

## 6.6: Harmonic Oscillator Selection Rules

Photons can be absorbed or emitted, and the harmonic oscillator can go from one vibrational energy state to another. Which transitions between vibrational states are allowed? If we take an infrared spectrum of a molecule, we see numerous absorption bands, and we need to relate these bands to the allowed transitions involving different normal modes of vibration.

The selection rules are determined by the transition moment integral.

$$\mu_T = \int_{-\infty}^{\infty} \psi_{v'}^*(Q) \hat{\mu}(Q) \psi_v(Q) dQ \quad (6.6.1)$$

To evaluate this integral we need to express the dipole moment operator,  $\hat{\mu}$ , in terms of the magnitude of the normal coordinate  $Q$ . The dipole moment operator is defined as

$$\hat{\mu} = \sum_{\text{electrons}} er + \sum_{\text{nuclei}} qR \quad (6.6.2)$$

where the two sums are over all the electrons and nuclei and involve the particle charge (-e or q) multiplying the position vector (r or R). We can obtain this dipole moment operator in terms of the magnitude of the normal coordinate,  $Q$ , in a simple way by using a [Taylor series expansion](#) for the dipole moment.

$$\mu(Q) = \mu_{Q=0} + \left( \frac{d\mu(Q)}{dQ} \right)_{Q=0} Q + \left( \frac{d^2\mu(Q)}{dQ^2} \right)_{Q=0} Q^2 + \dots \quad (6.6.3)$$

Retaining only the first two terms and substituting into Equation 6.6.1 produces

$$\mu_T = \mu_{Q=0} \int_{-\infty}^{\infty} \psi_{v'}(Q) \psi_v(Q) dQ + \left( \frac{d\mu(Q)}{dQ} \right)_{Q=0} \int_{-\infty}^{\infty} Q \psi_{v'}^*(Q) \psi_v(Q) dQ \quad (6.6.4)$$

In the above expressions,  $\mu_{Q=0}$  is the dipole moment of the molecule when the nuclei are at their equilibrium positions, and  $\left( \frac{d\mu(Q)}{dQ} \right)_{Q=0}$  is the linear change in the dipole moment due to the displacement of the nuclei in the normal mode. The derivative

is the linear change because it multiplies  $Q$  and not a higher power of  $Q$  in Equation 6.6.3. Both  $\mu$  and  $\left( \frac{d\mu(Q)}{dQ} \right)_{Q=0}$  are moved outside of the integral because they are constants that no longer depend on  $Q$  because they are evaluated at  $Q = 0$ .

The integral in the first term in Equation 6.6.4 is 0 because any two harmonic oscillator wavefunctions are orthogonal. The integral in the second term of Equation is zero except when  $v' = v \pm 1$  as demonstrated in Exercise 6.6.32. Also note that the second term is zero if

$$\left( \frac{d\mu(Q)}{dQ} \right)_{Q=0} = 0 \quad (6.6.5)$$

### Exercise 6.6.1

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation 6.6.4 is 0 unless  $v' = v \pm 1$ .

If we are to observe absorption of infrared radiation due to a vibrational transition in a molecule, the transition moment cannot be zero. This condition requires that the dipole moment derivative Equation 6.6.5 cannot be zero and that the vibrational quantum number change by one unit. The normal coordinate motion must cause the dipole moment of the molecule to change in order for a molecule to absorb infrared radiation. If the normal coordinate oscillation does not cause the dipole moment to change then  $\mu_T = 0$  and no infrared absorption is observed.

$$\text{For allowed transitions } \Delta v = \pm 1 \quad (6.6.6)$$

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero,  $\mu = 0$ . Since the vibrational motion (only bond stretching for a diatomic molecule) preserves this symmetry, the change in the dipole moment due to the vibrational motion also is zero,  $\frac{d\mu(Q)}{dQ} = 0$ . Consequently, oxygen and nitrogen cannot absorb infrared radiation as a result of vibrational motion.

This result has important practical consequences. Chemists can do infrared spectroscopy in the air. The spectrometer need not be evacuated to eliminate the absorption due to oxygen and nitrogen. This situation greatly simplifies the spectrometer design, lowers the cost of the instrument, and makes it more convenient to use.

