Chapter 11

Molecular electronic transitions

All the following material © P.W. Atkins and R.S. Friedman.

Exercises

11.1 See the discussion of the Hund coupling cases in Section 11.1.

(i) We focus on which of the quantum numbers for orbital and spin angular momenta are good quantum numbers. For case (a) \( \Omega, \Lambda, \Sigma \); for case (b) \( \Lambda, S \); for case (c) \( E, \Omega \), for case (d) \( L, S \).

(ii) In each case, the degeneracy of a rotational energy level is \( 2J + 1 \), where \( J \) is the total angular momentum.

Exercise: Describe mechanisms by which the angular momenta are decoupled.

11.2 Refer as needed to the discussion in Section 8.6. (i) A single electron (spin-1/2) gives rise to a doublet term. (ii) Since a d-orbital pertains to \( l = 2 \), the overlap of two d-orbitals, using the Clebsch-Gordan series (eqn 4.42), gives rise to terms with values of the orbital angular momenta of 0, 1, 2, 3, and 4, pertaining to \( \Sigma, \Pi, \Delta, \Phi, \) and \( \Gamma \) terms, respectively. (iii) The \( \Sigma \) term requires a label to describe its behaviour under reflection in a plane containing the internuclear axis. The molecular orbital constructed from face-to-face overlap of d_{xy} orbitals has the character of \( -1 \) under this operation so the term is \( \Sigma^- \). (iv) For the parity classification of the terms, the molecular orbital does not change upon inversion through the center of the diatomic molecule so it has gerade symmetry.
The following terms therefore arise: $^2\Sigma_g^-$, $^2\Pi_g$, $^2\Delta_g$, $^2\Phi_g$, $^2\Gamma_g$

11.3 Refer to the specification of the selection rules in Section 11.3.

(a) $^2\Pi \rightarrow ^2\Pi$ allowed by $\Delta \lambda = 0$

(b) $^1\Sigma \rightarrow ^1\Sigma$ allowed by $\Delta \lambda = 0$

(c) $\Sigma \rightarrow \Lambda$ forbidden ($\Delta \lambda = \pm 2$ not allowed)

(d) $\Sigma^+ \rightarrow \Sigma^-$ forbidden by $\Sigma^+ \leftrightarrow \Sigma^-$

(e) $\Sigma^+ \rightarrow \Sigma^+_u$ allowed by $\Delta \lambda = 0$ and $\Sigma^+ \leftrightarrow \Sigma^+_u$

(f) $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ allowed by $\Delta \lambda = 0$, $\Sigma^+ \leftrightarrow \Sigma^+_u$, and $g \leftrightarrow u$

(g) $^3\Sigma_g^+ \rightarrow ^3\Sigma_u^-$ forbidden by $\Sigma^- \leftrightarrow \Sigma^-$

**Exercise:** Which of $^2\Pi \rightarrow ^2\Sigma$, $^3\Pi_g \rightarrow ^3\Sigma_u^+$, and $^3\Delta_g \rightarrow ^1\Pi_u$ are allowed?

11.4 When a diatomic molecule with $S = 3/2$ dissociates, the two atoms that form may have spins $S_1$ and $S_2$, respectively, such that the Clebsch-Gordan series (eqn 4.42) for the resultant of $S_1$ and $S_2$ contains $S = 3/2$. For example, $(S_1 = 2, S_2 = 1/2)$ results in $S = 5/2$, $3/2$ so this combination of spins is allowed. The spin states, $(S_1, S_2)$, of the atoms that may form are

$(0, 3/2), (3/2, 0), (1/2, 1), (1, 1/2), (1/2, 2), (2, 1/2), (1, 3/2), (3/2, 1)$ and so on.

