

Photosynthetic Oxygen Evolution

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REDUCTION DEGREE IN PHOTOREDOX SYSTEMS

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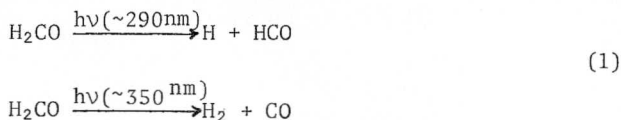
Abstract

By means of both literature examples and data of own research work it will be explained how to succeed in understanding photochemical reactions by processing chemical, spectroscopic, and molecular-physical results. The description of light-induced photoredox reactions is suitable to show, how the discussion of the thermal equilibrium position can lead to important information on the behaviour of an irradiated system. In virtue of model reflections a possibility for the initiation and maintenance of an intramolecular charge separation will be referred to in the last chapter.

Introduction

Photochemistry studies the chemical properties of molecules in excited state. Since each molecule can attain several states, the variety of this chemistry is not smaller than that of the ground state. Without any help of quantum theory the chemistry of the ground state has practically succeeded in developing a simple formalism, which can settle a lot of experimental data and sometimes allows to make predictions. The chemistry of the excited state was from the very beginning confronted with quantum theory. Although many interesting observations were made long before the development of this theory. However, with our

present knowledge it is no more reasonable to do photochemistry without the help of some results of quantum theory. Until now an exact quantum theoretical treatment of photochemistry is hardly possible. How extensive the difficulties are, demonstrates e.g. the detailed analysis of formaldehyde photolysis:



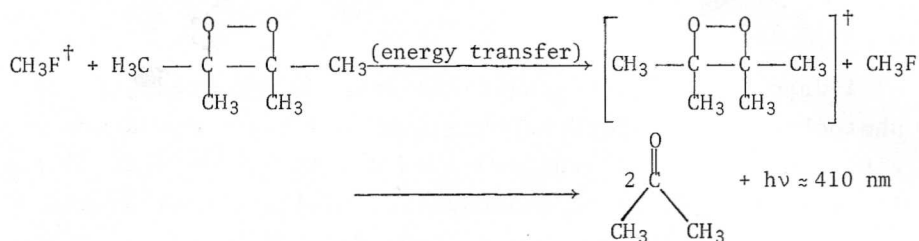
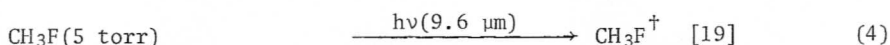
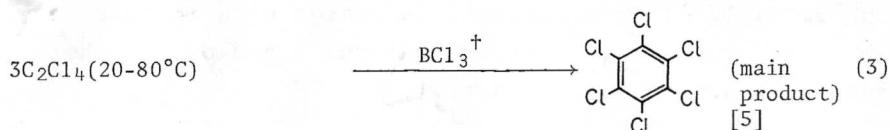
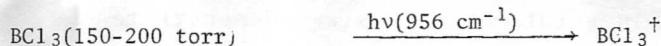
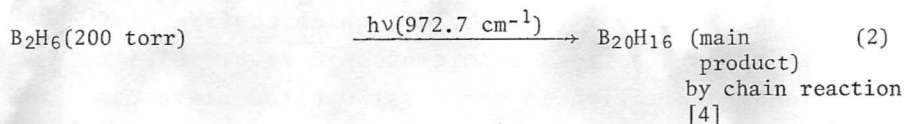
In spite of great efforts these relatively simple reactions are from the theoretical viewpoint only partly understood [26]. It is therefore our aim to find good models to work with. The particular difficulty - but at the same time the stimulus - of photochemistry consists in the necessity of processing chemical, spectroscopic and molecular-physical informations. This fact will be outlined by means of both literature examples and own research work. The arrangement chosen is for the most part incidental.

The insufficiently used possibility to have molecules reacting in a well-defined vibrational state - either by direct stimulation with infrared radiation or by the transfer of vibration energy - has gained remarkable interest with the development of infrared lasers¹

The following examples show in an impressive manner, that the electromagnetic energy - even in the infrared region - possesses not only quantitative, but also important qualitative aspects, with regard to chemical reactions.

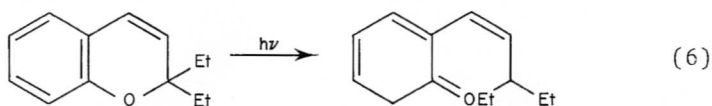
The pyrolysis of diborane leads to a product mixture, which does not contain icosaborane(16); normally tetra-

¹ By reason of the definition given above the chemistry with infrared radiation does not belong to photochemistry. This demonstrates a difficulty to be found, whenever one tries to describe a scientific discipline with the help of a simple definition.



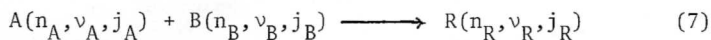
chloroethylene cannot be converted to hexachlorobenzene below 700°C . The authors could show in both cases, that vibrational excitation is responsible for the declared course of reaction. This appears even more clearly in the sensitization of chemiluminescence of the tetramethyl-1,2-dioxetane by vibrationally excited methylfluoride. It likewise appears in the reaction behaviour of vibra-

tionally excited hydrogenchloride, which confirms the postulated anticipations of microscopic reversibility. Vibrational excitation in the first excited state can also play a role in solutions. This was demonstrated by the example of 2,2-diethylchromene [6]. The fluorescence quantum yield of this compound decreases with increasing excitation energy, whereas the quantum yield of the photochemical reaction increases [29].



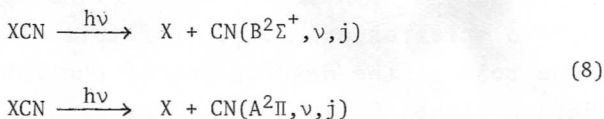
A dependence of this kind can only be expected, if the photochemical reaction happens within one or only a few vibrations after excitation, i.e. within $\sim 10^{-12} - 10^{-11}$ s. As we know by direct measurements [35,41], excess excitation energy is within this time dissipated by coupling of the molecules with their surroundings.

To describe a reaction, it would be an ideal situation to know the electronic (n), vibrational (ν) and rotational (j) state of the substrates A, B and the reaction products resulting from the first step.



The possibility of such a detailed analysis is restricted to the gas phase. The experimental and theoretical efforts are considerable. However, one approaches to information which is of great importance in connection with infrared lasers, isotope separation processes and research methods leading to a profound comprehension of chemical reactivity. The photodissociation of the cyano compounds XCN (with X = Cl, Br, I) was e.g. very thoroughly studied [3,39]. The distribution of the reaction energy on vibrational and

rotational levels in the CN fragment is fairly well known.



The potential curves of the cyanide radical for the three lowest electronic states together with the vibrational levels are given in Fig. 1 [40].

We would like to direct our attention only to the fact, that the states $\text{CN}(\text{B}^2\Sigma^+, \nu=0)$ and $\text{CN}(\text{A}^2\Pi, \nu=10)$ are accidentally degenerated, which - according to modern ideas - leads to a fast transfer between these two states [7,16, 18,30]. The experimental studies of this event - so-called "intersystem crossing" as function of the rotational states are in qualitative agreement with the theoretical ideas [3].

