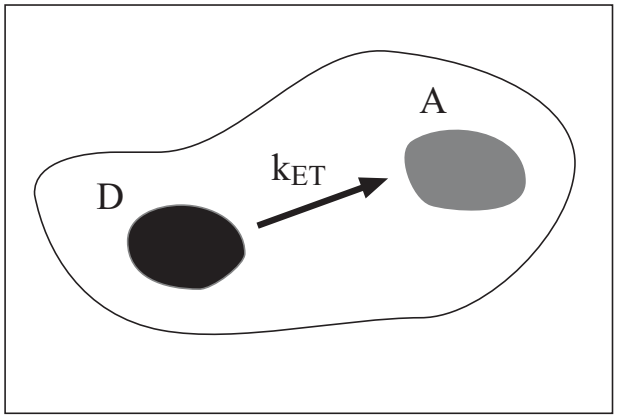

Figure 2.1: ET in a schematically drawn DA complex. The initial spatial localization of the transferred electron at the donor is shown by the left hatched area. The right hatched area corresponds to the final localization at the acceptor, and k_{ET} denotes the transfer rate.

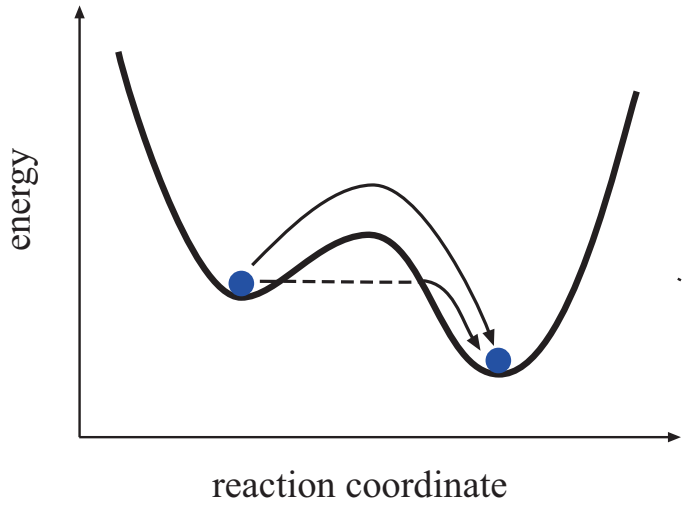

Figure 2.2: Double well–potential versus reaction coordinate which can be some collective nuclear coordinate triggering the adiabatic ET. In the initial state of the ET reaction the system is localized in the left metastable well. It can reach the right stable state by crossing the barrier (full line), or by tunneling through the barrier (broken line).

