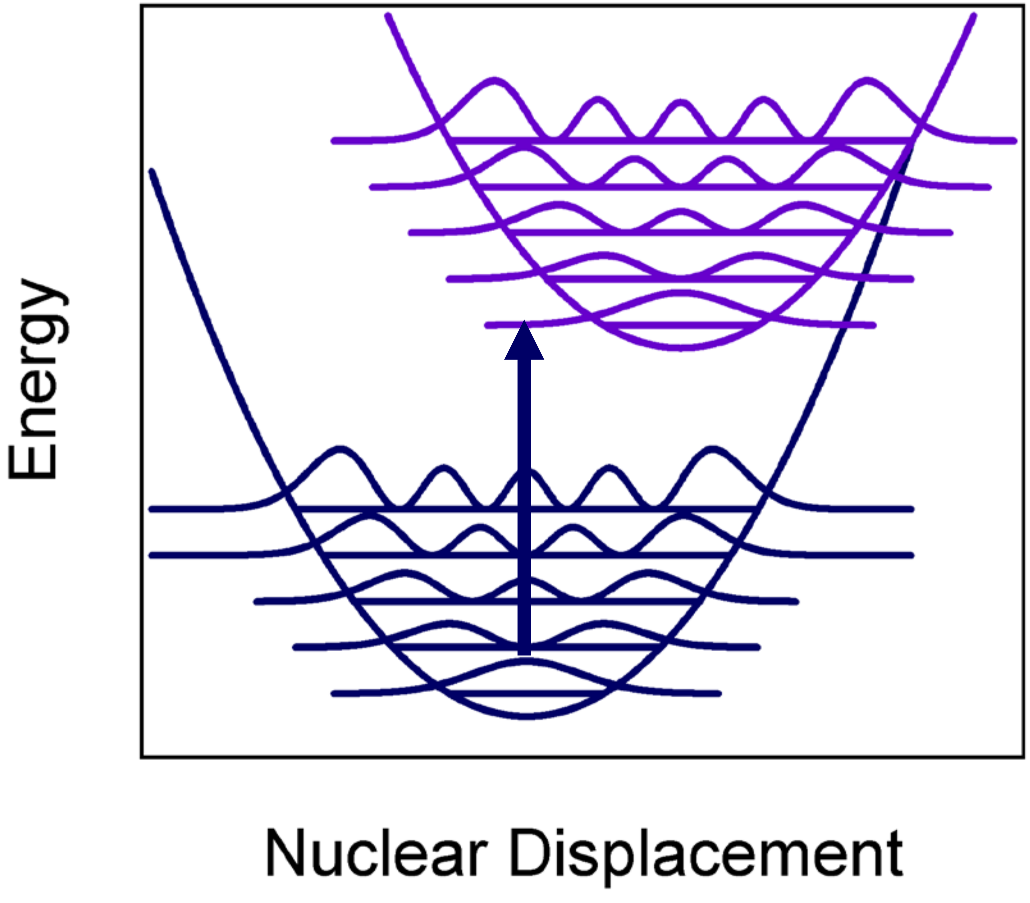
The nuclear part

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

