

Quantum Modeling of Optical and Magnetic Properties of the Triplet State

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Abstract

This thesis represents a quantum chemical treatment of optically detected magnetic resonance (ODMR) spectra of organic molecules excited to the triplet state (T). The T state is invariably of lower energy than the excited singlet (S) state, derived from the same single-electron transition. The triplet state has three spin sublevels which are split even in the absence of an external magnetic field. The zero-field splitting (ZFS) is determined mostly by spin-spin coupling (SSC) and is a unique characteristic of the orbital nature of the excited state. Each spin sublevel T_1^a has its own transition probability to the ground S_0 state, since it is governed by spin-orbit coupling (SOC) with specific selection rules. The difference in the magnetic sublevel radiative rates makes it possible to detect microwave transitions between triplet spin substates via changes in phosphorescence intensity, which is the origin of the ODMR technique in triplet state spectroscopy. The electric dipole activity of the spin sub-levels in the phosphorescent triplet-singlet transitions is estimated in this thesis by means of the quadratic response technique. The first *ab initio* attempt is performed in order to understand the origin of spin-selective solvent effects on ODMR signals. To the first order of perturbation theory SOC does not affect the energy of the triplet spin states. The second order SOC contribution to the splitting of the ${}^3\pi\pi^*$ states is found to be almost negligible. Solvent effects on the zero-field splitting constants induced by electron spin-spin coupling in the triplet states of azaaromatic molecules are calculated using multi-configuration self-consistent field wave functions and the polarized continuum model. The correlation between the solvent-induced shift in the ZFS and phosphorescence frequency that has been observed in ODMR experiments in low temperature glasses is reproduced by our direct SSC and SOC calculations. It is found that account of SOC perturbation produces only a minor influence on the solvent-induced ZFS shift even for ${}^3n\pi^*$ states. Solvent effects on hyperfine structure of triplet states are also studied in this thesis. The applicability of the MCSCF technique for ZFS and hyperfine constant calculations in organic triplet molecules is proved by similar studies of rotational fine-structure in optical spectra of diatomic molecules. Experimental research in these two branches of molecular spectroscopy are developed independently, but *ab initio* theory can treat both types of spectra on the same background of spin-selectivity in magnetic perturbations.

Using density functional theory (DFT) it is possible to treat also large molecular systems. In this respect special attention in this thesis is paid to theoretical studies of triplet state properties of the free-base porphyrin molecule. Comparative studies of singlet-triplet transition moments by time-dependent MCSCF and DFT methods in three-atomic molecules show similar results and indicate that DFT is a good approach of similar quality as explicitly correlated methods for small molecules.

Publications

Publications included in the thesis

1. *Physical properties and spectra of IO, IO⁻ and HOI studied by ab initio methods.*
B. Minaev, O.Loboda, O.Vahtras, H.Ågren, E.Bilan, **Spectrochimica Acta A** 58, 1039 (2002)
2. *Ab initio calculations of zero-field splitting parameters.*
O. Vahtras, O.Loboda, B.Minaev, H.Ågren, K.Ruud, **Chem. Phys.** 279, 133 (2002)
3. *Ab initio calculations of zero-field splitting parameters in linear polyacenes.*
O.Loboda, B.Minaev, O.Vahtras, B.Schimmelpfennig, H.Ågren, K.Ruud, D.Jonsson, **Chem. Phys.** 286, 127 (2003)
4. *CASSCF calculations of triplet-state properties. Applications to benzene derivatives.*
O.Rubio-Pons, O.Loboda, B.Minaev, B.Schimmelpfennig, O.Vahtras and H.Ågren, **Mol. Phys.**, 101, 2103 (2003).
5. *Ab initio study of non-homogeneous broadening of the zero-field splitting of triplet guest molecules in diluted glasses.*
O.Loboda, B.Minaev, O.Vahtras, H.Ågren and K.Ruud. **J. Chem. Phys.**, 119, 3120 (2003).
6. *Fine- and hyperfine- structure in three low-lying ³Σ⁺ states of molecular hydrogen.*
B.Minaev, O.Loboda, Ž. Rinkevičius, O.Vahtras, H.Ågren, **Mol. Phys.**, 101, 2335 (2003).
7. *Ab initio calculations of vibronic activity in phosphorescence microwave double resonance spectra of para-Dichlorobenzene.*
O. Rubio-Pons, B. Minaev, O. Loboda and H. Ågren. **Theor. Chem. Accounts**, accepted (2004).
8. *Solvent effects on optically detected magnetic resonance in triplet spin labels.*
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9. *Singlet-triplet transitions in three-atomic molecules studied by time-dependent MC-SCF and density functional theory.*
B. Minaev, I. Tunell, P. Salek, O. Loboda, H. Ågren. **Mol. Physics**, accepted (2004).
10. *Theoretical study of triplet state properties of free-base porphin.*
O. Loboda, I. Tunell, B. Minaev and H. Ågren. **Chem. Phys.**, accepted (2004).

11. *Theoretical study of isomerisation of free-base porphin.*
O. Loboda, F. Himo and B. Minaev. In manuscript

Publication not included in the thesis

- *A Quantum-chemical study of excited states of the HO₂ radical*
B.F.Minaev, O.M.Homenko, O.A.Loboda, **Rus. J. Phys. Chem.** 75, 1158,
(2001)

Own contributions

I carry the main responsibility for the papers where I am the first author (*Papers 3 and 5,10,11*). The papers where I have carried out all or the major part of the calculations are *Papers 1-3,5,6,8,10,11*. In the remaining *Papers 4,7,9* I have assisted with the performance of the studies.

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Contents

1	Introduction	1
2	Computational methods	5
2.1	MCSCF method	5
2.2	Density functional theory	6
3	Triplet state properties	9
3.1	Spin-spin coupling	10
3.2	Spin-orbit coupling	12
3.3	Hyperfine coupling	14
3.4	Nuclear quadrupole interaction	15
4	Electron paramagnetic resonance	19
5	ODMR Spectroscopy	23
5.1	Experimental technique	24
5.2	FDMR	25
5.3	Solvent effects in ODMR	27
5.4	Connections between magnetic resonance methods	28
6	Sample application: Porphyrins	31
6.1	Nomenclature and organization	32
6.2	Photoinduced isomerization	33
6.3	Phosphorescence	37
7	Overview of the presented projects	39

Chapter 1

Introduction

The characteristics of magnetic and optical properties of triplet state molecules is a central theme of study in the present thesis. The triplet state manifests itself in a long-lived emission which proceeds long after the termination of excitation. Optical and magnetic properties of triplet state molecules can be studied by various techniques. The most visible contribution of electron paramagnetic resonance (EPR) spectroscopy is in determining structures of free radicals, paramagnetic metal complexes and molecules in excited triplet states. Since the first EPR experiment on photoexcited organic molecules carried out by Hutchison *et al.* [1] in the late 1950's, the magnetic and spin selective research of the organic triplet state in condensed matter has been a steadily increasing field of interest among physicists, chemists and biologists [2, 3].

Most of the known spin selective processes are connected with phosphorescence studies, with electron transfer, conductivity in molecular solids, with photochemistry and with magnetic field effects on those processes [4]. The phosphorescence becomes allowed because of mixing of the singlet and triplet states induced by spin-orbit coupling (SOC). It is well-known that different vibronic bands in the phosphorescence spectra often are strongly polarized. This polarization indicates that SOC is highly selective in the sense that the three spin sublevels of the triplet state have different S-T mixing patterns and different phosphorescence rate constants [5].

By the same reasons the photochemical and photophysical nonradiative processes connected with the triplet state can also be spin-selective. Since the SOC interaction causes spin sublevel selective reactions from the triplet exciplex, the electron spin polarization should be observed in the transient radicals which escape from the non-equilibrated intermediates [4]. This also gives rise to the external magnetic field effects [2] and to the external heavy atom effects on the studied processes [6]. This is a background for spin catalysis concept [7].

Spin selectivity of photophysical and photochemical processes in molecules originates from energetic splitting of spin sublevels in the triplet excited states. For excited radicals, biradicals and molecules with spin $S \geq 1$ the spin sublevels with different M_s quantum numbers are split even in the absence of an external magnetic field. In particular, for excited triplet state molecules (T_1), which are responsible for phosphorescence, the spin splitting in zero external magnetic field was observed in EPR spectra [1]. The phosphorescence emission ($T_1 \rightarrow S_0$) has a long lifetime (from 100 s to 1 ms) due to the necessary spin reorientation which must accompany this spin forbidden transition. Doublet states with $S=1/2$ are always degenerate in the absence of external magnetic fields (Kramer's degeneracy). The energy of the zero field splitting (ZFS), the reactivity of isolated spin sublevels, and other kinetic constants which describe the radiative and non-radiative decay, are defined by internal magnetic interactions in molecules or in reaction centers of enzymes [4]. The most important among them are SOC and spin-spin coupling (SSC) interaction, that is dipole-dipole interaction of magnetic moments of electron spins. Apart from SOC and SSC, within certain conditions a crucial role is played by weak magnetic interactions depending on nuclear spin. This is hyperfine couplings (HFC) which include isotropic Fermi-contact interaction and dipole-dipole anisotropic hyperfine coupling. The nuclear quadrupole interaction can also influence the electron spin-selectivity via hyperfine couplings. The electron-nuclear HFC interaction together with the nuclear quadrupole coupling give rise to spin selectivity in molecular triplet states [6] and also in other higher multiplets in paramagnetic ions of transition metals in active sites of enzymes [8]. Additional peculiarities are related with the mixing of electronic spin sublevels by external fields. It is obvious that the strongest mixing of the ZFS electronic spin sublevels is induced by an external magnetic field. Hence, the well-known magnetic field effects on the rate constants of a large number of photophysical and photochemical processes in molecules can be explained [2]. This includes also some important biological process [9, 10, 11], for instance, reactions catalyzed by enzymes. Meanwhile, there is no doubt that saturation of microwave transitions between spin sublevels (in zero field as well as in magnetic field) should also change the speed of a spin-selected process. Certain well-known photophysical methods of analysis such as optical detected magnetic resonance (ODMR), electron nuclear double resonance (ENDOR), etc. rely on these principles.