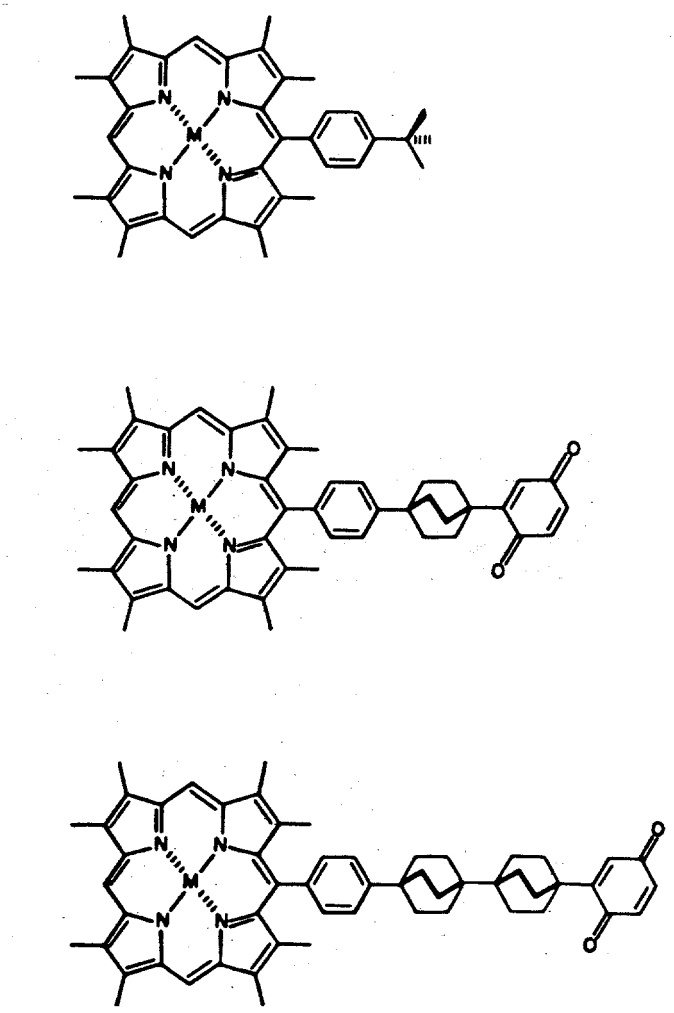

Figure 2.3: A porphyrin quinone complex (M = Zn) with different bridging molecules as a typical example for the through–bond ET reaction is shown. The ET proceeds from the photoexcited zinc porphyrin (left part) to the quinone (right part), and the ET rate is determined according to $k_{\mathrm{ET}} = 1/\tau_{\mathrm{obs}} - 1/\tau_0$, where τ_{obs} is the observed fluorescence lifetime and τ_0 denotes the natural fluorescence lifetime of the porphyrin taken from the upper compound. Varying the solvent, k_{ET} equals 5×10^9 to 1.5×10^{10} s^{-1} for the middle compound and is $\leq 10^7$ s^{-1} for the lower compound (reprinted from B. A. Leland, A. D. Joran, P. M. Felker, J. J. Hopfield, A. H. Zewail, and P. B. Dervan, J. Phys. Chem. **89**, 5571 (1985)).

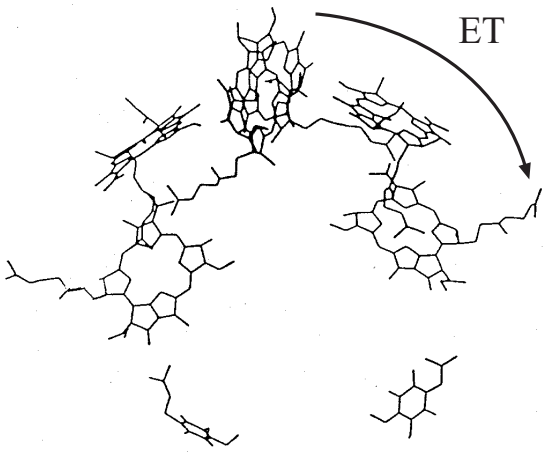

Figure 2.4: Chromophores of the photosynthetic bacterial reaction center (the protein the chromophores are embedded in is not shown). In the upper part the special pair of two bacteriochlorophyll molecules is shown acting after an excitation process as the ET donor. The ET takes place along the right branch of the reaction center formed by a further bacteriochlorophyll molecule, a metal–free bacteriochlorophyll molecule, and a quinone as the ET acceptor (from top to bottom).

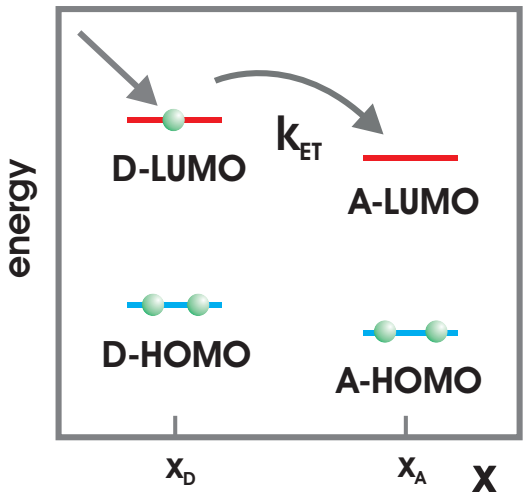

Figure 2.5: ET reaction of an excess electron in a HOMO–LUMO scheme of a DA complex with spatial donor position $x_{\mathrm{D}}$and acceptor position x_{A}. The reactant state electron configuration is shown. The curved arrow indicates the pathway the transferred electron takes toward the product state.