11.5 A $\Phi$ state pertains to $A = 3$. Therefore, the two atoms that form when the diatomic molecule dissociates may have may have orbital angular momenta $L_1$ and $L_2$, respectively, such that the Clebsch-Gordan series (eqn 4.42) for the resultant of $L_1$ and $L_2$
contains a value of 3. For example, the atomic terms \((F, D)\) pertain to \(L_1 = 3\) and \(L_2 = 2\) with resultant values of \(5, 4, 3, 2, 1, 0\); therefore, since a value of 3 is possible, the atomic terms \((F, D)\) are possible. The list of possible terms includes
\[(F, S), (S, F), (D, P), (P, D), (D, D), (F, D), (D, F)\) and so on.

11.6 Dissocation of \(O_2^+\) produces \(O + O^+\). (i) The \(^4\Pi_u\) state has a spin multiplicity of \((2S + 1) = 4\); that is, \(S = 3/2\). Therefore, if \(S_1\) is the total spin for the O atom (an integer since the atom has an even number of electrons) and \(S_2\) is the total spin for the \(O^+\) ion (a half-integer since the ion has an odd number of electrons), then possible values for \(S_1\) and \(S_2\) are those for which the Clebsch-Gordan series (eqn 4.42) for the coupling of \(S_1\) and \(S_2\) includes a value of 3/2. For example, the combination of \(S_1 = 0\) (a singlet term) and \(S_2 = 3/2\) (a quartet term) is possible. (ii) The \(^4\Pi_u\) pertains to \(\Lambda = 1\). Therefore, the states that form when the diatomic molecule dissociates may have orbital angular momenta \(L_1\) and \(L_2\) such that the Clebsch-Gordan series (eqn 4.42) for the resultant of \(L_1\) and \(L_2\) contains a value of 1. For example, the terms \((P, D)\) pertain to \(L_1 = 2\) and \(L_2 = 3\) with resultant values of \(5, 4, 3, 2, 1, 0\); therefore, since a value of 1 is possible, the terms \((P, D)\) are possible.

The list of possible terms includes
\[O(^1P) + O^+(^4S), O(^3P) + O^+(^4S), O(^3P) + O^+(^2S), O(^1D) + O^+(^4S), O(^3D) + O^+(^4S),
O(^1P) + O^+(^2D), O(^1S) + O^+(^2P),\] and so on.

11.7 The transition element \(\langle ^1A_2|\mu_q|^1A_1\rangle\) transforms as

\[A_2 \times \Gamma(\mu_q) \times A_1 = A_2 \times \Gamma(\mu_q);\]

but as \(\Gamma(\mu_q) = A_1, B_1, B_2\), it must vanish.
The normal coordinates of H$_2$O are of symmetry species 2A$_1$ + B$_2$. Since B$_2 \times A_2 = B_1$, the vibronic transition matrix element

$$\langle ^1A_2, ^1B_2|\mu_q| ^1A_1, ^0B_2\rangle$$

is of symmetry species A$_2 \times B_2 \times \Gamma(\mu_q) \times A_1 \times A_1 = B_1 \times \Gamma(\mu_q)$. It is A$_1$ when $\Gamma(\mu_q) = B_1$, which is so where $q = x$. Therefore, an $x$-polarized vibronic transition may occur.

**Exercise:** Show that the transition $^2B_2 \leftrightarrow ^2B_1$ is forbidden in ClO$_2$ (a C$_2v$ molecule), but may be vibronically allowed.

**11.8** Determine which states are mixed by rotations. In $D_{6h}$ rotations transform as A$_{2g}$ and E$_{1g}$.

Therefore, B$_{1u}$ × {A$_{2g}$, E$_{1g}$} = {B$_{2u}$, E$_{2u}$} and B$_{2u}$ × {A$_{2g}$, E$_{1g}$} = {B$_{1u}$, E$_{2u}$}. Therefore

$^1B_{2u}$ and $^1E_{2u}$ may be mixed into $^3B_{1u}$ and $^1B_{1u}$ and $^1E_{2u}$ may be mixed into $^3B_{2u}$.

**Exercise:** What triplet states may be mixed into the $^1E$ state of NH$_3$? What states would be mixed if the molecule were planar in the $^1E$ excited state?