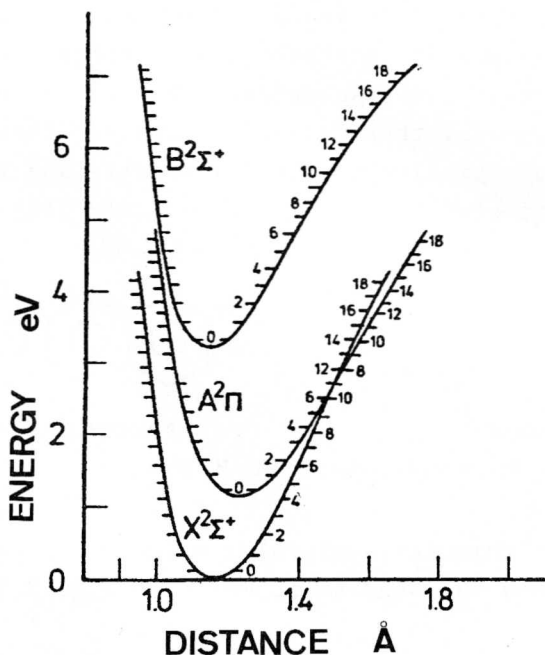
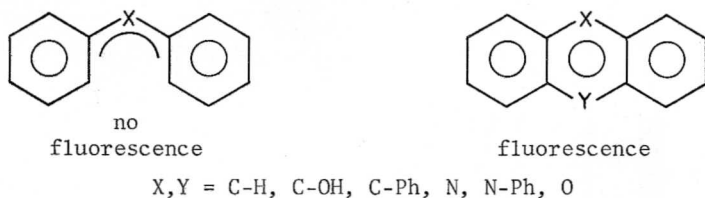


Fig. 1. Potential curves with vibration levels of the CN^\bullet radical in the lowest electronic states.

Intramolecular motions

In solutions rotational levels of molecules cannot be separated spectroscopically. Therefore they definitely play no role in the description of photochemistry in a condensed phase. However, the time during which a molecule can turn around its own axis - rotational diffusion - becomes an important figure. After excitation with polarized light a molecule emits polarized light only under the condition, that it cannot significantly rotate within the mean lifetime of the excited state. This circumstance has led to various methods to measure the rotational diffusion of electronically excited molecules [16,21,27,29,44]. We have found that the fluorescence quantum yield of methincyanines at room temperature rises considerably with increasing solvent viscosity [16]. According to the well-known principle, that for high fluorescence quantum yields the molecule skeleton has to be stiff [33], it was obvious to examine, whether this viscosity dependence is to be explained by hindrance of intramolecular movements with increasing viscosity. It was evident from former research work, that in general there exist no simple relations between the macroscopically measured viscosity and the viscosity as experienced by the single molecule [32]. The comparison already made by Th. Förster [21]



has shown that this intramolecular movement is probably a rotation around the bond axis, which in Fig. 2 is marked by an arrow.

It is reasonable to assume, that in methincyanines a hindrance of the rotation of the whole molecule entails

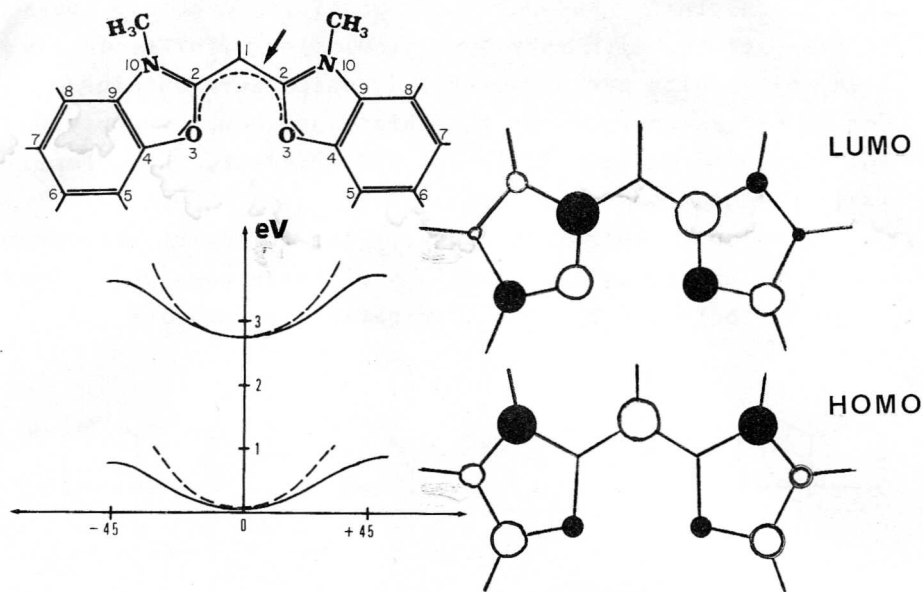


Fig. 2. Potential curves in the ground state and in the first excited state at twisting of the oxazole ligands. The straight lines give calculations with the EHT model [24]. The reason of the rotation barriers of ~ 1 eV are lower lying π orbitals. This is also the reason, why the barriers in the ground state and in the first excited state are nearly identical. The two hatched curves result, if the twisting of the two oxazole ligands is hindered by the viscosity of the solvent. The HOMO/LUMO behaviour as given in this figure and in Fig. 4 is realized, if no lower lying δ^* orbitals exist [12].

also a rotation aggravation around this bond axis. This idea could be verified by measuring the dynamic fluorescence depolarization [16,27].

Fig. 2 gives the highest occupied - HOMO - and the lowest unoccupied - LUMO - molecular orbitals as they are obtained by applying a one-electron model. The change of the charge distribution and of the binding forces connected with the transfer of the ground state to the first excited state can be estimated from these orbitals. The deficiencies of one-electron models are so well known, that

this must not be stressed here. The justification to use these models nevertheless lies in their practical advantage. If carefully handled, it is possible to obtain reasonable pictures with very low calculation efforts. In Fig. 3 (a, b) results are demonstrated, which were obtained for an oxygen analogue of the thiathiophthene by applying EHT (extended Hückel; [24]) and PPP (Pariser, Parr, Popel; [34]) calculations.

The calculation results suggest the following interpretation of photochemical reactions of these compounds; they could be confirmed by careful experimental studies [13].

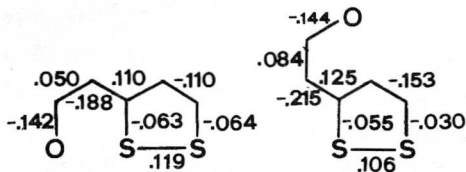
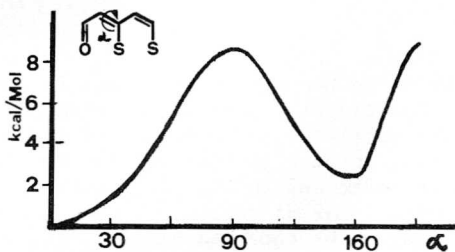
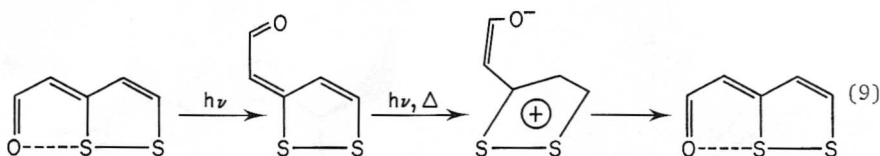


