

Introduction to nonlinear optics

- When high intensity electromagnetic radiation, e.g. laser, interacts with a non-linear optical material new electromagnetic fields may be generated.
- Inherent charges in the material interact with the electromagnetic field of the incident light causing its *phase, frequency, amplitude* or *polarization* to be altered. The study of these interactions is known as *non-linear optics (NLO)*.
- Materials able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing.
- In general, progress in these areas would be greatly enhanced by the availability of readily processed materials with sufficiently large NLO responses thus extensive research efforts have been directed at synthesizing more efficient photon-manipulating-materials.
- 1875 saw the birth of non-linear optics with publication of J. Kerr's observations of a *quadratic electric field induced change in the refractive index* of CS known as the Kerr effect.
- A similar but linear effect was observed in quartz in 1883 known as Pockel's effect. The use of these effects was limited until the invention of the laser in 1960, which was shortly followed by the discovery of *second harmonic generation (SHG)* in quartz by P. Franken in 1961.

Principles of linear polarizability

- In linear optics, when the fluctuating *electric field* E of monochromatic radiation of *frequency* ω strikes a molecule it sets the electron cloud into oscillatory motion thus causing an instantaneous displacement of the electron density of the molecule.
- In its distorted form the molecule is polarized, i.e. it *undergoes a momentary charge displacement forming an induced electric dipole moment known as polarization* P , which oscillates at the fundamental frequency of the incident monochromatic radiation.
- The magnitude of P depends on the strength of the perturbing electric field E and the ease with which E can distort the electron cloud of the molecule (eqn. 1).

$$P = \alpha \cdot E \cos 2\pi\omega t \quad (\text{eqn. 1})$$

- The parameter ' α ' is known as the *polarizability* of the molecule, a volumetric measure of its electron cloud displacement in the path of incident light, relative to the nuclear framework.
- The polarizability α is closely related to the structure and bonding properties of the molecule and is always non-zero .

Principles of linear polarizability (contd.)

- If the incident light frequency ω is in a transparent region of the molecular spectrum, much of the light passes through the sample, but a small fraction ($\sim 10^{-3}$) is scattered in all directions.
- Most of the scattered light emerges at the same frequency as the incident light and is known as **Rayleigh scattering**, the photons neither gain nor lose energy in their collisions with the molecules.
- A very small portion of these collisions ($\sim 10^{-6}$) are inelastic, however, and a net transfer of energy does occur giving rise to scattered light with modified frequencies. These frequency changes are associated with transitions between vibrational levels (ω_k) of the system, i.e. $\omega \pm \omega_k$, and can give rise to **Raman spectra** of the system involved.
- In the case of bulk or macroscopic materials equation 1 takes a different form where χ is the linear susceptibility of a collection of molecules (eqn. 2). The macroscopic susceptibilities are related to the corresponding molecular susceptibilities, or polarizabilities, by local field effects that take into account intermolecular interactions and molecular packing density.

$$P = \alpha \cdot E \cos 2\pi\omega t \quad (\text{eqn. 1})$$

$$P = \chi \cdot E \cos 2\pi\omega t \quad (\text{eqn. 2})$$

Principles of nonlinear polarizability

- The non-linear optical phenomenon arises from the breakdown of equation 1 at sufficiently intense electric fields, such as lasers.
- As the applied field strengths increase, the polarization response of the system is no longer linear.
- Only after the advent of the laser could optical fields of sufficient intensity be produced to observe this effect.
- The ***non-linear polarization of the molecule, which is a function of the applied electric field***, is now represented by a schematic power series expansion in the electric field.