The emergence of ODMR spectroscopy has served to both increase interest in magnetic properties of organic triplet molecules and to expand the scope of triplet-state systems with short lifetime. The recent emergence of the ODMR technique in the field of biology, where photoexcited triplet molecules are utilized as intermediates (photosynthesis) or as probes of the bioenvironment, is apparently a new important expansion [2, 3, 12]. One of the major problems in modern science is the relationship between structures of molecules and their chemical behavior. There is a large amount of techniques that help to solve this problem for the ground

state molecules, but the number of methods available for the study of electronically excited states is more limited. This is unfortunate, because excited states are often key intermediates in chemical reactions initiated by light, and they often exhibit reactivity that is completely different from that of the corresponding ground state. The development of theoretical *ab initio* methods, which together with ODMR measurements, allow the direct assessment of the structural and dynamic properties of short-lived excited states, must be regarded as one of the most significant advances in this field in the past decade [7, 13, 14]. This thesis provides an extension along this line with respect to spin-selective processes which occur in short-lived triplet excited states. The present summary is presented in the following way: The first part reviews aspects of the theory of quantum chemistry, the second part presents the different applications of this thesis.

Chapter 2

Computational methods

Advanced theoretical methods are called for in order to model the electronic structure and properties of molecules. Using theoretical methodology one can obtain the molecular structure quite accurately although for larger molecules it is computationally demanding. In this chapter two major groups of theoretical methods based on *ab initio* and DFT approaches will be discussed.

2.1 MCSCF method

The Multi-Configurational Self-Consistent Field (MCSCF) method can be regarded as a truncated configurational interaction expansion where the molecular orbitals and the coefficients in front of the determinants are optimized by the variational principle. Thus the MCSCF wave function can be represented as

$$|\Psi_{MCSCF}\rangle = \sum_I c_I |\Psi_I\rangle \quad (2.1)$$

where the expansion coefficients c_I and the orthonormal orbitals contained in $|\Psi_I\rangle$ are optimized. A crucial aspect in using MCSCF is to select a proper orbital space for electron correlation. There are several approaches to accomplish this. In our studies we mostly used MCSCF wave functions of complete active space (CAS) type, where the orbital space is divided into inactive and active spaces. The typical inactive space is doubly occupied and formed by the core orbitals and usually the number of active orbitals is equal to the valence orbitals in the molecule. Another approach in treatment of MCSCF wave functions is the Restricted Active Space Self-Consistent Field (RASSCF) method. In the RASSCF procedure the active molecular orbitals (MOs) are divided into three parts, RAS1, RAS2 and RAS3. RAS1 has MOs which are close to doubly occupied, RAS2 consists of fraction-

ally occupied MOs which are neither close to 2 or 0 in occupancy and the RAS3 space consists of MOs which have occupancies close to 0. RAS2 is a full active space, with all possible electron redistributions accounted for, and is in this sense analogous to CASSCF, while the RAS1 and RAS3 have restriction in excitations which allow only limit number of electrons to be excited from RAS1, respectively, to RAS3.

The drawback of the MCSCF method is that in order to select the proper configurations a pre-knowledge about the system is required. One way of overcoming this problem is running a preliminary Møller-Plesset perturbation theory MP2 or a UHF calculation. An inspection of orbital energies together with an analysis of occupation numbers of natural orbitals may be used for selecting the important orbitals.

There are several possibilities to study transitions between electronically excited states. In the present thesis we employ response theory, either linear response theory in which one of the excited states is chosen as reference state or quadratic response theory where the reference state is the electronic ground state. In our MCSCF calculations we employ both methods for studies of singlet-triplet as well as singlet-singlet transitions in different chemical systems. The formalism of response theory is reviewed in *Paper 9*.

2.2 Density functional theory

Density Functional theory (DFT) was first proved for an electron gas by Hohenberg and Kohn, and after that developed by Kohn and Sham. DFT is based on the idea that the ground-state energy is completely determined by the electron density ρ . In contrast to the MCSCF approach where the system is characterized by a wave function, the main focus in DFT is on the electron density ρ . A general DFT energy expression can be divided into four parts:

$$E[\rho] = T[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (2.2)$$

where the T is the kinetic energy, V_{ne} the nuclear-electron attraction, J describes the Coulomb interaction between electrons and E_{xc} represents the exchange-correlation energy. The last term is a key for DFT. The calculation of E_{xc} is often a computationally expensive task and the exact form of E_{xc} is unknown. In order to facilitate the calculation of E_{xc} and make it of a similar cost as the Hartree-Fock (HF) method various approximations are implemented in DFT. One of the most successful functionals is the hybrid B3LYP method in which the exact HF exchange is included. This method gives a good agreement with experimental data and is widely used in a large amount of applications.

The main advantages of DFT methods is the inclusion of correlation contributions and short computing time in particular for large systems in comparison to

ab initio methods. The DFT energies are often less sensitive to the size of basis set than wave-function methods.

The recently developed restricted Time Dependent DFT method utilizing response functions provides a valuable treatment for singlet-triplet transition moments and phosphorescence lifetimes. Comparison with *ab initio* and experimental data indicates that DFT exhibits results of similar quality as explicitly correlated methods. Indeed, it reproduces with high accuracy phosphorescent spectra for a large class of molecules.

Chapter 3

Triplet state properties

In this chapter the magnetic properties of the lowest triplet states of organic molecules will be briefly discussed in the context of the spin-selective processes in ODMR spectroscopy. A leading term of the spin Hamiltonian for electron interaction with a magnetic field is represented by the Zeeman interaction between the electronic spin at $L=0$ and the magnetic field at the nucleus. Usually it has an order of 1 cm^{-1} . The Zeeman operator can be written in the form:

$$H_Z = g_e \mu_B \mathbf{B} \cdot \mathbf{S} \quad (3.1)$$

where g_e is the spectroscopic factor, known as the g factor, which has a value of 2.0023 for a free electron, and $\mu_B = e\hbar/2m_e c$ is the Bohr magneton. The full spin Hamiltonian of the excited triplet state in the presence of an external field also includes electron-nuclear hyperfine terms

$$H_{HF} = \sum_{\text{nuclei}} \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} \quad (3.2)$$

nuclear quadrupole terms

$$H_{NQ} = \sum_{\text{nuclei}} \mathbf{I} \cdot \mathbf{P} \cdot \mathbf{I} \quad (3.3)$$

and nuclear Zeeman terms

$$H_{NZ} = \sum_{\text{nuclei}} \mu_N g_N \mathbf{B} \cdot \mathbf{I} \quad (3.4)$$

\mathbf{A} , \mathbf{P} are second-rank tensors, μ_N is the nuclear magneton and g_N is the nuclear g -factor.

A suitable spin Hamiltonian thus describes at least five magnetic interactions as

follows: the electronic Zeeman interaction, the interaction of the electron spins with each other

$$H_0 = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}, \quad (3.5)$$

the nuclear hyperfine interaction, the nuclear quadrupole interaction and the nuclear Zeeman interaction. For the most part we shall be concerned with the first four types of magnetic interactions in this thesis.

3.1 Spin-spin coupling

For molecules in the triplet state there is a possibility of a splitting even in the absence of an external magnetic field. This splitting arises from the magnetic interaction of the two unpaired electrons. Each electron exerts a magnetic field upon the other.

If one considers the naphthalene molecule (Fig. 3.1), the extent of the splitting is mainly determined by the magnetic dipole-dipole interaction between the electron spins, with spin-orbit coupling (SOC) contributing only to a minor extent. However, exceptions may occur in molecules with orbital degeneracy or near or-

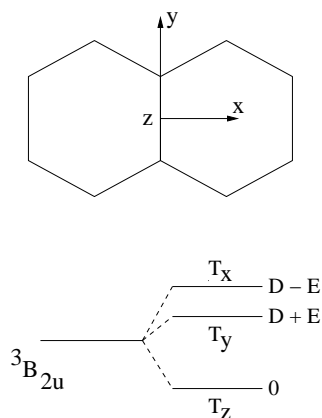


Figure 3.1: The molecular principal axes x , y , and z of the naphthalene molecule and the ZFS of the triplet state T_1

bit degeneracy, or in those containing heavy atoms [15]. Thus the ${}^3\Pi$ states of diatomics and of linear polyatomic molecules have a large splitting, determined entirely by spin-orbit coupling. As a matter of fact, for the lowest triplet π - π^* states of aromatic molecules the spin-orbit coupling is a weak interaction, which split the spin sublevels in the second order of perturbation theory, and the main

contribution to the zero field splitting origins in spin-spin interaction. This contribution occurs as an expectation value of the dipole-dipole interaction operator H_{ss} , which is given by

$$H_{ss} = \frac{\alpha^2}{2} \sum_{i,j} \left[\frac{\vec{s}_i \cdot \vec{s}_j}{r_{i,j}^3} - \frac{3(\vec{s}_i \cdot \vec{r}_{i,j})(\vec{s}_j \cdot \vec{r}_{i,j})}{r_{i,j}^5} \right] \quad (3.6)$$

where $s_i = \vec{s}_i$ and $s_j = \vec{s}_j$ are the spin angular momentum operators of electrons i and j , and r_{ij} describe the position of electron i with respect to electron j . In order to calculate this interaction energy, one must integrate over the spatial distribution of the electrons in the phosphorescent T_1 state. Introducing $S = \sum_i s_i$, the microscopic Hamiltonian Eq. (3.6), can within the triplet multiplet be written as a phenomenological spin Hamiltonian H_0 , Eq. (3.5), in which only operators for the total spin angular momentum are present. The elements of the zero-field splitting tensor D involve integrals of the operator (3.6) over the the electron wave functions and, possibly, additional contributions from SOC. When an x, y, z axis system is chosen in such a way that D is diagonal, and terms involving $S_x S_y$, etc. disappear, H_0 is reduced to

$$H_0 = -X S_x^2 - Y S_y^2 - Z S_z^2, \quad (3.7)$$

with $X + Y + Z = 0$ [16]. In general, the principal axes or "spin axes" of the tensor D coincide with the molecular axes x, y, z , if the molecule in the excited state belongs to the C_{2v} symmetry group, or to a symmetry group that contains C_{2v} as a subgroup. This is the case for the pyrazine, naphthalene, benzene and other molecules studied in this thesis.

The parameters X, Y, Z are equal to the zero-field energies of the three spin sublevels, and thus the form (3.7) of the spin Hamiltonian is particularly well suited for the discussion of an experiment in zero field. For a conventional EPR experiment in a magnetic field it is customary to express H_0 in the alternative form [17]:

$$H_S = D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2), \quad (3.8)$$

where $D = -\frac{3}{2}Z$ and $E = \frac{1}{2}(Y - X)$ (Fig. 3.1).

