

29.3: Electronic Spectroscopy

Electronic spectroscopy is concerned with the measurement of the energies of transitions between quantized electronic states of molecules. Electronic transitions are always associated with simultaneous changes in vibrational levels. In the gas phase vibronic transitions are also accompanied by changes in rotational energy.

Electronic transitions are typically observed in the visible and ultraviolet regions, in the wavelength range approximately 200 – 700 nm ($50,000 - 14,000 \text{ cm}^{-1}$). When the electronic and vibrational energy changes are drastically different, vibronic coupling (mixing of electronic and vibrational wave functions) can be neglected and the energy of a vibronic level can be taken as the sum of the electronic and vibrational (and rotational) energies; that is, the Born–Oppenheimer approximation applies. The overall molecular energy depends not only on the electronic state but also on the vibrational and rotational quantum numbers, v and J . In this context, it is conventional to add a double prime (v'', J'') for levels of the electronic ground state and a single prime (v', J') for electronically excited states.

Each electronic transition may show vibrational coarse structure, and for molecules in the gas phase, rotational fine structure. This is true even when the molecule has a zero dipole moment and therefore has no vibration-rotation infrared spectrum or pure rotational microwave spectrum.

It is necessary to distinguish between absorption and emission spectra. With absorption the molecule starts in the ground electronic state, and usually also in the vibrational ground state $v'' = 0$ because at ordinary temperatures the energy necessary for vibrational excitation is large compared to the average thermal energy. The molecule is excited to another electronic state and to many possible vibrational states $v' = 0, 1, 2, 3, \dots$. With emission, the molecule can start in various populated vibrational states, and finishes in the electronic ground state in one of many populated vibrational levels. The emission spectrum is more complicated than the absorption spectrum of the same molecule because there are more changes in vibrational energy level.

As we did for the previous two cases, we will concentrate below on the electronic absorption spectroscopy of diatomic molecules.

Electronic spectroscopy of diatomic molecules

The vibronic spectra of diatomic molecules in the gas phase also show rotational fine structure. Each line in a vibrational progression will show P- and R- branches. For some electronic transitions there will also be a Q-branch. The transition energies of the lines for a particular vibronic transition are given (in wavenumbers) by:

$$G(J', J'') = \bar{\nu}_{v'-v''} + B' J'(J' + 1) - B'' J''(J'' + 1). \quad (29.3.1)$$

The values of the rotational constants, B' and B'' may differ appreciably because the bond length in the electronic excited state may be quite different from the bond length in the ground state. The rotational constant is inversely proportional to the square of the bond length. Usually $B' < B''$, as is true when an electron is promoted from a bonding orbital to an antibonding orbital, causing bond lengthening.

The treatment of rotational fine structure of vibronic transitions is similar to the treatment of rotation-vibration transitions and differs principally in the fact that the ground and excited states correspond to two different electronic states as well as to two different vibrational levels. For the P-branch $J' = J'' - 1$, so that:

$$\begin{aligned} \bar{\nu}_P &= \bar{\nu}_{v'-v''} + B'(J'' - 1)J'' - B''J''(J'' + 1) \\ &= \bar{\nu}_{v'-v''} - (B' + B'')J'' + (B' - B'')J'' \end{aligned}$$

Similarly, for the R-branch $J' = J'' + 1$, and:

$$\begin{aligned} \bar{\nu}_R &= \bar{\nu}_{v'-v''} + B'J'(J' + 1) - B''J'(J' - 1) \\ &= \bar{\nu}_{v'-v''} + (B' + B'')J' + (B' - B'')J'^2. \end{aligned}$$

Thus, the wavenumbers of transitions in both P- and R- branches are given, to a first approximation, by the single formula:

$$\bar{\nu}_{P,R} = \bar{\nu}_{v',v''} + (B' + B'')m + (B' - B'')m^2, \quad m = \pm 1, \pm 2, \dots \quad (29.3.2)$$

Here positive m values refer to the R-branch (with $m = +J' = J'' + 1$) and negative values refer to the P-branch (with $m = -J''$).

The intensity of allowed vibronic transitions is governed by the Franck-Condon principle, which states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly. A diagrammatic representation of electronic spectroscopy and the Franck-Condon principle for a diatomic molecule is presented in figure 29.3.1.¹

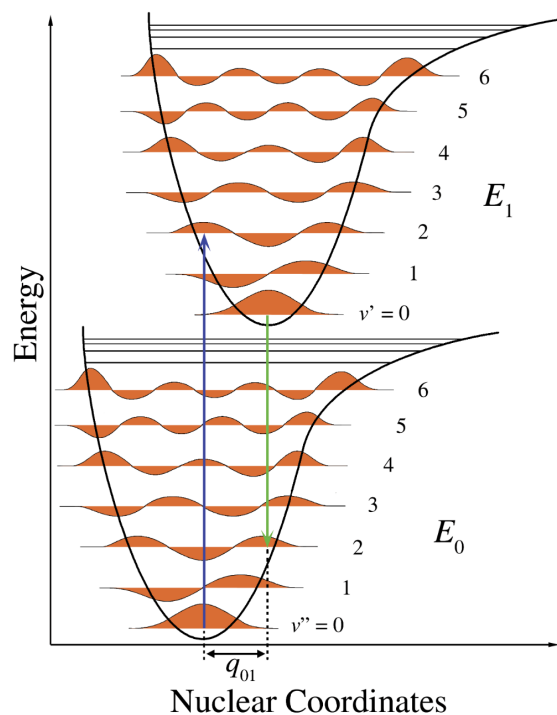


Figure 29.3.1: Energy level diagram illustrating the Franck-Condon principle.

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