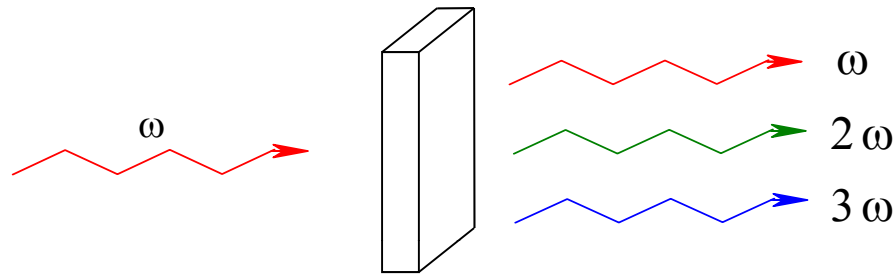
$$P_i = \mu_g + \alpha_{ij} \cdot E_j \cos 2\pi\omega t + \beta_{ijk} E_j E_k \cos^2 2\pi\omega t + \gamma_{ijkl} E_j E_k E_l \cos^3 2\pi\omega t + \dots \text{ (eqn. 3)}$$

where P_i is the i^{th} component of the polarization, μ_g is the permanent ground-state dipole moment and the frequency dependent α_{ij} , β_{ijk} and γ_{ijkl} represent the ***linear, quadratic*** and ***cubic polarizability tensors*** respectively (the subscripts i, j, k, \dots refer to the components expressed in a molecular frame).

- Accordingly, the macroscopic polarisation of a material is represented by a similar series expansion where P_0 is the static dipole of the material and $\chi^{(1)}, \chi^{(2)}$ and $\chi^{(3)}$ represent the linear, quadratic and cubic ***macroscopic susceptibilities*** respectively.

$$P_i = P_0 + \chi^{(1)}_{ij} E_j \cos 2\pi\omega t + \chi^{(2)}_{ijk} E_j E_k \cos^2 2\pi\omega t + \chi^{(3)}_{ijkl} E_j E_k E_l \cos^3 2\pi\omega t + \dots \text{ (eqn. 4)}$$

Principles of nonlinear polarizability



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The molecular quadratic polarizability (β)

- The **molecular quadratic polarizability** (β) is also known as the **second-order polarizability** or the **first-order hyperpolarizability**.
- The power series expansion of P for centrosymmetric systems cannot contain any even terms such as β or $\chi^{(2)}$, as the effect of symmetrically related polarizations cancel each other out.
- Incorporation of **achiral molecules**, **H-bonding**, **ionic chromophores** or **steric hindrance** into crystal matrices can enhance the chances of a non-centrosymmetric configuration.
- Most second-order NLO materials have therefore been composed of non-centrosymmetric one-dimensional charge-transfer molecules. Typically, molecules designed for SHG contain a conjugated π -electron system, asymmetrically substituted by donor and acceptor groups.

donor– π –acceptor

- Such systems, sometimes known as ‘push-pull’ or ‘donor- π -acceptor’ compounds, are characterized in solution by an intense absorption band in the UV-visible region that is associated with an **intramolecular charge transfer (ICT) transition**.
- It should also be noted that SHG requires phase matching where the waves of the fundamental frequency, ω , and of the doubled frequency, 2ω , should be in phase. With birefringent crystals phase matching can be achieved for certain directions of the incident and generated waves, as the refractive index is frequency dependent.

β contd....

- The transfer of energy involved in SHG results from the perturbation of the electronic wavefunction of the molecule by the electric field of the photon which, for a very short time interval ($< 10^{-14}\text{s}$), becomes indistinguishable from the potential and kinetic energy of the perturbed electrons.
- It can be viewed in terms of the electric field of the incident radiation modifying the electronic ground state of the molecule.
- The original electronic ground state is no longer a quantum state for the molecule when it is perturbed by the electric field. ***The new “virtual” quantum state can be described as a linear combination of the ground and excited states of the molecule in its unperturbed state.***
- As the ground and excited states of the molecule have different electronic distributions within the molecule, mixing of these states results in a net charge redistribution or polarization.
- Although the mixing introduces excited state character into the ground state, it does not result in a long lifetime population of any excited state.
- The instantaneous formation of these polarized states has been sometimes referred to as virtual transitions. Formally, the molecule is regarded as having attained a higher energy non-stationary energy level, i.e. a virtual state, it returns to a lower energy stationary state by emitting a photon. These processes are simultaneous and cannot be separated in time.

β contd....