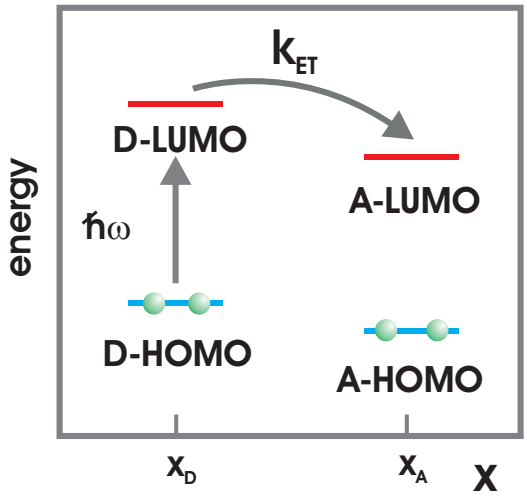

Figure 2.6: Photoinduced ET reaction in a DA complex.

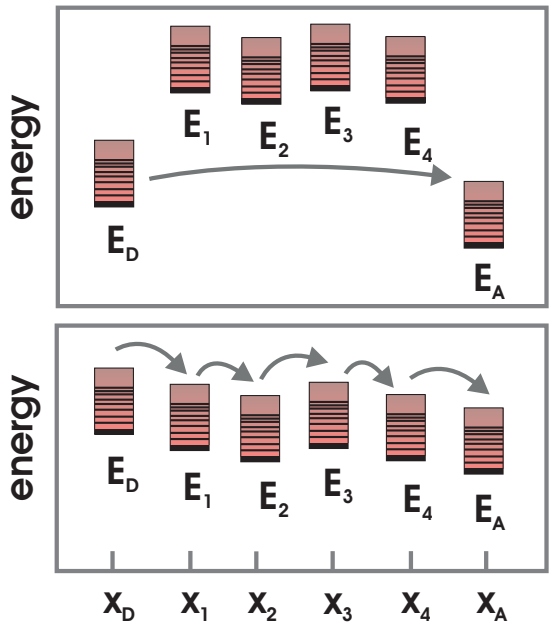

Figure 2.7: Bridge–mediated ET between a donor and an acceptor level connected by a linear chain of bridging units (thick lines – electronic levels, thin lines – vibrational levels). In the upper panel the bridge levels are energetically well separated from the donor and acceptor levels. In the lower panel a situation is shown where the energy levels of donor and acceptor are approximately resonant with the bridge levels.

