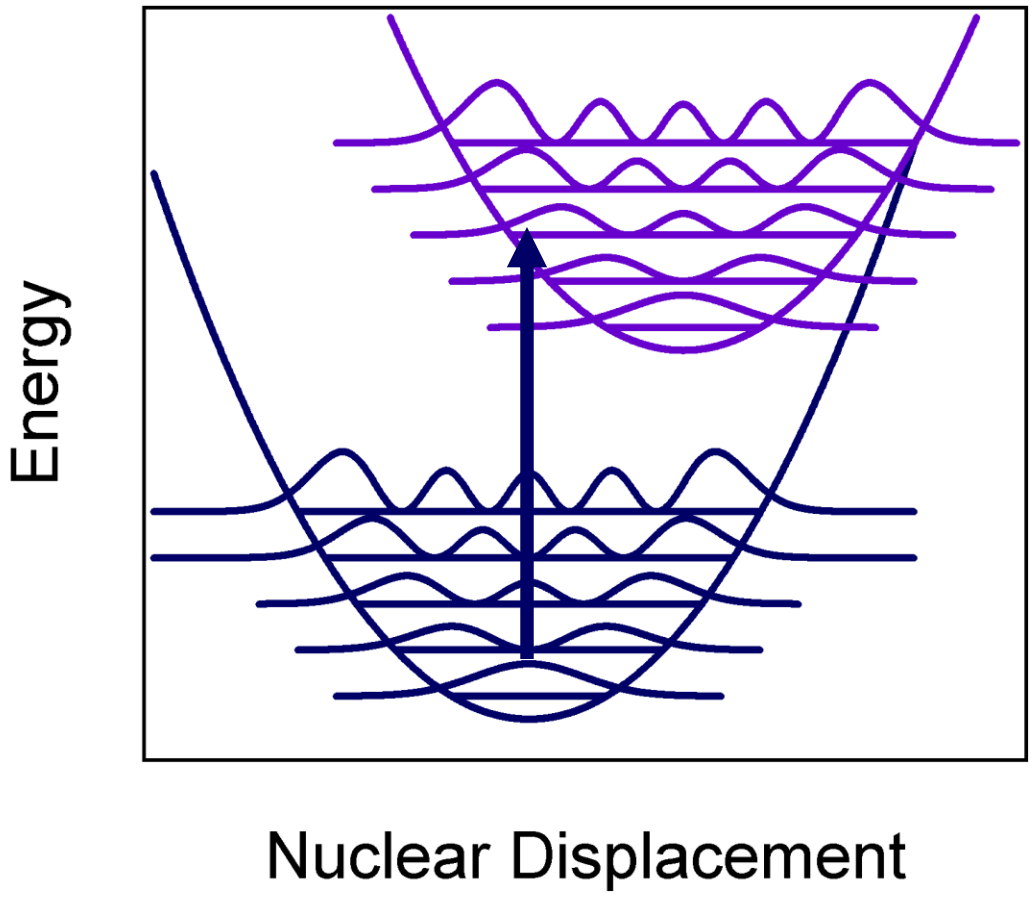


Excited state

0-1'

Ground state

The Franck-Condon factor is due to the overlap of ground state v=0 with excited state v'=0', 1', etc.