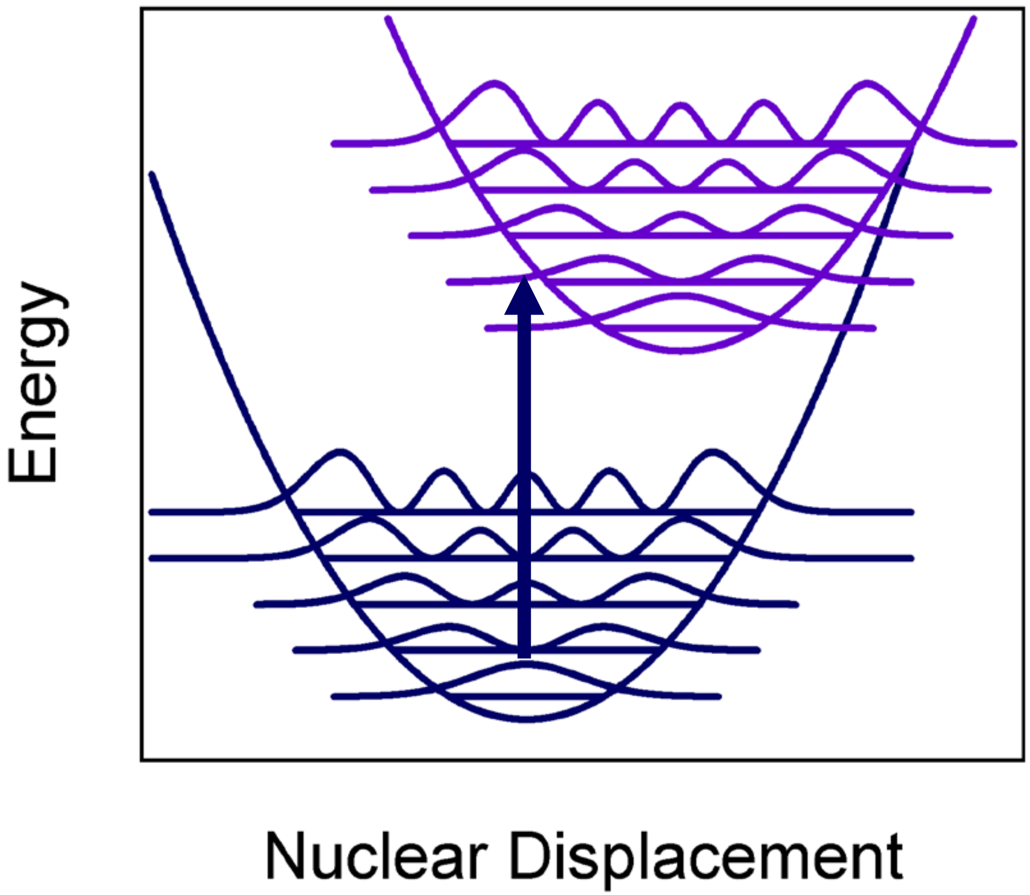


Excited state

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.

