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Solvent effects on optically detected magnetic resonance in triplet spin labels

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Abstract. We have calculated solvent effects on the zero-field splitting (ZFS) constants induced by electron spin–spin coupling (SSC) in the low-lying triplet states of azaaromatic molecules in solutions using multiconfiguration self-consistent-field wave functions and the polarizable continuum model. The second-order spin–orbit coupling (SOC) contribution to the splitting of the $^3\pi\pi^*$ states is found to be almost negligible, and the calculations therefore provide a good estimate of the ZFS parameters and their solvent dependence based only on the electron spin–spin coupling expectation values. The correlation between the shift in the ZFS and the phosphorescence frequency that has been observed in optically detected magnetic resonance experiments in low-temperature glasses is supported by our direct SSC calculations without taking SOC into account. This makes it possible to distinguish between the two theories that earlier were proposed to explain the inhomogeneous broadening of triplet state spectra, and discard the one that is exclusively based on the SOC-induced mixing of the singlet and triplet states.

Keywords: Zero-field splitting – Solvent effects – Triplet spin label – Optically detected magnetic resonance – Electron spin–spin coupling

1 Introduction

Electron paramagnetic resonance (EPR) spectroscopy has found numerous applications to biomedical and biochemical problems as a sensitive tool for the detection of free radicals and other paramagnetic species [1, 2]. This applies to the natural occurrence of free-radical intermediates in metabolic processes, to the observation of stable transition-metal ions and to the analysis of

paramagnetic probes introduced into biosystems. The success of the spin-probe technique is determined by the ability of the environment to influence the EPR spectrum of the probe. It is therefore important to understand how the probe–substrate interaction can modify the parameters of the spin Hamiltonian. A number of ab initio calculations have been carried out in order to simulate the effects on the EPR parameters (g -factor and hyperfine constants) arising from the interaction between the unpaired spin of a free radical and a diamagnetic environment, see for example Refs. [3, 4, 5]. In this paper we are going to investigate the solvent dependence of the parameters of the spin Hamiltonian for triplet excited-state spin labels.

Triplet spin labels are often used in a form of nitroxide biradicals [1] and also as natural constituents of biopolymers that contain chromophores which can be excited to the triplet state [6, 7, 8]. von Schutz et al. [6] observed optical detection of magnetic resonance (ODMR) for tryptophan phosphorescence in horse liver alcohol dehydrogenase and in hen egg-white lysozyme. The ODMR technique was used by Alfredson and Maki [7, 8] to investigate the effects of complex formation between DNAs and several species of *Streptomyces* antibiotics. These species contain two quinoxaline [7] and two quinoline moieties [8] that are attached by peptide linkages to the depsipeptide ring through a pair of serine residues. Among other natural products of *Streptomyces* the quinomycins (echinomycin and its bisquinolone analogues) were studied. Complexation with DNAs was found to influence the triplet state zero-field splitting (ZFS) of the phosphorescent quinoxaline and quinoline residues [7, 8]. It has been shown that the ODMR signals of organic molecules hosted as a dilute impurity in glassy or polycrystalline guests at low temperatures are strongly inhomogeneously broadened [6, 9, 10] as are the optical spectral lines [11]. The relative magnitude of the line broadening, $\Delta\nu/\nu$, is of the same order of magnitude for both types of spectra [9, 12].

In the excited triplet states of polyatomic molecules the ZFS operator H_S (the effective spin Hamiltonian) is given by [24]

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

where \mathbf{S} and S_x are the total spin operator and the spin projection operator, respectively; D and E are the measurable ZFS parameters. The ZFS parameter D determines the largest energy gap between spin sublevels and the most important ODMR signals $D \pm E$, since they usually induce the strongest modulation of the optical phosphorescence band signals.

When plotting the ZFS parameter D against the solvent shift monitored by narrow-band optical detection through the inhomogeneously broadened phosphorescence band, van Egmont et al. [9] found that the solvent-induced ΔE_{ST} shift of the optical line is linearly related to a shift in the microwave ODMR signal. Similar linear dependencies have also been found in many ODMR studies of aromatic molecules and amino acids frozen in glasses, biopolymers and other disordered environments at low temperatures [6, 7, 8, 10, 12, 13, 14, 15]. The first model employed to explain these results [9] was based on a solvent-induced mixing of the molecular triplet states with different ZFS patterns by an external electric field due to the environment (similar to the linear Stark effect on ODMR [16]). The fluctuation of the local field throughout the ensemble of the local field leads to inhomogeneous broadenings of the microwave transitions in the guest triplet [6, 9].

Later, two other models which take into account spin-orbit coupling (SOC) of the singlet S and triplet T states in order to explain the observed correlation between the optical frequency, ΔE_{ST} and the ODMR shift ΔD were introduced [13, 14]. The SOC matrix element in these models was treated as an empirical parameter which was fitted to the observed inhomogeneous broadening and has never been calculated directly from any reliable wave functions.

The first theoretical attempt to interpret the solvent effect on the ZFS parameters was presented by direct calculations of the lowest ${}^3n\pi^*$ state in the pyrazine molecule using an unrestricted Hartree-Fock wave function in the CNDO/2 approximation [17]. The influence of intermolecular interaction on the ODMR spectra in mixed crystals was studied by a model in which two water molecules were coordinated to the nitrogen atoms of the pyrazine molecule. It was predicted that the spin-spin coupling (SSC) contribution was reduced from $D = 0.556 \text{ cm}^{-1}$ to $D = 0.537 \text{ cm}^{-1}$ upon complexation with water. The reason for the decrease of the D value was connected with a small spin density penetration from the triplet pyrazine to the water molecules. The distance between the two spins thus increases and consequently the SSC parameter decreases. This result was in qualitative agreement with the experimental data of Refs. [18, 19], where it was found that the ZFS parameter for the pyrazine triplet state changes during a transition from one host crystal matrix to another, the ZFS parameters becoming smaller as the proton-donor nature of the solvent was increased.