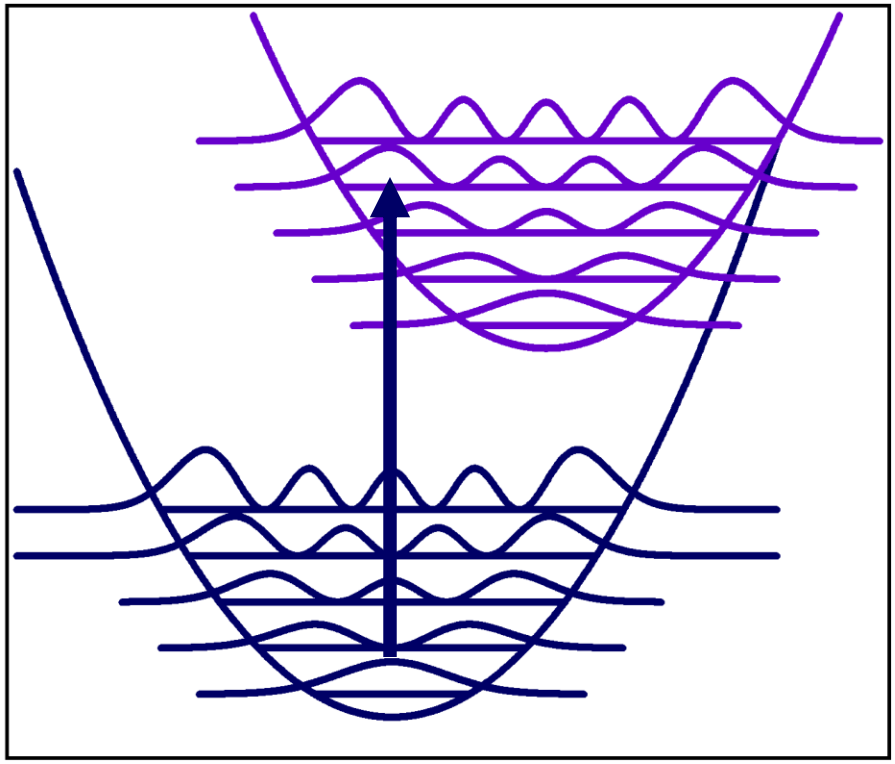


Excited state

0-2'

Ground state

The Franck-Condon factor is due to the overlap of ground state v=0 with excited state v'=0', 1', etc.

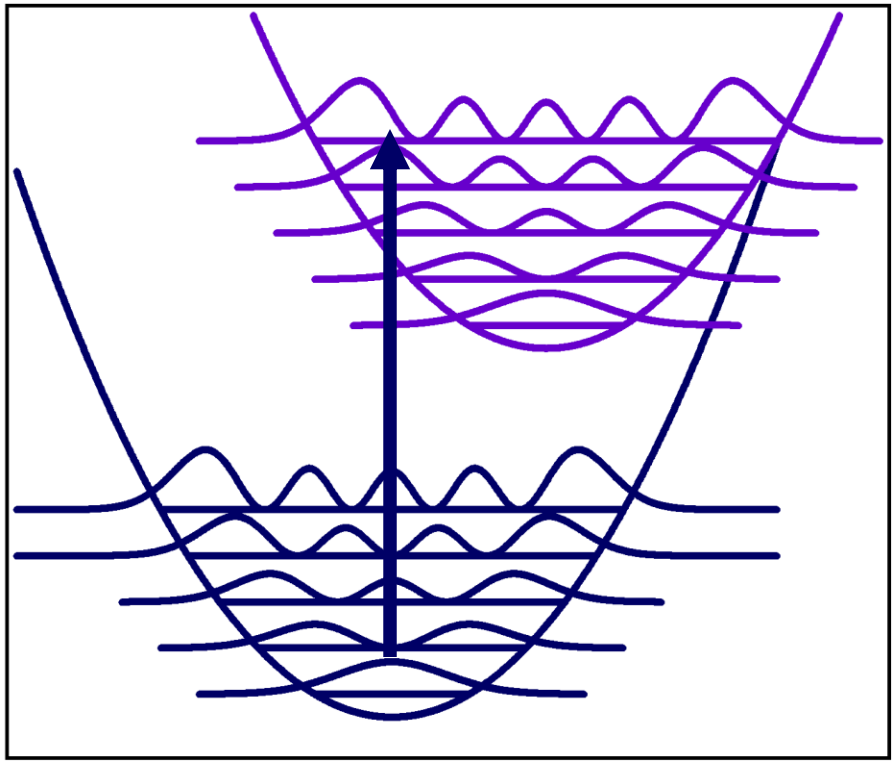


Excited state

0-3'

Ground state

The Franck-Condon factor is due to the overlap of ground state v=0 with excited state v'=0', 1', etc.