- These concepts are the basis of the quantum-mechanical '*sum-over-states*' (*SOS*) *perturbation theory* for the description of the molecular polarization.
- Thus, the electronic states created by the perturbing field are treated as an infinite expansion over a complete set of unperturbed excited states and the individual tensor components of the molecular first hyperpolarizability (β) can be related exactly to all the excited states of the molecule.
- Oudar and Chemla simplified this approach by ***assuming that the NLO response is dominated by the quadratic hyperpolarizability tensor β_{ijk}***
i.e. β is one dimensional along the ICT axis and thus restricted to one excited state.
- The second-order response was taken to be the sum of two contributions, i.e. β_{add} and β_{ct} , where β_{add} is the additive portion, accounting for the interaction between the individual substituents and the conjugated π -network, and β_{ct} the contribution arising from the interaction of donor and acceptor moieties.
- It was shown experimentally, however, that β_{ct} is responsible for a large proportion of the first hyperpolarizability, which was later confirmed theoretically by Zyss.

β contd....

$$\beta \cong \beta_{CT} = \frac{3}{2\varepsilon_0\hbar^2} \frac{\omega_{ge}^2 (\mu_{ee} - \mu_{gg}) \mu_{ge}^2}{[(\hbar\omega_{ge})^2 - (\hbar\omega)^2][(\hbar\omega_{ge})^2 - (2\hbar\omega)^2]} \quad (\text{eqn. 5})$$

$$= \beta_0 \frac{\omega_{ge}^4}{[(\hbar\omega_{ge})^2 - (\hbar\omega)^2][(\hbar\omega_{ge})^2 - (2\hbar\omega)^2]} \quad (\text{eqn. 6})$$

$$\beta_0 = \frac{3\varepsilon_0^2 (\mu_{ee} - \mu_{gg}) \mu_{ge}^2}{(\hbar\omega_{ge})^2} \quad (\text{eqn. 7})$$

where $\hbar\omega_{ge}$ is the energy difference between the ground and charge-transfer excited states, $\hbar\omega$ is the energy of the incident photon, $(\mu_{ee} - \mu_{gg})$ is the difference between the ground and excited state dipole moments and μ_{ge} is the transition dipole moment between the ground and excited states.

- Extrapolation to zero of equation 5 ($\hbar\omega = 0.0$ eV; $\lambda = \infty$) allows estimation of the **static first hyperpolarizability**, β_0 , which is used to compare the nonlinearity of different molecules.

- The two-level model therefore makes it possible to establish trends in the nonlinearity-molecular structure relationship in terms of relatively simple physical properties.
 - It is clear from eqn. 7 that the hyperpolarizability will be enhanced with
 - decreasing ICT transition energy
 - increasing oscillator strengths for the ICT transition
 - increasing transition dipole moment
 - increasing change of dipole moment
- $$\beta_0 = \frac{3\varepsilon_0^2(\mu_{ee} - \mu_{gg})\mu_{ge}^2}{(\hbar\omega_{ge})^2}$$
- It was shown by Marder using the two-state analysis of a four π -orbital system, i.e. single donor and acceptor orbitals linked via two bridge orbitals, that the ***optimum value for β is dependent on the coulombic energy difference between the donor and acceptor orbitals.***
 - It was found that the strongest donor-acceptor pair does not necessarily lead to the largest non-linearity and that the degree of ***bond-length-alternation***, i.e. bridge length, and the importance of the donor and acceptor orbital interaction with those of the bridge must be considered.
 - This two-level model holds quite well for many organic donor- π -acceptor type systems as it describes β in terms of an electronic charge transfer excitation between the ground and excited state, however, it fails for ***octopolar compounds***, some organometallics and some recently developed unconventional chromophores.

S.R. Marder, D.N. Beratan, L.-T. Cheng, *Science* **1991**, 252, 103.