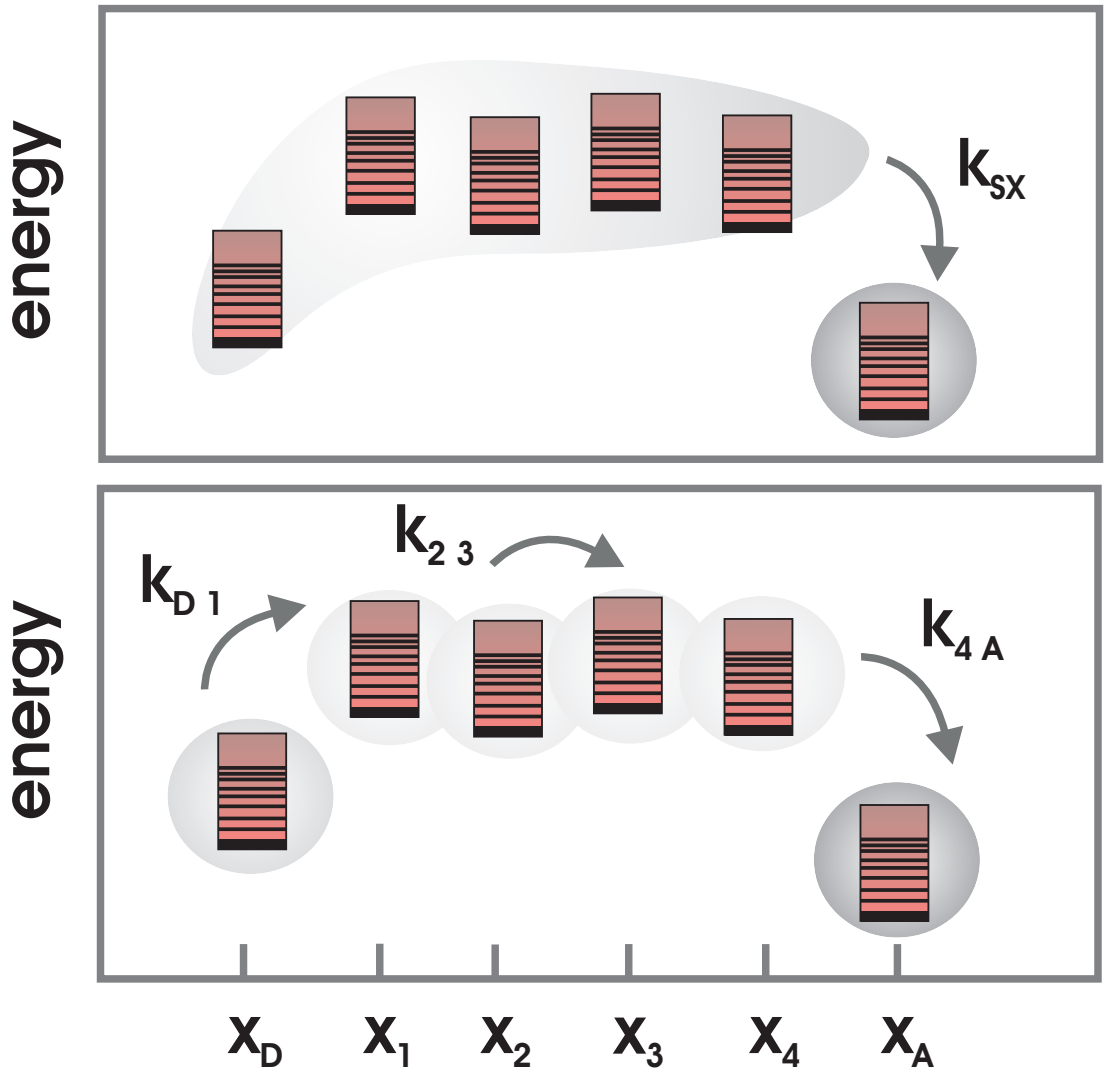

Figure 2.8: Bridge–mediated ET between a donor and an acceptor level. The upper part gives a scheme of the superexchange ET where the initial state wave function (shaded area) extends over the whole bridge. For the sequential ET (lower part) the electronic wave function is localized on the various sites during the transfer.

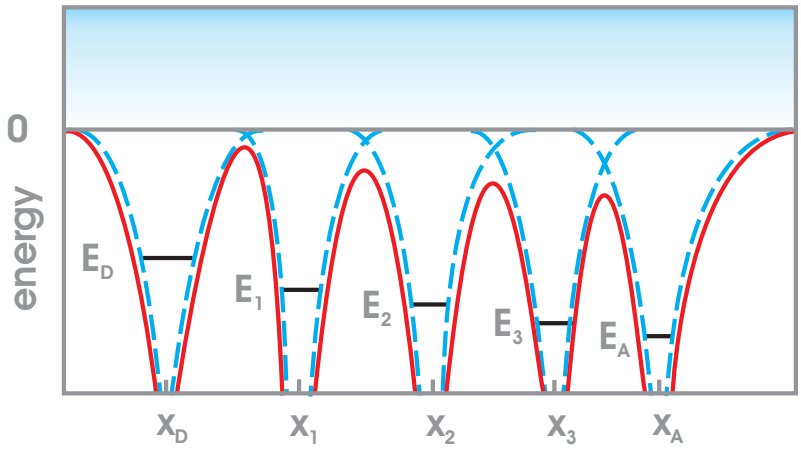

Figure 2.9: One–dimensional sketch of the pseudo–potential $V(\mathbf{r})$ (full line). x_D, x_1, etc. mark the spatial position of the different units of the ET system. The pseudo–potentials $V_m(\mathbf{r})$ of the individual molecular units (broken lines) and the levels E_m occupied by the excess electron are also shown. The motion of the excess electron among the various energy levels proceeds as a tunneling process through the barriers separating different potential wells.