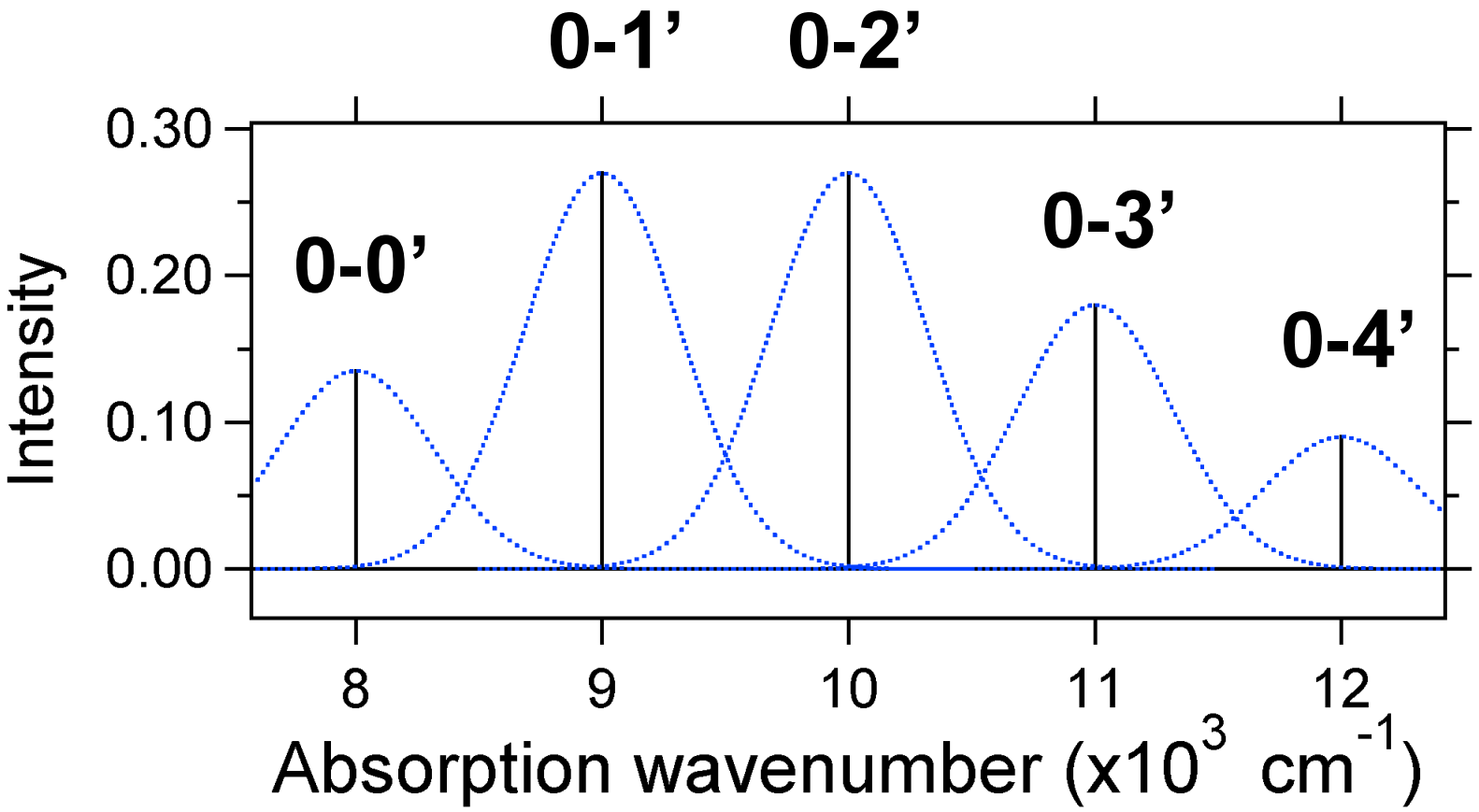


Excited state

0-4'

Ground state

Based on the FC factors we can construct a “stick” spectrum



Calculated assuming E(0-0’) = 8000 cm^{-1} and vibrational mode of 1000 cm^{-1}. 1 eV = 8065.6 cm^{-1}.

Vibrational overlap integrals

Transitions occur vertically, which means that the lowest vibrational state in the ground state manifold (v = 0) can have transitions to all of the excited state vibrational quanta (v' = 0', 1', 2', etc.). This would not be possible without the position shift. Recall that the vibrational wave functions are orthogonal. Therefore,

