Chapter 6

Internal Conversion and Intersystem Crossing

6.1. The States Between Which Transitions Occur

To understand the mechanisms by which a molecule can undergo a *radiationless transition* (Yardley, 1980; Lin, 1980) from one potential energy surface to another, the Schrödinger equation for combined electronic and nuclear motion given in Chapter 1 is needed. The electronic wavefunctions $\{\phi_a(\mathbf{r}|\mathbf{R})\}$ corresponding to the two interacting states between which transitions occur obey the equations

$$h_e\phi_{S_0} = E_{S_0}(\mathbf{R})\phi_{S_0} \tag{6.1}$$

and

$$h_e\phi_x = E_x(\mathbf{R})\phi_x \qquad (x = S_1 \text{ or } T_1). \tag{6.2}$$

Within the Born-Oppenheimer approximation, the internal (vibrational-rotational) wavefunctions belonging to the S_0 and excited potential surfaces obey the equations

$$(D_R^2 + E_{S_0})\chi_v^0 = \epsilon_v^0\chi_v^0 \tag{6.3}$$

and

$$(D_R^2 + E_x)\chi_{v'}^x = \epsilon_{v'}^x\chi_{v'}^x, \tag{6.4}$$

in which D_R^2 is the kinetic energy operator for all of the nuclear vibration and rotation. The energies ϵ_v^0 and $\epsilon_{v'}^x$ are the *total* Born-Oppenheimer energies of $\phi_{S_0}\chi_v^0$ and $\phi_x\chi_{v'}^x$, respectively. ϵ_v^0 can be decomposed into the electronic energy at the minimum of the S_0 surface plus the χ_v^0 internal energy (e_v^0)

$$\epsilon_v^0 = E_{S_0}(\text{min}) + e_v^0. \tag{6.5}$$

An analogous expression can be written for ϵ_v^x

$$\epsilon_v^x = E_x(\text{min}) + e_v^x \tag{6.6}$$

where E_x (min) is the electronic energy at the minimum of the excited-state surface. $E_x(\text{min}) - E_{S_0}(\text{min})$ gives the adiabatic *electronic* energy difference for the $S_0 \rightarrow X$ excitation; e_v^0 and e_v^x are simply the vibration/rotation energies (labeled by the quantum number v) on the S_0 and x surfaces, respectively.

In the approximation that the internal vibrations and rotations may be uncoupled, the functions χ_v^0, and $\chi_{v'}^x$ consist of products of appropriate rotational functions and of $3N - 6$ vibrational wavefunctions—one for each of the normal or local vibrational coordinates (Yardley, 1980) *including* the reaction coordinate Q_r. As pointed out in Chapter 1, motion along coordinates orthogonal to Q_r can often be thought of as involving approximately harmonic vibration. However, the components of χ_v^0 and $\chi_{v'}^x$ that describe motion along Q_r cannot be approximated by harmonic motion except near local minima. In regions of Q_r space in which S_0 has negative curvature, the Q_r component of χ_v^0 looks like a continuum wavefunction rather than a bound vibrational wavefunction.

We now consider the transitions used when a molecule hops from S_1 or T_1 to S_0. The S_1 or T_1 state has been populated by the mechanism $S_0 + h\nu \rightarrow S_n \rightarrow (S_1, T_1)$. In the Born-Oppenheimer approximation, the wavefunction of this excited state is given by

$$\psi_x = \phi_x(\mathbf{r}\,|\,\mathbf{R})\chi_{v'}^x(\mathbf{R}). \tag{6.7}$$

The vibrational energy level $\epsilon_{v'}^x$ may be high or quite low (e.g., in condensed-phase situations). Although $\epsilon_{v'}^x$ also contains rotational and, perhaps, relative translational energy, we will, for brevity, speak of this energy as being vibrational. If the density of states (states per cm^{-1} of energy) in the S_0 manifold is high at this energy level ($\epsilon_{v'}^x$), it is likely that there is a state of the S_0 manifold

$$\psi_0 = \phi_{S_0}(\mathbf{r}\,|\,\mathbf{R})\chi_v^0(\mathbf{R}) \tag{6.8}$$

that is *nearly degenerate* with ψ_x. These two zeroth-order states will be coupled by the terms in the true Hamiltonian that give rise to non-Born-Oppenheimer corrections. This coupling will be strong if the off-diagonal matrix elements $\langle \psi_x | H | \psi_0 \rangle$ are nonnegligible when compared to the energy difference $\epsilon_{v'}^x - \epsilon_v^0$ (Yardley, 1980). Therefore, in this situation the non-Born-Oppenheimer coupling is said to give rise to *transitions* between ψ_x and ψ_0, and these transitions are the hopping that has been discussed. If the excited state is a triplet, the non-Born-Oppenheimer terms alone would not couple ψ_x and ψ_0; H must