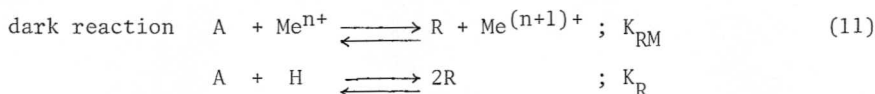
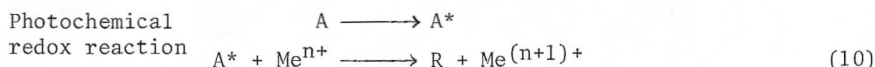
Fig. 3. (a) Energy profile in the ground state as function of the twist angle α , as obtained by an EHT calculation [13]. (b) Calculated change of the π bond order $\delta p_{\mu\nu}$ at the transition from the ground state to the electronically excited singlet state [13]:

$$\delta p_{\mu\nu} = p_{\mu\nu}^* - p_{\mu\nu}^{\circ}$$

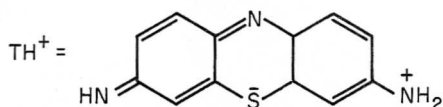
$p_{\mu\nu}^{\circ}$ symbolizes the π bond order between the centers μ and ν in the ground state, $p_{\mu\nu}^*$ in the excited state.

Photoredox reactions of the thionine type

With thermodynamic reflections and the help of a simple orbital scheme a clear picture of photochemical redox reactions of the thionine type can be obtained [42]. These reactions are defined by the following minimal scheme [14, 15].



In the case of the thionine we symbolize A with TH^+ [36],



R (the simple reduced form) according to the proton level with TH or TH^+ and H, the twice reduced form with TH^{2+} . The energy diagram together with the relevant redox potentials of the thionine are shown in Fig. 4 (a,b).

For the photochemical redox reactions the difference

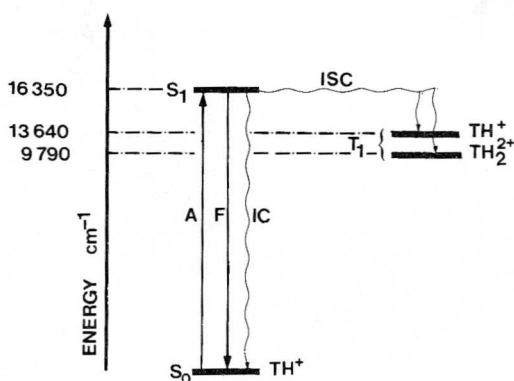


Fig. 4. (a) Energy level scheme of the thionine. A = absorption; F = fluorescence; IC = internal conversion; ISC = intersystem crossing; S_0 = ground state; S_1 = first excited state; T = triplet state [42].

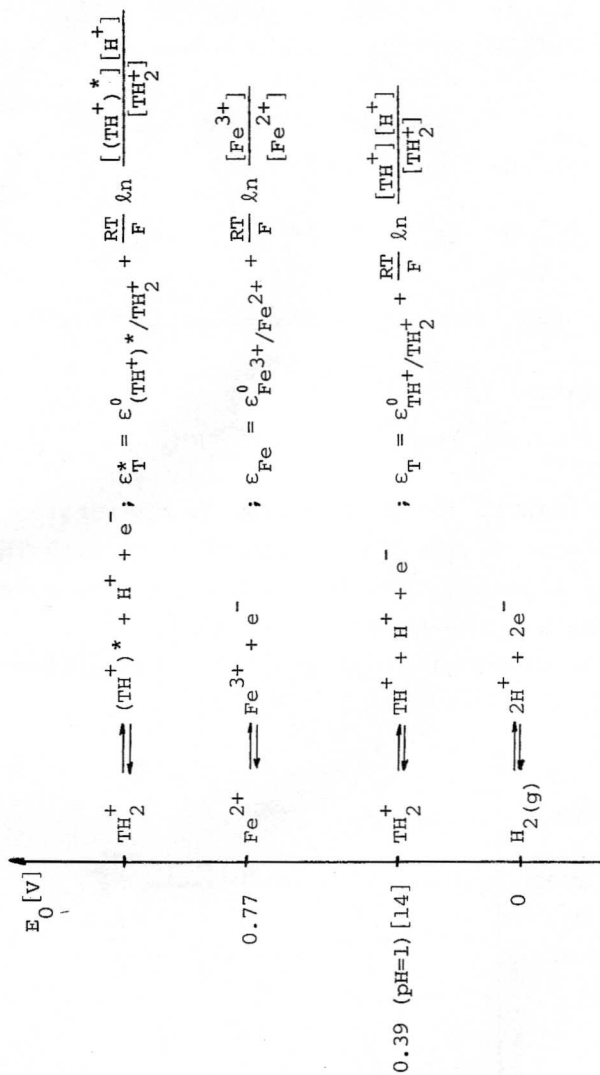


Fig. 4. (b) Redox potentials of the thionine in the ground state S_0 (ϵ_{T}) and the excited state triplet state T (ϵ_{T}^*) and of the iron ions (ϵ_{Fe}) [42].

$$\Delta^*_0 = \epsilon^0_{(\text{TH}^+)/\text{TH}_2^+} - \epsilon^0_{(\text{TH}^+)^*/\text{TH}_2^+} \quad (12)$$

is significant. The fact, that an iron(II) oxidation takes place can be demonstrated in a one-electron scheme (Fig. 5).

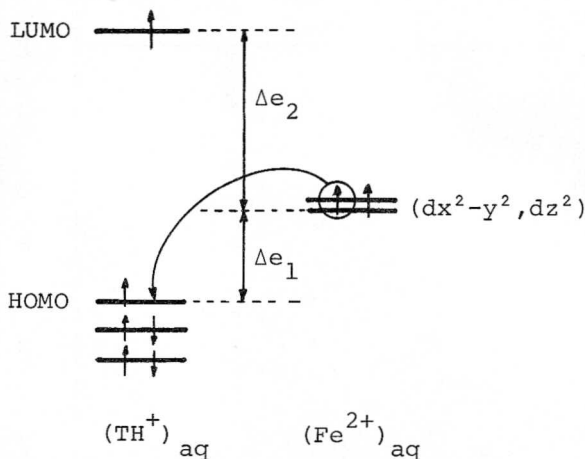


Fig. 5. One-electron scheme, demonstrating the oxidation of Fe(II) by electronically excited thionine. The orbital difference Δe_1 is given by $\Delta e_1 = e(dx^2-y^2, dz^2) - e_{\text{HOMO}}$

This scheme would gain valence, should it be possible to establish a quantitative connection between Δ^*_0 and Δe_1 . To find this connection we first examine the energy balance given in Fig. 6.