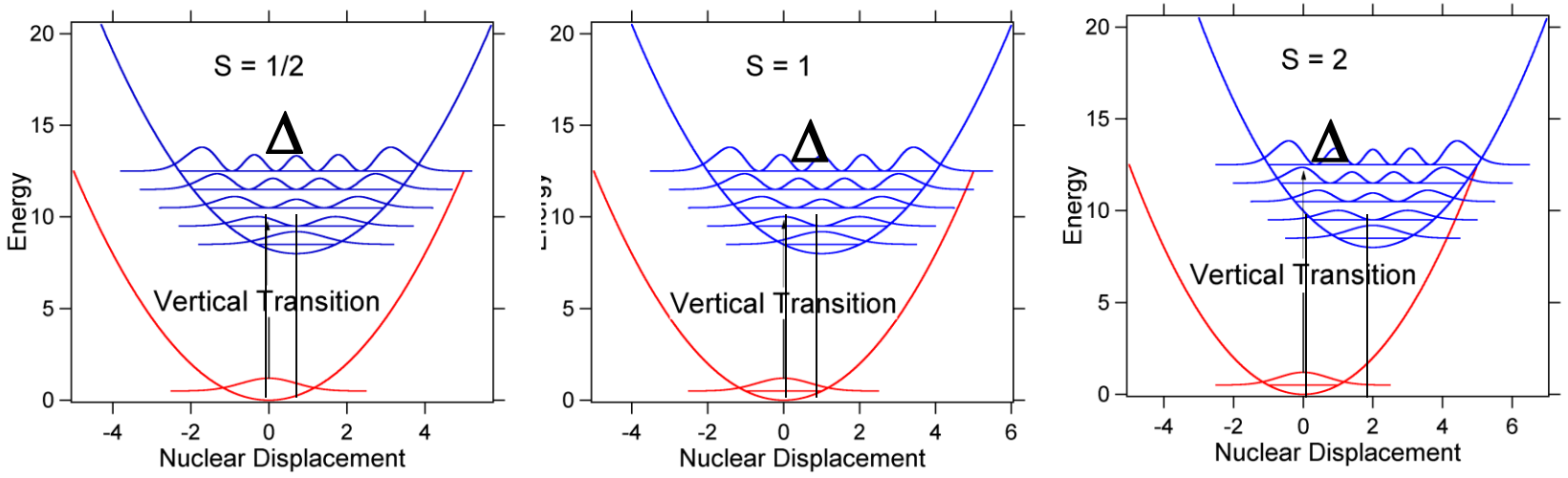
$$\int_{-\infty}^{\infty} \chi_i \chi_j dQ = \delta_{ij}$$

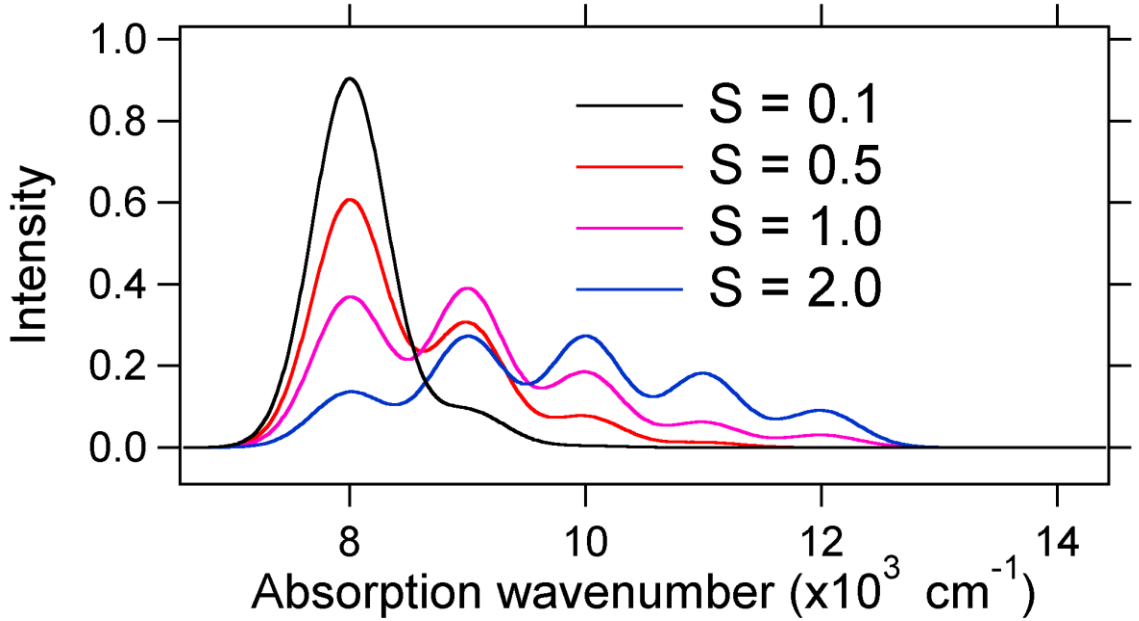
which means that the integral is non-zero only for i = j. However, when there is a position shift the wave functions are no longer orthogonal.

$$\int_{-\infty}^{\infty} \chi_i \chi_j, dQ \neq 0 \qquad \text{even for } j \neq i$$

The result is that electron transition bands are observed at 0-0', 0-1', 0-2', etc. and they depend on the extent of the position shift.