In the present paper the spin splitting is calculated for azabenzene and quinoline molecules taking into account both SSC and SOC perturbations using ab initio

methods. For the low-lying ${}^3\pi\pi^*$ states (the lowest triplet state for all molecules studied except pyrazine and pyrimidine) only SSC contributions are important since the SOC contribution occurs only at second order in perturbation theory; it is here found to be completely negligible for the ${}^3\pi\pi^*$ states. The solvent effects for the ZFS of the lowest triplet state, calculated using the polarizable continuum model (PCM), has therefore been studied retaining only the SSC expectation value.

2 Method of calculations

The multiconfigurational self-consistent field (MCSCF)-PCM method [20, 21, 22, 23] is here used to calculate the SSC expectation value and the fine-structure calculations of the triplet states of azaromatic molecules in different solvents. The SOC contribution to the ZFS constants was calculated only for isolated molecules through a direct diagonalization of the configuration interaction (CI) + SOC matrix.

Since our implementation of this model at the MCSCF level in the Dalton program [21] has already been described [22, 23], we here restrict ourselves to an outline of the characteristic features of our approach. Complete active space (CAS) wave functions were used to compute the electronic wave functions in the adiabatic approximation [20]. Relativistic corrections arising from the interaction between the spin and orbital angular momenta of the electrons were added to the electronic nonrelativistic Hamiltonian. The most important relativistic terms are the electronic SOC

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

and SSC

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

terms.

Both operators will, in general, contribute to the spin splitting in triplet states and higher multiplets.

The spin-splitting parameters D and E are determined by the electron SCC term to first order in perturbation theory and by SOC to second order [24]. The energy shifts, W , of the orbitally nondegenerate state of multiplicity $2S + 1$ due to the perturbations H_{ss} and H_{so} can be obtained by diagonalizing

$$|\mathbf{H} - W\mathbf{I}| = 0, \quad (4)$$

where \mathbf{H} is the matrix defined by

$$\mathbf{H} = \langle \Psi | H_{ss} + H_{so} R_0 H_{so} | \Psi \rangle \quad (5)$$

within the reference manifold

$$| \Psi_0 \rangle = (| \Psi_0^{-S} \rangle, \dots, | \Psi_0^S \rangle) \quad (6)$$

and where R_0 is the reduced resolvent operator [20, 22]. A conventional sum-over-state expansion of the resolvent gives for the case of a triplet reference state, sums over singlet, triplet and quintet states

$$H_{ij} = \langle {}^{2S+1}\Psi_0^i | H_{ss} | {}^{2S+1}\Psi_0^j \rangle - \sum_{n,\lambda} \sum_k \frac{\langle {}^{2S+1}\Psi_0^i | H_{so} | {}^\lambda\Psi_n^k \rangle \langle {}^\lambda\Psi_n^k | H_{so} | {}^{2S+1}\Psi_0^j \rangle}{{}^\lambda E_n - {}^{2S+1} E_0}. \quad (7)$$

In these expressions ${}^\lambda\Psi_n^k$ is the zeroth-order wave function, which is an eigenfunction of the nonrelativistic Schrödinger equation $H_0 {}^\lambda\Psi_n^k = {}^\lambda E_n {}^\lambda\Psi_n^k$. $\lambda = 2S + 1$ is the multiplicity of the state and S is the total spin quantum number

$$S^2 {}^\lambda\Psi_n^k = S(S + 1) {}^\lambda\Psi_n^k, \quad (8)$$

$$S_z {}^\lambda\Psi_n^k = k {}^\lambda\Psi_n^k. \quad (9)$$

The indices $i, j, k = M_S$ determine the projection of the total spin. The SOC contribution to the ZFS of the lowest $^3\Psi_1$ triplet state (Eq. 7) usually includes only a few of the nearest singlet, triplet and quintet excited states $\lambda = 0, 1, 2$ [25, 26]. In most cases, only the singlet and the triplet state perturbations are important. A proper balance of these states is, however, crucial for the SOC contribution to the ZFS [27] and accounting only for the singlet states ($\lambda = 1$) as perturbations in Eq. (7) [24] gives qualitatively incorrect results.

The matrix defined in Eq. (7) can be diagonalized by a principal-axis transformation. For the molecules considered in this work, the symmetry axes of the molecular frame coincide with the magnetic axes, and the matrix Eq. (7) is thus diagonal. The eigenfunctions of the $|SM\rangle$ basis in Eqs. (8) and (9) can be related to the ZFS eigenfunctions by [20]

$$|t^x\rangle = \frac{1}{\sqrt{2}}(|1, -1\rangle - |1, 1\rangle), \quad (10)$$

$$|t^y\rangle = \frac{i}{\sqrt{2}}(|1, -1\rangle + |1, 1\rangle), \quad (11)$$

and

$$|t^z\rangle = |1, 0\rangle. \quad (12)$$

The t^k functions correspond to the zero projections of the total spin on the three molecular axes. The quintet states together with the singlet and triplet states, (Eqs. 10, 11, 12), contribute to the ZFS parameters through the SOC operator. The connection between the ZFS eigenfunctions of the quintet state ($S = 2$) and the eigenfunctions of the $|SM\rangle$ basis is determined by [25, 28]

$$|t^{xz}\rangle = \frac{1}{\sqrt{2}}(|2, -1\rangle - |2, 1\rangle), \quad (13)$$

$$|t^{yz}\rangle = \frac{i}{\sqrt{2}}(|2, -1\rangle + |2, 1\rangle), \quad (14)$$

$$|t^{zz}\rangle = |2, 0\rangle, \quad (15)$$

$$|t^{xx-yy}\rangle = \frac{1}{\sqrt{2}}(|2, 2\rangle + |2, -2\rangle), \quad (16)$$

$$|t^{xy}\rangle = \frac{i}{\sqrt{2}}(|2, -2\rangle - |2, 2\rangle). \quad (17)$$