With the help of this scheme it is easy to get a quantitative relation between Δ^*_0 and Δe .

$$\begin{aligned} \Delta^*_0 \cdot F &= \Delta G^0_{\text{TH}^+/\text{TH}_2^+} - \Delta G^0_{(\text{TH}^+)^*/\text{TH}_2^+} = \\ &= \Delta H^0_{\text{TH}^+/\text{TH}_2^+} - \Delta H^0_{(\text{TH}^+)^*/\text{TH}_2^+} + T (\Delta S_{(\text{TH}^+)^*/\text{TH}_2^+} - \Delta S_{\text{TH}^+/\text{TH}_2^+}) \end{aligned} \quad (13)$$

It is reasonable to suppose, that the entropy difference

$$T \cdot \delta S = T (\Delta S_{(\text{TH}^+)^*/\text{TH}_2^+} - \Delta S_{\text{TH}^+/\text{TH}_2^+}) \quad (14)$$

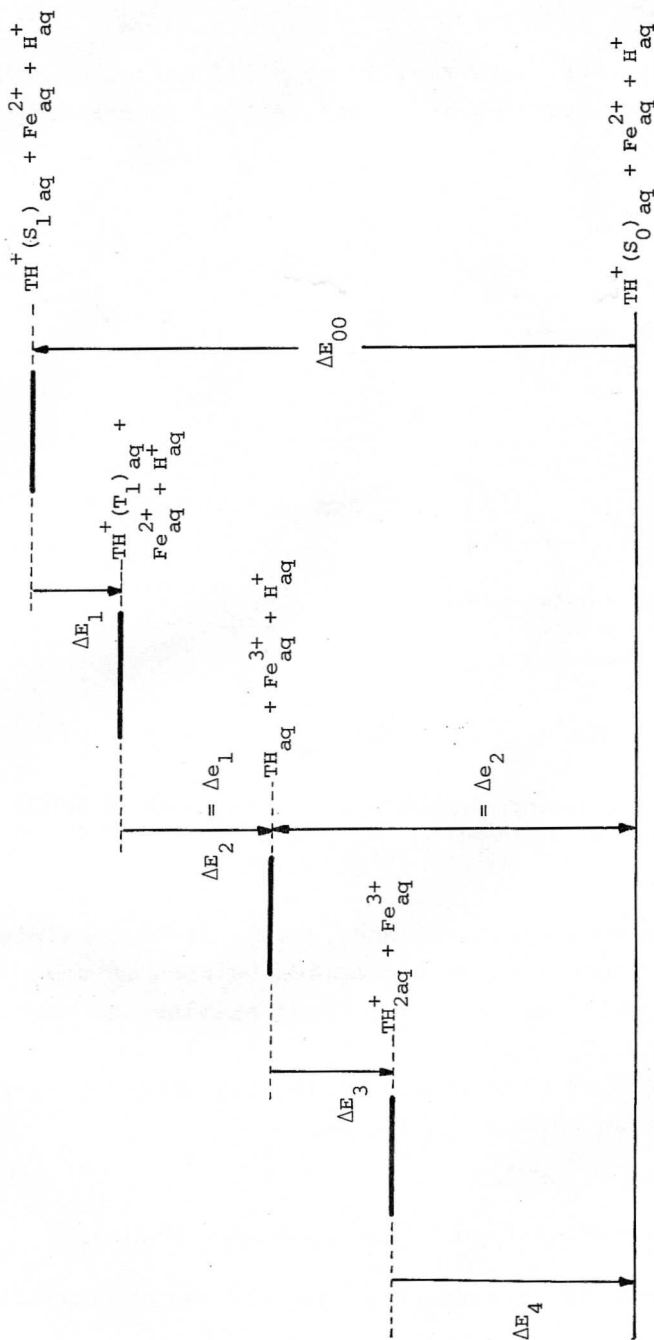


Fig. 6. Energy balance of the thionine/iron redox system [42]. Not considered is the disproportionation reaction, which splits ΔE_4 into $\Delta E_4(1)$ and $\Delta E_4(2)$. E_{00} = energy difference between the lowest vibrational level of the thionine in the ground state and in the first excited singlet state S_1 , compare Fig. 4a; ΔE_1 = energy difference between the singlet state S_1 and the triplet state T_1 , compare Fig. 4a; ΔE_2 = energy difference corresponding to Δe_1 as given in Fig. 5; ΔE_3 = protonation enthalpy ΔH_P^0

$\Delta G_P^0 = -RT \ln \frac{[\text{H}^+] \cdot [\text{TH}]}{[\text{TH}_2^+]}$. (Since the radical TH^\cdot is a strong base, it is immediately protonated.)

$\Delta E_4 = \text{redox enthalpy } \Delta H_T: \Delta G_T^0 = -RT \ln K_{\text{RM}} = \Delta H_T^0 - T\Delta S_T$

in general can be disregarded compared to the enthalpy difference. Under this condition there is

$$\begin{aligned}\Delta_0^* \cdot F &\approx \Delta H_{\text{TH}^+/\text{TH}_2^+}^0 - \Delta H_{(\text{TH}^+)^*/\text{TH}_2^+}^0 = \Delta E_{00} + \Delta E_1 \\ &= \Delta e_1 + \Delta H_P + \Delta H_{\text{TH}^+/\text{TH}_2^+}^0\end{aligned}\quad (15)$$

which gives the wanted connection between Δ_0^* and Δe :

$$\Delta_0^* \approx \frac{1}{F}(\Delta e_1 + \Delta H_P + \Delta H_{\text{TH}^+/\text{TH}_2^+}^0) \quad (15.a)$$

It is interesting to see, that ΔE_1 , ΔE_2 and ΔE_3 show deficit mechanisms referring to the finally stored energy of ΔE_{00} . The stored energy per mol is¹

$$\frac{\Delta E_{00} + \Delta E_1 + \Delta E_2 + \Delta E_3}{\Delta E_{00}} = \frac{-\Delta E_4}{\Delta E_{00}} \quad (16)$$

With this we come to a problem of primary interest in connection with all efforts to transform light energy into chemical or electrochemical energy. It is the question of the highest possible efficiency for such a transformation of a specific reaction.

Efficiency of a photoredox system

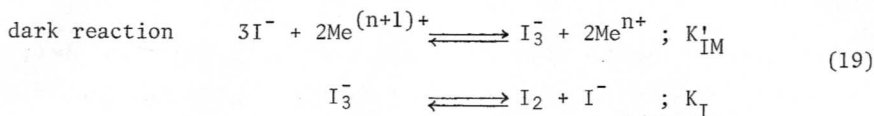
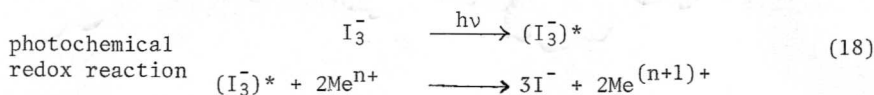
Calvert [8,9] has given the efficiency Q of such a transformation for monochromatic light of wavelength λ at the temperature T with

$$Q = \frac{\Delta G_T^0}{E} \Phi \quad (17)$$

E_λ is the light energy per Einstein at the wavelength λ , Φ the quantum yield and ΔG_T^0 the change of free molar enthalpy between the substrates and the photochemically produced end products. For polychromatic light this

¹Equation (16) does not yet contain the disproportionation reaction, which in the thionine example means another deficit mechanism.

equation can be changed accordingly referring to E_λ [1,15]. A careful analysis shows, that this change of the free molar enthalpy ΔG_T^0 is not always an appropriate measure for estimating Q. For this reason we regard the following photochemical redox reaction, which shall be denoted as the iodine type:



To describe this system, it is convenient to introduce a reduction degree r . It shall serve as measure for the number of the reduction equivalents, which are added in relation to $\text{Me}^{(n+1)+} = M_0$ and $3\text{I}_3^- = I_0$. With this M_0 is for the total concentration of metal ions and I_0 for the whole iodine amount:

$$\begin{aligned} M_0 &:= \text{Me}^{n+} + \text{Me}^{(n+1)+} \\ I_0 &:= \text{I}^- + 2\text{I}_2 + 3\text{I}_3^- \end{aligned} \quad (20)$$