The eigenfunctions of the ZFS operator (3.7) are labeled T_x, T_y, T_z :

$$T_x = \frac{1}{\sqrt{2}}(\beta\beta - \alpha\alpha), \quad (3.9)$$

$$T_y = \frac{i}{\sqrt{2}}(\beta\beta + \alpha\alpha), \quad (3.10)$$

$$T_z = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha), \quad (3.11)$$

$$(3.12)$$

where the eigenfunction T_x corresponds to the eigenvalue X , *et cetera*. Calculations of the ZFS parameters from the first principles is one of the main goals of the present work. By doing these calculations one can predict connections between magnetic, optical and photochemical properties of the triplet state molecules and also analyze all possible spin-selective processes.

3.2 Spin-orbit coupling

There is a magnetic interaction between the electron spin magnetic moment and the magnetic moment due to the orbital motion of an electron. In order to understand the nature of this interaction, one should consider the nucleus as if it were moving around the electron. We consider the motion from this reference point because we are more interested in its effects on the electron. The charged nucleus circles the electron, which is, essentially, equivalent to placing the electron in the middle of a coil of wire carrying current. Since a moving charge in a such solenoid creates a magnetic field in the center, the orbital motion produces a magnetic field at the electron position. This magnetic field can interact with the spin magnetic moment of the electron resulting in spin-orbit coupling (SOC). For a many-electron system the SOC operator has been obtained by Breit and Pauli in the form:

$$H_{\text{so}} = \frac{\alpha^2}{2} \left[\sum_{i,A} Z_A \frac{\vec{l}_{iA} \cdot \vec{s}_i}{r_{iA}^3} - \sum_{ij} \frac{\vec{l}_{ij} \cdot (\vec{s}_i + 2\vec{s}_j)}{r_{ij}^3} \right], \quad (3.13)$$

The coupling of the spin and orbital angular momenta leads to a splitting of the $2S + 1$ components of a spin multiplet without any external field. For orbitally non-degenerate triplet states the SOC expectation value is zero, thus the zero-field splitting is determined by spin-spin coupling in the first order. For diatomic and linear molecules with nonzero orbital angular momentum projection on the internuclear axis (Λ), for example for ${}^3\Pi$ states ($\Lambda = 1$), the SOC expectation value is not equal to zero and is much larger than the ZFS parameter for organic triplet-excited molecules. It is thus often referred to as spin-orbit splitting [6] and needs to be distinguished from the usual zero-field splitting for polyatomics. This effect is of great importance in high resolution rovibronic spectra of diatomic and small linear polyatomic molecules [6].

Since the spin-selective energy differences can be measured very accurately using spectroscopic methods, it is also a challenge for a number of theoretical methods to compute such multiplet splittings solely on the basis of quantum chemical calculations. Molecules suitable for ODMR experiments usually have strong SOC between excited states. They also tend to have low-lying $n\pi^*$ states. For instance, most of the aza-aromatic compounds, such as pyrazine, have low-lying excited triplets of $n\pi^*$ nature. In these molecules, there can be a substantial contribution

of the spin-orbit coupling effect to the ZFS, which occurs in the second order of perturbation theory. Thus for orbitally nondegenerate systems the first order SOC effect on the sublevel energy is zero. For the ${}^3\pi\pi^*$ states of aromatic hydrocarbons the second-order SOC contribution is negligible [6] and one expects the spin-spin interaction to dominate in the ZFS. We have shown for the first time by *ab initio* methods that the SOC contribution to the ZFS for the benzene molecule is negligibly small (*Paper 2*). Theoretical calculations of SOC contributions to the ZFS for benzene carried out by Hamerka and Oosterhoff in a π -approximation [18] indicate that the spin-orbit interaction energy is approximately 10^{-5} cm^{-1} . Account of σ -electrons by CNDO CI methods leads to zero SOC contribution to the ZFS [6]. The INDO CI methods give practically a negligible SOC contribution to the ZFS of the ${}^3\pi\pi^*$ states of aromatic hydrocarbons, since the perturbing $\sigma\pi^*$ states have very small S-T splitting, which finally determines, to a large extent, the SOC effect on ZFS [6]. Our calculations support these results of old semiempirical theories. Our calculated expectation value of the spin-spin coupling for the T_1 state of the benzene molecule $D = 0.1583 \text{ cm}^{-1}$, is remarkably close to the experimental value of $D = 0.159 \text{ cm}^{-1}$ (*Paper 2*).

Nondiagonal SOC interactions with higher electronic singlet and triplet states shifts the three spin sublevels almost equally. Meanwhile, there is often considerable SOC between one spin sublevel of the triplet state and a nearby singlet state. This rather strong interaction can shift the affected spin state relative to the others, resulting in a significant change of the ZFS. An extreme example is the oxygen molecule. The excited triplet state of molecular oxygen $A^3\Sigma_u^+$ has a relatively large value for the ZFS parameter ($D = 10 \text{ cm}^{-1}$) which results from quite a strong SOC mixing between the close-lying $c^1\Sigma_u^-$ and $A^3\Sigma_u^+$ states. These states are mixed by SOC very effectively, since the spin-orbit integral is comparable with the energy gap between them. The excited singlet $c^1\Sigma_u^-$ state elevates the $A^3\Sigma_{u,0}^+$ spin sublevel, while other sublevels with $\Omega = 1$ are almost unaffected. They only weakly interact with the high lying repulsive ${}^{1,3}\Pi_u$ state (*Paper 2*).

SOC also determines the intensity of spin-forbidden singlet-triplet transitions [17]. The most important is phosphorescence emission from the first excited triplet state T_1 to the ground singlet state (S_0) of organic molecules. In this thesis the radiative phosphorescence lifetime has been calculated by the quadratic response method [7]. The $S_0 - T_1$ transition dipole moment connected with a particular spin sublevel k $M_l(T^k) = \langle \tilde{S}_0 | r^l | \tilde{T}_1^k \rangle$ is determined in this case by the equation:

$$M_l(T^k) = \sum_n \frac{\langle S_0^0 | r^l | S_n^0 \rangle \langle S_n^0 | H_{so}^k | T_1^{k,0} \rangle}{E(T_1^0) - E(S_n^0)} + \sum_m \frac{\langle S_0^0 | H_{so}^k | T_m^{k,0} \rangle \langle T_m^{k,0} | r^l | T_1^{k,0} \rangle}{E(S_0^0) - E(T_m^0)} \quad (3.14)$$

where H_{so}^k is the k :th component ($k, l \in x, y, z$) of the SOC operator; T_1^0 and \tilde{T}_1 de-

note the zero and first order wave functions of perturbation theory. Results of quadratic response calculations for a number of benzene derivatives are presented in *Paper 5*. Together with calculations of the ZFS parameters, the radiative activity of different spin sublevels of the triplet state, estimated by Eq. (3.14), constitute the theoretical background for the most important spin-selective processes in ODMR spectroscopy.

3.3 Hyperfine coupling

Hyperfine coupling originates from interactions between magnetic nuclei and unpaired electrons. Experimentally, hyperfine measurements are carried out by means of EPR or ENDOR spectroscopy. In order to be able to perform an EPR experiment, an external magnetic field needs to be applied. The interactions between the magnetic moments of an unpaired electron or a magnetic nucleus with an external magnetic field, \mathbf{B} , and between the magnetic moments of the electron and nuclei, are described by the following *spin Hamiltonian*

$$H_{spin} = g_e \mu_B \mathbf{B} \cdot \mathbf{S} - g_N \mu_N \mathbf{B} \cdot \mathbf{I}_N - \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}_N, \quad (3.15)$$

where the first two terms describe the interactions between the electron and the field, and between the nuclei and the field, respectively, and are referred to as the electronic and nuclear Zeeman terms. The last term of equation Eq. (3.15) describes the magnetic hyperfine interaction between the magnetic moments of the electron and the nuclei. This interaction can be of two kinds. The first - the anisotropic (dipole-dipole) interaction, is dependent on the direction of the orbital with respect to the applied magnetic field, as well as to their separation. The anisotropic hyperfine tensor reads

$$T_{ij}(N) = g_e g_N \mu_B \mu_N \sum P_{\mu\nu}^{\alpha-\beta} \langle \varphi_\mu | r_{iN}^{-5} (r_{iN}^2 \delta_{ij} - 3r_{iN} r_{jN}) | \varphi_\nu \rangle, \quad (3.16)$$

where g_e and g_N are the g -factors of the free electron and nucleus N , respectively, μ_B and μ_N are the Bohr and nuclear magnetons, and $P_{\mu\nu}^{\alpha-\beta}$ is an element of the spin density matrix. The second term, the isotropic (or Fermi contact) interaction, is defined in terms of the unpaired spin density at the nucleus and is independent of the molecular orientation. It arises when there is a non-zero probability of finding the electron at a particular magnetic nucleus. Consequently, the interaction with a specific atom will be larger the more s -character there is in the MO on the particular atom, since only s -orbitals have the property that they do not vanish at the nucleus. Due to the tumbling motion of molecules in solution, averaging of the anisotropic field occurs; thus isotropic interactions can be obtained. However, in the solid phase the anisotropic effects are clearly detected.

The isotropic coupling constant A_{iso} is given by

$$a = (8\pi/3)g_e g_N \mu_B \mu_N \sum P_{\mu\nu}^{\alpha-\beta} \varphi_\mu(\mathbf{r}_N) \varphi_\nu(\mathbf{r}_N), \quad (3.17)$$

where \mathbf{r}_N is the nuclear position vector of nucleus N . A_{iso} is thus responsible for the isotropic part of the electron spin resonance, which measures the shift of the energy levels for an electron in the presence of a magnetic field.

The prediction of isotropic coupling constants has been a challenge in computational chemistry for many years. In general, accurate predictions of A_{iso} require *ab initio* methods that can recover large portions of the electron correlation, and the use of basis sets of large size. The main difficulty for calculating A_{iso} arises from the necessity to accurately describe electron density and the difference between α and β spin electron densities at the nuclei.

We used the multi-configuration self-consistent field (MCSCF) technique together with full configuration interaction for calculations of the hyperfine coupling constants (HFC) for the hydrogen molecule in *Paper 7*. It was found that convergence of the HFC constants requires large expansions of the basis set, for instance, using uncontracted so-called correlation consistent basis sets a number of additional tight s functions were needed. As this basis is found to be most flexible in the core and valence regions it can give a balanced description of electron correlation and electron density near the nucleus [19]. However, the anisotropic HFC constant does not depend so much on this extension, since it depends mostly on the quality of the p functions. Our results show a good agreement with the experimental value of the a constant for the hydrogen atom [20], and, indeed, *ab initio* methods can provide very accurate predictions of HFC in atoms.

