

The Shapes of Electronic Absorption Bands

Atomic spectra consist of very sharp ($< 1 \text{ cm}^{-1}$) lines. Molecular electronic absorption and luminescence bands can be extremely broad, sometimes as much as several thousand wavenumbers. The difference can be explained by the nature of the wavefunctions describing electronic states in molecules.

The Hamiltonian for a molecule has the form:

$$H = -\sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{k>l} \frac{Z_k Z_l e^2}{R_{kl}} - \sum_{m,n} \frac{Z_m e^2}{|R_m - r_n|} + \sum_{o>p} \frac{e^2}{r_{op}}$$

It is common to divide this into nuclear and electronic Hamiltonians (H_N , H_E):

$$H_N = -\sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 + V(R)$$

$$H_E = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{k>l} \frac{Z_k Z_l e^2}{R_{kl}} - \sum_{m,n} \frac{Z_m e^2}{|R_m - r_n|} + \sum_{o>p} \frac{e^2}{r_{op}}$$

The nuclear coordinates are treated as parameters in the Schrödinger equation with the electronic Hamiltonian:

$$H_E \psi_E(R, r) = V(R) \psi_E(R, r)$$

The eigenvalues for this electronic Schrödinger equation ($V(R)$) are functions of the nuclear coordinates. These energy functions are used as the potential energy in the nuclear Hamiltonian. The nuclear Schrödinger equation is:

$$H_N \chi_N(R) = E \chi_N(R)$$

If the nuclear potential energy function is approximated as harmonic, the wavefunctions $\chi(R)$ will be modified Hermite polynomials. The total molecular wavefunction, $\Psi(R, r)$ will be given by the product:

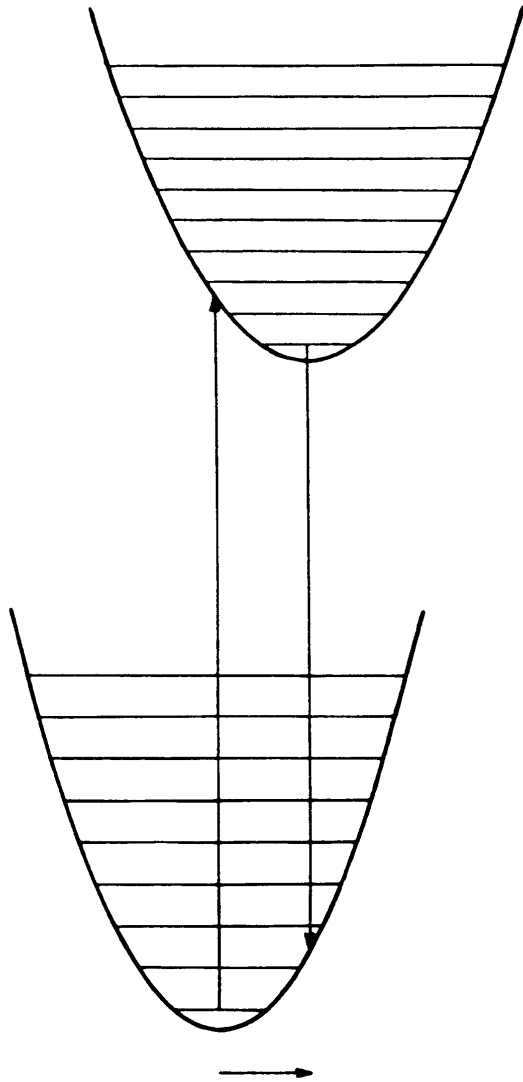
$$\Psi(R, r) = \chi_N(R) \psi_E(R, r)$$

This approximation of separating nuclear and electronic coordinates is known as the Born-Oppenheimer or adiabatic approximation. It is common to invoke the so-called crude Born-Oppenheimer or crude adiabatic approximation:

$$\psi_E(r) \approx \psi_E(R_0, r)$$

In this expression, R_0 is the equilibrium nuclear configuration for the electronic state.

The potential energy surfaces for different electronic states are represented as shown below (the vibrational levels in each surface are shown as horizontal lines):



The positions of the minima and the force constants for different electronic states need not be the same. The different electronic states will create different forces on the nuclei in the molecule resulting in a change in the equilibrium nuclear configuration as well as a change in vibrational force constants.