It is useful to define the reduction degree as follows:

$$r := \frac{\text{Me}^{n+} + \text{I}^-}{M_0 + I_0} ; 0 \leq r \leq 1 \quad (21)$$

With v the relation M_0 to I_0 will be indicated:

$$v := \frac{M_0}{I_0} \quad (22)$$

To discuss the system (18/19) as a function of the three most important degrees of freedom r , v and M_0 , it is reasonable to perform the following normalization of the

concentrations.

$$M\emptyset := \frac{M_0}{e_c} := 1 \quad (23)$$

$$[e_c] := \text{mol/l}$$

For clearness sake we assume that the balance $I_3^- \rightleftharpoons I_2 + I^-$ lies so much on the left side that the concentration of I_2 is neglectable in all following considerations. This assumption does not restrict the validity of the considerations and can in special cases be discarded right off. By definition [23] follows

$$K'_{IM} = \frac{[Me^{n+}]^2 [I_3^-]}{[Me^{(n+1)+}]^2 [I^-]^3} = \frac{MN^2 \cdot e_c^2 \cdot I_3 \cdot e_c}{MN I^2 \cdot e_c^2 \cdot I I^3 \cdot e_c^3} = \frac{K_{IM}}{e_c^2} \quad (24)$$

$$K_{IM} = K'_{IM} \cdot e_c^2 \quad (25)$$

If the normalized (equation 23) light-induced turnover of I_3^- is denoted with D , we gain for the photochemically produced change of the free Gibbs' enthalpy ΔG :

$$\Delta G = -RT \ln K_{IM} + RT \ln \frac{(MN-2D)^2 (I_3-D)}{(MN+2D)^2 (I+3D)^3} \quad (26)$$

If two ideal electrodes would be available, one of which reversible for I_3^-/I^- only, the other one for $Me^{(n+1)+}/Me^{n+}$ only, the potential difference

$$\Delta E = \frac{\Delta G}{2F} \quad (27)$$

between these two electrodes could be measured. Only in the special case $\Delta G = -RT \cdot \ln K_{IM}$ equation (25) would be applicable to get Q . In the general case it is necessary to use a formulation as given in equation (26). Fig. 7a gives the normalized equilibrium concentrations of the reaction partners Me^{n+} , $Me^{(n+1)+}$, I^- and I_3^- together with the redox potential $E_{Me^{(n+1)+}/Me^{n+}}$ - for the equilibrium

constant K_{IM} (equation (25)) and the ratio $v=1$ - as function of the reduction degree. For the calculation of the curves we used a formerly described method [15,17]. If at a fixed reduction degree a sample is irradiated, the photo redox reaction - as given by equation (18) - shifts the individual concentrations from the equilibrium in directions marked by arrows. Since no reduction equivalents are supplied to the system, the reduction degree r remains unchanged.

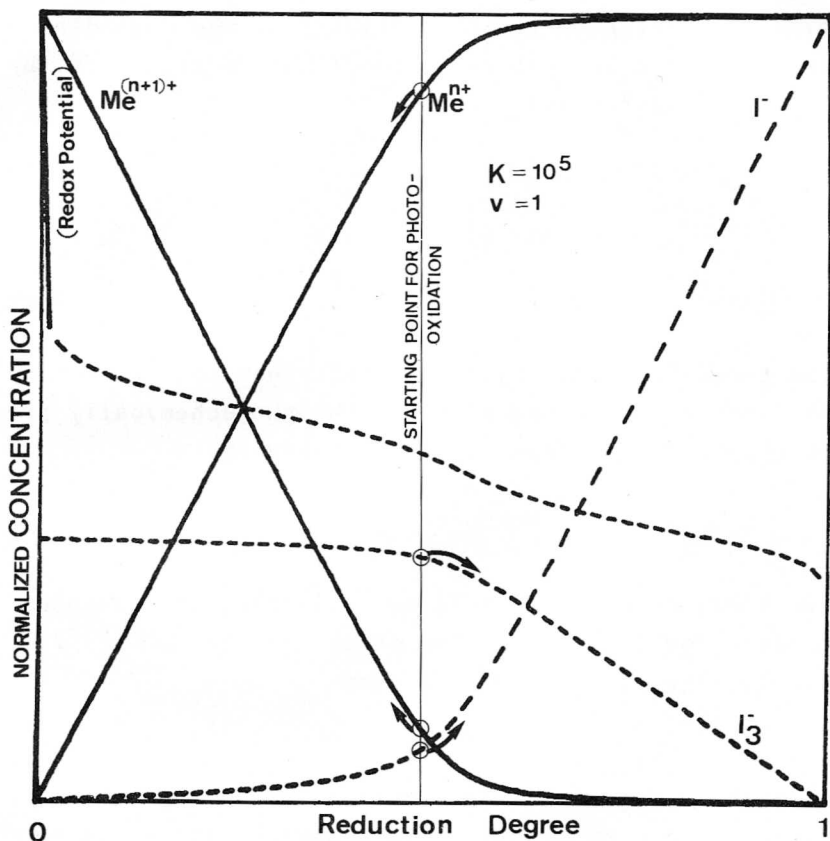


Fig. 7. (a) Normalized equilibrium concentrations of the redox partners Me^{n+} , $Me^{(n+1)+}$, I^- , I_3^- and the redox potential $E_{Me^{(n+1)+}/Me^{n+}}$ (for the equilibrium constant $K_{IM} = 10^5$ and the ratio $v = 1$) as function of the reduction degree r . For the redox potential the total ordinate corresponds to 1 V (The same is valid for the Fig. 7b and 8).

Fig. 7b is equivalent to Fig. 7a with the only exception, that in addition the potential differences starting from three different reduction degrees - as calculated by equation (27) - are added, which are produced with the photochemical turnover rate ΔI_3^- . According to the Nernst equation it is possible to obtain potential differences of any size. In the sharply decreasing part of Fig. 7b, the potential differences are, however, not anymore connected to a metabolic turnover. For this reason in this potential region a photogalvanic cell will not show any remarkable electric current.

A region where currents can be gained over a constant potential difference is (in Fig. 7b) marked with (1/2,

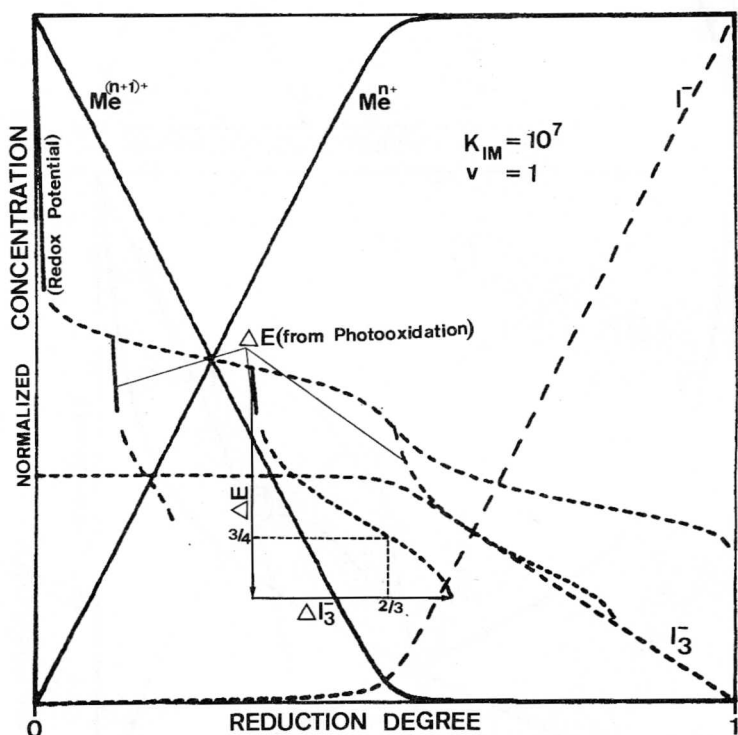


Fig. 7. (b) Like (a), but supplemented by the potential difference resulting from the photochemical turnover ΔI_3^- . The data were calculated by equation (26), starting from three different reduction degrees.

