

7.2.5.2 *Progressions and sequences*

Figure 7.18 shows sets of vibrational energy levels associated with two electronic states between which we shall assume an electronic transition is allowed. The vibrational levels of the upper and lower states are labelled by the quantum numbers v' and v'' , respectively. We shall be discussing absorption as well as emission processes and it will be assumed, unless otherwise stated, that the lower state is the ground state.

In electronic spectra there is no restriction on the values that Δv can take but, as we shall see in Section 7.2.5.3, the Franck–Condon principle imposes limitations on the intensities of the transitions.

Vibrational transitions accompanying an electronic transition are referred to as vibronic transitions. These vibronic transitions, with their accompanying rotational or, strictly, rovibronic transitions, give rise to bands in the spectrum, and the set of bands associated with a single electronic transition is called an electronic band system. This terminology is usually adhered to in high-resolution electronic spectroscopy but, in low-resolution work, particularly in the liquid phase, vibrational structure may not be resolved and the whole band system is often referred to as an electronic band.

Vibronic transitions may be divided conveniently into progressions and sequences. A progression, as Figure 7.18 shows, involves a series of vibronic transitions with a common

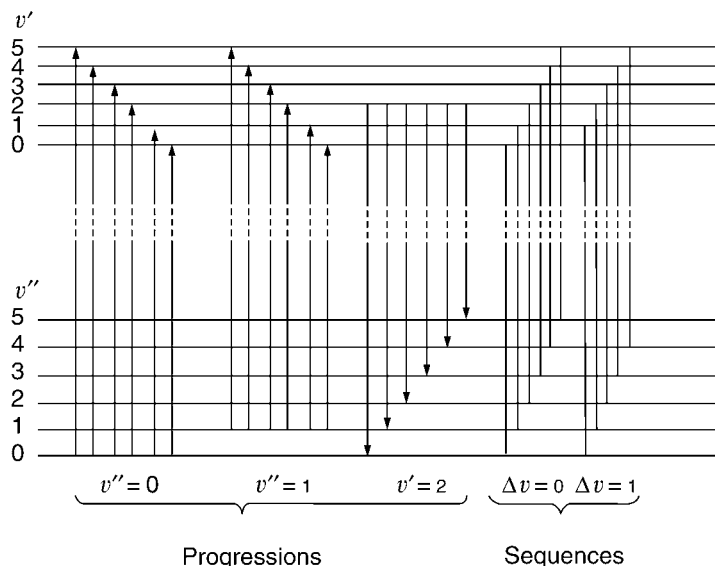


Figure 7.18 Vibrational progressions and sequences in the electronic spectrum of a diatomic molecule

lower or upper level. For example, the $v'' = 0$ progression members all have the $v'' = 0$ level in common.

Quite apart from the necessity for Franck–Condon intensities of vibronic transitions to be appreciable, it is essential for the initial state of a transition to be sufficiently highly populated for a transition to be observed. Under equilibrium conditions the population $N_{v''}$ of any v'' level is related to that of the $v'' = 0$ level by

$$\frac{N_{v''}}{N_0} = \exp \left\{ - \left[G(v'') - G(0) \right] \frac{hc}{kT} \right\} \quad (7.83)$$

which follows from the Boltzmann Equation (Equation 2.11).

Worked example 7.3

Question. Calculate the ratio of molecules in the $v = 1$ compared with the $v = 0$ vibrational level of the ground electronic state, at 293 K, for H_2 ($\omega_0 = 4161 \text{ cm}^{-1}$), F_2 ($\omega_0 = 895 \text{ cm}^{-1}$) and I_2 ($\omega_0 = 213 \text{ cm}^{-1}$). At what temperature, for each molecule, would the ratio be 0.5000?

Answer. Equation (7.83), derived from the Boltzmann equation, gives the ratio of the population N_1 of the $v = 1$ level to the population, N_0 , of the $v = 0$ level as

$$\frac{N_1}{N_0} = \exp \left(- \frac{hc\omega_0}{kT} \right)$$

where ω_0 is the $v = 1$ to $v = 0$ level separation. For H_2

$$\begin{aligned}\frac{N_1}{N_0} &= \exp\left(-\frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^{10} \text{ cm s}^{-1} \times 4161 \text{ cm}^{-1}}{1.3807 \times 10^{-23} \text{ J K}^{-1} \times 293 \text{ K}}\right) \\ &= \exp(-20.432) \\ &= 1.338 \times 10^{-9}\end{aligned}$$