6.2. Rates of Transitions

To evaluate *rates* of such transitions, the conventional Fermi "golden rule" can be used (Yardley, 1980; Lin, 1980); this rule states that transitions starting in $\phi_x\chi^x_{\nu'}$ and going to $\phi_{S_0}\chi^0_\nu$ and caused by the non-Born-Oppenheimer parts of $H - h_e$ occur at a rate given in sec^{-1} by

$$W = \frac{2\pi}{\hbar}\sum_\nu |\langle\phi_{S_0}\chi^0_\nu|H - h_e|\phi_x\chi^x_{\nu'}\rangle|^2\delta(\epsilon^0_\nu - \epsilon^x_{\nu'}). \tag{6.9}$$

The δ function guarantees that the states $\phi_{S_0}\chi^0_\nu$ contributing to the total radiationless transition rate have the same Born-Oppenheimer energy as $\phi_x\chi^x_{\nu'}$. When many vibrational or rotational modes are present, there may be many χ^0_ν functions, each having the same energy ϵ^0_ν. The number of such states is referred to as the density of states ρ at this total energy (ϵ^0_ν)

$$\rho(\epsilon^x_{\nu'}) = \sum_\nu \delta(\epsilon^0_\nu - \epsilon^x_{\nu'}). \tag{6.10}$$

If there is reason to believe that all of the states $\{\phi_{S_0}\chi^0_\nu\}$ in this degenerate manifold couple to the same extent with the initial state $\phi_x\chi^x_{\nu'}$, then the sum over ν in the above expression for W can be replaced by the appropriate state density

$$W = \frac{2\pi}{\hbar}|\langle\phi_{S_0}\chi^0_\nu|H - h_e|\phi_x\chi^x_{\nu'}\rangle|^2\rho(\epsilon^0_\nu) \tag{6.11}$$

in which $\chi^x_{\nu'}$ is any one of the degenerate states. Modern research on the behavior of electronically excited molecules indicates that, even for systems with high state densities, often only a small fraction of the modes play an active role in the radiationless transition. As a result, it may not be wise to use equation 6.11 when trying to understand radiationless transition rates; it is probably more appropriate to think in terms of equation 6.9.

Internal Conversion Rates

We now consider how equation 6.9 depends on the electronic energy difference and the vibrational wavefunctions χ^0_ν and $\chi^x_{\nu'}$ for the internal conversion case in which ϕ_x is a singlet state. The terms in $H - h_e$ that couple the initial state $\phi_{S_1}\chi^x_{\nu'}$ to the final state $\phi_{S_0}\chi^0_\nu$ are the non-Born-Oppenheimer terms, and the off-diagonal coupling matrix element described in Chapter 1 is

$$\langle\phi_{S_0}\chi^0_\nu|H - h_e|\phi_{S_1}\chi^x_{\nu'}\rangle = \langle\phi_{S_0}\chi^0_\nu|\chi^x_{\nu'}D^2_R\phi_{S_1} + 2D_R\phi_{S_1}\cdot D_R\chi^x_{\nu'}\rangle \tag{6.12}$$

As discussed in Chapter 1, the second term in this expression is usually larger than the first (except when the second term vanishes, owing to symmetry); hence, the analysis will proceed using only this term. The analysis of the first term can be performed in analogous fashion (Berry, 1966); to do so would not shed further light on the physical origins of internal conversion.

