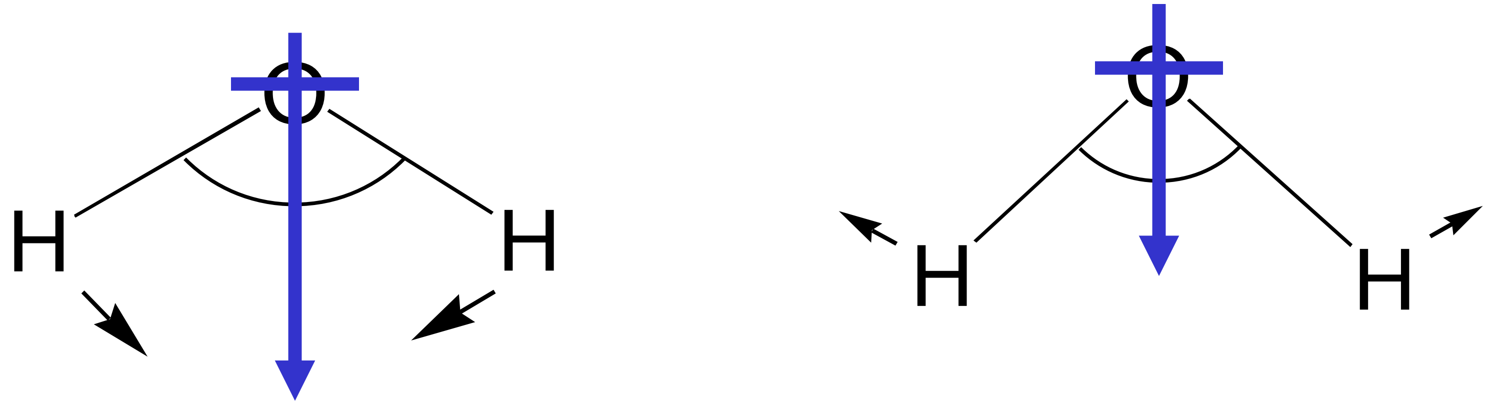
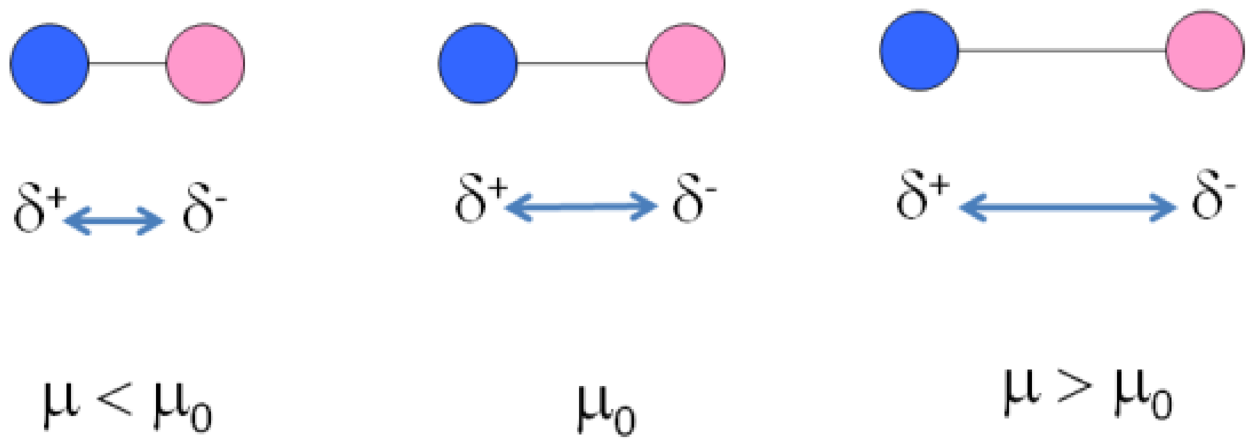
Transition dipole moment

In order for infrared light to be absorbed the polarization must be aligned with the direction of the transition moment. For a vibrational mode this is determined by the directional change in the dipole moment. This is shown below for the bending mode of H_2O.



The change in ground state dipole moment during vibration interacts with light.

$$\mu(Q) = \mu_0 + \left(\frac{\partial \mu}{\partial Q}\right) Q + \cdots$$



The first term is static and does not contribute to the transition. Calling the vibrational wave functions χ_i the transition moment is:

$$\left(\frac{\partial \mu_0}{\partial Q}\right) \langle \chi_0 | Q | \chi_1 \rangle$$

Infrared transitions occur because of changes in the dipole moment during oscillatory motion. This change can be described using a power series expansion of the dipole moment as a function of nuclear coordinate. The first term from the expansion can permit the product of χ_0 and χ_1 to have a non-zero value. This is transition dipole moment for the $0 \rightarrow 1$ transition

$$\left(\frac{\partial \mu_0}{\partial Q}\right) \int_{-\infty}^{\infty} \chi_0 \, Q \chi_1 dQ = \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{\partial \mu_0}{\partial Q}\right) \int_{-\infty}^{\infty} e^{-\alpha Q^2/2} \, Q\sqrt{2\alpha} Q e^{-\frac{\alpha Q^2}{2}} dQ$$