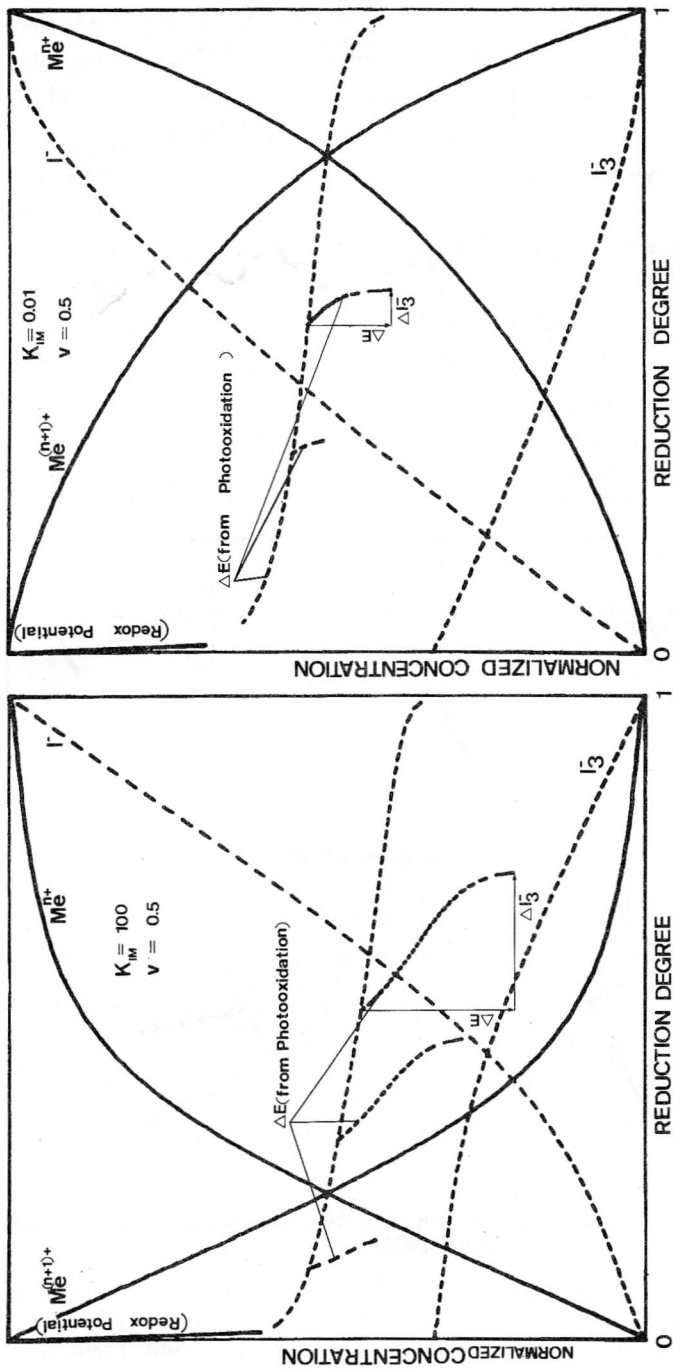


Fig. 8. For explanation see text and legends to Fig. 7 (a, b).

1/2). The electrode problems, which are to be solved for a photogalvanic cell of this kind were examined by Gerischer [22]. Since K_{IM} quadratically depends on the normalization constant e_c , its value will be changed with an alteration of the total concentration - e.g. for a factor of 100 by four orders of magnitude. The results of such a change for $K_{IM} = 10^2$, respectively $K_{IM} = 10^{-2}$ and $v = 0.5$ are demonstrated in Fig. 8. According to primary concentration and reduction degrees it is readily possible, that in a system which principally should be able to enter a photo redox reaction this cannot actually be observed due to unfavourable equilibrium conditions. With this it is shown, how important in some cases the discussion of the thermal equilibrium situation can be for the comprehension of the photochemical behaviour of chemical systems.

Perspectives

The intermolecular redox reactions shown in schemes (10) and (18) raise the question how far one succeeds by photochemical procedures in producing an intramolecular charge separation and maintaining this over a longer period. The complex chemistry knows a wide selection of charge transfer (CT) absorptions (see e.g. [11,20,28, 31, 37]). The life-time of such charge separations generally lies in the ns to μ s region. CT transfers are known, in which an electron from the central atom specifically migrates to a ligand, so that it is justified to talk about an "intramolecular charge separation". There is e.g. the pyrazine-pentacyanoferrate complex $[\text{Fe}(\text{CN})_5 \text{ pyrazine}]^{m-}$, $m=2,3$ [11,20]. In Fig. 9 the observed transfers in this compound and their attribution are demonstrated. The molecular orbitals received by an EHT calculation with quadratic charge iteration [11] serve to explain the charge displacement. In this connection the $d-\pi^*$ transfer marked with (1) is of interest. It is evident, that with this transfer one electron primarily mainly localized on

the central atom will be completely transferred to the pyrazine ligand. By this means both the basic character and the redox potential of the heterocycle are considerably changed.

In a binuclear complex it should be possible to stabilize such a charge displacement over a longer period against a potential gradient. Without going into details this statement shall be supported with the help of the following qualitative considerations. Here it is favourable to divide the most important one-electron orbitals of a common binuclear complex

$$(L_1)_n M_1 - B - M_2 (L_2)_m \quad (28)$$

into a part ϕ^{M_1} , ϕ^{M_2} for both centres M_1 and M_2 , a part ϕ^{L_1} , ϕ^{L_2} for the ligands $(L_1)_n$ and $(L_2)_m$ and finally a part ϕ_B for the bridging ligand.

$$\psi_i = (a_{1i}\phi_i^{M_1} + a_{2i}\phi_i^{M_2}) + (b_{1i}\phi_i^{L_1} + b_{2i}\phi_i^{L_2}) + c_i\phi_i^B \quad (29)$$

A specially simple example of a binuclear complex, where the importance of function (29) can be demonstrated, is the symmetrical binuclear (2,2)-pentacyanoferrate complex, which is bridged over a pyrazine. This compound possesses a "closed-shell" configuration. At the longest wavelengths the transfer with the (2,2)-complex shows definite MBCT (B = bridging ligand) character and may in very good approximation be described as $d-\pi^*$ (pyrazine) [11,20]. The local symmetry of both $\text{Fe}(\text{CN})_5$ fragments is C_{4v} . That means, the formal d_{xy} , d_{xz} and d_{yz} orbitals of these parts

Fig. 9. MO scheme for the $[\text{Fe}(\text{CN})_5 \text{pyrazine}]^{m-}$, $m=2,3$, and demonstration of some molecular orbitals. In the absorption spectrum of the $[\text{Fe}(\text{CN})_5 \text{pyrazine}]^{3-}$ in water (at room temperature) the longest wavelength band (1) ($22\,100\text{ cm}^{-1}$) and the band (3) ($38\,000\text{ cm}^{-1}$) can experimentally be identified as $d-\pi^*$ and $\pi-\pi^*$ transitions. The absorption bands denoted with (2) probably correspond to one $d-\delta^*$ and one $n-\pi^*$ transition.