For F_2

$$\begin{aligned}\frac{N_1}{N_0} &= \exp(-4.395) \\ &= 0.0123\end{aligned}$$

For I_2

$$\begin{aligned}\frac{N_1}{N_0} &= \exp(-1.046) \\ &= 0.351\end{aligned}$$

For H_2 , if $\frac{N_1}{N_0} = 0.5000$, then

$$\begin{aligned}0.5000 &= \exp\left(-\frac{hc\omega_0}{kT}\right) \\ \ln 0.5000 &= -0.6931 = -\frac{hc\omega_0}{kT}\end{aligned}$$

$$\begin{aligned}\therefore T &= \frac{hc\omega_0}{0.6931k} \\ &= 2.0758 \text{ cm K} \times 4161 \text{ cm}^{-1} \\ &= 8637 \text{ K}\end{aligned}$$

For F_2

$$\begin{aligned}T &= 2.0758 \text{ cm K} \times 895 \text{ cm}^{-1} \\ &= 1860 \text{ K}\end{aligned}$$

For I_2

$$\begin{aligned}T &= 2.0758 \text{ cm K} \times 213 \text{ cm}^{-1} \\ &= 442 \text{ K}\end{aligned}$$

Note that the values given for ω_0 limit the number of significant figures to four for H_2 and to three for F_2 and I_2 .

Because of the relatively high population of the $v'' = 0$ level the $v'' = 0$ progression is likely to be prominent in the absorption spectrum. In emission the relative populations of the v' levels depend on the method of excitation. In a low-pressure discharge, in which there are not many collisions to provide a channel for vibrational deactivation, the populations may be somewhat random. However, higher pressure may result in most of the molecules being in the $v' = 0$ state and the $v' = 0$ progression being prominent.

The progression with $v'' = 1$ may also be observed in absorption but only in a molecule with a vibration wavenumber low enough for the $v'' = 1$ level to be sufficiently populated. This is the case in, for example, iodine for which $\omega_0 = 213 \text{ cm}^{-1}$. As a result the $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$ visible system shows, in absorption at room temperature, not only a $v'' = 0$ but also a $v'' = 1$ and a $v'' = 2$ progression, as shown in Figure 7.19.

A progression with $v' = 2$, illustrated in Figure 7.18, can be observed only in emission. Its observation could result from a random population of v' levels or it could be observed on its own under rather special conditions involving monochromatic excitation from $v'' = 0$ to $v' = 2$ with no collisions occurring before emission. This kind of excitation could be achieved with a tunable laser.

A spin-allowed ($\Delta S = 0$) emission process is defined as fluorescence, and a spin-forbidden ($\Delta S \neq 0$) emission process as phosphorescence. Because of the spin-forbidden nature of phosphorescence the upper state concerned tends to have a long lifetime compared with that of the upper state of spin-allowed fluorescence. Consequently, there is a tendency to distinguish the two processes according to their lifetimes. The danger in using this distinction is that, in cases of strong spin-orbit coupling, the lifetime of a transition between states of differing multiplicity may be relatively short, leading to an erroneous description as fluorescence.

If emission is from only one vibrational level of the upper electronic state it is referred to as single vibronic level fluorescence (or phosphorescence).

A group of transitions with the same value of Δv is referred to as a sequence. Because of the population requirements long sequences are observed mostly in emission. For example, sequences of five or six members are observed in the $C^3\Pi_u - B^3\Pi_g$ band system of N_2 in emission in the visible and near-ultraviolet from a low-pressure discharge in nitrogen gas. The vibration wavenumber ω_e is high (2047.18 cm^{-1}) in the C state and equilibrium population of the vibrational levels is not achieved before emission.

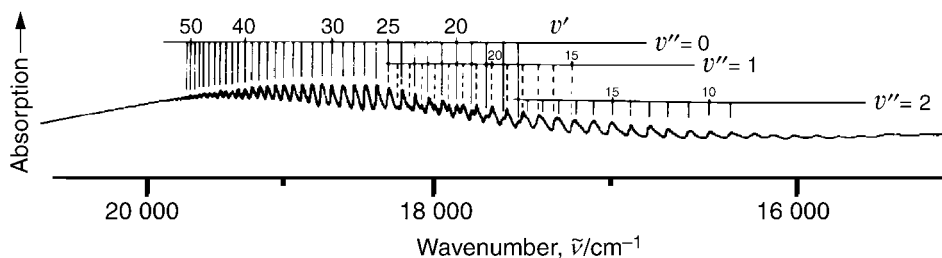


Figure 7.19 Progressions with $v'' = 0, 1$ and 2 in the $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$ system of I_2

It is clear from Figure 7.18 that progressions and sequences are not mutually exclusive. Each member of a sequence is also a member of two progressions. However, the distinction is useful because of the nature of typical patterns of bands found in a band system. Progression members are generally widely spaced with approximate separations of ω'_e in absorption and ω''_e in emission. In contrast, sequence members are more closely spaced with approximate separations of $\omega'_e - \omega''_e$.

The general symbolism for indicating a vibronic transition between an upper and lower level with vibrational quantum numbers v' and v'' , respectively, is $v' - v''$, consistent with the general spectroscopic convention. Thus the electronic transition is labelled 0–0.