Also, we studied the HFCs of the triplet state of aza-aromatics by density functional theory (DFT) (*Paper 6*).

Solvent effects on the isotropic hyperfine coupling constants for ^{13}C and ^{14}N nuclei of free-base porphyrin were predicted on the ground of the polarizable continuum model (*Paper 10*). In particular, a large reduction of the isotropic hyperfine coupling on the ^{13}C and ^{14}N nuclei was obtained in polar solvents such as toluene and water in comparison with the gas phase.

From a methodological point of view hybrid density functional methods (here B3LYP) have been shown to be reliable for the study of open shell systems. This opens the field for computing magnetic properties and interpretation of EPR, ENDOR and ODMR spectra of larger polycyclic organic molecules containing nitrogen.

3.4 Nuclear quadrupole interaction

The nuclear quadrupole interaction is the interaction between the electric quadrupole moment of a nucleus with the electric field gradient at the nucleus due to all electronic and other nuclear charges of the atom or molecule [21].

If a nucleus with an electric quadrupole moment (nuclear spin quantum number $I \geq 1$) is surrounded by a non-homogeneous electric field resulting from the asymmetry in the electron distribution, it will interact with this electric field to a different extent depending on various possible orientations. The elliptical quadrupolar nucleus has $2I + 1$ orientations, which are described by the nuclear magnetic quantum m , where m has values $I, I - 1, \dots, 0, \dots, -I + 1, -I$. The lowest quadrupole energy level corresponds to the orientation in which the largest density of positive nuclear charge is closest to the largest density of negative charge in the electron environment. The differences in energy between the orientations are not very large, but thermal agitation reduces the excess of nuclei in the lower energy state; consequently, at normal temperatures all states are nearly equally occupied.

In the case of a spherical electron environment around the nucleus, or spherical nucleus ($I = 0, \frac{1}{2}$), all nuclear orientations are equivalent and the corresponding quadrupole energy states are degenerate. However, for the nucleus with $I = \frac{1}{2}$ in the presence of an external magnetic field the degeneracy will be destroyed, and the $m_I = \frac{1}{2}$ state will have a lower energy relative to the $-\frac{1}{2}$ state. If the spins of all the particles (protons and neutrons) are paired, the nuclear spin quantum number I is equal to zero. The distribution of the positive charge is spherical, and the nucleus has a zero nuclear quadrupole moment eQ , where e is the unit of electrostatic charge and Q is a measure of the deviation of the charge distribution from spherical symmetry (which in case of $I = 0$ is zero). A positive value of Q indicates that the protonic charge is oriented along the direction of the applied field vector, while a negative value for Q corresponds to charge accumulation perpendicular to the principal axis. For instance, for the ^{127}I isotope the nuclear quadrupole moment is $eQ_I = -0.789 \cdot 10^{-24} \text{ e} \times \text{cm}^2$ [22], where the negative sign of the nuclear quadrupole moment indicates that the charge distribution is flattened relative to the spin axis.

The quadrupole energy level splitting is determined by the product of the field gradient q at the nucleus produced by the electronic distribution in the molecule, and the quadrupole moment. The components of the field gradient q along the x , y and z axes are denoted as q_{xx} , q_{yy} , and q_{zz} . Conventionally q_{zz} refers to the highest value of the field gradient, q_{yy} to the next highest one, and the q_{xx} is the lowest when all three values are different. When $q_{xx} = q_{yy} = q_{zz}$, which means that all orientations of the nucleus interact identically with the electronic charge, the field gradient is spherical and all quadrupole levels are degenerate. If $q_{zz} \neq q_{xx} = q_{yy}$ then there is axial symmetry around the z axis. We calculated the nuclear quadrupole coupling constant ($e^2 Q_D q_{zz} = -2e^2 Q_D q_{xx}(yy)$) of molecules of this type for the deuterium isotope in the ground and excited states of the D_2 and HD species (*Paper 7*) and for the ^{127}I isotope of the IO radical (*Paper 1*). The deuterium atoms in D_2 and the iodine atom in IO are axially symmetric, and the bond axis in D_2 and the $\text{I} - \text{O}$ bond axis in the IO radical are the z axes in these molecules. The energies of

different quadrupole states in an axially symmetric field can be expressed by

$$E_m = \frac{eQq[3m^2 - I(I+1)]}{4I(2I-1)}, \quad (3.18)$$

where I is the nuclear spin quantum number and m is the nuclear magnetic number which can have values of $I, I-1, \dots, -I$.

For deuterium $I = 1$, equation (3.18) can be rewritten in the following manner:

$$E_0 = \frac{-2eQq}{4I(2I-1)} \quad (3.19)$$

$$E_{\pm 1} = \frac{eQq}{4I(2I-1)} \quad (3.20)$$

Since m is squared, the value for $m=1$ will be the same as for $m = -1$, resulting in a doubly degenerate set of quadrupole energy states. Due to selection rules, the allowed transitions are $\Delta m \pm 1$. That is why for $I=1$ only a single line is observed in NMR spectra. Two lines in a quadrupole spectrum for a nucleus with $I=1$ may occur if the deviation from axial symmetry is appreciable (in other words, the asymmetry parameter η is nonzero) or for nuclei with $\eta=0$ located in two nonequivalent lattice environments. When the field gradients around a nucleus are described as $q_{zz} \neq q_{xx} \neq q_{yy}$, they are called nonsymmetric. The spectra of molecules of this type are more complex in comparison to those obtained for molecules with axially symmetric environments. We interpreted the NMR spectra of the HOI molecule which has an oxygen atom with a nonsymmetric field gradient (*Paper 1*). To evaluate nuclear quadrupole coupling constants from the spectra of nuclei in nonsymmetric fields, an asymmetry parameter η needs to be introduced:

$$\eta = (q_{xx} - q_{yy})/q_{zz} \quad (3.21)$$

In terms of the field gradient tensor and the nuclear quadrupole moment the Hamiltonian is given by the following equation [3]:

$$H_{NQ} = \frac{e^2Qq}{4I(2I-1)} [(3I_z^2 - I^2) + \eta(I_x^2 - I_y^2)], \quad (3.22)$$

The nuclear quadrupole resonance (NQR) technique provides a unique means for the study of structure, dynamics and chemical bonding in solids. There exists a number of atomic nuclei possessing nonzero electric quadrupole moments in the ground state. The interaction of a nuclear quadrupole moment with the local non-homogeneous electric field removes the degeneracy of the nuclear ground state. The transition frequencies between the nuclear quadrupole energy levels are usually in the MHz frequency region and depend on the electric field gradient (EFG)

tensor at the nucleus and on the nuclear quadrupole moment. The nuclear electric quadrupole moment is a well-defined property of a nucleus [23]. The EFG tensor depends on the electric charge distribution around the nucleus. Thus, the NQR frequencies indirectly give important information on the local structure around the observed atom and its chemical bonding. In solids, thermal motions partly average out the EFG tensor; meanwhile, thermal motions in isotropic liquids bring the values of the EFG tensor to zero. The temperature dependence of the NQR frequencies provides valuable information about the thermal behavior of solids. It is noteworthy that the quadrupole couplings in the triplet state provide information about the symmetry of the total charge distribution in the vicinity of the quadrupolar nucleus.

Chapter 4

Electron paramagnetic resonance

It is well-known that under suitable conditions the metastable triplet states of aromatic molecules may be populated via the absorption of ultraviolet light and decay with the emission of a long-lived (1 ms - 100 s) visible phosphorescence [3]. The first successful application of electron paramagnetic resonance (EPR) to the study of the paramagnetic triplet excited states was reported by Hutchison and Mangum [1]. They detected the photoexcited triplet state of naphthalene incorporated in a durene single-crystal host. Since that first experiment a large number of systems have been investigated in a similar way by EPR in an external magnetic field. In order to discuss the basic concepts of electron resonance spectroscopy we shall start to review the applicability of this technique. An EPR signal is always observed when the material has free electrons. There are several cases in which EPR can be applied. The most important for our aims are applications for materials containing free chemical radicals and biradicals and triplet excited molecules. The two parallel unpaired electrons of triplet states can have three different orientations with respect to an applied magnetic field. This is illustrated by Figure 4.1 which gives the energy levels for the triplet state molecule in the presence of a field aligned in turn along each of the principal axes. When the magnetic field is applied along one of the axes it does not affect the spinsublevel with zero projection, but cause splitting of the other two energy levels.

If two or more electrons are present in the system ($S > \frac{1}{2}$), the $H_0 = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ term (3.5) should be introduced, where \mathbf{D} is a second rank tensor with a trace equal to zero. Eq. (3.5) must be added to the Zeeman H_Z operator to produce the spin Hamiltonian for the triplet state $H = H_Z + H_0$. The last term does not depend on the external magnetic field and describes the so-called "zero-field splitting". In contrast to EPR spectra of the triplet state, the ODMR signals can be detected in

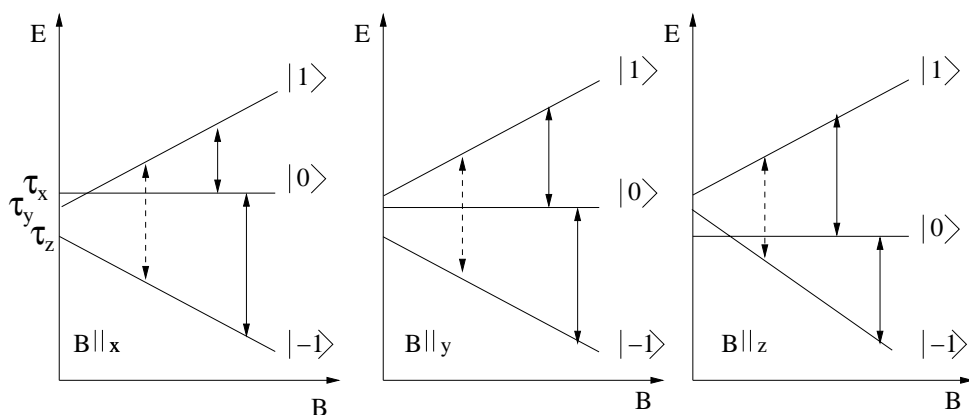


Figure 4.1: Triplet energy levels of naphthalene versus magnetic field (B)

a zero field; saturation of magnetic transitions between spin sublevels leads to changes in total equilibrium balance of the population for the T_1 state, as well as for the excited singlet state S_1 , since the rate constants for the radiative $T_1 - S_0$ transition and for nonradiative $S_1 - T_1$, $T_1 - S_0$ transitions are strongly selective for the spin projections T_1^a . Thus the ODMR signals can be observed by intensity changes in phosphorescence or in fluorescence emission, produced by microwave resonance.

