

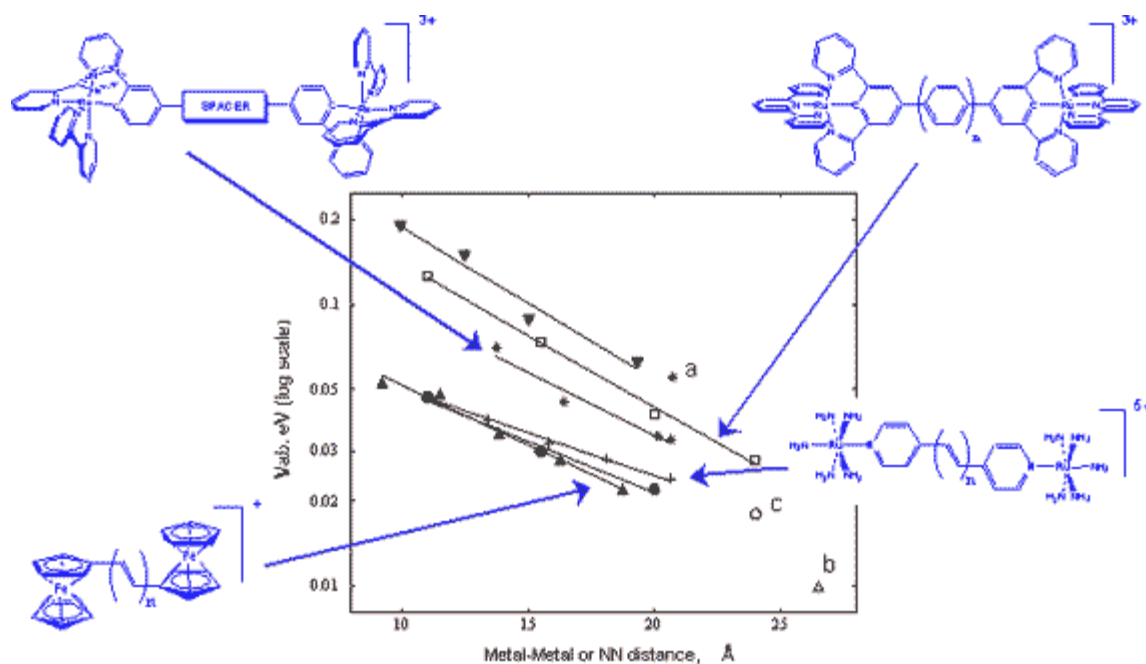
LONG DISTANCE INTERVALLENCE ELECTRON TRANSFER

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Study period : ca 1990 to now.

Long Distance Intervalence Electron Transfer can be monitored by the quantitative study of intervalence transitions in series of binuclear mixed-valent metal complexes. We consider systems in which the two metal atoms are linked by a long conjugated organic ligand, with metal-metal distances between 10 and 25 Å. The study of the intervalence band allows the determination of the electronic coupling V_{ab} , and its rate of decay with distance. Comparisons can be made between several series of compounds, and also with organic mixed-valent systems.

The decay is generally exponential with a coefficient varying in a relatively narrow range (0.08 to 0.12 Å⁻¹). Among all the compounds studied in the last ten years, we have found that *cyclometallated species* (compounds with a metal-carbon bond) are particularly efficient, since they lead to a relatively strong metal-metal coupling even for large distances. Organic mixed-valence systems can also lead to large couplings, with the advantage that both the *optical* (intervalence) and the *thermal* electron transfer can be probed.



DECAY LAWS $V_{ab} = V_{ab}^{\circ} \exp(-\gamma R)$, with $\gamma = 0.07$ to 0.1 \AA^{-1}

A related topic is the study of long-distance magnetic exchange coupling, i.e. spin-pairing of paramagnetic sites linked by a conjugated bridge. Such studies can be useful for the design of efficient molecules for Molecular Electronics, in particular the construction of nanoelectrode-molecule-nanoelectrode devices. In addition, when the distance between redox sites is large enough, it is possible to intercalate an active element in the structure, and thus investigate the possibility of switching at the molecular level.

References :

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