Electronic structure of metallocenes and their conjugated derivatives

- The interaction of ferrocene and ruthenocene donor moieties with conjugated substituents is more complex than that of organic donors as both metal-based and ligand-based orbitals of the metallocene interact with the π -orbitals of the acceptor.
- These complex interactions give rise to a variety of interesting properties including
 - non-linear optical activity in donor-acceptor systems
 - mixed-valence behaviour in bis(ferrocenyl) compounds
 - structural distortions in polymethines

Electronic structure of metallocenes (revision)

- The three highest filled levels of ferrocene are derived from the dxy , dx^2-y^2 (e_{2g} in staggered D_{5d} geometry) and the dz^2 (a_{1g}) orbitals.

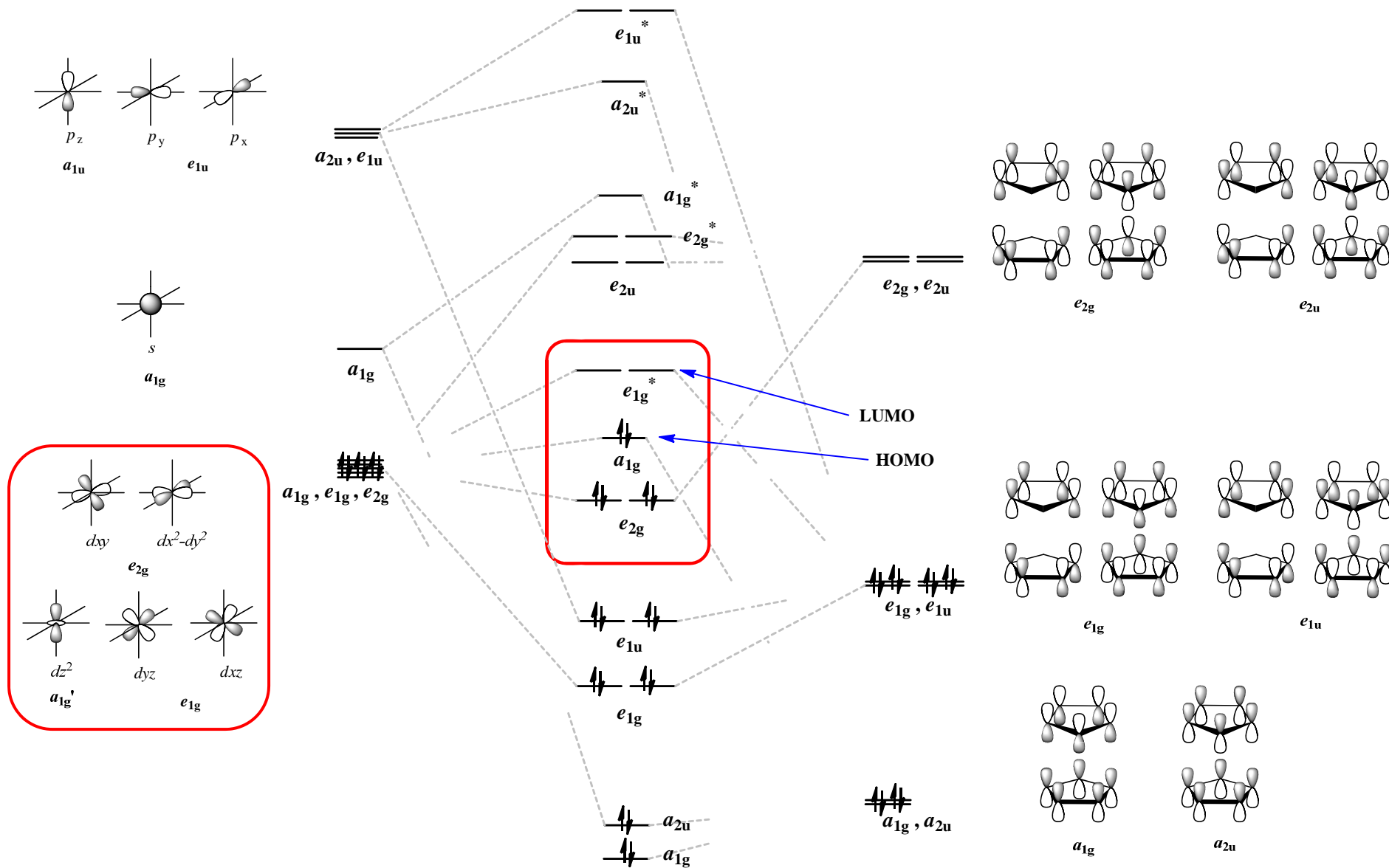
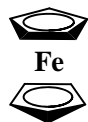
Note: the HOMO of the neutral molecule is a_{1g} , whilst the SOMO of the cation is e_{2g} .