The Franck-Condon factor determines the envelop of the absorption lineshape



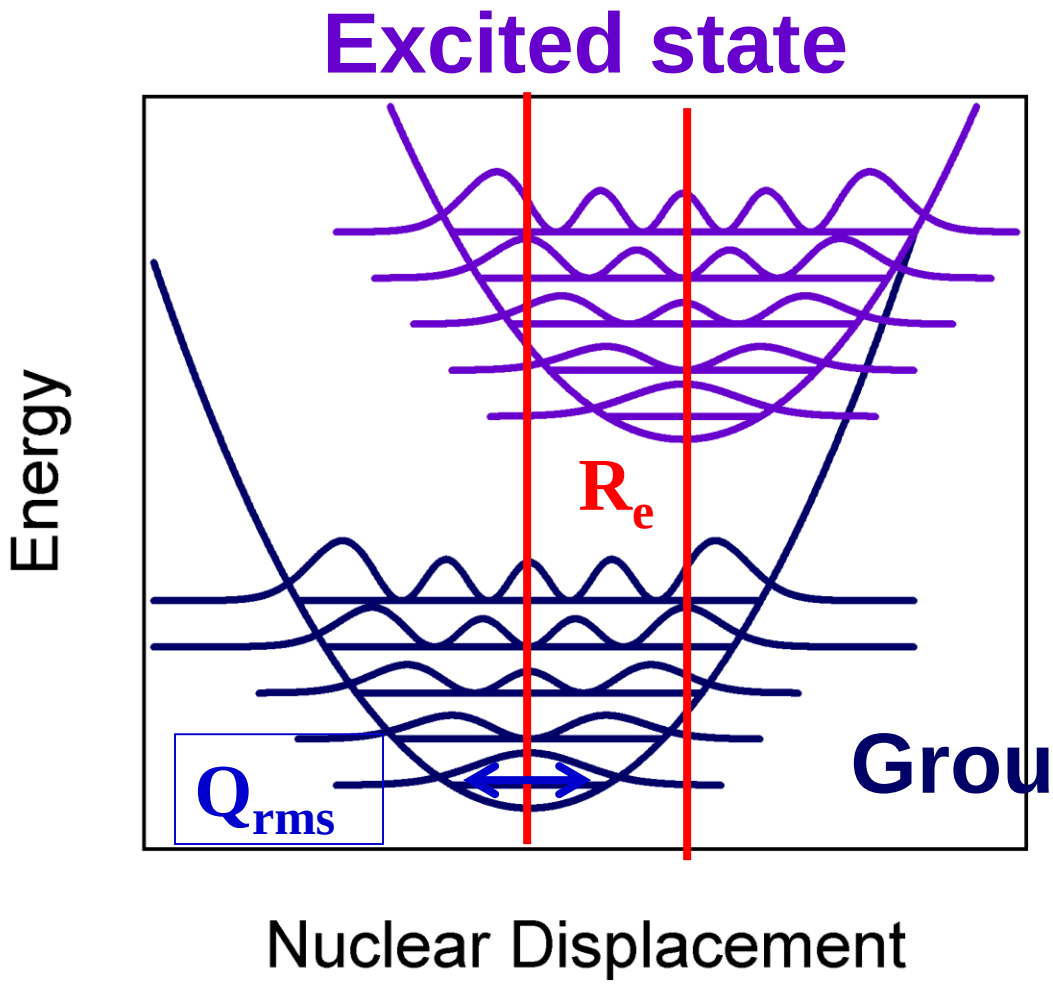


$S = \Delta^2/2$

S is electron-phonon coupling

Δ is nuclear displacement

Definition of the dimensionless displacement, Δ



Δ is the displacement R_e weighted by the r.m.s. zero point motion, Q_{rms}

$$\Delta = \frac{R_e}{Q_{rms}}$$

Calculation of the r.m.s. of zero-point motion

$$Q_{rms} = \sqrt{\langle Q^2 \rangle} = \sqrt{\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha Q^2/2} Q^2 e^{-\alpha Q^2/2} dQ}$$