An expression for the above coupling matrix element that is more physically useful can be obtained by applying the D_R operator to the Born-Oppenheimer Schrödinger equation, which ϕ_{S_1} obeys:

$$D_R(h_e\phi_{S_1} - E_{S_1}\phi_{S_1}) = 0. \tag{6.13}$$

Multiplying on the left by ϕ_{S_0} and integrating over the *electronic* coordinates only yields

$$\langle\phi_{S_0}|D_R h_e|\phi_{S_1}\rangle + \langle\phi_{S_0}|h_e D_R\phi_{S_1}\rangle - D_R E_{S_1}\langle\phi_{S_0}|\phi_{S_1}\rangle$$
$$- E_{S_1}\langle\phi_{S_0}|D_R\phi_{S_1}\rangle = 0. \tag{6.14}$$

Equation 6.14 can be solved for $\langle\phi_{S_1}|D_R\phi_{S_1}\rangle$, which can then be used to reexpress the coupling matrix element and, therefore, to write the transition rate as

$$W = \frac{2\pi}{\hbar}\sum_{v}\delta(\epsilon_v^0 - \epsilon_{v'}^0)$$
$$|\langle\chi_v^0|[E_{S_1} - E_{S_0}]^{-1}\langle\phi_{S_0}|D_R h_e|\phi_{S_1}\rangle\cdot 2D_R\chi_{v'}^{*}\rangle|^2 \tag{6.15}$$

This analysis shows that W is likely to be large if regions of nuclear configuration space (**R**) exist for which the electronic energy gap is small ($E_{S_1}(\mathbf{R}) \cong E_{S_0}(\mathbf{R})$) and the product $\chi_v^0(\mathbf{R})D_R\chi_{v'}^{*}(\mathbf{R})$ is nonvanishing. Therefore, molecular deformations that bring the two singlet-state potential surfaces close to one another should be sought. If χ_v^0 and $D_R\chi_{v'}^{*}$ have appreciable *overlap* in the region in which $E_{S_0} \cong E_{S_1}$, then internal conversion is likely. However, the *electronic* force matrix element $\langle\phi_{S_0}|D_R h_e|\phi_{S_1}\rangle$ must also be substantial; this integral will be large if (in the orbital-following sense introduced in Chapter 4) the distortion tends to evolve the orbital structure of ϕ_{S_1} into that of ϕ_{S_0}. Where symmetry is present, the direct product of the S_0 and S_1 symmetries must match that of $D_R h_e$. For example, in H_2CO, the $n\pi^*$ state is achieved by excitation from an occupied $b_2(n)$ orbital to the vacant $b_1(\pi^*)$ orbital. The kind of motion that is symmetry-consistent with $b_1 \times b_2$ is a_2. H_2CO does not have any vibration with a_2 symmetry. As a result, the $\langle\phi_{S_0}|D_R h_e|\phi_{S_1}\rangle$ matrix element should be small for $n\pi^*$ states in C_{2v} symmetry. In contrast, $\pi\pi^*$ S_1 states have $b_1 \times b_1 = a_1$ symmetry and, hence, D_R can be a, because S is also a. $H\,CO$ has three a vibrations (symmetric CH

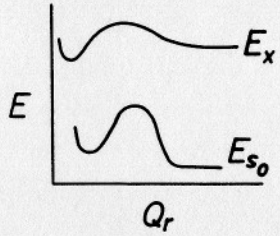

Figure 6-1
Energy surfaces that do not approach closely.

pected to have the largest effect on mapping the π^* orbital into the π orbital because the nature of these two orbitals is affected by the distance from C to O.

Let us review the procedure developed so far. If a coordinate exists along which E_{S_0} approaches E_{S_1}, the hopping rate for internal conversion is increased. Near this avoided crossing or near approach of the S_0 and S_1 surfaces, one considers whether symmetry or physical force are likely to make $\langle \phi_{S_0} | D_R h_e | \phi_{S_1} \rangle$ significant for deformations either along Q_r ($D_R = D_{Q_r}$) or along some direction perpendicular to Q_r. Directions in which both this electronic force matrix element is large and the vibrational product $\chi_\nu^0 D_R \chi_{\nu'}^x$ is substantial will play important roles as modes that *digest* the excess electronic energy $E_{S_0} - E_{S_1}$. That is, the direction along which E_{S_0} and E_{S_1} come close is important because this motion brings the molecule to the funnel geometry. Once the molecule is near the funnel, it can use *other* degrees of freedom (orthogonal to Q_r) to digest the excess electronic energy.

