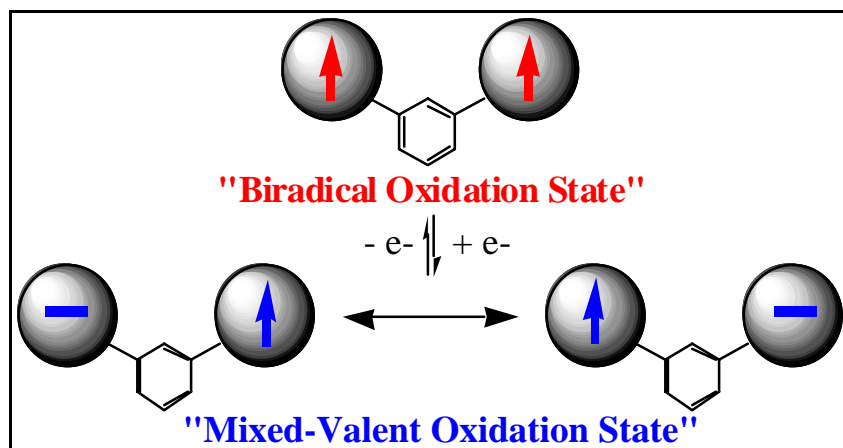


MIXED VALENCE

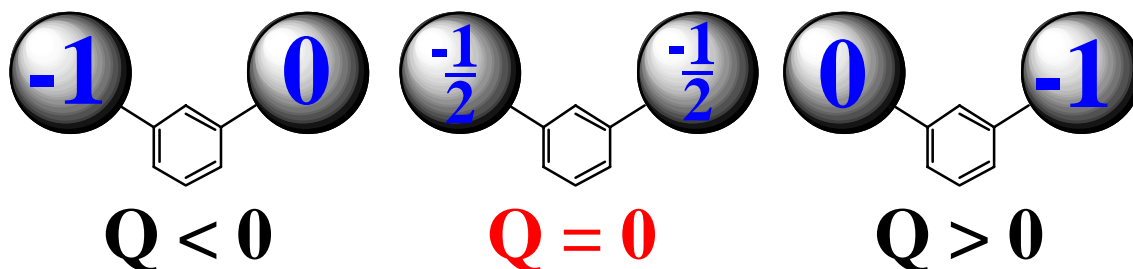
Mixed valence (MV) has been studied for over thirty years, primarily by inorganic chemists, although several examples of organic mixed-valent systems are known.¹⁻¹³

Consider the generic cross-conjugated system below composed of an anion and a radical species. As suggested, such molecules can be prepared by one-electron reduction of a symmetric biradical. The “delocalization” in this cross-conjugated MV system is Linker-modulated, similar to Linker-modulated exchange coupling in the biradical oxidation state.



Not surprisingly, the bonding in the anionic half (-1) of the MV molecule is quite different than in the radical half (0) of the molecule. Let us assume that the redox-active orbitals on each half of the molecule are antibonding, such that the normal mode frequencies are less for the anion than for the radical.

This asymmetry leads to a vibrational coordinate, Q , such that when $0 < Q$ or when $Q < 0$ the (-1) and (0) sites are localized on separate ends of the molecule. However, when $Q = 0$, the species is delocalized as shown below.



If there is no interaction between the two halves of the molecule, two potential energy wells exist with,

$$E_{Q<0} = (k/2)Q^2 + xQ \quad \text{and} \quad E_{Q>0} = (k/2)Q^2 - xQ$$

where x represents the magnitude of distortion along the Q coordinate, and k is the force constant for the Q vibration. The result is two energy curves with minima at,

$$\Delta E_{Q<0}/\Delta Q = kQ + x = 0, \text{ so } E_{\min(Q<0)} \text{ at } Q = -x/k$$