$$\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha Q^2} Q^2 dQ = \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{\pi}{4\alpha^3}\right)^{1/2} = \frac{1}{2\alpha}$$

$$Q_{rms} = \sqrt{\frac{1}{2\alpha}}$$

The root-mean-squared displacement

The magnitude of the shift is given first in Δ, where Δ is called the dimensionless displacement. The displacement is normalized (divided by) the root-mean-square of zero-point motion. This normalization automatically scales the displacement by a natural extent of fluctuation along a normal mode coordinate.

$$\sqrt{\langle Q^2 \rangle} = \sqrt{\int_{-\infty}^{\infty} \chi_i Q^2 \chi_i dQ}$$

In this expression,

$$\sqrt{\langle Q^2 \rangle} = 1/\sqrt{2\alpha}$$

The value of

$$\alpha = \frac{\sqrt{\mu k}}{\hbar} = \frac{\mu\omega}{\hbar}$$

The zero-point motion is a yardstick for the motion of a vibrational mode. If the displacement of a particular mode, Q_0, in the excited state is divided by the square root of two times the zero-point motion $1/\sqrt{\alpha}$, it becomes a dimensionless displacement.

$$\Delta = \sqrt{\alpha} Q_0$$

Thus, Δ represents a normalized shift of the excited state potential surface relative to the ground state. It is customary to express the shift in nuclear coordinates in terms of the electron-phonon (or electron-vibration) coupling parameter S.

$$S = \frac{\Delta^2}{2}$$

S is proportional to the energy of the shift since the position variable square is proportional to the energy in the harmonic approximation

$$V(Q) = \frac{k}{2} Q^2$$

Useful “rule of thumb” using S

S is useful as a description for the coupling of a vibrational mode to the electronic transition. The different line shapes arise because of nuclear coupling. The relative magnitude of 0-0’ and 0-1’ is given by S.

$$S = \frac{I(0-1')}{I(0-0')}$$

where I(0-0’) and I(0-1’) are the intensities of the 0-0’ and 0-1’ bands, respectively. S is also roughly equal to the quantum of the maximum of the transition, i.e. 0-S’ is closest to the maximum of the band shape. For example, when S = 0.1, i.e. S << 1 so 0’ is the largest band. When S = 2, the largest vibrational band is 2’ etc. These “rules of thumb” are quite useful, but it is more useful to find a general formula for the FC factor in terms of the nuclear displacement.

FC factor is the square of vibrational overlap integrals

We can express the overlap integrals in terms of S. For the first few integrals we find,

$$\left| \int_{-\infty}^{\infty} \chi_0 \chi_{0'} dQ \right|^2 = e^{-S}$$

$$\left| \int_{-\infty}^{\infty} \chi_0 \chi_{1'} dQ \right|^2 = S e^{-S}$$

$$\left| \int_{-\infty}^{\infty} \chi_0 \chi_{2'} dQ \right|^2 = \frac{S^2 e^{-S}}{2}$$

FC factor is the square of vibrational overlap integrals

The integrals can also be written using braket notation as,

$$|\langle 0|0'\rangle|^2 = e^{-S}$$

$$|\langle 0|1'\rangle|^2 = Se^{-S}$$

$$|\langle 0|2'\rangle|^2 = \frac{S^2 e^{-S}}{2}$$

The pattern can be given as follows,

$$FC = \sum_{n=0\prime}^{\infty} \frac{S^n e^{-S}}{n!} \delta(\omega - \omega_n)$$

Introduction of linewidth

The delta function,

$$\delta(\omega - \omega_n)$$

is an energy matching condition that is zero when

$$\omega \neq \omega_n.$$

The delta function is not a realistic representation of spectral line shapes since they must have some width.

The Uncertainty Principle requires that the lifetime of the excited state, $\Delta\tau$, give rise to an energy width, ΔE, and therefore a frequency width $\Delta\omega$.