Electronic absorption bands in molecules arise from electric dipole transitions. The transition moment operator has the form:

$$\mu(r) = e \sum_i r_i$$

The transition moment integral will have the form:

$$M_{if} = \langle \Psi^i(R, r) | \mu(r) | \Psi^f(R, r) \rangle$$

Substitution gives:

$$M_{if} = \langle \chi_N^i(R) \psi_E^i(R, r) | \mu(r) | \chi_N^f(R) \psi_E^f(R, r) \rangle$$

If we invoke the Condon approximation, $\psi_E(R, r) \approx \psi_E(R_0, r) \equiv \psi_E(r)$, we can separate the transition moment integral into two parts, an electronic component and a nuclear component.

$$M_{if} = \langle \chi_N^i(R) | \chi_N^f(R) \rangle \langle \psi_E^i(r) | \mu(r) | \psi_E^f(r) \rangle$$

The integral over the electronic coordinates (M_E) determines the overall intensity of the absorption band; the integral over the nuclear coordinates determines the intensity distribution within the absorption band. The overall intensity of an absorption or emission band depends on the square of the transition moment integral with a Boltzmann weighting of initial vibrational states and a sum over all possible final vibrational states:

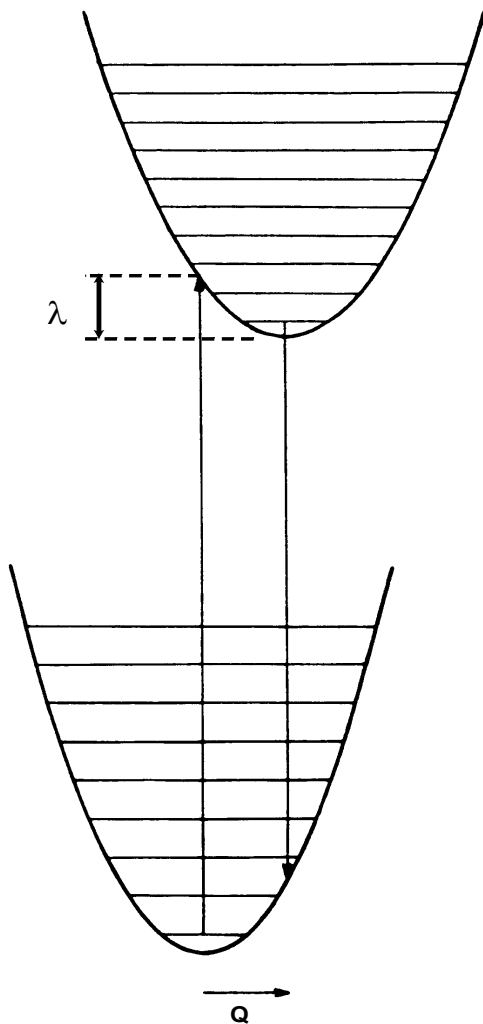
$$I \propto M^2 = \sum_{v_i=0}^{\infty} P(v_i) \sum_{v_f=0}^{\infty} \left| \langle \chi_N^i(R, v_i) | \chi_N^f(R, v_f) \rangle \right|^2 M_E^2$$

where $P(v_i)$ is the Boltzmann probability of being in initial vibrational level v_i . The squares of the vibrational overlap integrals are known as Franck-Condon factors. And the nuclear/electronic coordinate separation for electronic transitions is known as the Franck-Condon principle.

If the vibrational motions are treated semi-classically, then the predicted bandshape is Gaussian:

$$I(h\nu) = \exp\left\{-\frac{(h\nu - h\nu_{\max})^2}{4\lambda RT}\right\}$$

The parameter λ is related to the magnitude of the distortion of the excited-state potential surface along normal coordinate Q (see figure below).



But, nuclear motions cannot always be treated semi-classically. If we use the quantum mechanical solution to the harmonic oscillator problem, we expect to see vibrational fine structure in absorption and luminescence spectra (see figure on the next page). The bandshape consists of a progression of lines, separated by the vibrational frequency of the excited state in absorption, and the vibrational frequency of the ground state in luminescence. These progression must be in totally symmetric vibrational modes, otherwise the Franck-Condon factors would vanish for odd values of Δv (the difference in vibrational quantum number) Using modified Hermite polynomials for the vibrational wavefunctions leads to recursion relations for Franck-Condon factors.