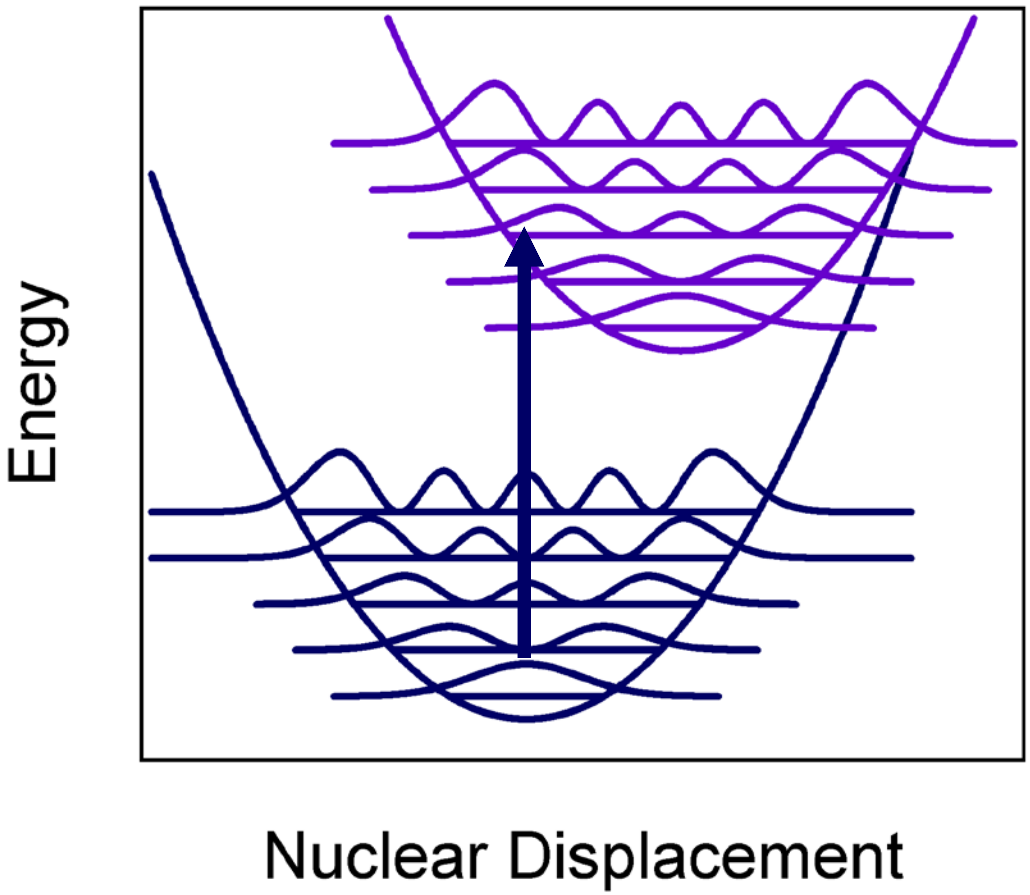


Excited state

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.

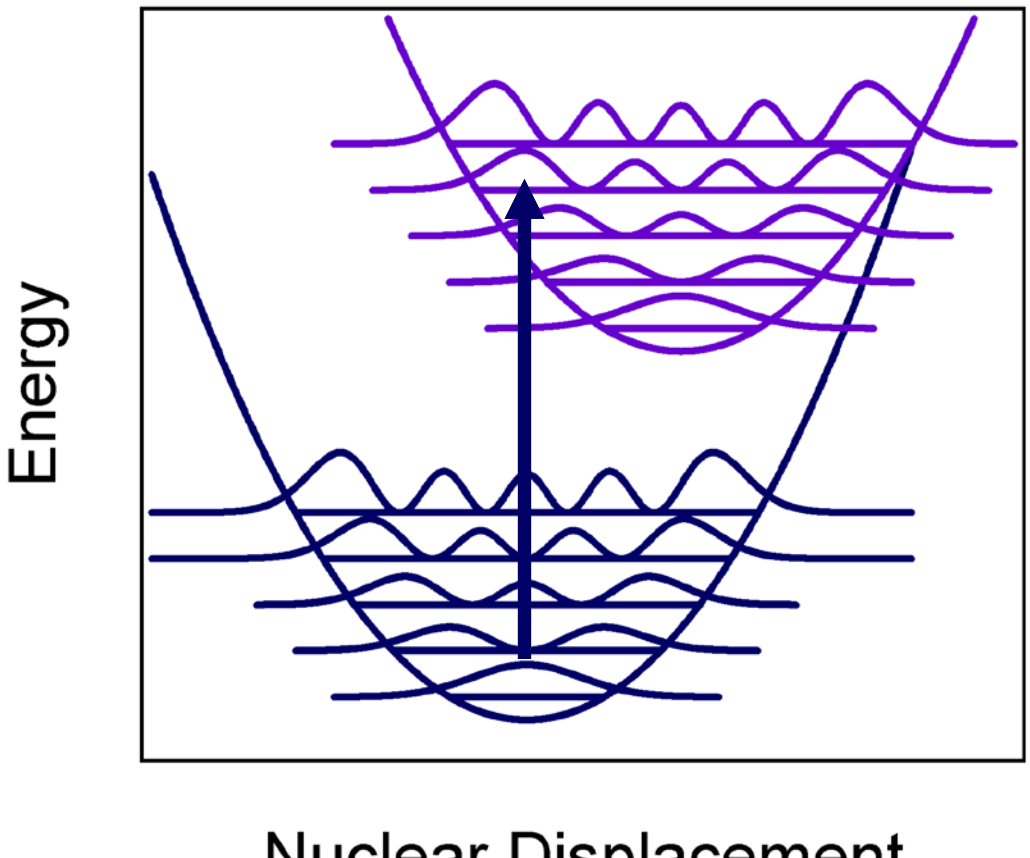


Excited state

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.