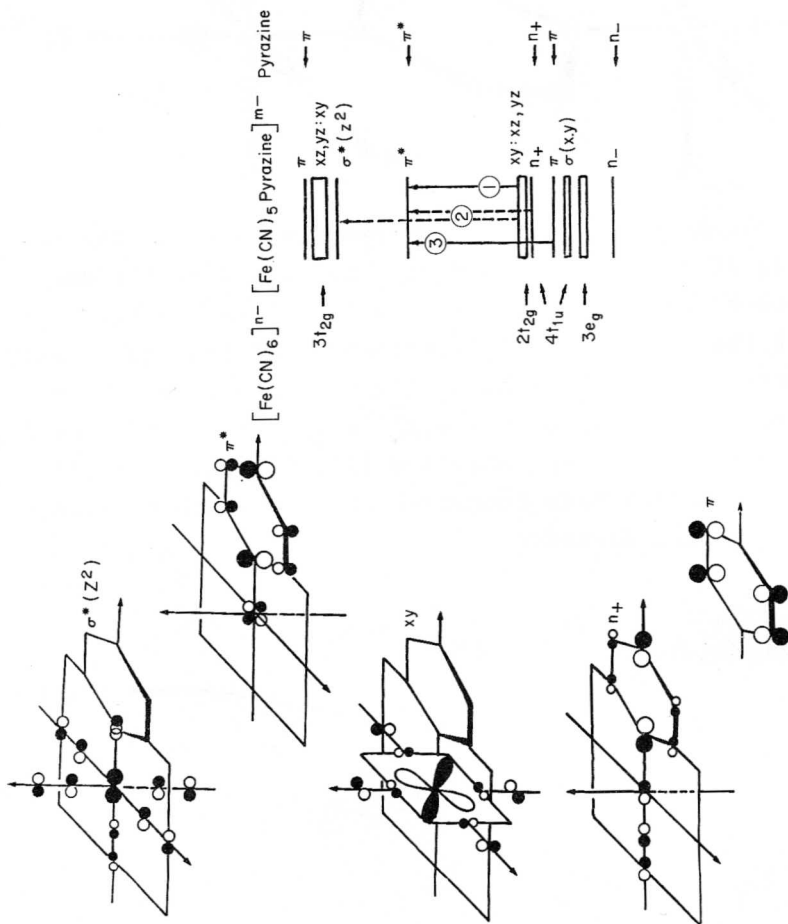
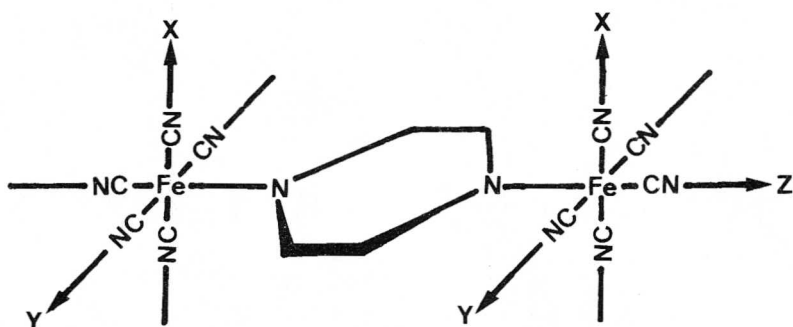


Fig. 9.



split into xy and (xz, yz) . For symmetry reasons the xy orbitals of both centres cannot - neither directly nor over the bridging ligand - interact with each other. Against that a small mutual influence between the xz and yz function over the bridging ligands occurs, which in non-symmetrical complexes - e.g. (2,3)-complexes - leads to intervalence absorptions (see [11,20,23,25,31,37,38, 45]). This interaction decreases with comparable ligands with increasing distances.

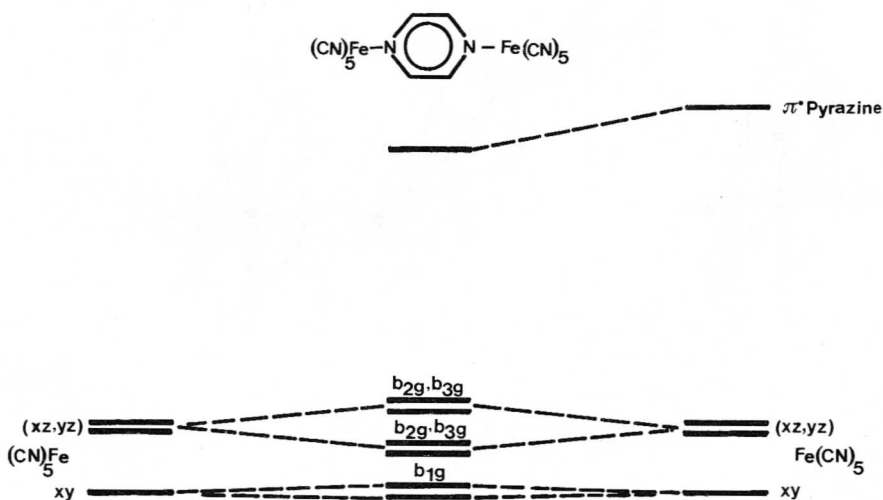
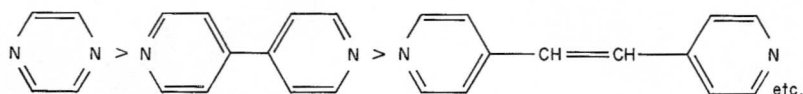


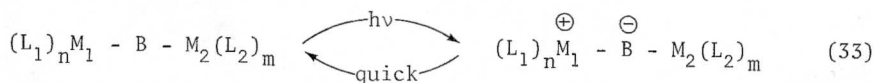
Fig. 10. Energy level scheme of the binuclear pentacyanoferrate compound as obtained by an EHT calculation [11].



The orbital scheme of the pyrazine-bridged compound as obtained by an EHT calculation is demonstrated in Fig. 10. The most important molecular orbitals in this connection are illustrated in Fig. 11. The splitting of these two b_{2g} orbitals from which the (in the z direction) polarized $d-\pi^*$ transfer results, is so small, that in the already broad - experimentally determined [20] - CT band only one transfer can be recognized. From the viewpoint of clearness the wave function given in equation (29) is in this form not especially favourable. It is better to write linear combinations, which lead to the following expressions:

$$\begin{aligned} \Psi_i(+)&= 2a_{1i}\phi_i^{M_1} + 2b_{1i}\phi_i^{L_1} + C_i(+)\phi_i^B(+), \\ \Psi_i(-)&= 2a_{1i}\phi_i^{M_2} + 2b_{2i}\phi_i^{L_2} + C_i(-)\phi_i^B(-). \end{aligned} \quad (32)$$

Here $\Psi_i(+)$ is localized at the centre M_1 , $\Psi_i(-)$ at the centre M_2 . One can consider the normally small error, which has its origin in the formulation of these linear combinations, as being contained in $C_i(+)$ respectively $C_i(-)$. The degenerated molecule orbitals ($d_{xz}^{(1)}$, $d_{xz}^{(2)}$) as given in Fig. 11 correspond to the functions (32). The illustrated $d-\pi^*$ transfer indicates, that during the lifetime of the π^* state one of the two iron centres possesses a higher oxidation degree, whereas the bridging ligand formally exists as B^- .