The SSC and SOC interactions in the excited triplet states determine the ZFS tensor D_{ij} , which is widely used to analyze EPR spectra. It defines the effective spin Hamiltonian given by [24]

$$H_S = \sum_{mn} D_{m,n} S_m S_n, \quad (18)$$

where S_m is the m th Cartesian component of the total electron spin operator. The effective spin Hamiltonian can in a coordinate system x, y, z with the ZFS eigenfunctions (Eqs. 10, 11, 12) be written as

$$H_S = -XS_x^2 - YS_y^2 - ZS_z^2, \quad (19)$$

where $D_{x,x} = -X$, $D_{y,y} = -Y$, and $D_{z,z} = -Z$. Since the $D_{m,n}$ is a traceless and symmetric tensor ($X + Y + Z = 0$), it is diagonal in its principal axis system [24] and can be described by only two independent parameters, D and E , Eq. (1). In Eq. (1) the choice of axes is such that $|t^z\rangle$ is the spin sublevel with the largest splitting, i.e., ($|Z| > |X|$, $|Z| > |Y|$), the z -axis being the main axis of the ZFS tensor:

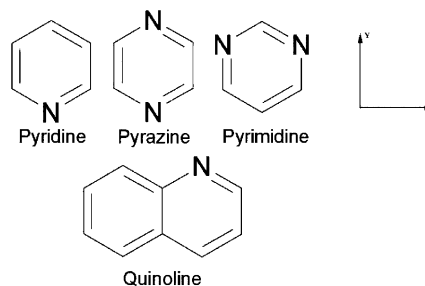


Fig. 1. Molecules and choice of axes

$$D = -\frac{3}{2}Z, \quad (20)$$

$$E = \frac{1}{2}(Y - X). \quad (21)$$

This ZFS tensor has been widely used for triplet states of polyatomic molecules studied by the EPR and ODMR methods in solid solvents and crystals. We note that the choice of z -axis, which determines the ZFS parameters D and E , depends on the molecule and on the symmetry of the triplet state. For all the molecules studied (Fig. 1), our choice of coordinate system can give rise to different main axes for the ZFS tensor of the triplet states. In order to avoid confusion we present the ZFS tensor for the isolated molecules using both Eqs. (1) and (19). Since the choice of the main axis for the ZFS tensor for the lowest triplet state of a given molecule is fixed (Fig. 1) we present the SSC contributions to the ZFS of the isolated molecules in the form of Eq. (19) in Table 1, which defines the main axis. Taking the SOC contribution to the ZFS parameters into account does not change this definition. All other calculated ZFS parameters are presented in Tables 2, 3, 4 and 5 in the standard form of Eq. (1), including those for the solvated molecules.

It has been demonstrated [22] that the ZFS tensor can be obtained by contracting two-electron field gradient integrals with a quintet two-electron density:

$$D_{kl} = \sum_{tuvw} d_{kl,tuvw} q_{tuvw}, \quad (22)$$

where $d_{kl,tuvw}$ is the integral over partially occupied orbitals t, u, v, w of the Cartesian k, l component of the two-electron field gradient operator and q_{tuvw} is a two-electron density matrix corresponding to the zeroth component of the quintet combination of two triplet operators. Calculations of this matrix in terms of molecular orbital and CI expansions are given elsewhere [24, 27]. We refer to Ref. [22] for other details.

In the PCM approach – which is based on the pioneering contributions of Tomasi [29] – the solute molecule is assumed to be placed in a cavity embedded in a polarizable, homogeneous dielectric medium with permittivity ϵ . The cavity is assumed to be shaped after the molecular structure, excluding volumes where solvent molecules cannot penetrate. In order to solve the appropriate Poisson equation with the related boundary conditions in the PCM-integral equation formalism (IEF) approach we use here [30, 31, 32] the cavity is discretized into small, finite elements, and the integrations over the volume and surface of the cavity are replaced by a summation over the finite number of surface elements:

Table 1. Spin-spin coupling contribution to zero-field splitting (ZFS) energy eigenvalues (cm^{-1}) in the gas phase. The definition of axes is given in Fig. 1

Molecule	X	Y	Z	D	E
Pyridine	0.1117	-0.0750	-0.0367	$D = -\frac{3}{2}X = -0.1676$	$E = \frac{1}{2}(Y - Z) = -0.0191$
Pyrazine	-0.3020	0.1538	0.1481	$D = -\frac{3}{2}X = 0.4530$	$E = \frac{1}{2}(Y - Z) = 0.0028$
Pyrimidine	0.0221	-0.1211	0.0989	$D = -\frac{3}{2}Y = 0.1817$	$E = \frac{1}{2}(Z - X) = 0.0383$
Quinoline	0.0530	0.0126	-0.0657	$D = -\frac{3}{2}Z = 0.0986$	$E = \frac{1}{2}(Y - X) = -0.0201$