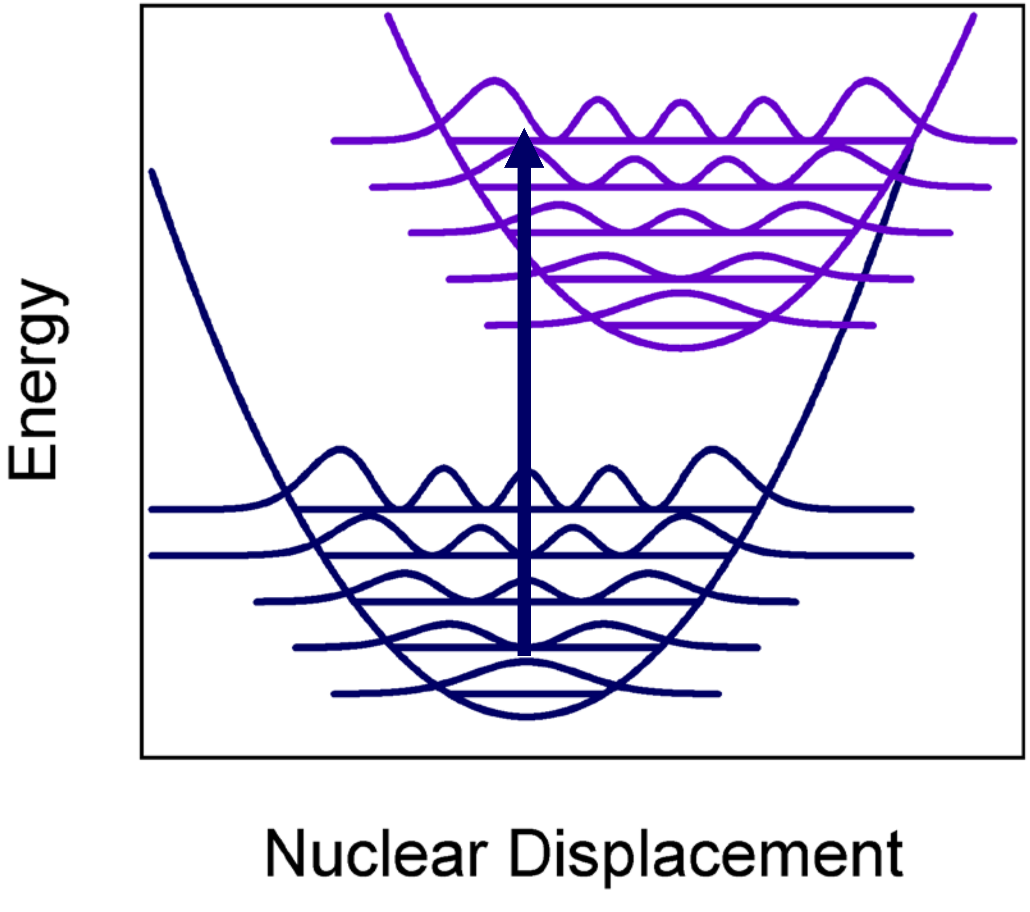


Excited state

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.