Energy-Digesting Modes

Two extreme cases of how the E_{S_0} and E_x surfaces might appear may be distinguished. The first case pertains to situations in which E_{S_0} and E_x do not approach one another closely—in other words, within an energy gap that is approximately equal to a non-Born-Oppenheimer matrix element. The shapes of two such surfaces are shown in Figure 6-1. Efficient internal conversion may still be possible by transfer of electronic energy to internal vibrational energy. To analyze the rates of such processes in this case, note first that the energy-denominator factor in equation 6.15—$[E_{S_0}(Q) - E_{S_1}(Q)]^{-1}$—is small and never undergoes rapid growth near some critical geometry as it would, for example, in the near-crossing situations (a second special case that will be treated shortly). Therefore, $E_{S_0} - E_{S_1}$ is approximated as a part that depends on the reaction coordinate Q_r, plus a part that describes the (approximately harmonic) motion perpendicular to Q_r:

Furthermore, the shapes of $E_{S_0}(\mathbf{R})$ and $E_{S_1}(\mathbf{R})$ are assumed to be sufficiently similar that $E_{S_0}(\mathbf{R}) - E_S(\mathbf{R})$ can be neglected relative to the presumed large value of $E_{S_0}(Q_r) - E_{S_1}(Q_r)$ splitting.

To continue the analysis, two additional assumptions are made: (1) Only one mode, whose spatial coordinate is R_a, plays an active role as an energy acceptor (Yardley, 1980). (2) In the initial S_1 state, the active mode is in its $v' = 0$ level. Assumption 2 is by no means fully justified or even necessary. In condensed media situations, it might be more justified, since vibrational energy would probably have been dissipated to the surroundings prior to the internal conversion process. This assumption is made only so the resulting integral containing $\chi_{\underline{v}}^0(R_a)$ and $D_{R_a}\chi_{\underline{v}'}^x(R_a)$ can be physically interpreted more easily. We will then argue that essentially the same physical picture would be obtained, after more tedious algebraic manipulation, if the more general ($v' \neq 0$) case were analyzed (see Yardley, 1980). Under the above outlined limitations, the rate expression (equation 6.15) becomes

$$W = \frac{2\pi}{\hbar} \sum_{\underline{v}} \delta(\epsilon_{\underline{v}}^0 - \epsilon_{\underline{v}'}^x) | \langle \chi_{\underline{v}}^0(Q_r) [E_{S_0}(Q_r) - E_{S_1}(Q_r)]^{-1} \chi_{\underline{v}'}^x(Q_r) \rangle$$

$$\Big(\prod_{b \neq a} \langle \chi_{v_b}^0 | \chi_{v_b'}^x \rangle \Big) \langle \phi_{S_0} | D_{R_a} h_e | \phi_{S_1} \rangle_{\text{eq}} \, 2 \langle \chi_{v_a}^0 | D_{R_a} | \chi_{v_a'}^x \rangle |^2. \tag{6.17}$$

Here the product Π_b extends over all modes *other than* Q_r and the active R_a and gives rise to simple Franck-Condon overlap factors for the passive modes. If these modes are fully passive, then the shapes of the S_0 and S_1 surfaces along these directions should be identical, in which case the $\langle \chi_{v_b}^0 | \chi_{v_b'}^x \rangle$ overlap factors would reduce to products of simple δ-functions $\Pi_b \, \delta_{v_b, v_b'}$. In writing the above expression for W, we assumed that the electronic force matrix element is rather insensitive to R_a. Consequently, $\langle \phi_{S_0} | D_{R_a} h_e | \phi_{S_1} \rangle$ was evaluated at the equilibrium value of the S_1 state of R_a ($R_a = R_a^{\text{eq}}$), which was denoted by the subscript "eq" in this integral. The vibrational quantum numbers appearing in $\epsilon_{\underline{v}}^0$ and $\epsilon_{\underline{v}'}^x$ are underlined because they contain the quantum numbers of *all* modes (for example, $\mathbf{v} = v_{Q_r}, v_a, v_b; b = 1 \ldots$).

With all of these observations, W reduces to

$$W = \frac{2\pi}{\hbar} \sum_{v_a v_r v_r'} \delta(e_{v_a}^0 + E_{S_0}(\text{min}) + e_{v_r}^0 - e_{v_a'}^x - E_{S_1}(\text{min}) - e_{v_r'}^x)$$

$$| \langle \chi_{v_r}^0(Q_r) | [E_{S_0}(Q_r) - E_{S_1}(Q_r)]^{-1} \chi_{v_r'}^x(Q_r) \rangle |^2$$