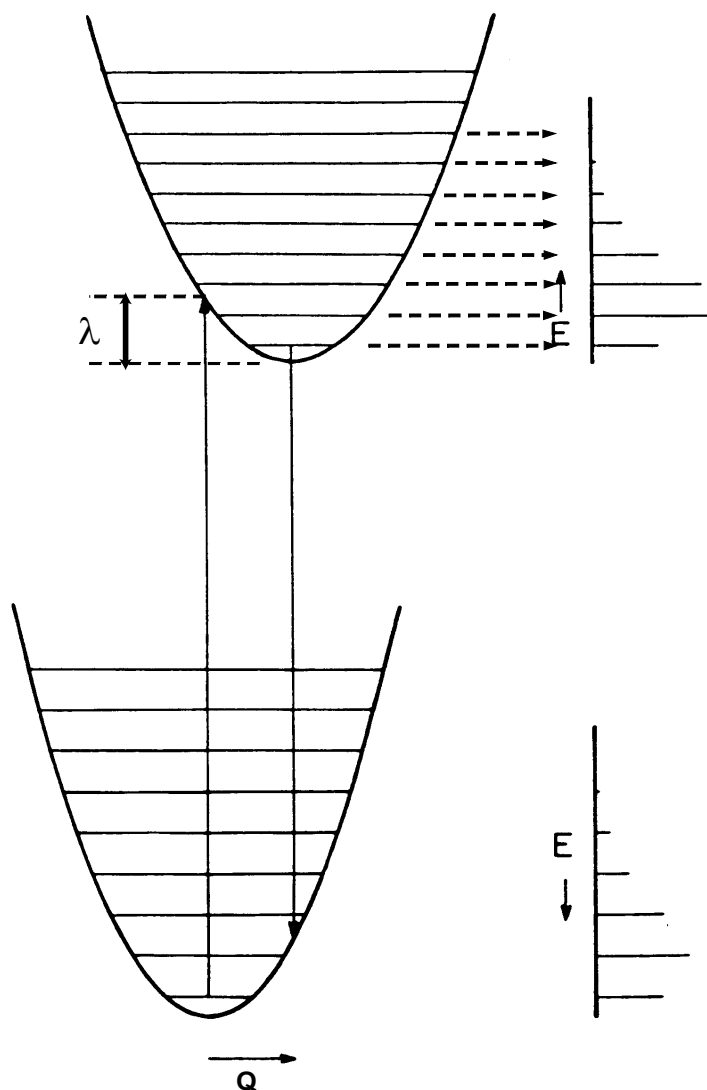
If we invoke the additional approximations that ground and excited state frequencies are equal ($\hbar\omega$), and that only the $v_i = 0$ level is populated, then the intensity distribution in an absorption band is described by the following equation:

$$I(h\nu) = \sum_{n=0}^{\infty} e^{-S_{HR}} \frac{S_{HR}^n}{n!} g(h\nu - (E_{00} + n\hbar\omega))$$

In the limit of large S_{HR} , this distribution approaches a Gaussian, as you would expect from the classical treatment of the bandshape. The parameter S_{HR} is sometimes called the Huang-Rhys parameter, and it is related to the magnitude of the distortion along Q . For reasonably large values of S_{HR} , it can be approximated by the following expression (where k is the force constant for the normal mode Q):

$$S_{HR} \approx n(I_{\max}) = \frac{\lambda}{\hbar\omega} = \frac{\frac{1}{2}k(\Delta Q)^2}{\hbar\omega}$$

In principle, then, analyses of absorption band profiles can provide information about the structures of molecules in electronic excited states. This information can be used to confirm assignments of absorption bands to specific electronic excitations.



In general, large excited-state distortions (ΔQ) lead to large S_{HR} values, and broader absorption profiles.

We can simulate the low-temperature absorption spectra for different values of S_{HR} for a distortion along a 400 cm^{-1} vibrational mode (a typical M-L stretching frequency).

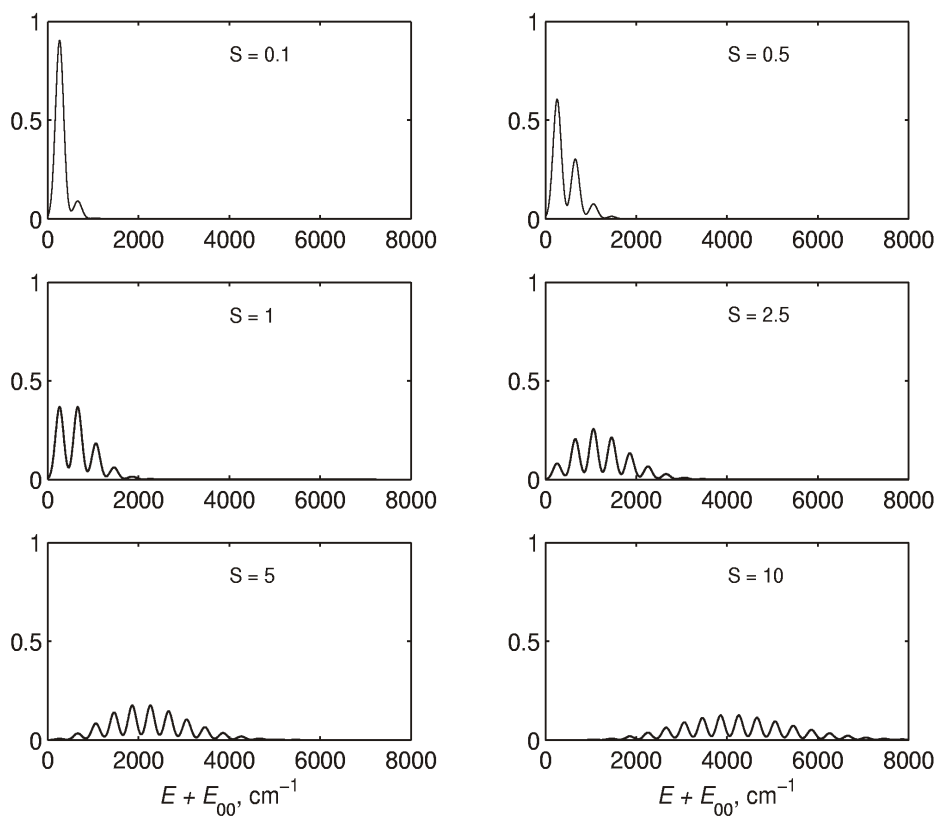
The intensity in bands with small excited state distortions ($S_{HR} < 1$) is carried mainly in the $v_i = 0 \rightarrow v_f = 0$ transition; the so-called 0,0-line. As distortions increase, the peak intensity decreases (because the oscillator strength remains constant). In addition, the bands become broader and look more like Gaussians.