Table 2. ZFS parameters for the lowest triplet (3B_2) state of pyridine

ZFS parameter	No solvent	Benzene	Aniline	Ethanol	Nitromethane	Water
Dielectric constant	1	2.25	6.89	24.55	38.20	78.39
Triple-zeta Dunning basis set						
D_{ssc} (cm^{-1})	-0.1676		-0.1636	-0.1626	-0.1624	-0.1623
E_{ssc} (cm^{-1})	-0.0191		-0.0179	-0.0175	-0.0174	-0.0174
D_{soc} (cm^{-1})	0.0050					
Double-zeta polarized Dunning basis set						
D_{ssc} (cm^{-1})	-0.1555	-0.1527	-0.1504	-0.1493	-0.1491	-0.1490
E_{ssc} (cm^{-1})	-0.0130	-0.126	-0.0117	-0.0112	-0.0112	-0.0111
D_{soc} (cm^{-1})	0.0090					

Table 3. ZFS parameters for the lowest triplet (${}^3B_{1u}$) state of pyrazine using the triple-zeta Dunning basis set

ZFS parameter	No solvent	Benzene	p -Dichlorobenzene	Ethanol	Nitromethane	Water
Dielectric constant	1	2.25	2.40 ^a 2.86 ^a	24.55	38.20	78.39
D_{ssc} (cm^{-1})	0.4530	0.4477	0.4474 0.4465	0.4418	0.4416	0.4413
E_{ssc} (cm^{-1})	0.0028	0.0040	0.0041 0.0043	0.0055	0.0055	0.0056
D_{soc} (cm^{-1})	-0.1245	-0.1275	-0.1275 ^b -0.1275 ^b		-0.1280	-0.1271
D_{tot} (cm^{-1})	0.3285	0.3202	0.3199 0.3190		0.3136	0.3142
D_{exp} (cm^{-1})		0.3450 ^d	No data 0.3392 ^c			
E_{exp} (cm^{-1})		-0.0070 ^d	No data -0.0072 ^c			

^a Two dielectric constants correspond to different temperatures; Ref. [43]

^b The same spin-orbit coupling effect as in benzene is assumed

^c Ref. [42]. Experimental temperature (4.2 K) is lower than that which is used for dielectric constant measurement; the last value $\epsilon = 2.86$ is more appropriate

^d Refs. [18,19]

Table 4. ZFS parameters for the lowest triplet (3B_1) state of pyrimidine using the triple-zeta Dunning basis set

ZFS parameter	No solvent	Cyclohexane	Dioxane	Benzene	Ethanol	Water
Dielectric constant	1	2.02	2.20	2.25	24.55	78.39
D_{ssc} [cm^{-1}]	0.1817	0.1767		0.1761	0.1699	0.1694
E_{ssc} [cm^{-1}]	0.0383	0.0371		0.0369	0.0354	0.0353
D_{exp}^a [cm^{-1}]		± 0.1653	± 0.1605	± 0.1726		
E_{exp} [cm^{-1}]		∓ 0.0135	∓ 0.0132	∓ 0.0154		
D_{soc} [cm^{-1}]	0.0120					

^aRef. [18]

Table 5. ZFS parameters for the lowest triplet (A'') state of quinoline using the triple-zeta Dunning basis set

ZFS parameter	No solvent	Benzene	Aniline	Ethanol	Nitromethane	Water
Dielectric constant	1	2.25	6.89	24.55	38.20	78.39
D_{ssc} [cm^{-1}]	0.0986	0.0979	0.0973	0.0970	0.0970	0.0969
D_{soc} [cm^{-1}]	0.0010					0.0011
E_{ssc} [cm^{-1}]	-0.0201	-0.0200	-0.0199	-0.0199	-0.0199	-0.0199
D_{exp}^a [cm^{-1}]						0.1040
E_{exp} [cm^{-1}]						0.0170

^aRef. [8]

$$V_{\rho\sigma}(\mathbf{x}) = \sum_k^K \frac{q_k(s_k)}{|\mathbf{x} - s_k|} . \quad (23)$$

Here the so-called apparent surface charges, $q_k(s_k)$, are determined by the surface charge distribution $\sigma(s_k)$, and the area of the finite surface element a_k , through

$$q_k(s_k) = \sigma(s_k)a_k . \quad (24)$$

In these equations, \mathbf{x} is an arbitrary position vector and s_k is the vector indicating the center of surface element k . We refer the interested reader to Refs. [23,33] for further details.

The solvated molecule is assumed to be described by a free-energy functional, $\mathcal{G}(\Psi)$, that is a function of the electronic wave function of the solute. This solvent energy functional depends on

the electronic parameters of the solute as well as on the mutual polarization of the solute and the solvent, described in terms of an effective operator \hat{G} defined in such a manner that

$$\mathcal{G}(\Psi) = \langle \Psi | \hat{G} | \Psi \rangle = \left\langle \Psi \left| \hat{H}_0 + \frac{1}{2} \hat{V}_{\rho\sigma} \right| \Psi \right\rangle . \quad (25)$$

In this equation \hat{H}_0 is the conventional electronic Hamiltonian of our isolated and unperturbed molecule, and $\hat{V}_{\rho\sigma}$ describes the interaction between the solvent and the solute.

