Visible Absorption Spectra of Substituted Ferricenium Cations

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Summary The magnitude of the extinction coefficient and the shift on substitution show that the band at 16,200 cm^{-1} in the absorption spectrum of $Fe(C_5H_5)_2^+$, which formerly was attributed to a $3d$–$3d$ ligand-field transition, is due to a ligand-to-metal $e_{1u} \rightarrow e_{2g}$ charge-transfer transition.

IN the visible absorption spectrum of the ferricenium cation there is a band at 16,200 cm^{-1}. Levy and Orgel[1] and Scott and Becker[2] attributed this band to the $^2E_{2g} \rightarrow {}^2A_{1g}$ transition, in which an electron is promoted from the $a_{1g}(3d)$ to the $e_{2g}(3d)$ orbital. This assignment to a parity-forbidden $3d$–$3d$ transition is, however, questionable. The extinction coefficient of this band (ϵ 420) is one order of magnitude larger than extinction coefficients of $3d$–$3d$ bands in the absorption spectra of dibenzenechromium cation (ϵ 10),[1–3] vanadocene, nickelocene, and ferrocene ($10 < \epsilon < 50$),[4] and a similar assignment for the 16,200 cm^{-1} band therefore seems improbable.

Our absorption measurements on substituted ferricenium cations support a different assignment. Substitution with methyl groups gives a red-shift of 700 cm^{-1}, while the acetyl group gives a blue-shift of 2700 cm^{-1} (*cf.* Table). These shifts are much larger than those observed for the $3d$–$3d$ bands of substituted ferrocenes[5] and indicate that at least one of the orbitals involved in the 16,200 cm^{-1} transition is a ligand orbital. Since in other metallocenes no band around 16,000 cm^{-1} is observed,[4] a ligand-to-ligand transition can be ruled out as a possible explanation and we conclude that the 16,200 cm^{-1} band is a charge-transfer band. Furthermore, the observation that the electron-donating methyl groups give a red-shift and the electron-withdrawing acetyl group gives a blue-shift shows that the band is due to a ligand-to-metal charge-transfer transition. Comparison with an MO calculation on ferrocene[6] indicates that the transition most probably is the symmetry-allowed $^2E_{2g} \rightarrow {}^2E_{1u}$ transition, in which an electron is promoted from the filled e_{1u} ligand orbital to the partly filled[7] e_{2g} iron orbital.

Additional evidence in favour of this assignment comes from photoelectron measurements by Turner.[8] In the photoelectron spectrum of ferrocene there are peaks at 6·85, 7·2, 8·8, and 9·3 ev, and several others at higher energies. The lower two ionization potentials are due to removal of electrons from the e_{2g} and a_{1g} iron $3d$-orbitals.[8] The next two IP's are somewhat larger than the lowest one (8·7 ev) of the C_5H_5 radical[9] and may therefore be attributed to ionization from the e_{1u} and e_{1g} ligand π-orbitals. Subtraction of the first from the third and fourth IP's of $Fe(C_5H_5)_2$ gives energy differences of 1·95 and 2·45 ev, that is 15,700 and 19,800 cm^{-1}. These values should be close to the excitation energies of the $^2E_{2g} \rightarrow {}^2E_{1u}$, $^2E_{1g}$ bands in the absorption spectrum of $Fe(C_5H_5)_2^+$. No real coincidence is expected, because all energies refer to vertical transitions and the dimensional changes differ when going from $Fe(C_5H_5)_2$ to $Fe(C_5H_5)_2^+$. Since in the absorption spectrum of $Fe(C_5H_5)_2^+$ there is a moderately strong band at 16,200 cm^{-1} and a weak band near 19,000 cm^{-1}, we attribute the former to the symmetry-allowed $^2E_{2g} \rightarrow {}^2E_{1u}$ transition and the latter to the forbidden $^2E_{2g} \rightarrow {}^2E_{1g}$ transition.

The photoelectron results not only confirm the $^2E_{2g} \rightarrow {}^2E_{1u}$ assignment of the visible absorption band, but also give information on the order of the a_{1g} and e_{2g} iron $3d$-orbitals. Subtraction of the first from the second IP gives an energy difference of 0·35 ev (=2800 cm^{-1}) between the $^2A_{1g}$ and $^2E_{2g}$ states of $Fe(C_5H_5)_2^+$. A ligand-field analysis of this value in terms of one- and two-electron integrals[1,2] shows that the a_{1g} level is 7200 cm^{-1} above the e_{2g} level. This means that ionization of $Fe(C_5H_5)_2$ to $Fe(C_5H_5)_2^+$ in its ground state takes place by ejection of an electron from an orbital (e_{2g}) which is not the highest filled orbital. The reason for this paradoxical situation is that two-electron integrals favour the $^2E_{2g}$ configuration relative to the $^2A_{1g}$ configuration.[1,2]

The present as well as former[4] results demonstrate that the order and character of the highest filled and lowest empty orbitals in ferrocene are:

$$e_{1g}(\pi\text{-Cp}) < e_{1u}(\pi\text{-Cp}) < e_{2g}(3d) < a_{1g}(3d) < e^*{}_{1g}(3d).$$

Position and extinction coefficients of the visible absorption bands

Compound	σ, cm^{-1}	ϵ, l.mole^{-1}.cm^{-1}
$Fe(C_5H_4CH_3)_2^+$	15,500	290
$Fe(C_5H_5)_2{}^+$	16,200	420
$Fe(C_5H_5)(C_5H_4{\cdot}COCH_3)^+$ ..	18,900	920

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