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$$= \left(\frac{2}{\pi}\right)^{1/2} \alpha \left(\frac{\partial \mu_0}{\partial Q}\right) \int_{-\infty}^{\infty} e^{-\alpha Q^2} \, Q^2 dQ = \left(\frac{\partial \mu_0}{\partial Q}\right) \left(\frac{1}{2\alpha}\right)^{1/2}$$

Mathematical note

Gaussian integrals have the solutions:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

A Gaussian times an odd polynomial has a value of zero over the even limits of –infinity to infinity.

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} x dx = 0$$

The even polynomials time Gaussians are not zero.

Mathematical note

If multiply any two vibrational functions that differ by 1 quantum then we will necessarily have one even and one odd function. The integral over even limits will be zero.

$$\int_{-\infty}^{\infty} \chi_0 \chi_1 dQ = 0$$

We can see this by plugging in the wave functions.

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

However, radiation can couple the vibrations by the term

$$\left(\frac{\partial \mu}{\partial Q}\right) Q$$

Mathematical note

We have instead that

$$\left(\frac{\partial\mu}{\partial Q}\right)\int_{-\infty}^{\infty}\chi_0 Q\chi_1 dQ = 0 \ \ ?$$

We can see this by plugging in the wave functions that the result is an even function times a Gaussian, which is not zero.

$$\left(\frac{\partial\mu}{\partial Q}\right)\left(\frac{\alpha}{\pi}\right)^{1/2}\sqrt{2\alpha}\int_{-\infty}^{\infty}Q^2 exp\{-\alpha Q^2\}dQ \neq 0$$

We note the general property of Gaussians, which permits us To calculate any even polynomial times a Gaussian:

$$(-1)^n\frac{\partial^n I_0(\alpha)}{\partial\alpha^n} = \int_{-\infty}^{\infty}x^{2n}x^{-\alpha x^2}dx = (-1)^n\frac{\partial^n}{\partial\alpha^n}\left(\frac{\pi}{\alpha}\right)^{1/2}$$