**Problems**

**11.1** $\psi_{2s} = (Z/a_0)^{3/2}(1/2\sqrt{2})(2 - \rho)e^{-\rho^2}Y$ [Table 3.4] with $\rho = Zr/a_0$

(a)

$$\langle r \rangle = \int_0^\infty rR^2r^2dr = \int_0^\infty \rho^3R^2(\rho)d\rho(a_0/Z)^4$$

$$= (a_0/Z)(1/8)\int_0^\infty \rho^3(2 - \rho)^2e^{-\rho}d\rho \quad [Z = 2]$$

$$= 12a_0/Z (318 \text{ pm}) \quad \left[ \int_0^\infty x^3(2 - x)^2e^{-x}dx = 96 \right]$$
(b)

\[ P(R) = \frac{(Z/a_0)^3}{(1/8)} \int_0^R (2 - \rho)^2 r^2 e^{-\rho} \, dr \]

\[ = \frac{1}{8} \int_0^A (2 - \rho)^2 \rho^2 e^{-\rho} \, d\rho = 0.90 \quad [A = ZR/a_0] \]

That is, we need to solve

\[ \text{Integral}(A) = \int_0^A (2 - \rho)^2 \rho^2 e^{-\rho} \, d\rho = 7.20 \quad \text{for } A \]

The graph of this integral as a function of \(A\) is shown in Fig. 11.1. We see that it has the value 7.20 at \(A = 9.12539\), so

\[ R = \frac{9.12539a_0}{Z} \quad (241 \text{ pm}) \]
Figure 11.1: The integral in Problem 11.1 as a function of $A = ZR/a_0$.

**Exercise:** Repeat the calculation for a 3s-orbital.

11.4 The vibrational wavefunctions are:

- Lower: $\psi_0 = N_i H_i(y) e^{-\frac{1}{2}y^2}$, \hspace{1em} $y = (m\omega/\hbar)^{1/2}x$ \hspace{1em} $[x = R - R_c]$

- Upper: $\psi_r = N_r H_r(y') e^{-\frac{1}{2}y'^2}$, \hspace{1em} $y' = (m\omega/\hbar)^{1/2}(x - \Delta R)$

Then the overlap integral is

$$S_{r0} = N_i N_0 \int_{-\infty}^{\infty} H_r(y')H_0(y)e^{-\frac{1}{2}(y^2+y'^2)} \, dx$$
\[ S_{10} = (2/\pi)^{1/2} \int_{-\infty}^{\infty} y e^{-\frac{1}{2}(y^2 + y'^2)} \, dy' \]

\[ S_{10} = (2/\pi)^{1/2} e^{-\frac{1}{2}z^2} \int_{-\infty}^{\infty} e^{-(y' + \frac{1}{2}z)^2} \, dy' \]

\[ S_{10} = (2/\pi)^{1/2} e^{-\frac{1}{2}z^2} \int_{-\infty}^{\infty} (w - \frac{1}{2}z) e^{-w^2} \, dw \quad [w = y' + \frac{1}{2}z] \]

\[ S_{10} = (2/\pi)^{1/2} e^{-\frac{1}{2}z^2} (-\frac{1}{2}z) \int_{-\infty}^{\infty} e^{-w^2} \, dw = -(z/\sqrt{2}) e^{-\frac{1}{2}z^2} \]

\[ S_{10} = \frac{1}{2} z^2 e^{-\frac{1}{2}z^2} = (m\omega^2/\hbar)\Delta R^2 \exp\{- (m\omega^2/\hbar)\Delta R^2\} \]

11.7 H\textsubscript{2}CO belongs to \textit{C}\textsubscript{2v}, and \( \mu_q \) transforms as \( B_1, B_2, A_1 \) for \( x, y, z \), respectively. The transition \( ^1A_2 \leftarrow ^1A_1 \) is therefore allowed only if it is vibronic \([\langle A_2|\mu_q|A_1\rangle \) does not span \( A_1 \). Since the six vibrations of \textit{H}_2\textit{CO} span \( 3A_1 + B_1 + 2B_2 \), possible singly excited vibronic states of the \( A_2 \) electronic state are of symmetry species \( A_1 \times A_2 = A_2, B_1 \times A_2 = B_2, \) and \( B_2 \times A_2 = B_1 \). These vibronic states may be stimulated from the \( A_1 \) state by \( y \)-polarized (\( B_2 \)) or \( x \)-polarized (\( B_1 \)) radiation.