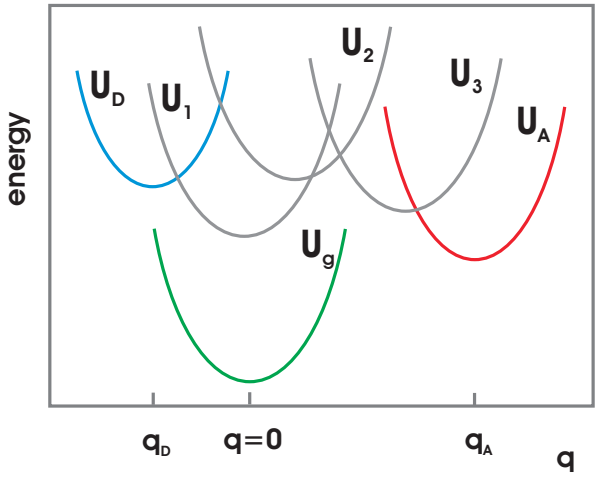

Figure 2.10: PES of the DA complex versus a single normal mode coordinate $q_\xi \equiv q$ (all other coordinates with $\xi' \neq \xi$ are fixed at $q_{\xi'}^{(m)}$ for every PES U_m). While U_g is the electronic ground–state (reference) PES of the neutral complex, the PES U_m correspond to the situation where one excess electron is present at the donor ($m = D$), the acceptor ($m = A$) or at a bridge unit ($m = 1, 2, 3$, note that the position of the PES along the q–axis has nothing to do with the spatial position of the related electronic wavefunctions φ_m).

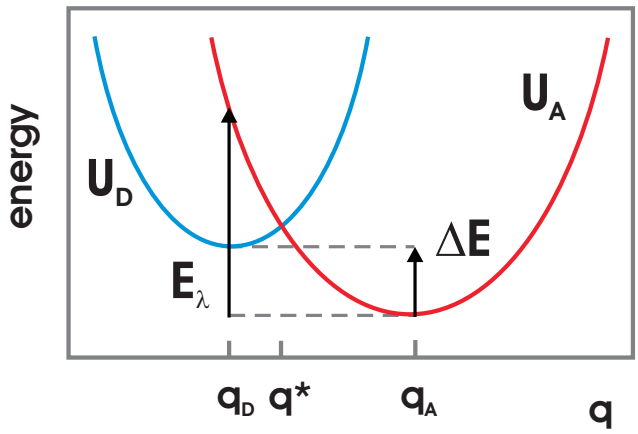

Figure 2.11: Potential energy surfaces for a DA complex in harmonic approximation. The definition of the driving force ΔE and the reorganization energy E_λ are indicated.

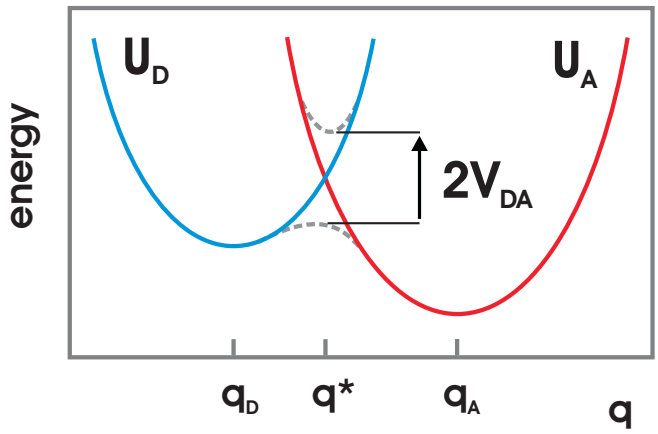

Figure 2.12: Donor and acceptor PES versus a single reaction coordinate. The diabatic (full line) as well as adiabatic curves (dashed line) are shown. There is a splitting between the adiabatic curves which has a magnitude of $2|V_{DA}|$ at the crossing point q^*.

