

ZFS-TENSOR OF THE TRIPLET STATES OF

[2.2]PHANES AS STUDIED BY ESR

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In the last ten years considerable effort and progress has been made in order to understand the excited states of charge-transfer (CT) complexes, being predominantly non-ionic in their ground state, but experiencing a considerable charge-transfer when be excited into higher electronic singlet states. Far less is known about the lowest excited triplet states of these complexes.

The complexes we studied were [2.2]Phanes such as 4,5,7,8-Tetracyano-[2.2]-Paracyclophane (1) or 4,7-Dicyano-12, 15-Dimethoxy-[2.2]Paracyclophane. They are models for either complexes or exciplexes with well known relative orientations of the molecular subunits. Because of the face to face orientation of the conjugated rings in the phane molecule, they are especially suited for a study of π -electron interaction. We investigated the lowest excited triplet states by ESR - and ODMR experiments on X-traps in single crystals at 1.3 K and 4 K.

The complete fine structure (zfs) tensor and the main axes orientations with respect to the molecular frame, were derived for the first time by the angular dependence of the $\Delta m_s = \pm 1$ ESR-transitions.

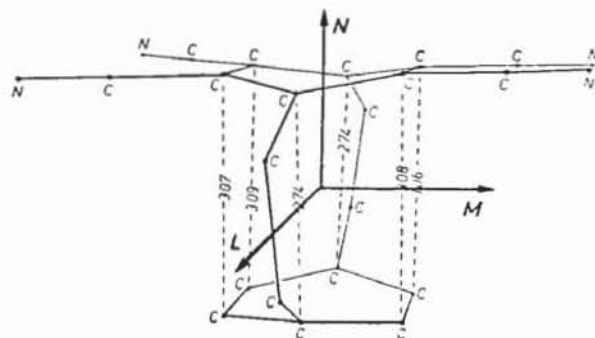
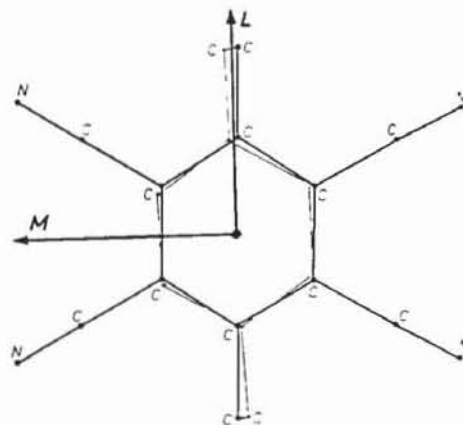
The evaluation of the CT character χ was performed up to now by using zfs constants derived from zero field experiments.

The use of the relation

$$\chi = \frac{D_{\text{complex}} - D_{\text{monomer}}}{D_{\text{ion}} - D_{\text{monomer}}} \quad (1)$$

implies, that for both, monomer and phane molecules, D is assigned via

$D = -\frac{3}{2}Z$ to a common fine structure axis. In addition the model assumes that the phane triplet state can be approximated by constructing the wavefunction from monomer and ionic CT contributions only.



4,5,7,8-Tetracyano[2.2]Paracyclophane: orientation of the main axes L,M,N of the fine structure tensor with the corresponding eigenvalues: L=(+)1129MHz, M=(+)185 MHz and N=(-)1314 MHz

The high-field experiments show, that in the case of appreciable CT as for 4,7-Dicyano-12,15-Dimethoxy-[2.2]Paracyclophane in the triplet state the relative ordering of the zfs eigenvalues may change. In such a case relation (1) can no longer be used.

In addition we found, that a construction of a zfs-tensor for the complex from monomer and CT terms alone is no longer possible for a strongly coupled system.

REFERENCES

1. P. Wahl, Dissertation, Universität Heidelberg 1980