Ethene belongs to \textit{D}\textsubscript{2h}, and \( \mu_q \) transforms as \( B_{3u}, B_{2u}, B_{1u} \) for \( x, y, z \), respectively. Therefore \( B_{2u} \leftarrow A_g \) is allowed for \( y \)-polarized radiation. The vibrations of ethene span

\[ 3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u} \]

[Problem 10.23], and so the possible vibronic states of the \( B_{2u} \) electronic state are

\[ B_{2u} \times (A_g, B_{1g}, B_{2g}, A_u, B_{1u}, B_{2u}, B_{3u}) = B_{2u}, B_{3u}, A_u, B_{2g}, B_{3g}, A_g, B_{1g} \]
[Refer to the character table, form $\chi(R)\chi'(R)$ for $\Gamma \times \Gamma'$, and identify the set of characters so produced]. Of these, $B_{2u}$ and $B_{3u}$ may be reached by an electric dipole transition from the $A_g$ ground state.

**Exercise:** Assess the polarization of the $^1B_2 \leftrightarrow ^1B_1$ transition in $H_2CO$ and the $B_{1g} \leftrightarrow A_g$ transition in ethene.

11.10

$$P_2(t) = (2V/\Omega)^2 \sin^2 \left( \frac{1}{2} \Omega t \right)$$

$$\Omega^2 = \omega_{21}^2 + 4V^2 \ [\text{eqn 6.63}].$$

$$\hbar \omega_{21} = \hbar J.$$ For state 2 taken as $T_0$, $\hbar V = \hbar \xi/\sqrt{2}$ [Problem 11.9];

for state 2 corresponding to $T\pm$, $\hbar V = \hbar \xi/2$. Therefore,

$$P(T_0) = \frac{\{2\xi^2/(J^2 + 2\xi^2)\} \sin^2 \left\{ \frac{1}{2} (J^2 + 2\xi^2)^{1/2} t \right\}}{\{2\xi^2/(J^2 + 2\xi^2)\} \sin^2 \left\{ \frac{1}{2} (J^2 + 2\xi^2)^{1/2} \right\}}$$

$$P(T\pm) = \frac{\{\xi^2/(J^2 + \xi^2)\} \sin^2 \left\{ \frac{1}{2} (J^2 + \xi^2)^{1/2} t \right\}}{\{\xi^2/(J^2 + \xi^2)\} \sin^2 \left\{ \frac{1}{2} (J^2 + \xi^2)^{1/2} \right\}}$$

$$P(T) = P(T_0) + P(T_\pm) + P(T_-)$$

For a range of initial times, $0 \leq t_0 \leq T$; the time $t$ then corresponds to the duration since initiation, which is $t - t_0$ for a given member of the system. Therefore, since $t_0$ ranges from 0 to $T$, the average population is:

$$P(T_0) = \{2\xi^2/(J^2 + 2\xi^2)\} (1/T) \int_0^T \sin^2 \left\{ \frac{1}{2} (J^2 + 2\xi^2)^{1/2} (t - t_0) \right\} dt_0$$

$$= \{2\xi^2/(J^2 + 2\xi^2)\} (1/T) \int_{t_0}^T \sin^2 (a \tau) d\tau \quad [\tau = t - t_0, a = \frac{1}{2} (J^2 + 2\xi^2)^{1/2}]$$

$$= \{\xi^2/(J^2 + 2\xi^2)\} \{1 - \gamma/2aT\}$$
\[ \gamma = [1 - \cos(2aT)] \sin(2at) + \sin(2aT) \cos(2at) \]