At the condition of high fields, when the spin is totally quantized by the influence of a magnetic field, we may assign the levels accordingly to their M_s value. The M_S term can have $(2S + 1)$ different values: $+S, (S - 1), (S - 2) \dots (-S)$. The S quantum number can be equal to 0 (singlet state) and 1 (triplet state) for two electrons. In case of 4 electrons the possible quantum numbers are $S = 0, 1$ and 2 (quintet state). When the possible values of M_S differ by one and vary from $-S$ to $+S$, then three possible values of M_S for the triplet state are found: $+1, 0$ and -1 . According to magnetic dipole selection rules only the $\Delta M_s = \pm 1$ transitions are allowed. However, at low fields a new "forbidden" $\Delta M_s = \pm 2$ transition can be resolved due to mixture of spin sublevels. In general, they are due to transitions between the two outermost energy levels. In Figure 4.1 they are shown by a dashed line.

The interaction energy between the external magnetic field and the electron magnetic moment is defined as:

$$E = -\mu_z B \quad (4.1)$$

where B is the strength of the external magnetic field along the z axis and μ_z is the

projection of the magnetic dipole moment. In quantum mechanics the μ vector is replaced by the corresponding operator which leads to the following Hamiltonian for the Zeeman perturbation

$$H_z = g_e \mu_B B S_z \quad (4.2)$$

so that the energy is given by $E = g_e \mu_B M_S B$. In a high field the difference between two spin sublevels is directly proportional to the externally applied magnetic field, since $\Delta E \propto B$. It is possible to induce transitions ($\Delta M_s = \pm 1$) between the two Zeeman sublevels by absorption of a microwave photon of energy $h\nu$, equal to the energy difference between the two sublevels

$$\Delta E = g_e \mu_B B = h\nu, \quad (4.3)$$

where ν is frequency of the electromagnetic radiation (microwave range). The presence of Zeeman sublevels, and also the possibility to induce transitions from the lower energy level to the upper energy level, is the very basis of EPR spectroscopy. It implies, for instance, that the position of absorption varies directly with the applied magnetic field.

At thermal equilibrium the relative populations of the two Zeeman spin sublevels is given by the Boltzmann equation:

$$\frac{N_1}{N_2} = e^{-\Delta E/kT} \quad (4.4)$$

At room temperature ($T = 300$ K) and in a field of 0.3 T the ratio of Eq. (4.4) is almost equal to unity, but a slight excess exists in the lower sublevel E_2 and it is this excess that gives rise to a net EPR signal. But the EPR signal would very quickly disappear as the absorption of electromagnetic microwave would equalize the population of these two states. To maintain the population excess, electrons in the upper level must be able to return back to the low energy state (to equilibrium). They must be able to transfer their excess magnetic energy to the surrounding lattice. The spin-lattice relaxation is due to molecular tumblings in solids and liquids, which have a frequency comparable to that of the Larmor precession, Eq. (4.3). If the spin-lattice relaxation time is too fast then the upper state is populated for a very short time; this gives rise to a broadening of the spectral line width (as a consequence of the uncertainty principle of Heisenberg). In this thesis we have calculated the EPR line broadening in triplet molecules which has a completely different nature, namely a non-homogeneous broadening. In fact, the application of ODMR spectroscopy implies a very low helium temperature ($T = 1-4$ K) in order to suppress the spin-lattice relaxation. For optical detection of the microwave transition (the ODMR signal) the spin-lattice relaxation time should be longer than the phosphorescence lifetime [6, 3].

Chapter 5

ODMR Spectroscopy

The optical detection of microwave transitions relies on the following principle. Firstly the sample is irradiated by light with the energy sufficient to populate the triplet state and its sublevels. Then, applying the microwave radiation to the sample, the changes in the phosphorescence emission intensity are registered as function of microwave frequency.

There are several approaches which provide population of the triplet sublevels. One of them is optical pumping of the molecule to the first excited singlet state with the following intramolecular intersystem crossing to the triplet manifold. The population of the triplet sublevels can also be achieved by singlet-triplet absorption, host-guest energy transfer, etc.

For optimal optical detection of microwave resonances the following conditions must be fulfilled: 1) the triplet state has to be luminescent; 2) there should exist some mechanism responsible for creating the triplet state in a state of spin alignment, and finally: 3) the difference in population of the spin sublevels should be preserved for a time sufficient to allow interaction between microwaves and the system.

Concerning the first condition a lot of organic as well as inorganic molecules exhibit phosphorescence when they are in solid solution or glass environments at low temperatures. The intersystem crossing processes are also intrinsic properties for many molecular systems and maintains spin-orbit symmetry selection rules in selective population of specific sublevels in the triplet manifold. Considering the third condition, the population imbalance depends on the rates of the spin-lattice relaxation processes. In order to preserve steady population the rates of sublevel interconversion have to be much slower than the rates at which the sublevels depopulate back to the singlet manifold. A reduction of the spin-lattice relaxation rates can be effectively achieved by cooling the system at liquid helium temperatures. It is possible to process optical detection of microwave resonances even

under condition of fast spin-lattice relaxation at 77K when the pulsed light source makes an instantaneous triplet sublevel population sufficient to observe the microwave effect before relaxation.

5.1 Experimental technique

The basic ODMR experiment requires an excitation light source usually equipped with lenses and filters to pump the sample radiatively to an electronic excited state from which the triplet state then can be populated. Furthermore, a microwave generator with variable-frequency in the 0.2-12GHz range, a liquid helium Dewar assembly for spectroscopic measurements and a phototube for the detection of the emission are needed. A schematic illustration of components for an ODMR experiment is shown in Figure 5.1. To prepare for an ODMR measurement the sample

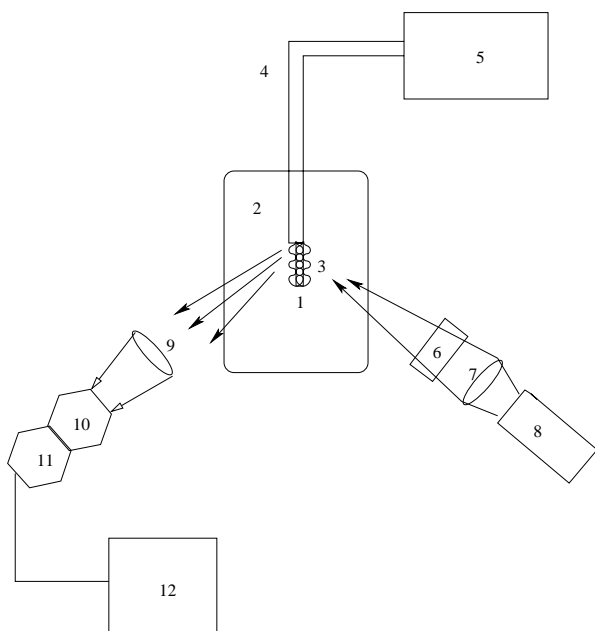


Figure 5.1: Block diagram of a simple ODMR experiment. 1) sample, 2) liquid helium cryostat, 3) copper coil helix, 4) coaxial waveguide, 5) microwave generator, 6) filters, 7) quartz lens, 8) light source, 9) collecting lens, 10) monochromator, 11) photomultiplier, 12) electrometer and recorder.

is inserted into a copper coil slow-wave helix structure attached to a stainless steel

coaxial waveguide. The whole apparatus is immersed in a liquid helium Dewar assembly. Exciting light from a u.v. light source is focused on the sample through the filters which prevent unexpected light. The light emitted from the sample is gathered by a system of lenses. It then passes through the monochromator or suitable filter and is detected by a phototube. The output of the phototube is amplified and displayed by electronics. By changing the frequency output of the microwave generator one observes the intensity change in the phosphorescence.

5.2 FDMR

Optically-detected magnetic resonance spectroscopy explores the intensity of an electronic transition in the optical spectral domain and acts as a detector for electron spin (or also nuclear spin) resonances, which are induced by simultaneous irradiation using microwaves or high-frequency radiation of the appropriate frequency. There are numerous variations on this method. *Ab initio* MCSCF calculations (*Paper 3*) of the ZFS parameters of the polyacene group like benzene, naphthalene, anthracene, naphthacene and pentacene illustrate how ODMR spectra of triplet excited states can be modeled by theoretical means. A diagram of the lowest electronic states of the pentacene molecule is given in Fig. 5.2.

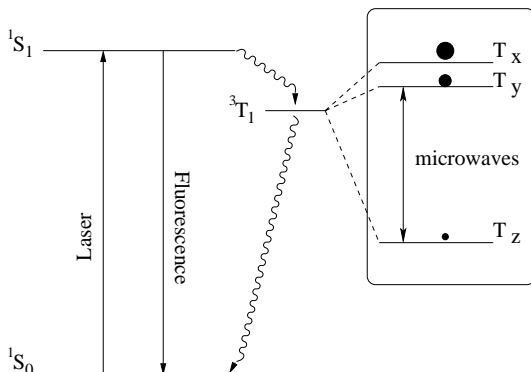


Figure 5.2: Diagram of the lowest electronic levels and transitions between the levels of the pentacene molecule. Arrows indicate radiative transitions, wavy lines - non-radiative transitions. The relative population of the three sublevels of the lowest triplet T_1 state are indicated by the solid dots.

In the ground state of the molecule all molecular orbitals are double occupied, resulting in a singlet state, 1S_0 . The molecule can be electronically excited by a π - π^* transition of the π -electrons, which leaves, in general, two possibilities for the

final state. Either all electrons still have pairwise opposite spins and consequently the molecule is in the singlet state 1S_1 ; or two electrons have parallel spins in the excited state and the molecule is in the triplet state 3T_1 . In the first case only the $^1S_1 \leftarrow ^1S_0$ transition is electronically allowed due to the spin conservation rule. After excitation to the 1S_1 state, the molecule decays to the ground singlet state by emitting a photon, and the fluorescence effect is observed. In another approximation there is a small but finite probability that a molecule crosses over from the singlet state 1S_1 to the triplet state 3T_1 due to the process called intersystem crossing (ISC). The ISC is a radiationless process that becomes possible due to intramolecular interactions such as spin-orbit coupling, which mixes some singlet character into the triplet state and vice versa. From the triplet state the molecules decay nonradiatively via a second intersystem-crossing process to the 1S_0 ground state. It should be noted that the molecules in the triplet state do not take part in the excitation-emission cycles contributing to the detected fluorescence intensity.