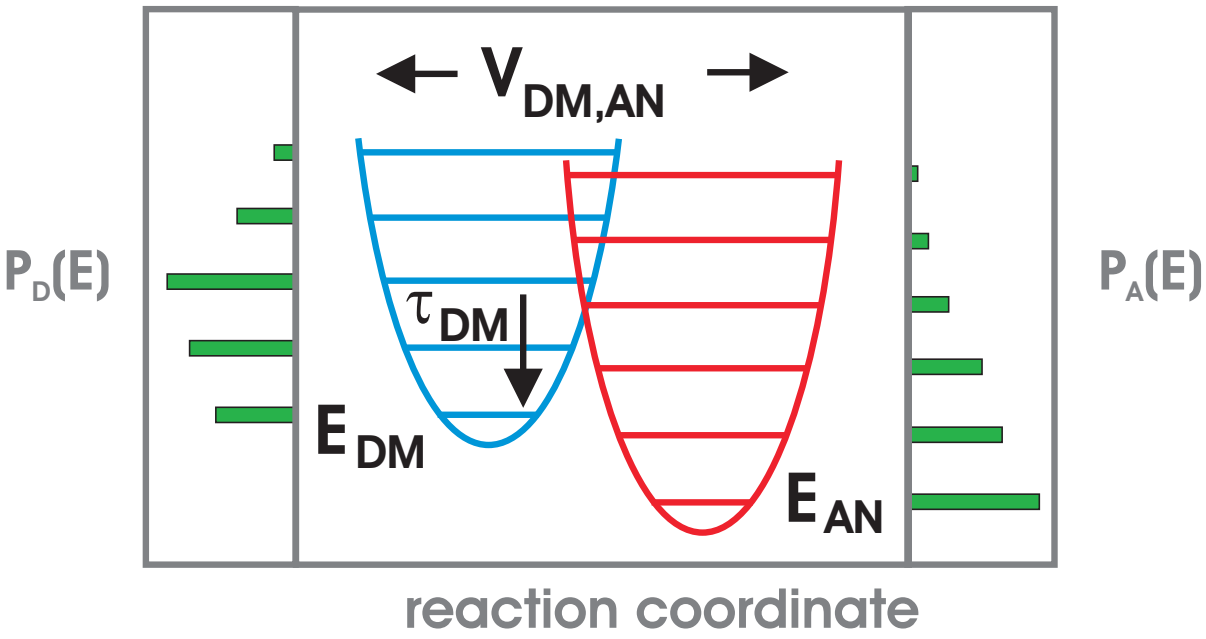

Figure 2.13: Ultrafast ET in a system of two coupled PES with donor vibrational levels E_{DM} and acceptor vibrational levels E_{AN} (the coupling matrix elements $V_{DM,AN}$ are also drawn). Left scheme: population P_D of the donor levels after optical excitation, right scheme: population P_A of the acceptor levels after relaxation took place. (If both spectra are degenerated a direct transfer from a selected level E_{DM} to a level E_{AN} becomes possible, probably connected with a back transfer. If degeneracy is absent a set of different levels is coupled simultaneously.)