The PCM-IEF representation of the solute-solvent interaction [23] gives three electronic contributions to $\hat{V}_{\rho\sigma}$:

$$\hat{V}_{\rho\sigma}(\tilde{0}) = \frac{1}{2} (\hat{J} + \hat{Y}) + \hat{X}(\tilde{0}) . \quad (26)$$

\hat{J} and \hat{Y} here represent the interaction of the solute's electronic structure with the nuclear apparent surface charges and the interaction of the solute's nuclei with the apparent surface charges generated by the electronic structure of the solute, respectively. $\hat{X}(0)$ represents the interaction of the solute's electron density with the apparent charges generated by the electron density of the solute, and is the cause of the nonlinearity of the free-energy functional (Eq. 25). In addition to these three terms, there is also a term that only depends on the nuclear framework, arising from the interaction of the nuclear charges with the apparent surface charges generated by the nuclear framework. This term is, however, independent of the electronic structure of the molecule.

We will not elaborate on this formalism for the case of an MCSCF wave function any further here, referring the interested reader instead to the paper describing the implementation we use in the DALTON program [23]. Here we only note that since the ZFS tensor can be obtained from the unperturbed two-electron density (Eq. 22), no changes need to be introduced for evaluating the ZFS tensor of a solvated molecule, as this is uniquely determined from the optimized density of the solvated molecule.

The cavities we used in our calculation were built from interlocking spheres centered on each atom of the molecule, using conventional radii for the various elements, see, for instance, Ref. [23]. The geometry was optimized using the first-order geometry-optimization scheme implemented in the DALTON program [34] and extended to include the PCM contributions [35]. The full point-group symmetry was used in the construction of the molecular cavity as described elsewhere [36]. In the SSC and SOC calculations the basis set dependence of the results was tested by employing the double-zeta polarized (DZP) and triple zeta (TZ) basis sets [37] with different numbers of contracted functions. Since these basis sets give almost identical D values, we mainly present results obtained using the TZ basis set.

The geometries of the singlet ground state and of the first excited triplet state were optimized for molecules in a vacuum and in solvents by the MCSCF-PCM method [35]. The singlet-triplet energy gap (ΔE_{ST}) was obtained at these optimized geometries. In order to analyze the solvent effect on the ODMR spectral shifts, the ZFS constants were also calculated in different solvents using the vacuum-optimized geometry of the singlet ground state. The singlet-triplet energy gaps obtained by the PCM method are in this case denoted by ΔE_{ST}^0 . The shift in the ZFS parameter, D , was calculated for each of these two sets of optimized geometries and is plotted versus ΔE_{ST} in Figs. 2 and 3, respectively.

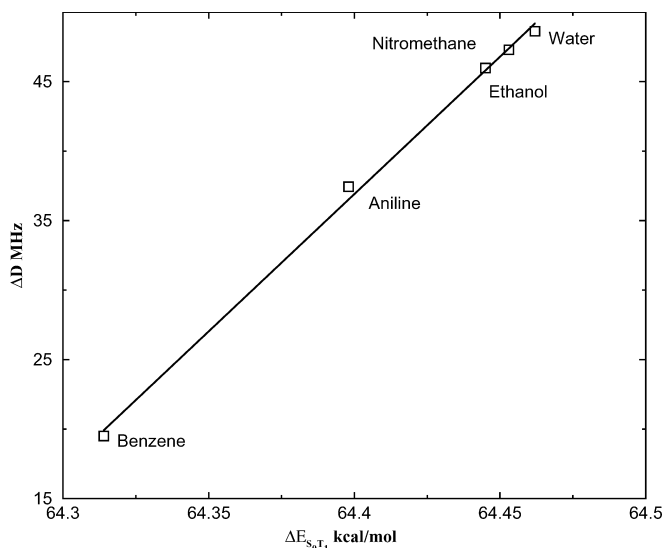


Fig. 2. Dependence of the ΔD parameter on the $\Delta E_{S_0, T_1}$ energy gap for the quinoline molecule in different solvents. The geometries of the singlet S_0 and triplet T_1 states are optimized in each solvent. Correlation coefficient $R = 0.9988$

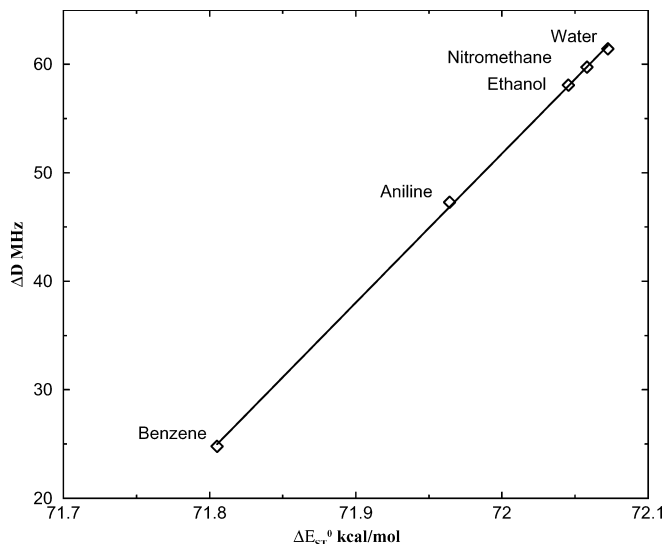


Fig. 3. Dependence of the ΔD parameter on the $\Delta E_{S_T^0}$ energy gap for the quinoline molecule in different solvents. All calculations were done at the geometry of the singlet S_0 state optimized in vacuum. Correlation coefficient $R = 0.9998$

The C_{2v} representation of the point group symmetry was employed for pyridine and pyrimidine molecules. In C_{2v} symmetry, the Hartree-Fock orbital configuration for this molecules is $11a_1, 7b_2, 2b_1, 1a_2$. We kept the $10a_1$ and $7b_2$ orbitals inactive in pyridine and $10a_1$ and $6b_2$ in pyrimidine. The CAS for all basis sets includes $1a_1, 4b_1, 2a_2$ with eight active electrons for pyridine and $2a_1, 2b_2, 4b_1, 2a_2$ with ten active electrons for the pyrimidine molecule. a_1 and b_2 are here σ orbitals and b_1 and a_2 are π orbitals. For the pyrazine molecule, which has D_{2h} symmetry, two occupied σ and six π orbitals with ten active electrons were included in the CAS. The C_s point group and an active space including 12 electrons in ten π and two σ orbitals was employed for the quinoline molecule. The SSC contribution to the ZFS parameters was calculated with a local version of the DALTON program [21]. The spin-orbit contribution to the splitting of the lowest triplet state of the different molecules was calculated using Dunning's cc-pVTZ basis set [38] by diagonalizing the spin-orbit Hamiltonian using MOLCAS [39], where the SOC integrals were estimated using the atomic mean-field approximation [40].