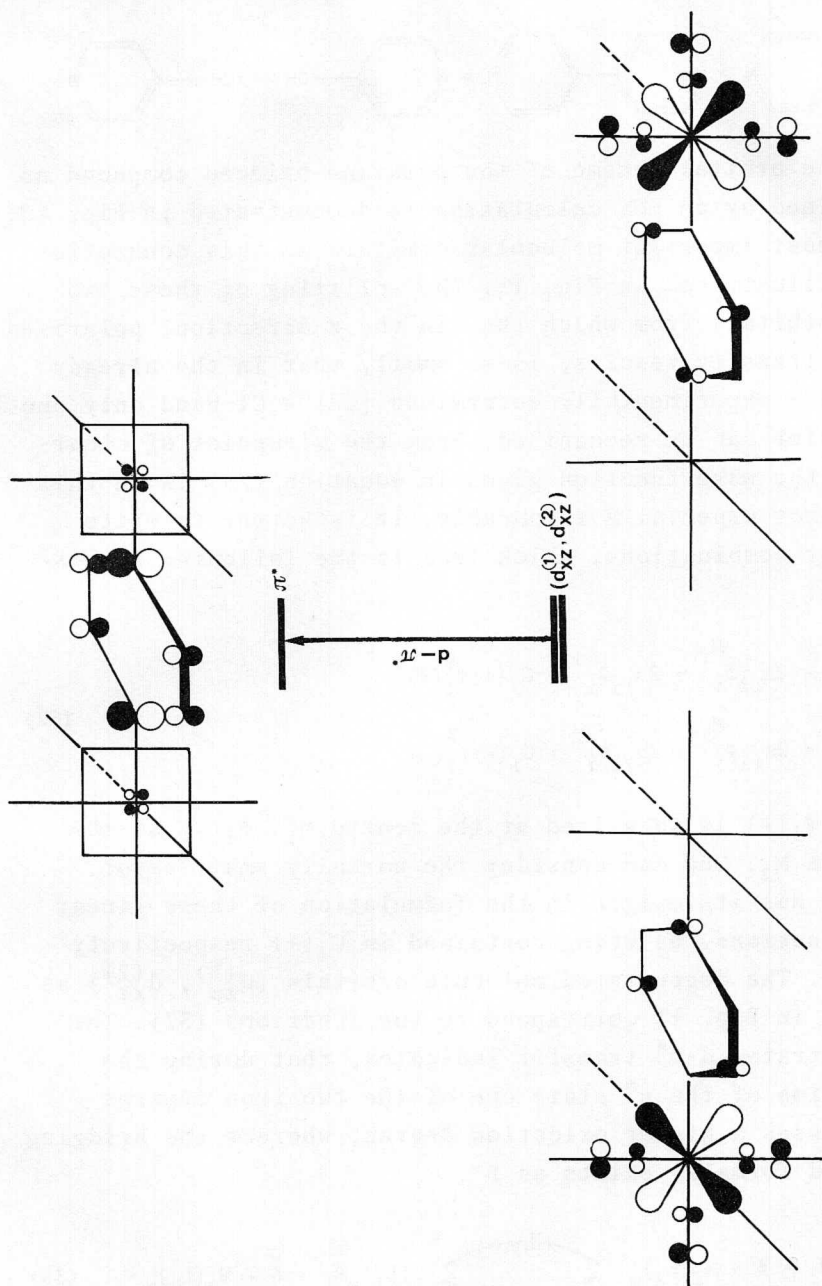


Fig. 11. Demonstration of the $d-\pi^*$ transition in the binuclear pentacyanoferrate(II)-pyrazine complex with localized orbitals [11,28].

A charge separation of this kind can be maintained at most during some ns or μ s. That depends whether the relaxation takes place under conservation or change of the spin multiplicity. However, we are interested in transfers, which lead to a charge separation with a much higher lifetime. One succeeds in this, when the electron can be kept in a potential trough. In a suitable complex the central atom M_2 can play the role of such a potential trough.

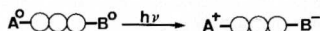
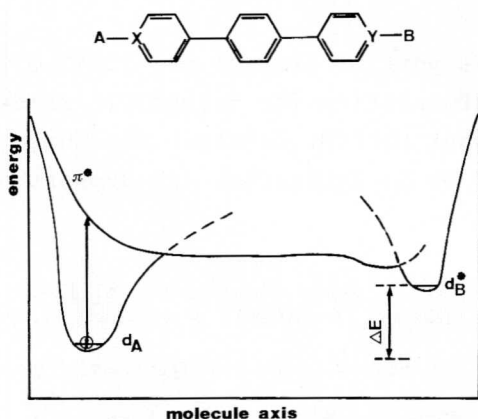
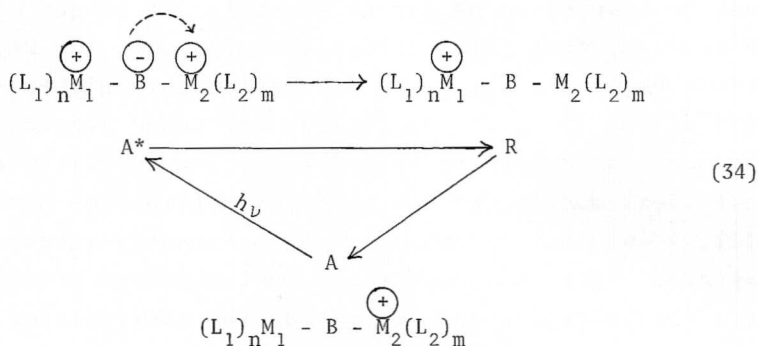


Fig. 12. One-electron model for the demonstration of a photochemically produced intramolecular charge separation in binuclear complexes. The figure gives the potential trough for an electron as a function of its position along the molecule axis [10].

The one-electron energy in function of the longitudinal axis of a model molecule is demonstrated in Fig. 12. By light absorption an electron which is located at the centre A will reach the π^* level of the bridging ligand. It possesses a certain probability - which should be as high as possible - to relax into the empty level d_{B^*} at the centre B, which lies about ΔE higher than the level A. From this level d_{B^*} there are various deactivation mechanisms back to d_A - not further discussed here [10] - which must be suppressed as far as possible. It is not difficult to realize, that there should be compounds, for which the life-time of the d_{B^*} state is considerably higher than that of the π^* state. In analogy one could denote such compounds as molecular photodiodes. They possibly represent ideal models for the study of multiphoton processes [10]. A somewhat different - quite recently successfully employed - possibility for the photochemical production of a charge separation depends on the exploitation of d-d transfers in two-dimensional crystal arrays [43].

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