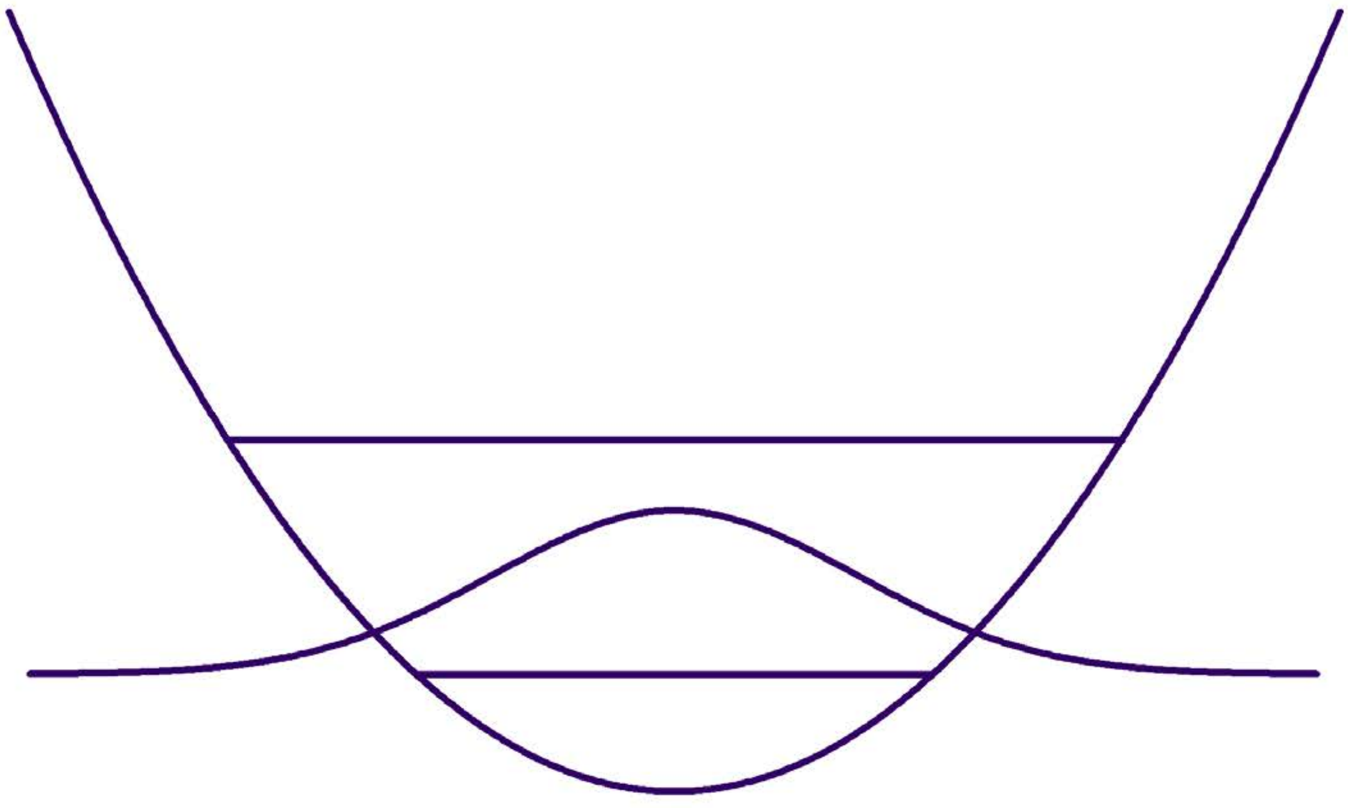
Selection rule

Within the harmonic approximation transitions can only occur between states separated by one quantum number ($\Delta v = 1$ or $\Delta v = -1$).

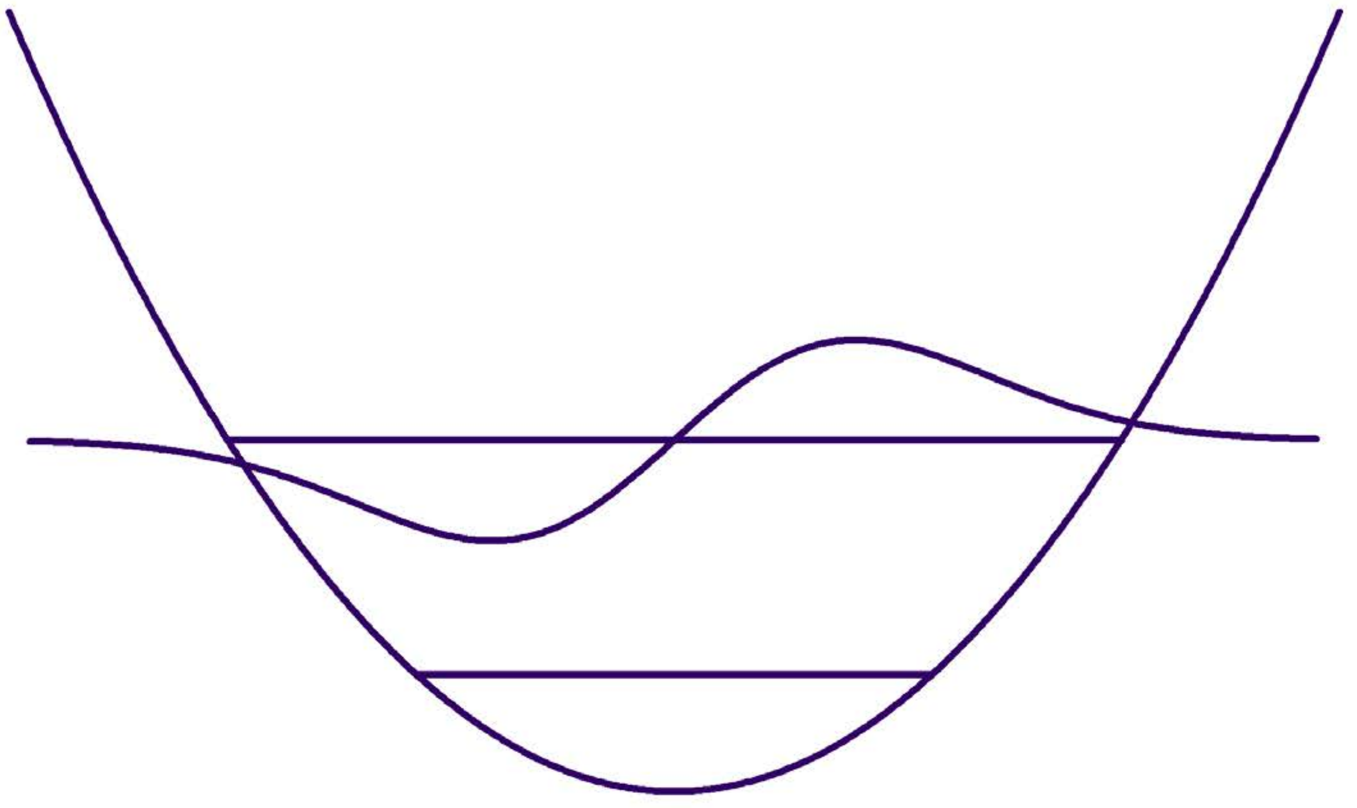
The change of $\Delta v = +1$ corresponds to absorption and $\Delta v = -1$ to emission.

This is known as a selection rule. We have Illustrated this rule on the following slides.

Vibrational Transition



Vibrational Transition



Vibrational Selection Rule