- The e_{2g} orbitals are somewhat d -back-bonding, through interaction with combinations of the cyclopentadienyl (Cp) anion LUMOs, whilst the a_{1g} has some interaction with the metal s orbital and with the Cp rings. Nonetheless, these orbitals may be regarded as essentially metal-based.
- The next highest orbitals (e_{1u}) of the metallocene are principally ligand-based, possibly with some contribution from the p_x and p_y metal orbitals.
- The lower energy orbitals involve bonding combinations of Cp orbitals with the metal d_{yz} , dxz , s and p_z orbitals and do not concern us further.
- The LUMO of ferrocene has symmetry e_{1g} (in D_{5d}) and is derived from an out-of-phase p interaction between the dxz/dyz , and Cp orbitals.

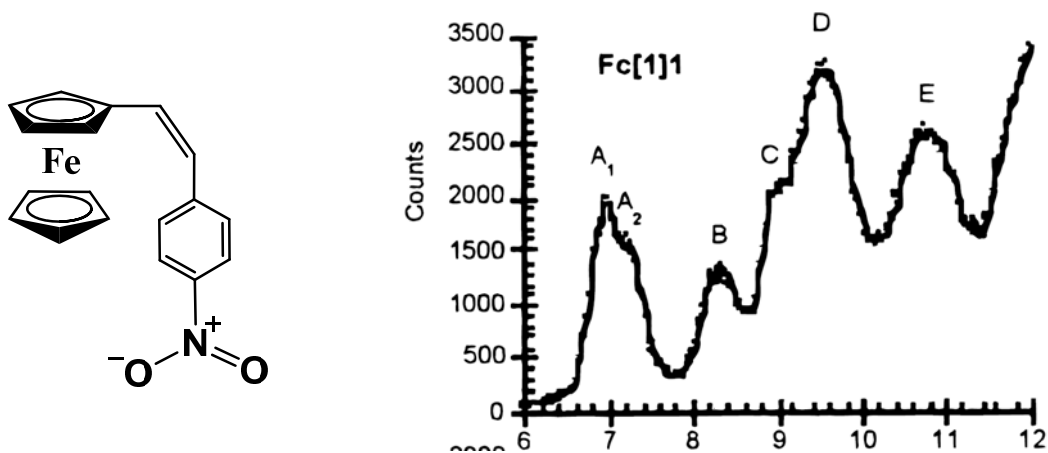
A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}