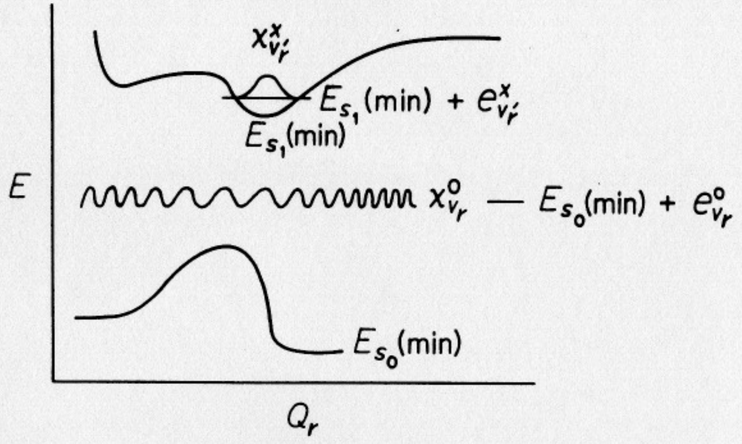

Figure 6-2
Energies relevant to internal conversion.

in which $e^0_{v_r}$ and $e^x_{v_r'}$ are the *internal* energies in the Q_r mode in the two states. The energy-conservation δ-function requires that the excess energy

$$E_{S_0}(\min) - E_{S_1}(\min) + e^0_{v_r} - e^x_{v_r'} \equiv \Delta E_r,$$

which is equal to an adiabatic electronic energy difference plus the amount of energy *along* Q_r that has to be "digested," is balanced by the change in vibrational energy of the energy-accepting mode. This modified energy gap is shown in Figure 6-2.

If $\chi^0_{v_a}$ and $\chi^x_{v_a'}$ are approximated by simple harmonic oscillator functions having identical frequencies ω but equilibrium bond lengths that differ by ΔR_a, the evaluation of the $\chi^0_{v_a}|D_{R_a}|\chi^x_{v_a'}$ integral is straightforward. For the case of $v_a' = 0$ (Yardley, 1980)

$$\langle \chi^0_{v_a}|D_{R_a}|\chi^x_0\rangle = \sqrt{\frac{\omega}{\hbar}}\left[\sqrt{\frac{v_a}{2}}\,(-\sqrt{X})^{v_a-1}((v_a-1)!)^{-1/2} - \sqrt{\frac{v_a+1}{2}}\,(-\sqrt{X})^{v_a+1}((v_a+1)!)^{-1/2}\right]\exp(-X/2) \quad (6.19)$$

is obtained, in which $X \equiv \omega/(2\hbar)\Delta R^2$. Substitution of this result into equa-

$$W = \frac{4\pi\omega}{\hbar^2}\sum_{v_r,v'_r}|\langle\phi_{S_0}|D_{R_a}h_e|\phi_{S_1}\rangle_{eq}|^2$$
$$|\langle\chi^0_{v_r}(Q_r)[E_{S_0}(Q_r)-E_{S_1}(Q_r)]^{-1}\chi^x_{v'_r}(Q_r)\rangle|^2$$
$$e^{-X}\quad\frac{\Delta E_r^2}{2\pi\hbar\omega(\Delta E_r-\hbar\omega)}^{1/2}$$
$$\exp\left[-\quad\frac{\Delta E_r-h\omega}{\hbar\omega}\left(\ln\left(\frac{\Delta E_r-h\omega}{\hbar\omega X}\right)-1\right)\right] \tag{6.20}$$

in which ΔE_r is the *excess energy* or gap defined earlier.

Notice that ΔE_r depends upon $e^0_{v_r}-e^x_{v'_r}$, the energy change along the mode Q_r. Since for this special case $E_{S_0}(Q_r)-E_{S_1}(Q_r)$ does not become small for any value of Q_r, the element $\langle\chi^0_{v_r}|(E_{S_0}-E_{S_1})^{-1}|\chi^x_{v'_r}\rangle$ is likely to be small unless $\chi^0_{v_r}$ and $\chi^x_{v'_r}$ have very similar shapes. This will *not* be the case if $\Delta E_r \cong 0$, since then $\chi^0_{v_r}$ would correspond to a wave packet having high kinetic energy and a short de Broglie wavelength (as in Figure 6-2). This function could have little overlap with any low-energy $\chi^x_{v'_r}$. Hence, the dominant contribution is for $v'_r = 0$ and small v_r, and therefore it is reasonable to set $v'_r = v_r = 0$ in equation 6.20.