In zero field, the lowest triplet state T_1 is split into three sublevels: T_x , T_y and T_z . As mentioned above microwaves are used to induce transition between these sublevels that can be detected through the resulting fluorescence. The magnetic-dipole transitions between any two of the triplet sublevels are possible. For example, T_x and T_z levels which are characterized by a large difference in population (T_x as the highest spin sublevel is more populated than the lowest T_z sublevel) are coupled by resonant microwaves. Then a fraction of population from the short-lived T_x level is moved into the long lived poorly occupied T_z level. As a result, the more molecules per time unit are in the triplet state, the fewer molecules reappear per time unit in the ground state. Therefore, if there are fewer molecules present in the ground state, then less molecules can be excited to the 1S_1 state. As a consequence the fluorescence intensity is decreased. Thus, a resonance in the triplet manifold leads to a change of the fluorescence between the singlet states, though the steady-state population of all five states are determined by the transition rates between them, and any change of these rates will lead to a redistribution of population in all states. This is the basis for the method of detection of magnetic resonance using $S_1 \rightarrow S_0$ fluorescence, namely, Fluorescence Detected Magnetic Resonance (FDMR); or using $S_1 \leftarrow S_0$ absorption called Absorption Detected Magnetic Resonance (ADMR). These methods become especially important when the intensity of the phosphorescence $T_1 \rightarrow S_0$ is too weak to allow detection.

The double resonance technique can also be applied for measuring the optical absorption spectrum $S_1 \leftarrow S_0$ or the phosphorescence spectrum $T_1 \rightarrow S_0$ with simultaneous irradiation of one of the microwave transitions between the T_x , T_y and T_z spin sublevels. If the detection apparatus is modulated at this microwave frequency, one observes only the absorption or phosphorescence spectrum of that particular molecule which has its microwave resonance at the applied frequency. It serves therefore as a fingerprint of each molecule. These methods are termed Microwave Induced Absorption (MIA) or Phosphorescence Microwave Double

Resonance (PMDR). It should be noted that the ODMR method can be successfully applied not only in zero field, but also in an external field.

5.3 Solvent effects in ODMR

Solvent effects on the ZFS constants induced by electron spin-spin coupling (SSC) in the low-lying triplet states of azaaromatic molecules have been calculated in this thesis using multi-configuration self-consistent field wave functions and the polarized continuum model (PCM). These results are presented in *Papers 4* and *6*. The second order spin-orbit coupling (SOC) contribution to the splitting of the $^3\pi\pi^*$ states is found to be almost negligible. The ZFS parameter and its SOC contribution are much larger for the $^3n\pi^*$ state (pyrazine) in comparison with the $^3\pi\pi^*$ states (quinoline, pyridine, pyrimidine). The correlation between the shift in the ZFS and phosphorescence frequency that has been observed in ODMR experiments in low temperature glasses is supported in our work by direct *ab initio* SSC calculations without SOC account. Even for the pyrazine molecule, where the SOC contribution to the ZFS of the $^3\pi\pi^*$ state is quite appreciable (about 30 %), the SOC effect does not contribute much to the non-homogeneous EPR (microwave) line broadening (*Paper 6*). Thus we have shown that the theory [28] which takes only into account spin-orbit coupling of the singlet S and triplet T states in order to explain the observed correlation between the optical frequency shift, ΔE_{ST} , and the EPR shift, ΔD , is inappropriate. The SOC matrix elements in this theory [28] have been considered as empirical parameters which were fitted to the observed non-homogeneous broadening and have never been calculated directly from any reliable wave functions.

The other semi-empirical theory [27] is based on a solvent-induced mixing between two triplet excited states ($T_1 - T_2$) with different ZFS patterns ($D_1 < D_2$) by an external electric field, V , due to the environment: $V_{1,2} = \langle T_1 | V | T_2 \rangle$. The $T_1 - T_2$ mixing leads to the shift of the T_1 level which is equal to

$$S = \frac{V_{1,2}^2}{{}^3E_1 - {}^3E_2} \quad (5.1)$$

Under the assumption that the polarizability of the ground S_0 state is much smaller than that of the excited triplet T_1 state and that the shift of the S_0 state is negligible, the solvent induced shift of the phosphorescence is equal to Eq. (5.1).

The $T_1 - T_2$ mixing leads also to the shift of the ZFS transition, which is approximately equal to

$$s = \frac{V_{1,2}^2(D_2 - D_1)}{({}^3E_1 - {}^3E_2)^2} \quad (5.2)$$

Thus the ratio of s and S is

$$\frac{s}{S} = \frac{(D_1 - D_2)}{{}^3E_1 - {}^3E_2} \quad (5.3)$$

That is, the shift of the ODMR microwave transition divided by the phosphorescence line shift should equal the difference in ZFS parameters of the T_1 and T_2 states divided by their energy gap. Thus the ratio, Eq. (5.3), should be approximately constant. For quinoxaline phosphorescence, non-homogeneously broadened in glass at 4.2 K, the ratio, Eq. (5.3), is equal to $+(2.8 \pm 0.2) \cdot 10^{-6}$ [27]. Thus it is constant within experimental error across the phosphorescence band in agreement with the simple model of the T_1 and T_2 states mixing by the solvent field. The most important attribute is the positive sign of this ratio. Our calculations for quinoline phosphorescence give the ratio $\frac{\delta}{\epsilon} = 1.6 \cdot 10^{-5}$ in agreement with the sign and in semiquantitative agreement with the order of magnitude of the experimental ratio mentioned above (*Paper 6*).

5.4 Connections between magnetic resonance methods

There are important connections between EPR, ODMR, MIA and other microwave induced methods, from one side, as ordinary optical spectroscopy methods, from the other side, in respect to determination of the ZFS parameters of the triplet states [24]. For diatomic and linear polyatomic molecules in $^3\Sigma$ states (when the electronic orbital angular momentum Λ projected on the molecular axis is zero) the electron spin is weakly coupled to the molecular rotation in Hund's case (b) [24]. Each rotational level (except the one with $N = 0$) is split into three components F_1, F_2, F_3 corresponding to $J = N + 1, N, N - 1$, respectively. This splitting is given by Eqs. 3-5 in *Paper 7*, where λ is a notation for the ZFS parameter: $D = 2\lambda$. The E parameter is equal to zero for diatomic and linear polyatomic molecules in $^3\Sigma$ states. In this way the ZFS parameter λ has been determined for a number of excited states in the O_2 molecule, which we have calculated *ab initio* for the first time (*Paper 2*). For the ground state $^3\Sigma_g^-$ of the O_2 molecule the ZFS parameter λ was determined for the first time by EPR method for solid oxygen in ref. [17]. Thus experiment and theory complement each other, but usually they do develop separately [17, 6, 25]. The aim of theoreticians is to unite all approaches. Rotational structure is much more complicated for nonlinear molecules, however the high-resolution spectra obtained with cavity-ring-down spectroscopy and the Fourier transform technique for singlet-triplet transitions in some polyatomic molecules yielded in recent years ZFS parameters with similar accuracy as typical for the EPR and ODMR methods [6, 25].

For large polyatomic molecules the ZFS parameters of the triplet states have been obtained by EPR and ODMR methods [17, 3]. The EPR method is used for single crystals and long lived triplet states. The ODMR methods can be used for mixed crystals and even for glassy solutions. It is well known [26], that the non-homogeneous broadening is a general feature of electronic spectra of molecules

in low temperature solids. Monochromatic light can be used in order to excite selectively few molecules in nearly identical environments of the mixed crystal or glassy solution. The resulting phosphorescence spectrum is much sharper than that obtained with broad band excitation [26, 27, 28]. This selective excitation technique has been used for a long time to study highly resolved vibronic lines in phosphorescence spectra of large organic molecules [26, 29]. Similar selective excitation methods have been applied with the ODMR techniques for detection of the non-homogeneous broadening of microwave transitions [12, 27, 28]. From the first measurements [27] a linear correlation between non-homogeneous broadening of the optical $T_1 \rightarrow S_0$ lines and microwave transitions $D \pm E$ have been obtained. The magnitude of the line broadening ($\Delta\nu$) divided by the line frequency (ν) - the relative line broadening ($\Delta\nu/\nu$) - is of the same order of magnitude for optical and EPR lines for a wide sequence of studied organic molecules and amino acids frozen in glasses, biopolymers and other disordered environments at low temperatures [12, 27, 28].

Chapter 6

Sample application: Porphyrins

Porphyrin systems have great biological importance. Porphyrins which contain iron, called hemes, participate in oxygen transport and electron transfer in biosystems. Many of the porphyrin, chlorin and bacteriochlorin ring systems are members of the protochlorophyll, chlorophyll and bacteriochlorin photosynthetic pigments. Due to this fact a lot of studies concerning the electronic structure and photophysical properties of porphyrin systems have been carried out during the past decades. Most investigations concern the biological role of this class of compounds. In our theoretical research of free-base porphin the main focus was on the lowest photoexcited triplet state T_1 .

It should be noted that the development of new ODMR spectroscopy techniques provide detailed information in this area. However, instrumental limitations of the experimental devices often leads to difficulties in investigations of triplet state properties of porphyrins. In this respect, theoretical studies of electronic structure of excited states are handy as relatively cheap and reliable tools.

Since many porphyrin molecules lack detectable phosphorescence, the microwave induced fluorescence method has proved to be the most appropriate approach to ODMR spectroscopy of nonphosphorescent porphyrins.