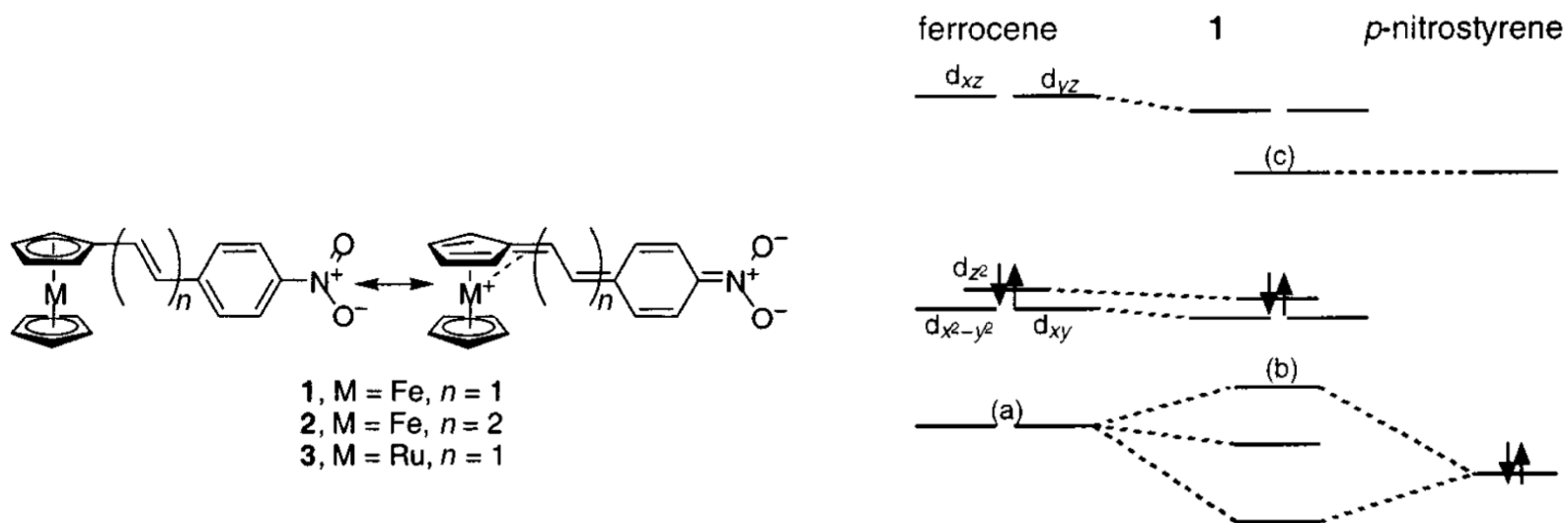
SALC's



- The bonding in ruthenocene (and osmocene) is qualitatively the same, but PES reveal substantial differences in metal-based orbital energies.
- The first vertical ionisation potentials (IPs) for ferrocene and ruthenocene are 6.86/6.89 and 7.45 eV, respectively, whilst the highest ligand-based levels lie at rather similar energies with e_{1u} vertical ionisations at 8.72/8.77 and 8.47/8.51 eV, respectively.
- Thus, ferrocene is clearly the stronger donor in an electron-transfer sense.
- Methylation of the cyclopentadienyl rings raises the energy of both the filled d -orbitals (the first IP of decamethylferrocene is 5.88 eV) and the highest ligand-based orbitals (lowest ligand ionisation of decamethylferrocene is 7.31 eV).
- However, it does not necessarily follow that a stronger electron transfer donor will lead to a greater perturbation of an attached π -conjugated system, since the detail of the electronic coupling between the donor and the π -system is also critical (vide infra).



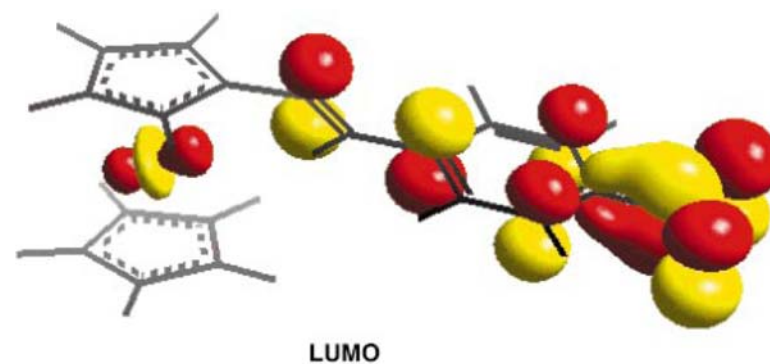
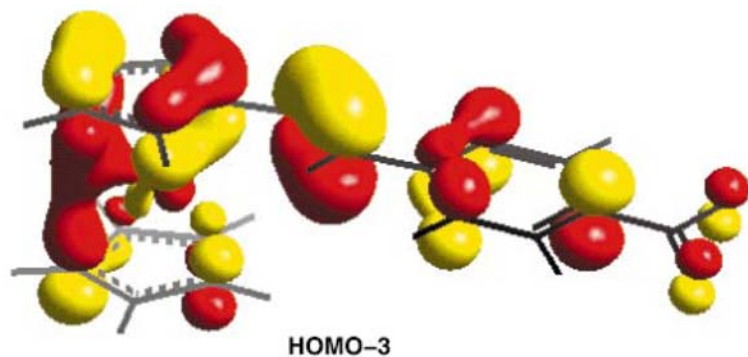
- When a conjugated system is attached to a metallocene the most significant perturbation is not to the metal-based HOMOs. For example,