3 Results

The ZFS constants D and E of the spin Hamiltonian (Eq. 1) can give important information about the symmetry and electronic structure of the triplet state. With a proper theoretical analysis of the ZFS parameters one can also get information about intermolecular interactions and even about the structure of a solvent or other environments in which the triplet probe is located. Ab initio calculations using the MCSCF method for the ZFS parameters of isolated molecules and for solvents present a good example of such a theoretical analysis. The ZFS parameters of the pyridine, pyrazine, pyrimidine and quinoline molecules excited to the first triplet state are presented in Tables 2, 3, 4, and 5 as calculated in different solvents using the PCM method. In Table 1, the ZFS parameters determined by the SSC expectation values in the form of the spin Hamiltonian (Eq. 19) are presented with respect to the axes given in Fig. 1. We

first consider the ZFS of the isolated molecules in vacuum (Table 1).

The second-order SOC contribution to the splitting of the ${}^3\pi\pi^*$ states is almost negligible, and the calculations therefore provide a good estimate for the ZFS even when only the electron SSC values are considered. The results do not strongly depend on the basis set choice. This is illustrated by the calculations on pyridine (Table 2). Similar results are obtained for pyridine in the basis set of Schäfer et al. [49]: $D_{\text{SSC}} = -0.1582 \text{ cm}^{-1}$; $D_{\text{SOC}} = 0.005 \text{ cm}^{-1}$. The energy gap between the lowest ${}^3\pi\pi^*$ state and the second triplet, ${}^3n\pi^*$, state is rather small. In perturbation theory the SOC contribution to ZFS occurs in the second order and seems to be strongly dependent on the small $\Delta E({}^3n\pi^* - {}^3\pi\pi^*)$ value since the SOC mixing between the ${}^3\pi\pi^*$ and ${}^3n\pi^*$ states is rather large [24, 27]. In the basis set of Schäfer et al. we get $\Delta E({}^3n\pi^* - {}^3\pi\pi^*) = 0.4 \text{ eV}$ and a SOC contribution that is small (0.005 cm^{-1}), while for the DZP basis the gap is 0.23 eV and the SOC contribution is larger (0.009 cm^{-1}). SOC mixing with the close-lying singlet ${}^1n\pi^*$ state is also very important for the T_1 state spin splitting [27]. Special precaution has to be taken in the case of the cc-pVTZ basis set; we obtain the T_1 state in the pyridine molecule as having ${}^3n\pi^*$ nature in this basis set with a relatively large ZFS parameter, $D = 0.0675 \text{ cm}^{-1}$.

The ZFS parameter is much larger for the ${}^3n\pi^*$ states since it is determined by one-center SSC and SOC integrals ($D \simeq 1 \text{ cm}^{-1}$), while for the ${}^3\pi\pi^*$ states only the two-center integrals are important ($D \simeq 0.1 \text{ cm}^{-1}$) [27]. The SOC contribution to ZFS is about 30% for pyrazine (Table 3), which is quite natural since the T_1 state has ${}^3n\pi^*$ character (${}^3B_{1u}$ symmetry).

Our MCSCF calculation predicts the lowest triplet state in the pyrimidine molecule to be of ${}^3n\pi^*$ type (3B_1) in agreement with experimental data [18, 24]. Two nitrogen atoms in meta positions produce a rather small ZFS for this ${}^3n\pi^*$ state, with the t^y sublevel being the lowest one (y -axis bisects the N–N line). The SOC contribution is also unusually small (Table 5). All these predictions reproduce the experimental ZFS parameters [18, 44]. In spite of the clearly established ${}^3n\pi^*$ nature of the lowest triplet state in pyrimidine its D value is more similar to that of the ${}^3\pi\pi^*$ states.

For the choice of axes given in Fig. 1, the lowest triplet state in the pyrazine molecule (${}^3B_{1u}$) is the ${}^3n\pi^*$ state. The SSC-induced D value can be determined by the x -axis $D = -3/2X = 0.453 \text{ cm}^{-1}$, in good agreement with semiempirical intermediate neglect of differential overlap for spectroscopy (INDO/S) CI calculations (0.462 cm^{-1}) [17, 27]. The SOC contribution to the D value in the ${}^3n\pi^*$ state of the pyrazine molecule is also large (-0.124 cm^{-1}) and agrees qualitatively with earlier INDO/S CI data (-0.083 cm^{-1}) [17, 27].