Notice that equation 6.20 leads to the conclusion that *high frequency vibrational modes* should be most effective in digesting the excess energy. For such modes, $(\Delta E_r-\hbar\omega)/\hbar\omega$ is as small as possible. The *exponential dependence* of W on the energy gap ΔE_r is thought to give rise to the observations leading to the Kasha rule. For most molecules the S_0-S_1 spacing (near the S_0 equilibrium geometry populated in the Franck-Condon absorption process) is larger than the S_1-S_2, S_2-S_3, . . . splittings. Hence, internal conversion from S_1 to S_0 is slower than between higher states, since ΔE_r is larger for the $S_1 \rightarrow S_0$ transition.

Equation 6.20 also shows that if experimentally one desired to modify the rate of internal conversion by isotopic substitution, the high frequency variations should be modified. For example, substitution of deuterium for hydrogen should produce substantial changes in the rate of internal conversion.

In the other extreme case (see Figure 6-3) in which $E_{S_0}(Q)-E_{S_1}(Q)$ becomes small along Q_r (of the order of magnitude of the non-Born-Oppenheimer matrix elements), we assume for motion along directions perpendicular to Q_r that $E_{S_0}-E_{S_1}$ can be written as two components—one consisting of motion along Q_r and a second comprised of harmonic segments (having the same geometries and frequencies). These harmonic potentials are assumed to be identical on S_0 and S_1 and, hence, cancel yielding

$$E_S - E_S \cong E_S(Q\ ) - E_S(Q\ ) \tag{6.21}$$

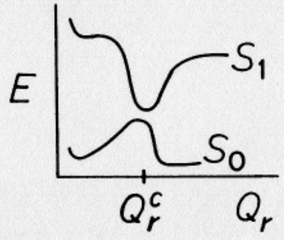

Figure 6-3
Energy surfaces that do approach closely.

In this case, Q_r itself is the energy-digesting mode.

The treatment in this section of the special case in which E_{S_0} and E_{S_1} do not approach closely can also be made for this case in Figure 6-3 to the point at which

$$W = \frac{2\pi}{\hbar} \sum_{\nu_r} \delta(E_{S_0}(\min) + e^0_{\nu_r} - E_{S_1}(\min) - e^x_{\nu_r'})$$

$$4 |\langle \chi^0_{\nu_r} | (E_{S_0}(Q_r) - E_{S_1}(Q_r))^{-1} \langle \phi_{S_0} | D_{Q_r} h_e | \phi_{S_1} \rangle D_R | \chi^x_{\nu_r'} \rangle |^2 \qquad (6.22)$$

Because $(E_{S_0} - E_{S_1})^{-1}$ enhances contributions to the integral over Q_r near the point of closest-approach Q_r^c, the electronic force matrix element and the energy difference can be approximated by their values at Q_r^c to obtain

$$W = \frac{8\pi}{\hbar} \sum_{\nu_r} \delta(E_{S_0}(\min) + e^0_{\nu_r} - E_{S_1}(\min) - e^x_{\nu_r'})$$

$$| [E_{S_0}(Q_r^c) - E_{S_1}(Q_r^c)]^{-2} | \langle \phi s_0 | D_{Q_r} h_e | \phi s_1 \rangle |^2 \langle \chi^0_{\nu_r} | D_{Q_r} | \chi^x_{\nu_r'} \rangle |^2 \quad (6.23)$$

Unfortunately, an energy-gap law is not easily obtained for this case because the $\langle \chi^0_{\nu_r} | D_{Q_r} | \chi^x_{\nu_r'} \rangle$ integral does not include two bound harmonic oscillator functions; $\chi^0_{\nu_r}$ describes *free* (unbound) motion along the S_0 surface. However, transitions will be *favored* if the electronic energy gap $E_{S_0}(Q_r^c) - E_{S_1}(Q_r^c)$ is small and the electronic-force matrix element is large. Moreover, the *kinetic energy* of motion along Q_r in the product S_0 state is $E_{S_1}(\min) + e^x_{n_r'} - E_{S_0}(Q_r^c)$, at $Q = Q_r^c$.