Thus, we may replace the delta function with a function that represents the linewidth for in individual transition, 0 → 0', 0 → 1', etc. The Lorentzian is such a function.

$$L(\omega) = \frac{1}{\pi} \frac{\Gamma}{(\omega - \omega_n)^2 + \Gamma^2}$$

Justification of the assumptions behind T = 0 K approximation

In summary, we see that the nuclear displacement determines the line shape of the absorption band. Note that the integrated area does not change as the FC factor changes. The Franck-Condon factor does not alter the overall intensity of the band, but just the line shape. The square of electronic transition moment $(M_{12})^2$ determines the overall intensity. We have used the so-called zero temperature approximation where all of the population initially is in the v = 0 vibrational state. This is actually a reasonable approximation even at room temperature, provided,

$$h\nu \gg k_B T$$

Since $k_B T$ is approximately 209 cm^{-1} at 300 K, this approximation will hold for all high frequency modes.

A look at the overlap integrals

The Franck-Condon factors can be derived from the solutions to the harmonic oscillator problem. If we imagine that the ground state nuclei are at position Q = 0 and the excited state nuclei have moved to Q_0, then the overlap factors can be calculated explicitly using the wave functions.
For the overlap of χ_0 and $\chi_{0'}$ we have

$$\langle 0|0'\rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} exp\left\{-\frac{\alpha Q^2}{2}\right\} exp\left\{-\frac{\alpha(Q-Q_0)^2}{2}\right\} dQ$$

Expanding the terms in the exponent we have

$$-\alpha Q^2 - \alpha(Q-Q_0)^2 = -\alpha\left(2Q^2 - 2QQ_0 + {Q_0}^2\right)$$

Complete square as a method to solve the overlap integrals

To convert this into a Gaussian integral that is exactly soluble, we use the method called “complete the square”. We assume that there exists a β such that

$$\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} exp\left\{\frac{\beta}{2}\alpha {Q_0}^2\right\} \int_{-\infty}^{\infty} exp\{-\alpha(Q-\delta Q_0)^2\}dQ$$

Where we have added $\exp\{-\alpha\beta Q_0^2/2\}$ inside the integral and $\exp\{+\alpha\beta Q_0^2/2\}$ outside the integral. We may compare the terms in each form of the exponent:

$$-\alpha\frac{\left(2Q^2-2QQ_0+{Q_0}^2+\beta {Q_0}^2\right)}{2} = -\alpha(Q-\delta Q_0)^2$$

Solve for the terms that complete the square

To solve for the unknowns, β and δ, that have introduced using the method of "completing the square" we expand both sides:

$$-\alpha\left(Q^2 - QQ_0 + \frac{(1+\beta){Q_0}^2}{2}\right) = -\alpha\left(Q^2 - 2\delta QQ_0 + \delta^2{Q_0}^2\right)$$

And solve for the unknowns β and δ.

$$\frac{1}{4} = \frac{(1+\beta)}{2} \qquad \beta = -\frac{1}{2}$$

$$\delta^2 = \frac{(1+\beta)}{2} \qquad \delta = \frac{1}{2}$$

Solution for 0 – 0’

$$\langle 0|0'\rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\} \int_{-\infty}^{\infty} exp\left\{-\alpha\left(Q-\frac{Q_0}{2}\right)^2\right\} dQ$$

$$\langle 0|0'\rangle = exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\} = exp\left\{-\frac{\Delta^2}{4}\right\}$$

Where, as before, the dimensionless displacement is

$$\Delta = \sqrt{\alpha} Q_0$$

The Franck-Condon factor for the 0 – 0’ term is:

$$|\langle 0|0'\rangle|^2 = exp\left\{-\frac{\Delta^2}{2}\right\} = e^{-S}$$

Solution for 0 – 1’

The integral of $\langle 0|1' \rangle$ is

$$\langle 0|1'' \rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} exp\{-\alpha Q^2/2\}\sqrt{2\alpha} Q exp\{-\alpha(Q-Q_0)^2/2\} dQ$$

The analysis is carried out by noting that

$$-\frac{Q^2+(Q-Q_0)^2}{2} = -\left(Q^2 - QQ_0 + \frac{Q_o^2}{2}\right) = -\left(Q-\frac{Q_0}{2}\right)^2 - \frac{Q_o^2}{4}$$