If \( T \) is long in the sense that \( 2aT \gg 1 \),

\[ \mathcal{P}(T_0) \approx \frac{\xi^2}{(J^2 + 2\xi^2)} \]

Likewise

\[ \mathcal{P}(T_\pm) \approx \frac{1}{2} \frac{\xi^2}{(J^2 + \xi^2)} \]

Overall, therefore,

\[ \mathcal{P}(T) \approx \frac{\xi^2}{(J^2 + 2\xi^2)} + \frac{\xi^2}{(J^2 + \xi^2)} = \frac{(2J^2 + 3\xi^2)\xi^2}{(J^2 + \xi^2)(J^2 + 2\xi^2)} \]

When \( J^2 \gg \xi^2 \), \( \mathcal{P}(T) \approx \frac{2\xi^2}{J^2} \).

**Exercise:** Suppose a magnetic field is present. How does \( \mathcal{P}(T) \) depend on it?

### 11.13
\[ H\Psi = \mathcal{E}\Psi, \quad \Psi = a\psi + \sum_n b_n\phi_n; \quad H^{(\text{bath})}\phi_n = E_n\phi_n. \]

\( \psi \) should be interpreted as \( \psi_{\text{system}}f_{\text{bath}} \) and \( \phi \) as \( \phi_{\text{bath}}g_{\text{system}} \), with \( H^{(\text{bath})}f_{\text{bath}} = 0 \) and \( H^{(\text{sys})}g_{\text{system}} = 0 \) (so that in each case no energy resides in the relevant component).

Then

\[ H\Psi = aE\psi + \sum_n b_n E_n \phi_n + H'a\psi + \sum_n b_n H'\phi_n \]

\[ = \mathcal{E}a\psi + \sum_n b_n \mathcal{E}\phi_n. \]
Multiply by (a) $\psi^*$ and integrate, (b) $\phi_n^*$ and integrate (follow that by setting $n' \to n$):

\[
(E - \varepsilon)a + V \sum_n b_n = 0 \quad \langle \psi|\phi_n \rangle = 0, \quad \langle \psi|H'|\psi \rangle = 0
\]

\[
V_a + (E_n - \varepsilon)b_n = 0 \quad \langle \phi_n|\psi \rangle = 0, \quad \langle \phi_n|H'|\phi_n \rangle = 0
\]

Then, $b_n = \{V/(E - E_n)\}a$.

Substitute this expression for $b_n$ back into the first equation of the pair:

\[
(E - \varepsilon) + V^2 \sum_n \{1/(E - E_n)\} = 0
\]

Then, with $E - E_n = \gamma \varepsilon - n \varepsilon$ and $\rho = 1/\varepsilon$,

\[
E - \varepsilon = -(V^2/\varepsilon) \sum_n \{1/(\gamma - n)\}
\]

\[
= (V^2 \rho)\pi \cot(\pi \gamma)
\]

As $\Psi$ is normalized to unity, $a^2 + \sum_n b_n^2 = 1$; consequently [from above]

\[
a^2 + a^2 V^2 \sum_n \{1/(E_n - \varepsilon)^2\} = 1
\]

Since

\[
\sum_{n=-\infty}^{\infty} (\gamma - n)^{-2} = \pi^2 \csc^2 \pi \gamma
\]

[Handbook of mathematical functions]

\[
a^2 = \{1 + \pi^2 \rho^2 V^2 \csc^2 (\pi \gamma)\}^{-1}
\]
\begin{align*}
&= \left\{ 1 + \pi^2 \rho^2 V^2 + \pi^2 \rho^2 V^2 \cot^2(\pi \gamma) \right\}^{-1} \\
&= \left\{ 1 + \pi^2 \rho^2 V^2 + \pi^2 \rho^2 V^2 \left[ \frac{(E - \epsilon)}{\pi \rho V^2} \right]^2 \right\}^{-1} \\
&= \frac{V^2}{(E - \epsilon)^2 + V^2 + (\pi V^2 \rho)^2} \\
\end{align*}

**Exercise:** Find an expression for \( \sum_n b_n^4 \).