The distortion parameters for the different S_{HR} values ($\hbar\omega = 400 \text{ cm}^{-1}$) are:

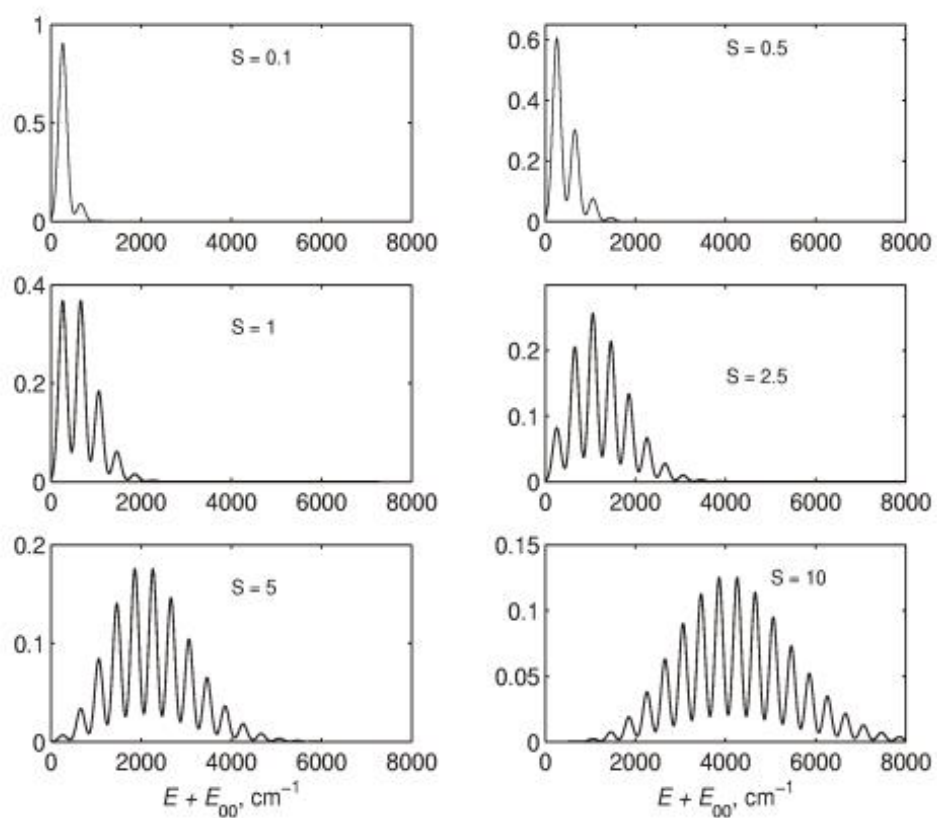
S_{HR}	$\lambda, \text{ cm}^{-1}$
0.1	40
0.5	200
1.0	400
2.5	1000
5.0	2000
10.0	4000

Notice in the following figures that the widths of these absorption bands are on the order of these λ values.

Vibrational fine structure and the magnitudes of excited state distortions can be extremely helpful when trying to assign electronic absorption spectra.



Predicted bandshapes for $S_{HR} = 0.1, 0.5, 1, 2.5, 5, 10$ (fixed ordinate)



Predicted bandshapes for $S_{HR} = 0.1, 0.5, 1, 2.5, 5, 10$ (scaled ordinate)