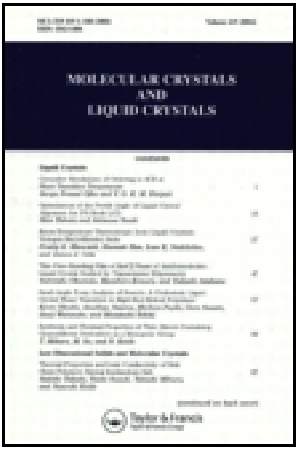

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Spin Distribution of Triplet States in Various Environments

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Spin Distribution of Triplet States in Various Environments

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Measurements have been made of the zero-field parameters of both ground state and metastable triplets in a variety of environments. These parameters provide an averaged distance between the unpaired electrons and thus are sensitive to the spin density distribution. The distance is found to increase in the series of matrices saturated fluorocarbons, saturated hydrocarbons, benzene derivatives and naphthalene. A detailed examination indicates that transfer of charge is occurring with electrons being donated into unfilled orbitals. Donation can occur from filled orbitals of the solvent into half-filled orbitals of the triplet or from the triplet to vacant orbitals of the solvent. The effect is essentially independent of local electric moments or the presence of heavy atoms so that polarization or spin-orbit contributions are likely to be of secondary importance.

Examination in fluorocarbon environments of the ground state triplet NCN, for which a zero-field splitting had been determined in the gas phase,[1] showed that even here 1–2% delocalization of spin occurred in the condensed medium. Important to this conclusion was correction for motion at the cryogenic temperatures at which the fluorocarbon measurements were carried out.

Variations in packing of the solvent about the solute triplet are able to alter the observed parameters. Triplets prepared in solids which were directly deposited from the vapor onto a surface at 5°K consistently gave shorter averaged distances and less charge transfer than those observed in solutions

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obtained by freezing. Such vapor-deposited solids are known to be of higher porosity than those obtained from the liquid.

An experiment was performed which we regard as equivalent to increasing the pressure on the sample. A one to one photodimer of naphthalene and anthracene was cleaved photolytically in a solid environment to yield naphthalene and anthracene in close proximity.[2] The zero-field parameter of the phosphorescent anthracene indicated 8% charge transfer to be compared with 9% for anthracene in a naphthalene host. Since the latter sample would have two naphthalenes in proximity to the anthracene guest we are observing a two-fold larger delocalization under the "high pressure" conditions.

The presence of charge transfer in all of the host investigated including saturated fluorocarbons and hydrocarbons leads us to conclude that the phenomenon is general for all organic solids. This delocalization is expected not only for triplets but for other systems with unfilled orbitals such as doublets and excited singlet states.

1. G. Herzberg and D. N. Travis, *Can. J. Phys.*, **42**, 1658 (1964).
2. E. A. Chandross and A. H. Schiebel, *J. Am. Chem. Soc.*, **95**, 1671 (1973).