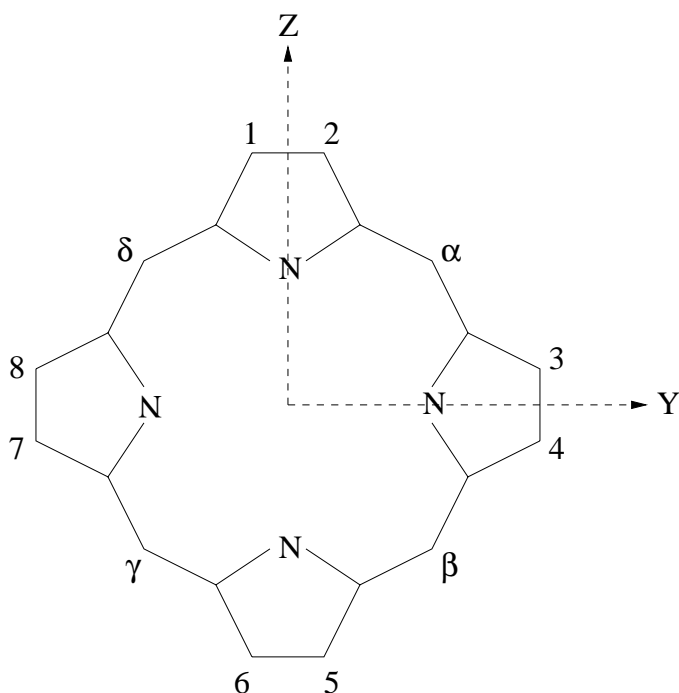


Figure 6.1: Basic porphyrin structure

6.1 Nomenclature and organization

The basic porphyrin skeleton with the rings and positions labeled and with axes chosen is shown in Figure 6.1. When there is a single H atom at each position of the labeled carbon atoms and two H atoms in the center attached to opposite nitrogens, the compound is called *free base porphin* (H_2P). The outer H atoms can be substituted as in benzene. The molecules so derived are referred to as porphins. Another type of substitution replaces the central H atoms by any of a variety of metals, thus changing from the free base to a metal salt. The benzoporphin series arises by fusing benzene rings across the outer bonds 1-2, 3-4, etc. A metal derivative of the unsubstituted porphin ring has D_{4h} symmetry and the lowest triplet state is predicted to be orbitally degenerate. By replacing the central metal ion by two protons thus forming free-base porphin the symmetry of the molecule is lowered from D_{4h} to D_{2h} and the degeneracy is lifted.

6.2 Photoinduced isomerization

It is known that the two inner hydrogens in free-base porphin show a tautomerism. This effect has been studied by 1H and ^{13}C NMR in liquid solution [30, 31]. The fluorescence emission spectrum of H_2P in n -octane host crystals at liquid helium temperature is shown in Figure 6.2. From this figure it can be seen that the fluorescence spectrum consists of a superposition of two almost identical spectra mutually displaced by 65cm^{-1} . H_2P molecules with 0-0 at $16\,331\text{cm}^{-1}$ are assigned as type (1) and H_2P molecules with 0-0 at $16\,266\text{cm}^{-1}$ are assigned as type (2). Such a doublet structure of the fluorescent spectrum arises from the presence of

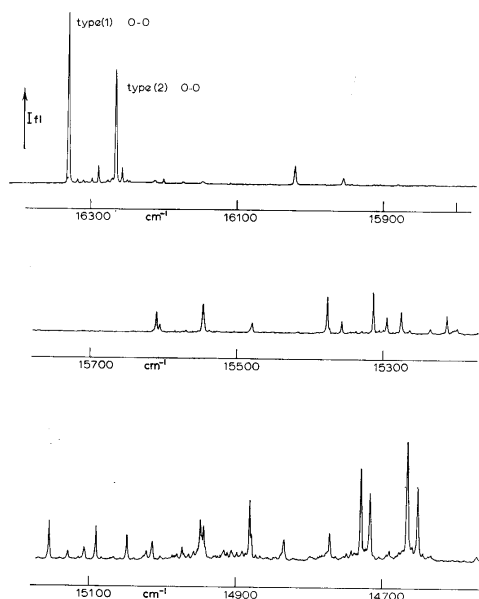


Figure 6.2: Fluorescence emission spectrum of free base porphin in a single crystal of n -octane at $T=4.2\text{K}$. The line width is 2cm^{-1}

two distinct H_2P molecules in the host crystal. The two types of H_2P molecules occupy equivalent positions in the lattice but have different orientation due to in-plane rotation over $\frac{1}{2}\pi$. It was concluded that this is a result of phototransformation. During this process the tautomeric displacement of central protons occurs and results in a formation of two types of H_2P molecules (Figure 6.3). Völker and van der Waals [32] proposed that the photoinduced shift of two inner protons may be associated with the vibrational relaxation that follows the intersystem crossing from the S_1 state to the triplet manifold. From our results (*Paper 10*) obtained

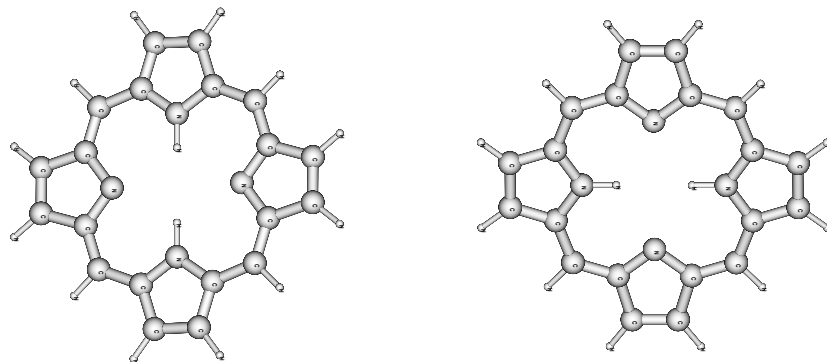


Figure 6.3: Two types of orientation of free base porphin in a host crystal

by time dependent DFT it follows that the first excited singlet and triplet states in the H_2P molecule are separated by less than one eV, whereas the two lowest triplet states are even closer to each other. The energy gap between the two lowest triplet states is almost four times smaller than the S_1-T_1 energy gap. This is in consistency with the proposed theory. However, the exact mechanism of the excited-state proton transfer in H_2P is not known. Indeed, it is not clear whether the proton tunneling occurs in a concerted way by a simultaneous two-proton shift or via an intermediate *cis*-isomer, where the two N-H groups are sitting on the neighboring pyrrole rings (Figure 6.4). In order to establish these two possible pathways of isomerisation we performed DFT calculations (*Paper 11*). A simulation of a stepwise mechanism was succeeded by elongating one of the N-H bond of the normal *trans*-isomer. Upon the *trans*→*cis* transformation the N-H bond cleaves and a new bond is forming with the adjacent nitrogen via passing a transition state (TS). Vibrational frequencies analysis of the TS provided a single imaginary frequency which indicates a large amplitude in-plane motion of the inner proton. The energy barrier was estimated to be equal to 17.6 kcal/mol, see Figure 6.5. Since the energy difference between the *cis* and *TS* structures is significantly smaller than the energy difference corresponding to the transition from the *trans* to *TS* structure, the latter should be the rate-determining step of isomerisation. This step can be accelerated by temperature. The experiment [33] shows that when the temperature increases the reaction yield increases considerably whereas at low temperatures the tautomerisation is found to be temperature independent. We anticipate that at low temperature conditions the molecule is able to reach the

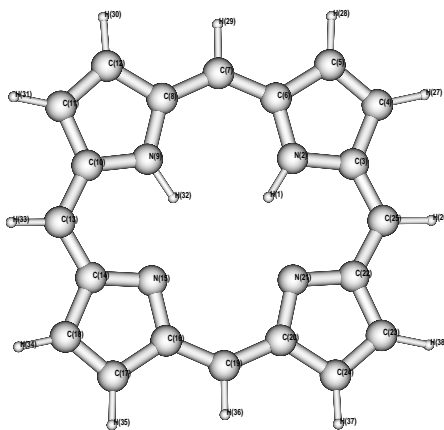


Figure 6.4: *cis*-isomer of free base porphyrin.

cis minima of the triplet state via intersystem crossing since it lies higher than the normal *trans* minima. The *cis*-isomer stability can be explained by an avoided crossing between the lowest singlet or triplet state and the corresponding excited state which has a deep minimum at the *cis*-structure point. Inspecting optimized structures with the extended basis set we find not much influence on the results of our work, something that makes us confident in our observations. It should be noted that a photoinduced transformation of the H_2P molecule has been observed only in excited states but never in a dark state, i.e. in a ground state. Nevertheless, we studied also *cis*, *trans* and *TS* optimized structures in the singlet ground state. The comparison of optimized singlet and triplet structures of H_2P allows to notice that isomer structures seem to be more relaxed in the triplet states. The computed bond length of bridged carbons which connect pyrrole rings in free base porphyrin are significantly larger than in the ground state. Meanwhile, the excitation from the singlet to the triplet state does not affect the N-H and C-H bonds (*Papers* 10 – 11). It is interesting to point out that the energy barrier in the singlet state for *trans*→*cis* transformation as well as the *trans*-*cis* energy difference is smaller than in the excited triplet state. However, the rate of the dark ground state reaction is equal to zero [33].

We also simulated the concerted pathway of isomerisation when the two central

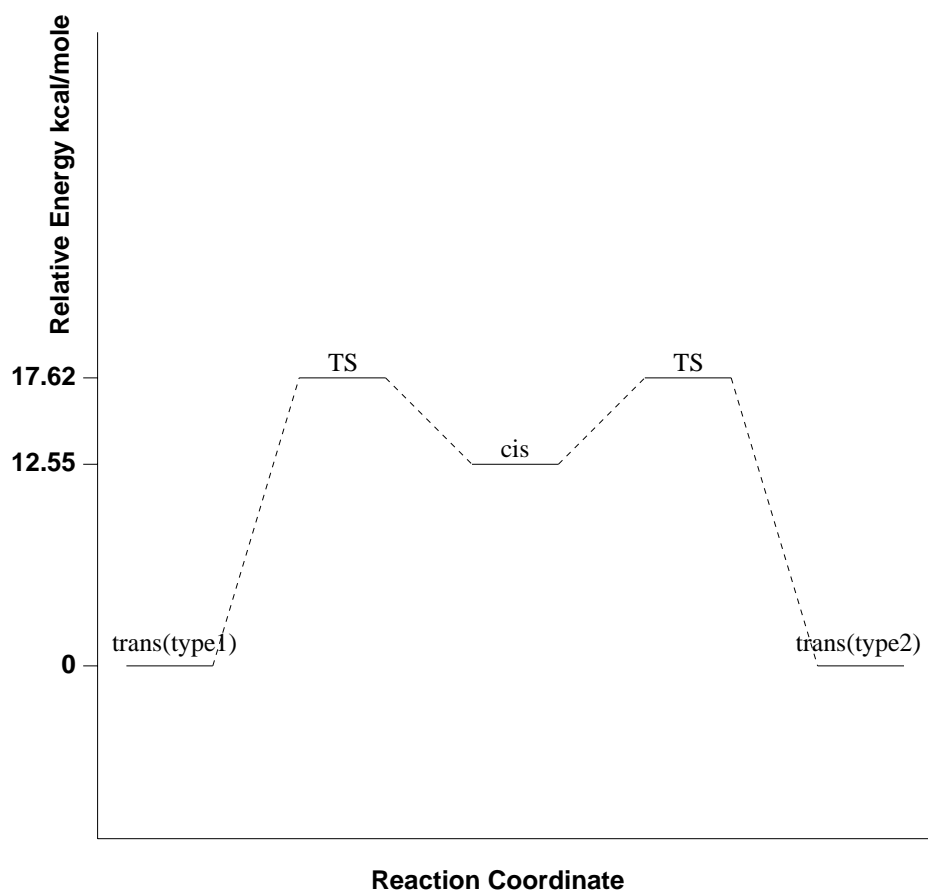


Figure 6.5: Schematic diagram of tautomerisation of free base porphin. Energies for the transition states and *cis* intermediate are relative to *trans* reactant.

protons are shifted simultaneously. Surprisingly, optimization of the transition state gave us the structure which was identical to the transition state of the stepwise isomerisation. The transition state geometry is similar to the *cis*-isomer, but in contrast it does not exceed C_s symmetry point group while the *cis*-isomer has the higher C_{2v} symmetry. As conclusion we found that a stepwise mechanism of isomerisation via an intermediate *cis*-isomer is the most favorable one.