The total ZFS parameter D for the pyrazine molecule is equal to 0.329 cm^{-1} , which is in good agreement with experimental measurements ($0.345 - 0.309 \text{ cm}^{-1}$) in different hosts with different techniques [18, 19, 41, 42]. Our designation of the molecular axes differs from that in Ref. [18, 19, 41, 42] but the main axis of the ZFS tensor (Eq. 1) being perpendicular to the N–N direction (Fig. 1), agrees with the results of Refs. [19, 41, 42]. We

support previous findings [19, 27] that the negative sign of D (as reported in Ref. [41]) is wrong. The positive sign of D is evident from studies of the optical Zeeman effect [19] and from INDO CI calculations [27]. The choice of D and E parameters given by Burland and Schmidt [18] is in disagreement with the general convention that $|D| > |E|$; thus we have transformed their values to $D = 0.345 \text{ cm}^{-1}$ and $E = -0.00705 \text{ cm}^{-1}$ for pyrazine in a benzene host. The $|E|$ value is much smaller than $|D|$ (Table 3) in agreement with our results, but the sign of the E value is opposite. The SSC contribution to E is definitely positive. In our restricted active space State Interaction calculations, SOC does not produce any appreciable E value and we note that the assignment of the axes for the determination of the E parameter may therefore be wrong in previous ODMR studies since it is difficult to assign what is the upper spin sub-level between two close-lying spin states t^y or t^z . The D parameter decreases in more polar and more polarizable host crystals ($D = 0.3392 \text{ cm}^{-1}$ in *p*-dichlorobenzene [42] in comparison with 0.345 cm^{-1} benzene), but the $|E|$ value increases (0.00719 cm^{-1} in *p*-dichlorobenzene [42] in comparison with 0.00705 cm^{-1} in benzene). This trend is reproduced in our PCM calculations (Table 3). We calculated solvent effects in *p*-dichlorobenzene at two different temperatures (322 and 293 K for which the dielectric constants are measured as 2.4 and 2.86, respectively [43]). The dielectric constant increases with decreasing temperature and we should expect a slightly lower value of D in *p*-dichlorobenzene under experimental conditions (4.2 K) [42]. In this context the predicted D -shift from benzene to *p*-dichlorobenzene (0.0012 cm^{-1}) and the experimentally observed one (0.0058 cm^{-1}) [18, 42] are not at variance. The SOC contribution to the ZFS for the pyrazine molecule in different solvents was found to be almost independent of the dielectric constant (Table 3).

The pyrazine molecule differs from those that have been studied in biopolymers (quinoline [8], quinoxaline [7], tryptophan [6]), all of which have ${}^3\pi\pi^*$ as the lowest excited state. Our calculations for the quinoline molecule indicates that the SOC-induced contribution to the ZFS parameter constitutes less than 1% of the D value (Table 5). In the present work we therefore ignore the influence of SOC on the ZFS parameters when we study solvent effects on the ODMR spectra.

The SOC-induced mixing of the ground singlet 1S_0 state and the first excited triplet ${}^3\pi\pi^*$ state is forbidden in the isolated azabenzene molecule (only small two-center SOC integrals contribute), but is allowed when the molecule interacts with a solvent [25]. This mixing is induced by exchange interactions and can be explained as a result of the violation of the σ – π separation in the molecular complex in the presence of the solvent [45]. Our preliminary estimates indicate that these SOC contributions to the ODMR solvent shift would be negligible.

Quite appreciable shifts in the ODMR transitions $D \pm E$ versus the solvent dielectric constant were obtained by SSC calculations with the PCM method for all the triplet excited molecules studied (Tables 2, 3, 4, 5). Solvent effects on the ZFS parameters in the low-lying triplet states of azaaromatic molecules are found to be

linearly dependent on solvent-induced shifts in phosphorescence frequency in agreement with experimental data on inhomogeneous broadening [8, 9, 10]. Such a correlation is shown in Fig. 4 for the pyrimidine molecule, which also illustrates the linear dependence of ΔD versus ΔE_{ST} . At the same time the D -shift in different host matrices with small dielectric constants seems to contradict this trend (benzene seems to be an exception in Table 4). One has to note that pyrimidine as a guest in benzene and dioxane host crystals has been studied at different temperatures [18, 44]. The benzene host crystal has C_i site symmetry [18] and the guest might be expected to enter substitutionally into the host lattice in three different ways. Thus the D -shift in different crystals must be determined not only by the dielectric constant of the host, but also by other factors, like crystallization conditions. The ZFS shift plotted against the solvent shift monitored by narrow-band optical detection through the inhomogeneously broadened phosphorescence band in the same host crystal is more informative for the study of the dependence of the microwave ODMR signal on solvent polarizability.

For the quinoline molecule we get a shift in the D value in water of $0.0016 \text{ cm}^{-1} = 48 \text{ MHz}$. This is in good agreement with experimental observations of the typical ODMR solvent shift, which is of the order of 30–50 MHz for similar molecules [8, 15]. The calculated values for the ZFS parameters of quinoline coincide fairly well with the spectral measurements. The total D value for the free quinoline molecule obtained taking into account the small SOC correction (Table 5) is 0.0996 cm^{-1} ; this can be compared with 0.1028 cm^{-1} measured for quinoline in a durene host crystal [46]. The agreement between the calculated and observed E values of -0.020 cm^{-1} (Table 5) and -0.017 cm^{-1} [46], respectively, is also good.