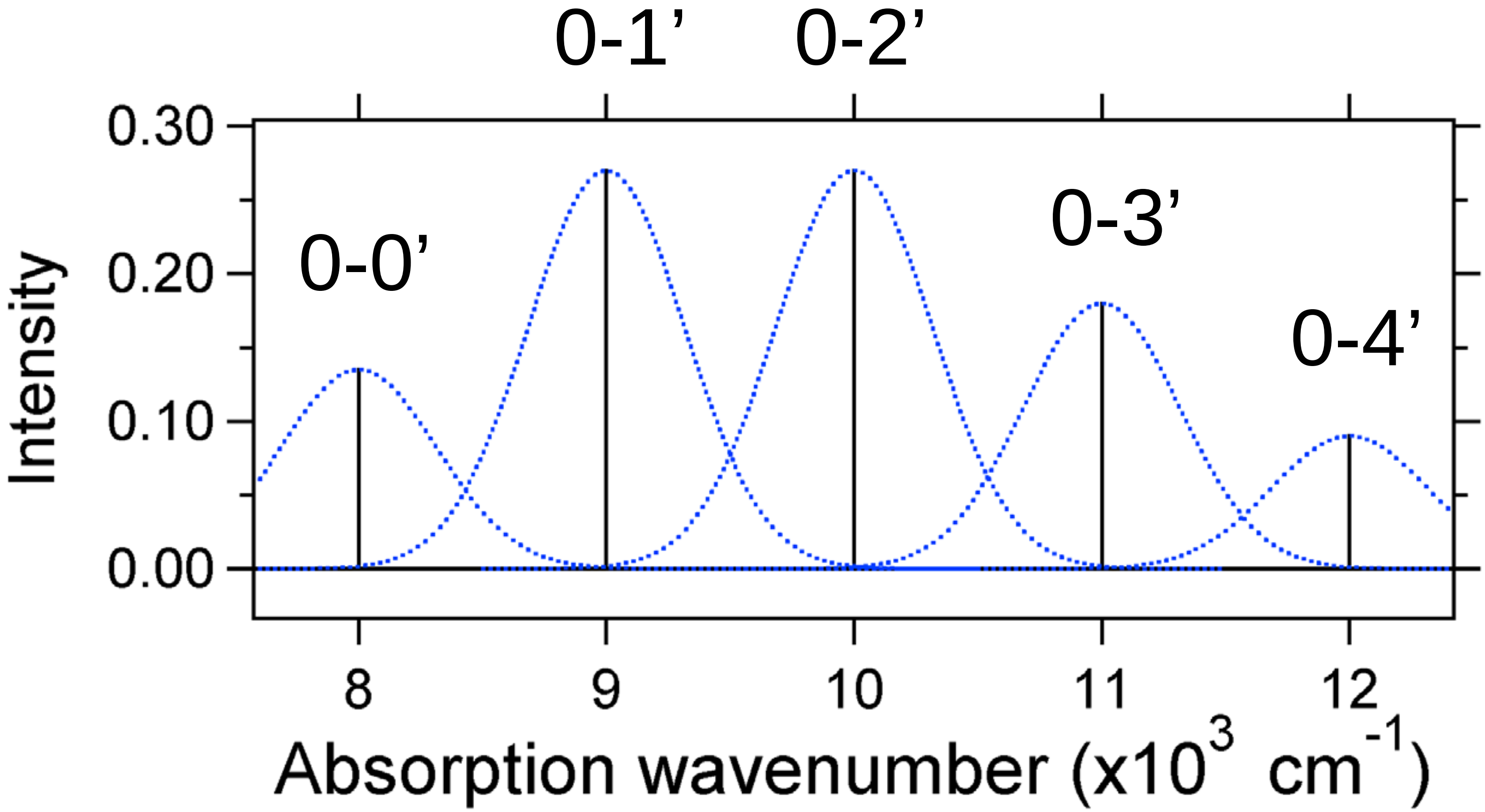


Excited state

0-4'