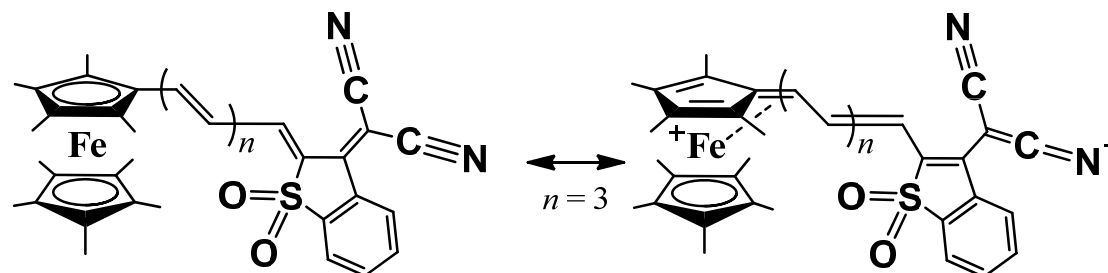
- The first IP (6.97 eV) and electrochemical oxidation potential (+25 mV vs. Fc^+/Fc) of **1** are close to those of ferrocene.
- The highest ligand level (e_{1u}) of the metallocene shows a much greater perturbation.
- An ionisation is found at 8.36 eV, i.e. lower in energy than that e_{1u} ionisation of ferrocene, or the first ionisation of nitrostyrene. This is attributed to ionisation of a π -orbital formed by an out-of-phase combination of one of the e_{1u} pair with the HOMO of the nitrostyrene fragment (MO *b* above in diagram)

- Compound 1 exhibits a molecular reduction at the same potential as *p*-nitrostyrene (−1.67 V vs. Fc⁺/Fc).
- The extended analogue 2 is reduced at −1.64 V, whilst nitrobenzene is reduced at −1.73 V.
- These results suggest that the LUMO is centred on the acceptor moiety, with some delocalisation onto the π -bridge (the empty *dxz* and *dyz* orbitals of the metallocene are at relatively high energy).
- An EPR study of [1]^{•−} shows the unpaired electron to be largely localised on the nitrophenyl ring, consistent with electrochemical data.

- The orbital picture deduced from PES, electrochemical and EPR data is consistent with that derived from extended-Hückel and DFT calculations.
- This model can be successfully extended to other donor–acceptor metallocene derivatives so long as the acceptor is sufficiently strong that the empty acceptor orbital lies below the metal dxz and dyz orbitals in energy.
- However, as the acceptor gets very strong it is necessary to further refine the simple model described above.
- Crystallographic and NMR data indicate that with electron acceptors of moderate strength, the structure is well approximated by the neutral valence-bond picture.



- However, as the acceptor (or donor) is strengthened the zwitterionic resonance form gains in importance.
- This results in a reduction in the bond-length alternation (BLA) of the alkene bridge.



- For example, in the above complex (strong acceptor) the polyene protons show coupling constants of ca. 13 Hz over both formally double and formally single bonds
- When replaced with the weakly accepting formyl group (CHO) coupling constants alternate between ca. 15 Hz across formally double bonds and ca. 10 Hz across formally single bonds.
- More evidence for the increased importance of the charge-transferred resonance form in strong-acceptor compounds comes from electrochemistry, for example, in the Fc analogues:
 - When $n = 1$ oxidation occurs at +325 mV vs. Fc^+/Fc , suggesting a much more severe effect of the acceptor on the metal than in the nitrophenyl analogue (+25 mV vs. Fc^+/Fc).
 - Moreover, the effect is strongly chain-length dependent; oxidation potentials for $n = 2$ and $n = 3$ are +200 and +110 mV, respectively, indicating a decrease in donor–acceptor coupling as the chain length increases.