### Exercise 6.6.2

Explain why the absorption coefficient in Beer's Law is larger for some normal modes than for others.

The case  $v' = v + 1$  corresponds to going from one vibrational state to a higher energy one by absorbing a photon with energy  $h\nu$ . The case  $v' = v - 1$  corresponds to a transition that emits a photon with energy  $h\nu$ . In the harmonic oscillator model infrared spectra are very simple; only the fundamental transitions,  $\Delta = \pm 1$ , are allowed. The associated transition energy is  $\hbar\omega$ , according to Equation ???). The transition energy is the change in energy of the oscillator as it moves from one vibrational state to another, and it equals the photon energy.

$$\Delta E = E_{final} - E_{initial} = h\nu_{photon} = \hbar\omega_{oscillator} \quad (6.6.7)$$

In a perfect harmonic oscillator, the only possibilities are  $\Delta = \pm 1$ ; all others are forbidden. This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of only one strong line, as shown in Figure 6.6.1, because as you showed in your energy level diagram in Exercise 6.6.2Q the energy levels are equally spaced in the harmonic oscillator model. If the levels were not equally spaced, then transitions from  $v = 0$  to 1 and from  $v = 1$  to 2, etc. would occur at different frequencies.

The actual spectrum is more complex, especially at high resolution. There is a fine structure due to the rotational states of the molecule. These states will be discussed in the next chapter. The spectrum is enriched further by the appearance of lines due to transitions corresponding to  $\Delta = \pm n$  where  $n > 1$ . These transitions are called overtone transitions and their appearance in spectra despite being forbidden in the harmonic oscillator model is due to the anharmonicity of molecular vibrations. Anharmonicity means the potential energy function is not strictly the harmonic potential. The first overtone,  $\Delta v = 2$ , generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the  $\Delta v = 1$  transition.

### Exercise 6.6.2

Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at  $2886 \text{ cm}^{-1}$ .

Also note that hot bands, those involving transitions from thermally populated states having  $v > 0$ , can be present in the spectra. The number density of molecules,  $n_v$ , in a particular energy level,  $v$ , at any temperature is proportional to the Boltzmann factor.

$$n_v \propto e^{-\frac{E_v}{k_B T}} \quad (6.6.8)$$

For molecules at room temperature or below, the  $v = 0$  vibrational state is the one that is most heavily populated.

### Exercise 6.6.3

Using the Boltzmann distribution, determine the ratio of the number of HCl molecules in the  $v = 1$  vibrational state compared to the  $v = 0$  state at room temperature. Comment on the expected intensity of the hot-band transition from the  $v = 1$  state at room temperature. At what temperature might the hot band for HCl have an intensity that is 25% of the fundamental band at that temperature?

These considerations explain the low-resolution absorption spectrum of a diatomic molecule shown in Figure 6.6.1. Such spectra are simple because only the fundamental ( $v = 0$  to 1) is intense. The overtones ( $v = 0$  to  $v > 1$ ) are very weak and are not shown in the spectrum. They only appear at all because the actual molecular potential is slightly anharmonic, making the harmonic oscillator

model and selection rules only an approximation. This anharmonicity becomes more important for the higher energy states ( $v \gg 0$ ) that involve larger displacements from equilibrium, i.e. larger values of  $Q$ . We conclude that the harmonic oscillator approximation is very good because the forbidden overtone transitions are indeed weak.

Generally each intense peak that is seen in an infrared spectrum of a polyatomic molecule corresponds to the fundamental transition of a different normal mode because the overtones are forbidden in the harmonic approximation and hot bands are weak at room temperature. However in a polyatomic molecule, combination bands that involve the excitation of two normal modes also can be intense. They arise from a higher order term in the expansion of  $\mu(Q)$ ; namely,

$$\left( \frac{\partial^2 \mu}{\partial Q_A \partial Q_B} \right)_{Q=0} Q_A Q_B \quad (6.6.9)$$

This derivative gives the change in the dipole moment due to the motion of two normal modes simultaneously.

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