One has to note that the scale of the shift in the D value for the ${}^3n\pi^*$ state (pyrimidine, Fig. 4) is much higher (150–350 MHz in different solvents) than in

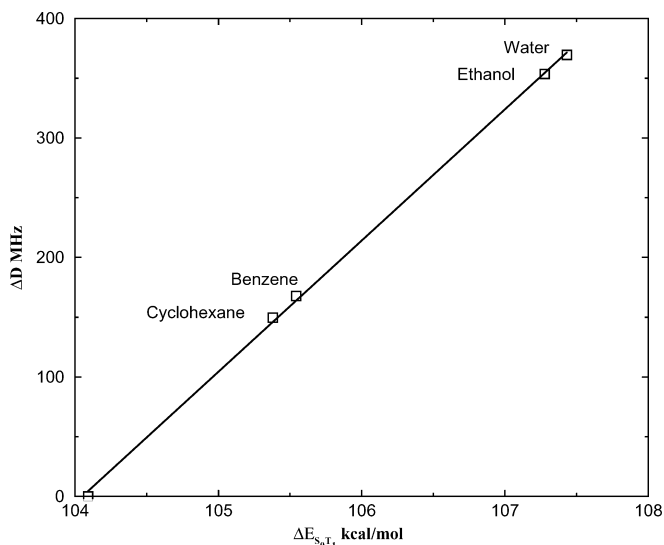


Fig. 4. Dependence of the ΔD parameter on the ΔE_{ST} energy gap for the pyrimidine molecule in different solvents. All calculations were done at the geometry of the singlet S_0 state optimized in vacuum. Correlation coefficient $R = 0.9997$

quinoline-type (${}^3\pi\pi^*$) molecules (cfs. Figs. 3, 4). The scale of the experimental D -shifts (Table 4) supports this qualitative conclusion.

Finally, the linear correlation between the solvent shift in the ZFS parameter and in the singlet–triplet energy gap (ΔE_{ST}) was reproduced in our MCSCF-PCM calculations for the quinoline molecule using the optimized singlet and triplet state geometries in each solvent (Fig. 2) and also using the fixed ground-state geometry optimized in a vacuum for the ZFS parameters calculated in different solvents (Fig. 3). In the latter case we find an even better correlation. This means that geometry relaxation in the solvent does not play any significant role in the origin of the ZFS shift. Similar correlations were obtained for the other molecules. The energy gap ΔE_{ST} determines the phosphorescence frequency and our linear correlation between solvent shifts of the ODMR and optical lines is in good agreement with experimental findings [8, 9, 12, 15].

4 Discussion

In the field of spectroscopy of molecular crystals it is known that the narrowest emission lines are observed when the guest molecule studied is incorporated into a single crystal of a suitable host material at low concentration, since each guest molecule in this case sees the same local environment in the single crystal. This is the so-called Shpol'skii effect [47]. In solid solvents used in ODMR studies of biopolymers and in other disordered environments at low temperatures, the solute molecule experiences local fields produced by randomly oriented neighbors, and the phosphorescence lines of such glasses are therefore broadened [6, 11]. Magnetic transitions between spin sublevels of the triplet state detected by ODMR techniques are also found to be strongly inhomogeneously broadened [8, 9, 10, 12, 13, 14, 15]. Two theories have been proposed to explain these observations. In one of the theories the intramolecular SOC is considered to be the origin of the solvent-induced shift of the ZFS levels: the SOC mixes T and S states and produces a second order contribution to the ZFS, which now depends on the energy gap, ΔE_{ST} . The solvent-induced shift of the optical line ΔE_{ST} is therefore linearly related to a shift in the microwave ODMR signal [13, 14]. The other theory [8, 9, 10] considers the solvent-induced mixing between the triplet states with different ZFS parameters. Though both types of models were fitted to experimentally measured inhomogeneously broadened ODMR and phosphorescence lines, the mixing parameters are not theoretically justified. In the present work we confront the results of these models by calculations of the solvent effects on ODMR and phosphorescence lines from ab initio principles.

If magnetic and optical frequency broadening are related through the SOC mechanism, a strong heavy-atom effect (internal and/or external) on the inhomogeneous broadening of ODMR transitions is expected [12]. Owing to the very small heavy-atom effect observed by Gradle and Coworkers [12, 48], they concluded that SOC is not the leading mechanism, in disagreement with

the models developed in Refs. [13, 14]. At the same time, the absence of a heavy-atom effect on the inhomogeneous broadening of ODMR signals is in good agreement with our results, since we have reproduced the linear correlation between the solvent-induced shift of the optical line ΔE_{ST} and the solvent-induced ODMR shift ΔD (Fig. 2) without taking SOC contributions into account. Indeed, even the SSC expectation value of the triplet state alone reproduces all changes in the ZFS parameters induced by the solvent.

In conclusion, the ZFS constants induced by electron SSC in the low-lying triplet states of the azaaromatic molecules pyridine, pyrazine, pyrimidine, and quinoline and their solvent shifts have been calculated by the MCSCF method and the PCM. The SOC contribution to the ZFS was shown to be very small for all molecules except pyrazine, for which it still amounts to only a quarter of the SSC value. For this reason the analysis of solvent effects was restricted to the SSC contribution alone.

The calculated ZFS shifts are in a good agreement with available experimental data for dilute solid solvents. The phosphorescence lines of such glasses and ZFS transitions between spin sublevels of the triplet state detected by ODMR techniques are strongly inhomogeneously broadened [9]. Using a narrow slit in the emission monochromator or by hole burning one can observe phosphorescence lines from a particular subset of molecules in the disordered solid and measure the ZFS parameters of that subset by ODMR techniques. In this way the linear dependence between the ZFS and the phosphorescence line broadening was observed [9]. The correlation between the shift in the ZFS and optical ΔE_{ST} parameters suggests that these perturbations have a common origin, namely the intermolecular electrostatic perturbation (similar to the Stark effect) which shifts the ground-state and excited-state energies and simultaneously influences the magnetic SSC through the deformation of the wave function. We have supported this finding by direct ab initio calculations with a new MCSCF-PCM method accounting only for the SSC contribution to the ZFS.

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