The Landau-Zener Point of View

Before discussing the rates of intersystem crossing, it is useful to point out the looking at rates of surface hopping (Eyring, Walter, and Kimball, 1944), a method that pertains *only* to the second case treated above (the close approach of S_0 and S_1 depicted in Figure 6-3). In the Landau-Zener approach the near crossing of the S_0 and S_1 surfaces is parameterized by the slopes (f_0 and f_1) of the surfaces near their avoided crossing and the closest-approach energy $2\epsilon_{10} \equiv 2(E_{S_1}(Q_r^c) - E_{S_0}(Q_r^c))$. The probability of a surface hop (per vibration along Q_r, as dictated by $\chi^x_{v'}$) is then expressed as

$$P = 1 - \exp[-(4\pi^2\epsilon_{10}^2)(hv\,|f_0 - f_1|)^{-1}] \tag{6.24}$$

in which v is the velocity of the nuclei as they pass through the avoided-crossing region. The dependence of P on the vibrational level ($\chi^x_{v'_r}$) of the initial S_1 state comes from this velocity—if v'_r is large, the velocity is high. Equation 6.24 shows that three things—a close approach (small ϵ_{10}), fast-moving nuclei (high frequency vibration), and a small difference in slope (small change in force)—favor surface hopping. This influence of the change in slope (which is the change in the *forces* felt by the nuclear framework of the molecule along the Q_r direction) is obscured somewhat in the earlier expression for W (equation 6.23). This force effect is contained in the $\chi^0_{v_r}(Q_r)D_{Q_r}\chi^x_{v'_r}(Q_r)$ factor. If S_0 and S_1 have very different slopes near Q_r^c, the wavefunctions $\chi^0_{v_r}$ and $\chi^x_{v'_r}$ will have greatly different *local* de Broglie wavelengths in this region, and $\chi^0_{v_r}$ and $\chi^x_{v'_r}$ are not likely to have large local overlap. In contrast, similar slopes of S_0 and S_1 near Q_r^c will lead to large overlap of $\chi^0_{v_r}$ and $\chi^x_{v'_r}$ (i.e., similar shapes in $\chi^0_{v_r}$ and $\chi^x_{v'_r}$).

6.3. Intersystem Crossing Rates

In intersystem crossing rates the electronic wavefunctions ϕ_0 and ϕ_x are singlet and triplet, respectively. However, the spin-orbital operator

$$h_{\mathrm{SO}} = \frac{e^2\hbar}{2m^2c^2}\left\{\sum_{i,a}\frac{Z_a}{r_{ia}^3}(\mathbf{r}_{ia}\times\mathbf{P}_i)\cdot\mathbf{S}_i + \sum_{i\neq j}\left[\frac{(2\mathbf{P}_j - \mathbf{P}_i)\times\mathbf{r}_{ij}}{r_{ij}^3}\right]\cdot\mathbf{S}_i\right\} \tag{6.25}$$

couples ϕ_0 and ϕ_x to give *perturbed* wavefunctions $\tilde{\phi}_0$ and $\tilde{\phi}_x$ that contain both singlet and triplet components. Intersystem crossing is viewed as occurring between these perturbed functions by a mechanism similar to that just discussed for internal conversion. The perturbed electronic wavefunctions are approximated by

$$\tilde{\phi}_{S_0} = \phi_{S_0} + \langle\phi_{S_0}|h_{\mathrm{SO}}|\phi_{T_1}\rangle(E_{S_0} - E_{T_1})^{-1}\phi_{T_1} \tag{6.26}$$

and

$$\tilde{\phi}_{T_1} = \tilde{\phi}_{T_1} + \langle \phi_{T_1} | h_{\mathrm{SO}} | \phi_{S_0} \rangle (E_{T_1} - E_{S_0})^{-1} \phi_{S_0} \tag{6.27}$$

(Eyring, Walter, and Kimball, 1944; Pilar, 1968). These functions can now be used in the Fermi golden-rule formula to evaluate W for intersystem crossing. In doing so, the electronic-force matrix element (or even the second non-Born-Oppenheimer factor $\langle \tilde{\phi}_{S_0} | D_Q^2 h_e | \tilde{\phi}_{T_1} \rangle$ that was not analyzed earlier) is modified because $\tilde{\phi}_{S_0}$ and $\tilde{\phi}_{T_1}$ are now of mixed spin character:

$$\begin{aligned} \langle \tilde{\phi}_{S_0} | D_Q h_e | \tilde{\phi}_{T_1} \rangle = {} & \langle \phi_{S_0} | D_Q h_e | \phi_{T_1} \rangle \\ & + \langle \phi_{S_0} | D_Q h_e | \phi_{S_0} \rangle \langle \phi_{T_1} | h_{\mathrm{SO}} | \phi_{S_0} \rangle (E_{T_1} - E_{S_0})^{-1} \\ & + \langle \phi_{S_0} | h_{\mathrm{SO}} | \phi_{T_1} \rangle \langle \phi_{T_1} | D_Q h_e | \phi_{T_1} \rangle (E_{S_0} - E_{T_1})^{-1} \\ & + \text{terms second order in } h_{\mathrm{SO}}. \end{aligned} \tag{6.28}$$