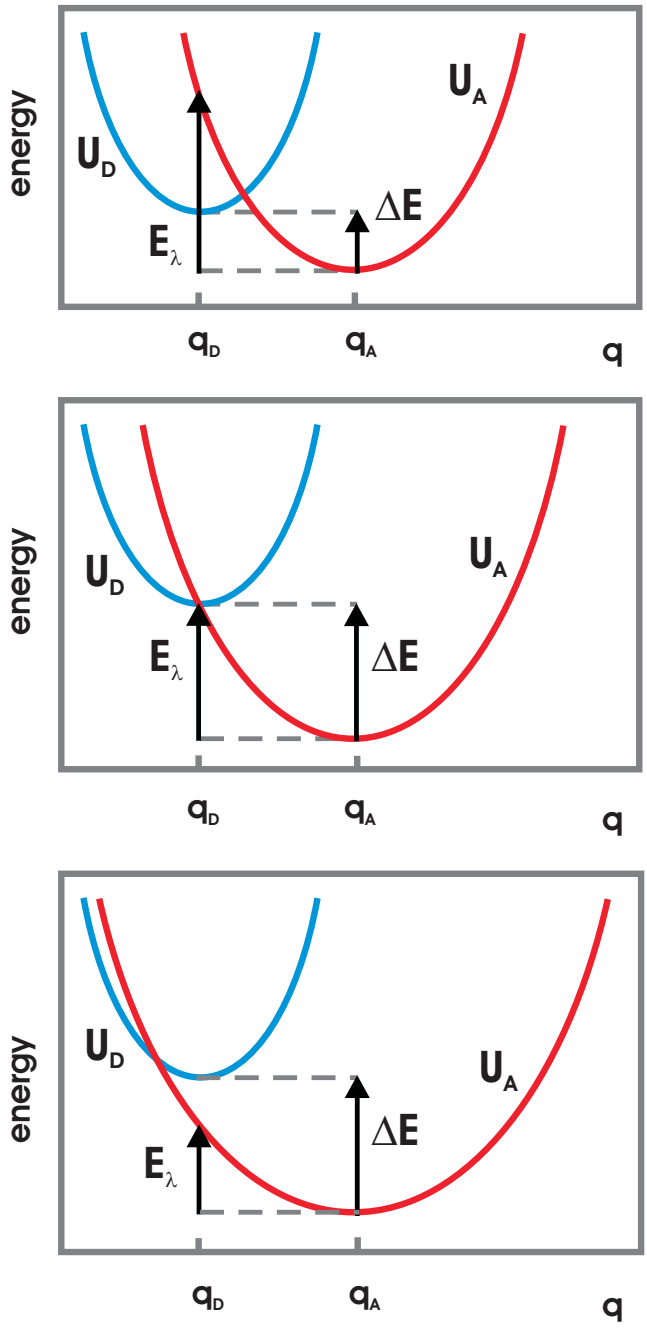

Figure 2.14: The normal region (upper panel), the activationless case (middle panel) and the inverted region (lower panel) of ET in a DA complex.

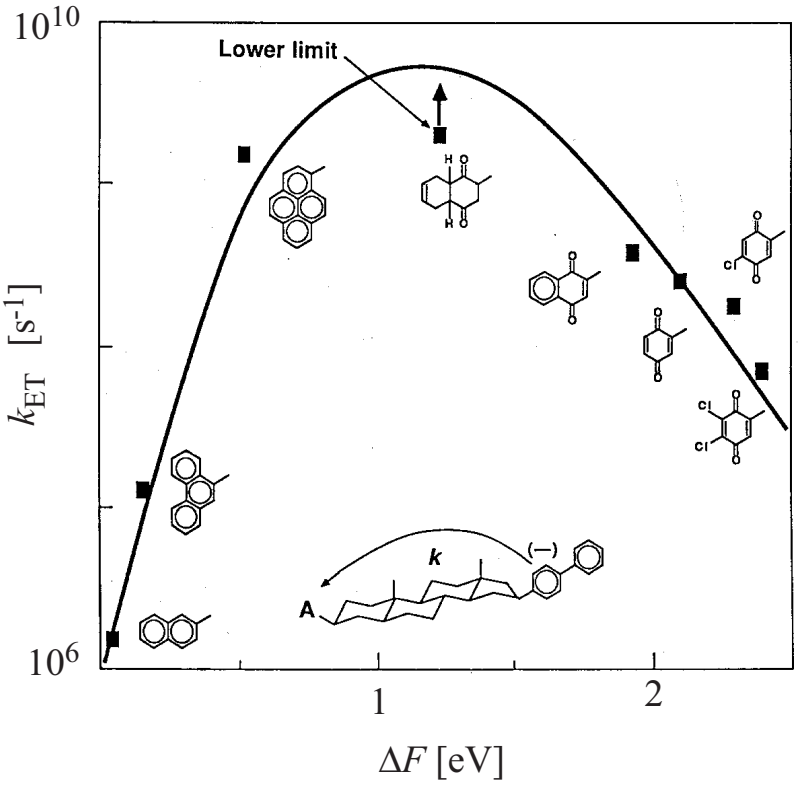

Figure 2.15: ET rate versus driving force of the reaction for a DA complex showing transfer in the inverted region. A steroid spacer (androstane) links a 4-biphenylyl donor group with different acceptors (shown below the curve). An excess electron has been attached to the donor by means of a pulsed electron beam. The complex was dissolved in methyltetrahydrofuran (reprinted from G. L. Closs and J. R. Miller, Science **240**, 440 (1988)).