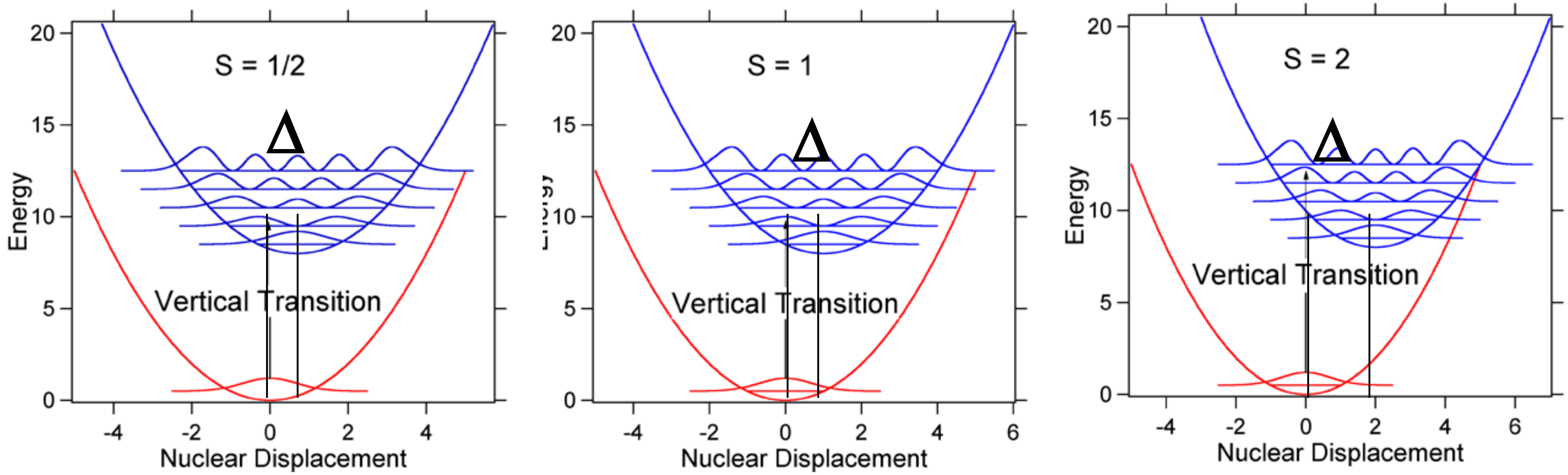
Ground state

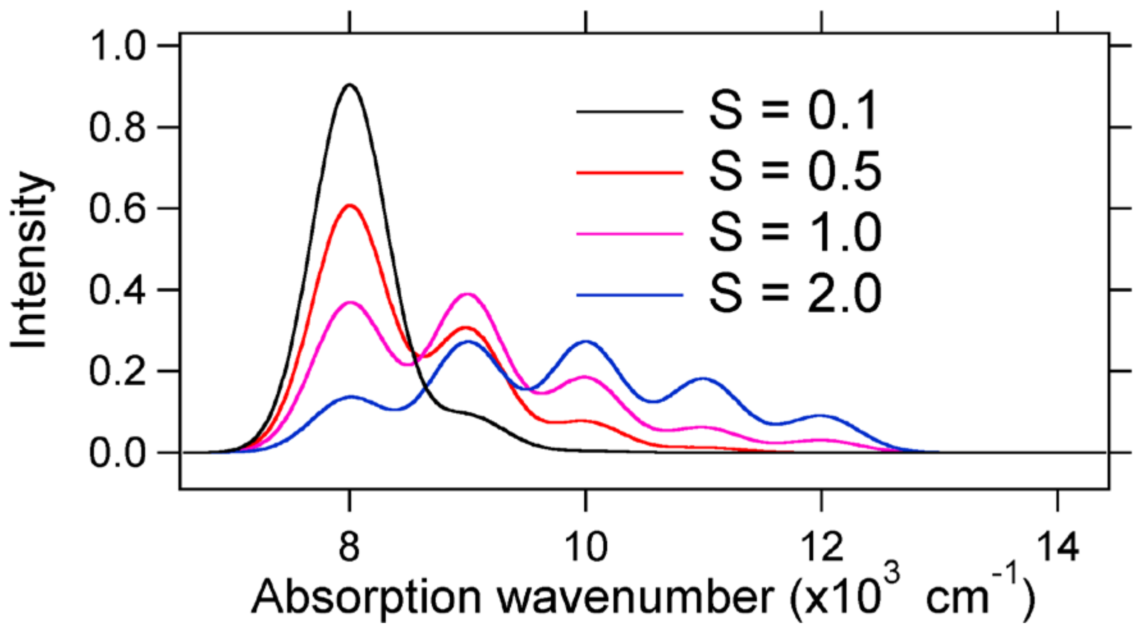
Based on the FC factors we can construct a “stick” spectrum



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

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





$S = \Delta^2/2$

S is electron-phonon coupling

Δ is nuclear displacement

Analytical expression for the FC factor

The Franck-Condon factor is a vibrational overlap term. It depends on nuclear displacement, which is treated using the parameter S, the electron-vibration (or electron-phonon) coupling. The big the displacement the bigger is S. There is a progression of lines with relative intensities given by:

$$FC = \sum_{n=1}^{\infty} \frac{S^n e^{-S}}{n!} \delta(\varepsilon - n\hbar\omega)$$

The delta function gives a stick spectrum spaced by energy equal to the vibrational frequency. This function is also known as a Poisson distribution. For large S this function approaches a Gaussian shape.