6.3 Phosphorescence

Phosphorescence of free base porphyrin is normally difficult to detect. Moreover, no phosphorescence has been observed from H₂P in solid solvents which are usually used for detection of phosphorescence. To enhance the phosphorescence intensity and permit the determination of triplet state energy, solvents containing high ethyl iodide concentrations have been used. In this case the recorded $T_1 \rightarrow S_0$ emission has been induced by the external heavy atom (EHA) effect. However, the use of solvent mixtures with heavy atom content also affects the radiationless decay. Since the radiative contribution to the triplet state decay in H₂P is very small it is problematic for experimental observation. In order to estimate the real radiative decay in free bases we applied the time dependent density functional theory (TD DFT) method. Among the three spin sublevels of the triplet state only one spin sublevel, T_z in our notation of axes, is radiative. In accord with the ODMR measurements of Ref. [34, 35] the remaining two spin sublevels are non-active in the radiative decay. This picture is well-reproduced in our calculations. The T^y spin sublevel is non-active by symmetry selection rules for spin-orbit coupling and electric dipole operators. The calculated radiative decay rate constant for the out-of-plane T^y spin sublevel is equal to 0.76×10^{-6} and can be considered as negligible. The calculated radiative decay rate of the T^z spin sublevel $k_z = 2.65 \times 10^{-3} \text{ s}^{-1}$ is in a good agreement with the estimated radiative decay rate from an analysis of the microwave-induced fluorescent signal of van Dorp [34]. However, elsewhere reported experimental rate constants [3] for different spin-sublevels by the fluorescent-detected ODMR techniques are much higher than the calculated radiative decay constants. This is because the experimental rate constants refer to the nonradiative decay. Meanwhile, a good quantitative agreement of our results with the k^z value extracted from kinetic analysis of the ODMR signals confirms our interpretation of the observed decay. The ODMR signals of H₂P in *n*-octane were detected via changes in the $S_1 \rightarrow S_0$ fluorescent intensity since the phosphorescence is absent at these conditions. Our results reproduce the fluorescent frequency and radiative constant quite well and prove capability of the quadratic time-dependent density functional theory.

Chapter 7

Overview of the presented projects

Applying *ab initio* methodology we investigated fine and hyperfine structure of a wide class of chemical systems with open shells from diatomic radicals to the excited triplet states of large polycyclic aromatic compounds and porphyrins. In *Paper 1* we considered physical properties of the iodine-containing species, which play an important role in atmosphere chemistry and, in particular, participate in the ozone destruction catalytic cycle in the troposphere. Employing the multi-configuration self-consistent field method (MC SCF) we optimized ground and excited state geometries of the IO, IO⁻ and HOI species. Magnetic properties and spin-forbidden transitions were analyzed. Since iodine oxide, its anion and hypoiodous acid are very unstable species, the detailed knowledge of their electric and magnetic susceptibility, nuclear quadrupole resonances (NQR), NMR chemical shifts, spin-rotation coupling constants, *g*-factors, can be useful for their identification in the laboratory and in the troposphere. For the ground $X^2\Pi$ state of the IO radical we obtained a reasonable agreement with the EPR and optical spectra: the spin-orbit coupling (SOC) constant calculated as a function of internuclear distance was in accordance with rovibronic spectral analysis, as well as the NQR parameters for iodine ¹²⁷I. The predication of the singlet-triplet (*S* – *T*) avoided crossing in IO⁻ anion seems to be interesting. Photodissociation in the S-T absorption bands of hypoiodous acid is the most important prediction of *Paper 1*. The study of these simple molecules with strong spin-orbit coupling was a very instructive starting point in my simulations of spin-selective processes.

In *Paper 2* calculations of electronic spin-spin coupling (SSC) expectation values are presented. This is a very important point in our strategy for the search of spin-selective phosphorescence and ODMR interpretations. The SSC contribution to the zero-field splitting (ZFS) was found to be dominating in the triplet state of

benzene in contrast to the oxygen molecule. The dependence of the ZFS parameters (D_{SO} and D_{SS}), as a function of the internuclear distance r in the ground and in a number of excited states of the oxygen molecule were discussed. We interpreted for the first time a very large ZFS in the $A^3\Sigma_u^+$ state of the first Herzberg band system in the oxygen spectrum. This ZFS ($D = 10 \text{ cm}^{-1}$) is produced mostly by the second-order SOC contribution; it is much higher than the well-known spin splitting in the upper state of the Schumann-Runge system.

We extended the technique developed in the previous project to calculations of ZFS parameters in linear polyacenes in *Paper 3*. The role of electron correlation was discussed in terms of comparison of different approaches (MCSCF, ROHF) with experimental data. It was shown that the zero field splitting in aromatic hydrocarbons arises almost solely from the spin-dipolar interaction. With a correlation between sign and magnitude of the ZFS parameter D the geometry optimization and hence the molecular shape and size was found reliable. Theoretical calculations for the zero-field D parameter were more successful than for the E parameter.

In *Paper 4* we performed CASSCF calculations of triplet-state properties of benzene derivatives. A qualitative agreement with experiment for nuclear quadrupole coupling constants was found for para-dichlorobenzene and aniline molecules. The radiative phosphorescence lifetimes for dihalobenzenes calculated by the quadratic response CASSCF method using different active spaces were also reported. Reasonable estimations of the radiative phosphorescence lifetimes for benzene derivatives (*Paper 4, 7*) and quinoline (*Paper 5*) were obtained.

In order to predict the pure spin-spin coupling term we studied H_2 as benchmark molecule (*Paper 6*) since the second order spin-orbit coupling contribution to the hydrogen $^3\Sigma^+$ states splitting is negligible. It is strange, but so far spin-splittings in the $^3\Sigma_u^+$ and $^3\Sigma_g^+$ states of hydrogen molecule have not been reported. Fine structure measurements and calculations are known only for the $^3\Pi_u$ state where SOC provides a non-zero first-order contribution. The fine structure constant and the hyperfine structure parameters in three low-lying $^3\Sigma^+$ states of molecular hydrogen were calculated by full configuration interaction and MCSCF wave functions (*Paper 6*). Large ZFS ($\simeq 1 \text{ cm}^{-1}$) was predicted for the repulsive $b^3\Sigma_u^+$ state (it can be measured, in principle, by electron scattering experiments). For the bound $a^3\Sigma_g^+$ and $a^3\Sigma_u^+$ states the spin-splitting was found negligible, it is less than 0.01 cm^{-1} , i.e. less than the half line width.

The next challenge for us was to investigate solvent effects on the ZFS constants in the lowest triplet states (*Paper 5* and *Paper 8*). For simulations of the solvent effect the polarizable continuum model was used. A linear correlation between the solvent shift in the ZFS parameter of azaaromatic molecules and the singlet-triplet energy gap was found, which is supported by ODMR measurements of phosphorescence frequency shifts in low-temperature glasses. The intermolecular electrostatic perturbation in solution determines shifts in the ground

and excited state energies; at the same time it influences the magnetic spin-spin coupling. Thus the D parameter decreases with increase of the dielectric constant of the solvent. The non-homogeneous broadening of the phosphorescence line and of the microwave signal in optical detection of magnetic resonance were calculated for ${}^3\pi\pi^*$ states (quinoline, pyridine, pyrimidine) and for the ${}^3n\pi^*$ state of the pyrazine molecule. For the latter species the SOC contribution is much larger and it was studied here in order to check the theory of Lemaistre and Zewail, which explains non-homogeneous broadening of EPR lines on the basis of an account of SOC. An explicit account of the second-order SOC contribution to the splitting of the ${}^3n\pi^*$ state in the pyrazine molecule indicates, however, no appreciable dependence of ZFS on the solvent dielectric constant. This raises some doubts in the theory of Lemaistre and Zewail. Calculations of the solvent effects on the hyperfine tensors in the lowest triplet state of the pyrazine molecule indicated appreciable solvent-induced rotation of the anisotropic hyperfine tensor axes. This leads to non-homogeneous broadening of ENDOR spectra and to spin-lattice relaxation between triplet state sublevels in molecular solids.

The response technique based on the time-dependent density functional theory was employed to the study of singlet-triplet transitions in three-atomic molecules and in free-base porphyrin (*Papers 9 – 10*). Comparative calculations indicate that DFT produces results of similar quality as the explicitly correlated methods (*Paper 9*). The calculated radiative rate constant of free-base porphyrin for the most active spin sublevel is in a good agreement with that estimated from kinetic analysis of microwave-induced fluorescent signals (*Paper 10*). The obtained results indicate that the observed decay of the lowest triplet state of the free-base porphyrin molecule is determined by nonradiative deactivation. The mechanism of photoinduced isomerisation of the free-base porphyrin molecule was finally studied (*Paper 11*). The stepwise pathway of isomerisation via an intermediate *cis* isomer was found preferable.

In total, a number of optical and magnetic properties of molecular triplet states were studied on the ground of MC SCF and TD DFT response theory, including fine and hyperfine structure of the triplet spin sublevels, which usually are measured by EPR, ENDOR and ODMR spectra. Spin-selective phosphorescence rate constants, vibronic line polarization, spin-selective solvent effects and spin-lattice relaxation mechanisms were analyzed in that context.

Thus a complete interpretation of all ZFS parameters and spin-selective rate constants for a number of photoprocesses studied by ODMR spectroscopy has been attempted in this thesis.

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