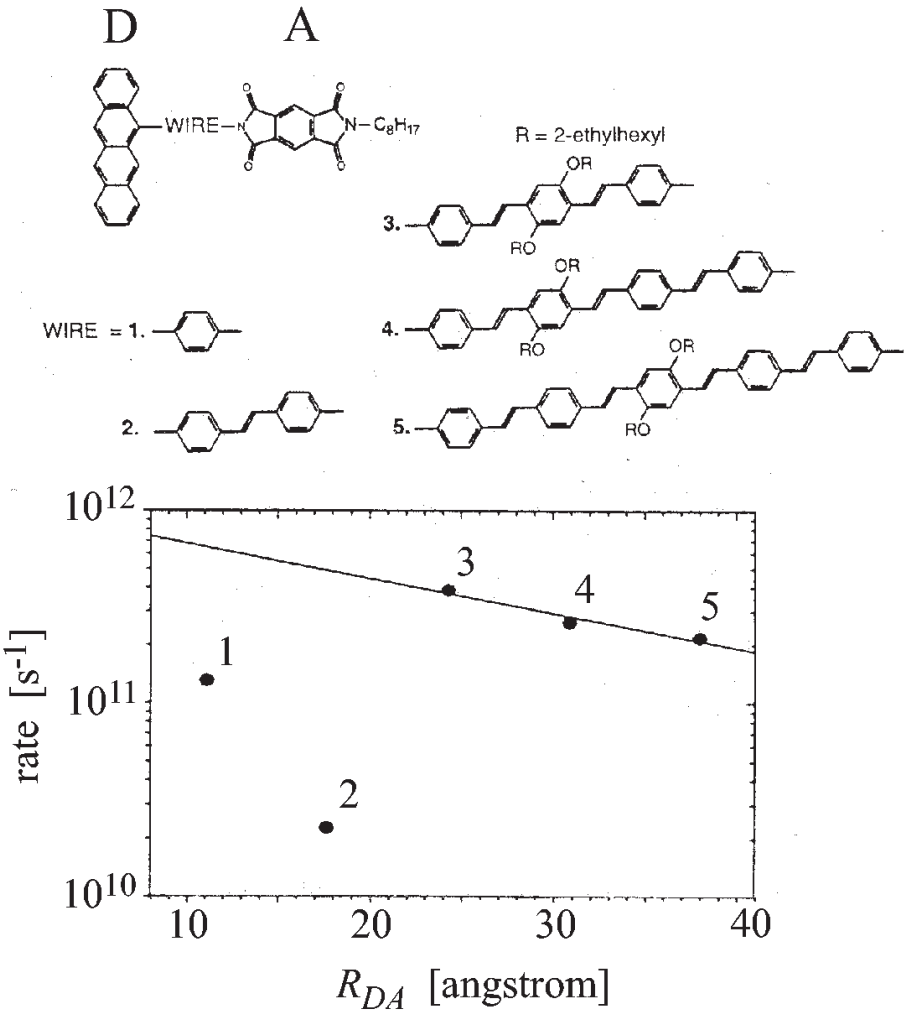

Figure 2.16: Bridge–mediated ET using a molecular wire of p–phenylenevinylene oligomers. The donor is given by tetracene and the acceptor by pyroelectricity. The five different types of wires together with the donor and acceptor are shown in the upper panel (DA distances R_{DA} for wire **1** up to **5** are 11.1, 17.7, 24.3, 30.9, and 38.0 Å). The distance dependence of the transfer rate is shown in the lower panel. (reprinted from W. B. Davis, W. A. Svec, M. A. Ratner, and M. R. Wasielewski, Nature **396**, 60 (1998)).