The first term vanishes because of spin orthogonality since $D_Q h_e$ contains no spin-dependent terms. The other two terms contain electronic-force expectation values, $E_{S_0} - E_{T_1}$ energy denominators, and spin-orbit matrix elements. When squared and substituted into the expression for W (equation 6.23), these integrals give an expression for the rate of intersystem crossing. The treatment of *digesting modes* other than Q_r (if S_0 and T_1 remain far apart) and the treatment of the case of Q_r accepting the excess energy (when S_0 and T_1 cross or come very close) proceed in the same way as that for intersystem crossing; therefore, we need not repeat the analysis of the dependence of this radiationless rate on the energy gap, accepting-mode frequencies, and so forth.

The primary difference between the expressions for internal conversion (W_{IC}) and intersystem crossing (W_{ISC}) is contained in the spin-orbit integrals $\langle \phi_{S_0} | h_{\mathrm{SO}} | \phi_{T_1} \rangle$ whose squares enter into W_{ISC}. These integrals require further discussion (Turro, 1978). The spin-orbit operator h_{SO}, consists of the dot product $(L_+S_- + L_-S_+ + 2L_zS_z)$ of a *spatial electronic angular-momentum* operator and an *electric spin* operator. Clearly, it is the spin-operator components (S_+, S_-, but not S_z) that map the triplet spin function into the singlet spin function in the $\langle \phi_{S_0} | h_{\mathrm{SO}} | \phi_{T_1} \rangle$ integral. When operating on ϕ_{T_1}, the corresponding spatial angular-momentum operator components can alter the angular characteristics of the spatial wavefunction in ϕ_{T_1}. More specifically, since the components L_x, L_y, L_z (or L_+, L_-, L_z) of the angular-momentum operator transform like rotation operators under point-group symmetry (see Appendix C or Cotton, 1963), the direct product of the spatial symmetries of ϕ_{S_0} and ϕ_{T_1} must match that of at least one of the components L_x, L_y or L_z for the spin-orbit matrix element to be nonvanishing. This is another important factor to keep in mind when deciding when intersystem crossing is likely to occur. For example, in H_2CO, the intersystem crossing transitions $(\pi\pi^*)^1 \rightarrow (n\pi^*)^3$ or $(n\pi^*)^3 \rightarrow n^2$ are spin-orbit *favored* because they utilize transitions between $\pi(b_1)$ and $n(b_2)$ orbitals or $\pi^*(b_1)$ and $n(b_2)$ orbitals whose direct product a_2 has the symmetry of a rotation about the symmetry axis of the molecule. Pictorially, this is represented by noting that a 90° *rotation* of the $n(b_2)$ orbital maps it into a π-like b_1 orbital. Likewise, the intersystem crossing rates $(\pi\pi^*)^1 \rightarrow (\pi\pi^*)^3$ and $(n\pi^*)^1 \rightarrow (n\pi^*)^3$ should be smaller because they are forbidden by first-order perturbation analysis —that is, the molecule has no rotation having $b_1 \times b_1 = a_1$ or $b_2 \times b_2 = a_1$ symmetry.

In the Landau-Zener method, which applies only to two surfaces (T_1 and S_0) that intersect or approach closely, the probability of intersystem crossing is given as before (equation 6.24) except that now the energy splitting $2\epsilon_{01}$ is *caused* by the spin-orbit coupling and is given by

$$\epsilon_{01} = \langle \phi_{S_0} | h_{SO} | \phi_{T_1} \rangle_{Q_r^c}. \tag{6.29}$$

Hence, the same conditions that favor internal conversion also favor intersystem crossing, except that the rate of intersystem crossing also includes the spin-orbit matrix element in a multiplicative manner. This element will be small unless heavy atoms are present and the two states can be connected by any of L_x, L_y, or L_z.