and

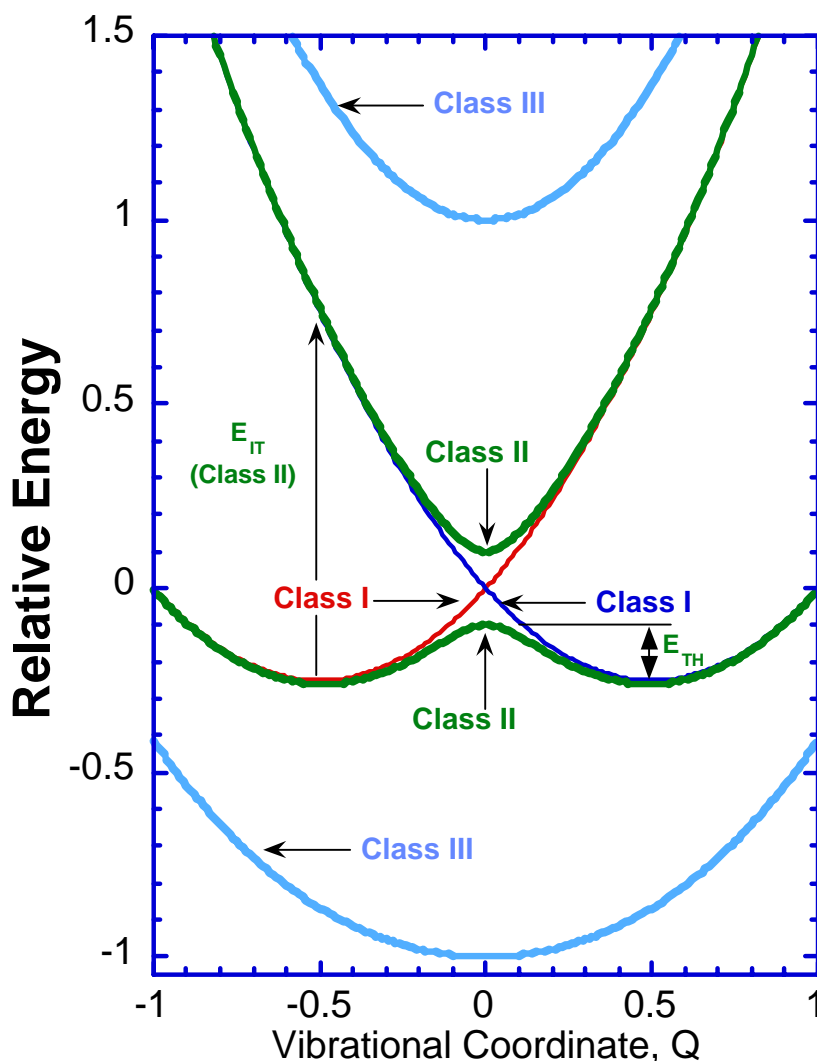
$$\Delta E_{Q>0}/\Delta Q = kQ - x = 0, \text{ so } E_{\min(Q>0)} \text{ at } Q = x/k$$

These curves are shown in **red** and **dark blue** in the graph below for $x = 1$ and $k = 2$. Such a system is classified as MV Class I (no interaction).¹⁴

Now let's consider the case where there is a small interaction between the two halves of the molecule given by the transfer integral, β_{12} . In this case, the energies are,

$$E_{\text{ground}} = (k/2)Q^2 - (x^2Q^2 + \beta_{12}^2)^{1/2} \quad \text{and} \quad E_{\text{excited}} = (k/2)Q^2 + (x^2Q^2 - \beta_{12}^2)^{1/2}$$

Such a system is classified as either MV Class II ($\beta_{12} = 0.1$, weak interaction, **green** potential energy curves below) or Class III ($\beta_{12} = 1$, delocalized, **light blue** potential energy curves below).¹⁴



It can be shown that Class II behavior will be observed when $\beta_{12} < x^2/k$ and Class II behavior will occur for $\beta_{12} > x^2/k$.

Class II behavior is very interesting due the energy barrier (E_{TH}) that exists between the two energy minima, and the unique optical transition, E_{IT} (the intervalence transition). It has also been shown that $E_{\text{IT}} = 2x^2/k = 4E_{\text{TH}}$.¹⁵

REFERENCES

- (1) Utamapanya, S.; Rajca, A. *J. Am. Chem. Soc.* **1991**, *113*, 9242-9251.
- (2) Le Mest, Y.; L'Her, M.; Hendricks, N.H.; Kim, K.; Collman, J.P. *Inorg. Chem.* **1992**, *31*, 835-847.
- (3) Bonvoisin, J.; Launay, J.P.; Vanderauweraer, M.; DeSchryver, F.C. *J. Phys. Chem.* **1994**, *98*, 5052-5057.
- (4) Bonvoisin, J.; Launay, J.P.; Rovira, C.; Veciana, J. *Angew. Chem. Int. Ed.* **1994**, *33*, 2106-2109.
- (5) Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **1995**, *117*, 9172-9179.
- (6) Domingo, V.M.; Castaner, J. *J. Chem. Soc., Chem. Commun.* **1995**, 895.
- (7) Sedó, J.; Ruiz, D.; VidalGancedo, J.; Rovira, C.J.; Bonvoisin, J.; Launay, J.P.; Veciana, J. *Adv. Mat.* **1996**, *8*, 748.
- (8) Bonvoisin, J.; Launay, J.P.; Verbouwe, W.; Vanderauweraer, M.; DeSchryver, F.C. *J. Phys. Chem.* **1996**, *100*, 17079-17082.
- (9) Sedó, J.; Ruiz, D.; VidalGancedo, J.; Rovira, C.J.; Bonvoisin, J.; Launay, J.P.; Veciana, J. *Syn. Met.* **1997**, *85*, 1651-1654.
- (10) Sedó, J.; Ruiz, D.; VidalGancedo, J.; Rovira, C.J.; Bonvoisin, J.; Launay, J.P.; Veciana, J. *Mol. Cryst. Liq. Cryst.* **1997**, *A 306*, 125-132.
- (11) Domingo, V.M.; Castañer, J.; Riera, J.; Brillas, E.; Molins, E.; Martinez, B.; Knight, B. *Chem. Mater.* **1997**, *9*, 1620-1629.
- (12) Karafiloglou, P.; Launay, J.P. *J. Phys. Chem. A* **1998**, *102*, 8004-8012.
- (13) Shultz, D.A.; Lee, H.; Kumar, R.K.; Gwaltney, K.P. *J. Org. Chem.* **1999**, in press.
- (14) Robin, M.B.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247.
- (15) Hush, N.S. *Prog. Inorg. Chem.* **1967**, *8*, 391-444.