biphenyl chromophore. The activated process makes up for the large distance of separation for the phenanthrene and naphthalene by achieving energy transfer in two steps; that is, step 1 is \( ^3 \text{phenanthrene} + \text{biphenyl} \rightarrow ^3 \text{phenanthrene} + ^3 \text{biphenyl} \), and step 2 is \( ^3 \text{biphenyl} + \text{naphthalene} \rightarrow \text{biphenyl} + ^3 \text{naphthalene} \). The various energy-transfer steps for this system are summarized in Scheme 7.6.

### 7.9 Electron Exchange Processes: Energy Transfer Resulting from Collisions and Overlap of Electron Clouds

Bimolecular chemical interactions are usually viewed as occurring via collisions between molecular reaction partners. By collisions, we mean that the participants in the reaction are sufficiently close that their electron clouds overlap significantly (the separation of the colliding partners is slightly smaller than their van der Waals radii). In any region of orbital overlap, electron exchange always occurs. The following processes of interest to photochemists can result from electron exchange interactions produced by molecular collisions:

1. Triplet–triplet energy transfer.
2. Singlet–singlet energy transfer.
4. Electron transfer.

We deal with energy-transfer processes that occur by electron exchange in Section 7.10, and then deal with electron-transfer processes in Section 7.13. For a discussion of energy transfer in organic photochemistry see Section 10.4.

### 7.10 Electron Exchange: An Orbital Overlap or Collision Mechanism of Energy Transfer

For the simple case of two spherical orbitals of \( ^* \text{D} \) and \( \text{A} \), the overlap between the orbitals falls off exponentially as the separation \( R_{\text{DA}} \) between \( ^* \text{D} \) and \( \text{A} \) increases. This exponential falloff is a characteristic distance dependence of orbital overlap. Since the degree of exchange for energy transfer is directly related to the orbital overlap of \( ^* \text{D} \) and \( \text{A} \), the rate constant for exchange energy transfer (\( k_{\text{ET}} \)) is also expected to fall off as an exponential function of the distance separating \( ^* \text{D} \) and \( \text{A} \). In addition to the dependence of the rate of exchange energy transfer on the separation of \( ^* \text{D} \) and \( \text{A} \), the rate of energy transfer will also be directly related to \( J \), the spectral overlap integral (Fig. 7.3), which, as expected from the golden rule for energy transfer between states (Eq. 7.24), is a measure of the number of states that are capable of satisfying the resonance condition, once \( ^* \text{D} \) and \( \text{A} \) are coupled by the electron exchange interaction as the result of finite orbital overlap. The rate constant of energy transfer by electron exchange\(^\text{11}\) is given by an equation of the form of Eq. 7.35a:

\[
k_{\text{ET}} \text{ (exchange)} = KJ \exp\left( -\frac{2R_{\text{DA}}}{R_{\text{DA}}^0} \right)
\]  

(7.35a)
where $K$ is a parameter related to the specific orbital interactions, such as the dependence of orbital overlap on the instantaneous orientations of $^*D$ and A. The parameter $J$ is the normalized spectral overlap integral (Eq. 7.14), where normalized means that both the emission intensity ($I_D$) and extinction coefficient ($\varepsilon_A$) have been adjusted to unit area on the wavenumber ($\bar{\nu}$) scale. It is important to note that $J$, because it is normalized, does not depend on the actual magnitude of $\varepsilon_A$. This difference is an important distinction from the situation for dipole–dipole energy transfer for which the magnitude of $\varepsilon_A$ is a direct factor in determining the overall value of $J$ (Eq. 7.29). The overlap integral $J$ can be identified with $\rho$, the density of degenerate states that couple $^*D$ and A (Eqs. 3.8 and 7.24).