Which can be rewritten

$$\langle 0|1' \rangle = exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \sqrt{2\alpha}\left\{Q-\frac{Q_0}{2}+\frac{Q_0}{2}\right\} exp\left\{-\alpha\left(Q-\frac{Q_0}{2}\right)^2\right\} dQ$$

Introduction of a substitution

Let

$$z = Q - \frac{Q_0}{2}$$

Then

$$\langle 0|1''\rangle = exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty}\sqrt{2\alpha}\left\{z+\frac{Q_0}{2}\right\}exp\{-\alpha z^2\}dz$$

There are two terms, first

$$exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\sqrt{2\alpha}\int_{-\infty}^{\infty} z\, exp\{-\alpha z^2\}dz = 0$$

Relationship between 0-0’ and 0-1’

However, the second term is not zero:

$$\langle 0|1'\rangle = \sqrt{\frac{\alpha}{2}} Q_0 exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} exp\{-\alpha z^2\} dz$$

$$\langle 0|1'\rangle = \sqrt{\frac{\alpha}{2}} Q_0 \langle 0|0'\rangle = \frac{\Delta}{\sqrt{2}} \langle 0|0'\rangle$$

Therefore, when we square the 0-1’ term we see its relation to the 0-0’ term, which was discussed previously.

$$|\langle 0|1'\rangle|^2 = \frac{\Delta^2}{2} exp\left\{-\frac{\Delta^2}{2}\right\} = S e^{-S}$$

Overlap of 0-2’

- We can continue with

$$\langle 0|2'\rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} exp\{-\alpha Q^2/2\} \frac{(2\alpha Q^2 - 1)}{\sqrt{2}} exp\{-\alpha(Q - Q_0)^2/2\} dQ$$

which can be rewritten as

$$\langle 0|2'\rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\} \int_{-\infty}^{\infty} \left(\frac{2\alpha\left(z + \frac{Q_0}{2}\right)^2}{\sqrt{2}} - \frac{1}{\sqrt{2}} \right) e^{-z} dz$$

which has four terms. We can see this by expanding the quantities inside the parentheses.

$$\frac{2\alpha z^2 + 2\alpha z Q_0 + 2\alpha Q_0^2 - 1}{\sqrt{2}}$$

Overlap of 0-2’

This integral has four terms. The first two cancel.

$$\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \left(\frac{2\alpha z^2}{\sqrt{2}}\right) e^{-z} dz = \frac{1}{\sqrt{2}} \qquad \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \left(-\frac{1}{\sqrt{2}}\right) e^{-z} dz = -\frac{1}{\sqrt{2}}$$

Term 1 Term 4

The second term gives an odd integral over even limits and is zero. The surviving term

$$\int_{-\infty}^{\infty} e^{-z} dz = \left(\frac{\alpha {Q_0}^2}{2\sqrt{2}}\right) exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\}$$

integrates to:

$$\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \left(\frac{\alpha {Q_0}^2}{2\sqrt{2}}\right) exp\left\{-\frac{\alpha {Q_0}^2}{4}\right\}$$

Generalization to 0-n’

$$\langle 0|2'\rangle = \frac{\Delta^2}{2\sqrt{2}}\langle 0|0'\rangle$$

Finally, we see that

$$|\langle 0|2'\rangle|^2 = \frac{\Delta^4}{8} exp\left\{-\frac{\Delta^2}{2}\right\} = \frac{S^2 e^{-S}}{2}$$

The general formula for a transition starting from v = 0 in the ground state is,

$$|\langle 0|n'\rangle|^2 = \frac{S^n e^{-S}}{n!}$$

Recursion relations: extension of the FC factor concept beyond T=0K

Manneback found recursion relations between any successive levels,

$$\langle m+1|n\rangle = \left(\frac{n}{m+1}\right)^{1/2} \langle m|n-1\rangle - \frac{\Delta\langle m|n\rangle}{(2(m+1))^{1/2}}$$

$$\langle m|n+1\rangle = \left(\frac{m}{n+1}\right)^{1/2} \langle m-1|n\rangle + \frac{\Delta\langle m|n\rangle}{(2(m+1))^{1/2}}$$

where m and n are the vibrational levels of the excited and ground electronic states, respectively. Using the recursion relations the Franck-Condon factors FC = $|\langle\chi_f|\chi_i\rangle|^2 = |\langle m|n\rangle|^2$ can be calculated.