Equation 7.35b is a convenient expression of the distance dependence for the rate constant for energy transfer by electron exchange, $k_{ET}$. The parameter $R_{DA}$ is the separation of $^*D$ and A; $R_{DA}^0$ is the separation of $^*D$ and A when they are in van der Waals contact; and $k_0$ represents the rate of energy transfer when $^*D$ and A are in van der Waals contact (when $R_{DA} = R_{DA}^0$, then for Eq. 7.35, $\exp[-\beta(R_{DA} - R_{DA}^0)] = 1$). The $\beta$ term in Eq. 7.35 is a parameter that represents the sensitivity of $k_{ET}$ to a distance of separation ($R_{DA}$) for a given $^*D$ and A pair. Typical values of $\beta$ are on the order of $1 \text{ Å}^{-1}$ and generally do not depend significantly on the electronic characteristics of $^*D$ and A when energy transfer is exothermic. This finding means that the rate constant for energy transfer falls off by $\sim 1/e$ as the value of $R_{DA}$ increases by 1 Å. Values of $\beta < 1$ mean that $\beta$ is not very sensitive to separation; for small values of $\beta$, energy transfer can occur over very large distances. The maximum value of $k_0$ is expected to be on the order of $10^{13} \text{ s}^{-1}$. From Eq. 7.35b, for $k_0 = 10^{13} \text{ s}^{-1}$, the rate of energy transfer is $10^{13} \text{ s}^{-1}$ when $^*D$ and A collide and are in contact; that is, $R_{DA} = R_{DA}^0$.

$$k_{ET} \sim k_0 \exp[-\beta(R_{DA} - R_{DA}^0)] \quad (7.35b)$$

In comparing dipole–dipole interactions and electron exchange energy-transfer processes, we note the following differences in their characteristics.

1. The rate of dipole-induced energy transfer decreases as $1/R_{DA}^6$, whereas the rate of exchange-induced transfer decreases as $\exp(-R_{DA}/R_{DA}^0)$. Quantitatively, this means that $k_{ET}$ (exchange) drops to negligibly small values (relative to the lifetime of $^*D$) as the intermolecular distance between $^*D$ and A increases to values that are more than one or two molecular diameters (5–10 Å), as shown in Fig. 7.5.

2. The rate of dipole-induced transfer depends on the extinction coefficients ($\varepsilon$) of the $^*D \rightarrow D$ and $A \rightarrow ^*A$ radiative transitions, but the rate of the exchange-induced transfer is independent of the extinction coefficients of the $^*D \rightarrow D$ and $A \rightarrow ^*A$ transitions.

3. The efficiency of energy transfer (fraction of transfers per donor lifetime $\sim k_{ET}/k_D$) by the dipole mechanism depends mainly on the oscillator strength of the $A \rightarrow ^*A$ transition (since a smaller extinction coefficient for the $^*D \rightarrow D$ transition is compensated for by a slower radiative rate constant) and is directly related to the quantum yield for emission of $^*D$, whereas the efficiency of
energy transfer by the exchange interaction cannot be as directly related to experimental quantities.

4. Both Förster\textsuperscript{12} and Dexter\textsuperscript{11} theories predict a direct dependence of $k_{\text{ET}}$ on $J$, the spectral overlap integral, but the Förster theory includes the extinction coefficient of the $A \rightarrow \^A$ transition in the computation of $J$.

### 7.11 Electron-Transfer Processes Leading to Excited States

The formation of excited states of $\^A$ via electron exchange can be imagined to occur by way of a simultaneous two-electron transfer (Scheme 7.7), requiring simultaneous orbital overlap between both HO of $\^D$ and HO of A, as well as orbital overlap between LU of $\^D$ and LU of A.

Excited states of $\^A$ can also be obtained via electron- or hole-transfer processes starting from radical ion pairs ($D^{\bullet+}, A^{\bullet-}$) as shown in Scheme 7.7b, hole transfer, $D^{\bullet+} + A^{\bullet-} \rightarrow D + A$, and in Scheme 7.7c, electron transfer, $D^{\bullet-} + A^{\bullet+} \rightarrow D + \^A$. Note that charge-separated structures, as illustrated on the right of Scheme 7.7, may make some contribution to energy transfer if the two-electron exchange is not “fully concerted”; that is, exciplex-like structures (Section 4.36), for which CT is a significant contributor, may be involved as intermediates. From fundamental considerations, we expect that, depending on the systems under investigation, there will be a continuum of structures with differing degrees of CT character, all the way from weak CT exciplexes to complete electron transfer.

Scheme 7.7  Mechanisms for forming D and $\^A$ via electron-exchange processes. The conversion from the left to the center box corresponds to energy transfer, while those originating from the boxes on the right illustrate electron transfer, where D acts as a hole donor (top) or as an electron donor (bottom).