

Magnetic Field Dependence of Ultrafast Intersystem-Crossing: A Triplet Mechanism on the Picosecond Time Scale?

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Abstract: The influence of strong magnetic fields up to 9 T on the decay kinetics of Ni²⁺–bacteriochlorophyll a was studied by femtosecond pump–probe spectroscopy. The appearance of a magnetic field effect depends on the initial electron spin state of the molecule, which can be switched by using suitable solvents. In toluene, where the central Ni²⁺ is tetraordinated, the ground state has singlet multiplicity, while in pyridine, where in addition two solvent molecules bind to the Ni²⁺ ion, it is a paramagnetic triplet state. In toluene, no field dependence of the excited-state decay kinetics is observed, whereas in pyridine the decay is accelerated by strong magnetic fields, on a time scale of 10 ps. The field-dependent process has been identified as a loss of axial pyridine ligands which is accompanied by intersystem crossing to a singlet state. The field dependence is discussed in terms of a triplet mechanism, which is applicable if an electron spin relaxation time of ≥ 100 ps and a large zero-field splitting of ~ 20 cm⁻¹ are assumed.

Introduction

Recently, it has been demonstrated that recombination kinetics of a photogenerated radical pair can be subject to magnetic field modulation on the time scale of a few picoseconds,¹ which is nearly 4 orders of magnitude shorter than that in the processes studied heretofore. It was shown that the presence of a transition metal moiety in the electron-transfer system is crucial for the appearance of magnetic field effects in this time regime. The effect rests on field-induced coherent transitions between the singlet and triplet states of the radical pair. These transitions can occur only if the singlet–triplet splitting of the radical pair states, i.e., the exchange interaction, is small compared to the Zeeman energy, which is on the order of several wavenumbers in the large fields (up to 9 T) applied. In this radical pair recombination, the unpaired electrons reside on different molecules, so their distance is rather large, resulting in a small exchange interaction.

Here, we report a magnetic field effect (MFE) on an intramolecular deactivation process—where the distance of the unpaired electrons is expected to be small—which is observed some 10 ps after photoexcitation. Again, the molecular system showing such an effect contained a transition metal, a nickel(II) ion bound to the four pyrrole nitrogen atoms of bacteriochlorophyll a ([Ni]–BChl). This molecule as well as Ni²⁺–porphyrins^{2,3} shows the phenomena of solution paramagnetism:⁴ in noncoordinating solvents such as toluene, the molecule has

a diamagnetic singlet ground state⁵ because of the low-spin configuration of the close to square-planar coordination sphere of the Ni²⁺ ion. In coordinating solvents such as pyridine, the central Ni²⁺ binds two solvent molecules and hence becomes hexacoordinated. This change in the coordination sphere induces a low spin–high spin transition; thus, the ground state is a paramagnetic triplet state.⁶

We studied the excited-state dynamics of [Ni]–BChl after excitation to the lowest singlet state of the tetrapyrrole π -system using femtosecond transition absorption and fluorescence spectroscopy.⁷ Solvent-specific decay patterns were observed, with characteristic time constants ranging from 100 fs to 25 ps in toluene and from 150 fs to >2 ns in pyridine. Analysis of the time-dependent spectra led to the conclusion that the different behavior in the two solvents is related to the different multiplicities. In toluene, the decay seems to occur only via singlet states, i.e., only internal conversion (IC) processes are involved. In pyridine, the deactivation processes include changes of multiplicity, i.e., intersystem crossing processes (ISC). Experimental verification of this interpretation is obstructed by the insensitivity of optical spectroscopy toward the overall spin state of the complex.⁸ Time-resolved paramagnetic resonance techniques, which would be ideal to probe the spin states, are restricted to the nanosecond time regime.⁹

(5) The ground state of the tetrapyrrole π -system is a diamagnetic singlet state in both cases; thus, the overall multiplicity of the complex is determined by the multiplicity of the Ni²⁺ spin system.

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(8) The multiplicity of the complex depends on the combination of the two spin systems of the complex. Consequently, the overall spin state of the complex can change without changing the spin state of one subsystem or may remain the same while the spin states of the subsystems change simultaneously. The transient absorption experiment probes only within one subsystem, i.e., the π -system, and is therefore almost insensitive toward the overall spin state.

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Here, we try to demonstrate that, by examining the modulation of the decay kinetics by external magnetic fields, it is possible to gain insight into the spin dynamics accompanying the excited-state deactivation. Such an approach has been proven useful in the study of the photophysics of organic molecules, where the modulation of ISC processes by static and oscillating magnetic fields has been probed optically in techniques such as optically detected magnetic resonance (ODMR).¹⁰ These techniques have been applied to processes occurring on the micro- to millisecond time scale, and modulations were achieved by applying rather small fields in the range of 0.1 T.¹¹ Analogous effects on the picosecond time scale can be expected only if the inverse of the Zeeman energy (in frequency units) is of the order of some picoseconds, a condition fulfilled by the fields of several teslas which are applied in the experiments presented here.

Materials and Methods

For the time-resolved absorption measurements, a femtosecond transient absorption setup based on a 76-MHz Ti:sapphire oscillator and a regenerative amplifier with a repetition rate of 1 kHz for excitation at 780 nm was used. The typical pulse duration of the pump and the probe beam is about 100 fs (fwhm). Detailed descriptions are given in refs 12 and 13. In the measurements of the magnetic field effect, pump and probe pulses were crossed under a small angle (5°) in the center of a superconducting magnet (Oxford Instruments, Spectromag 4000-9). The propagation vectors of the two beams were perpendicular to the magnetic field. The polarization of the pump beam was parallel to the magnetic field in the experiments presented here. However, turning the pump polarization perpendicular to the magnetic field did not influence the effect. The probe beam polarization was set to magic angle with respect to the polarization of the pump beam to avoid contributions from rotational diffusion.

Preparations of the Ni²⁺-centered BChl and the sample solutions are given in detail in refs 7 and 12.

Results

The pump wavelength of our laser systems was tuned to 780 nm, allowing a direct $S_0 \rightarrow S_1$ excitation within the tetrapyrrole π -system for [Ni]-BChl dissolved in toluene and in pyridine. The field effect was monitored at 680 nm. At this wavelength, all kinetic components involved have considerable absolute and relative amplitudes in both solvents.⁷

[Ni]-BChl in Toluene. The dominating part of the transient absorption of [Ni]-BChl in toluene after excitation at 780 nm (Figure 1) decays with a time constant of 450 fs, and additional components with smaller amplitudes have characteristic lifetimes of 4 and 25 ps. The small sigmoidal feature around 0 ps is due to wings in the temporal behavior of the pump pulse which is caused by a nonideal setting of the compressor. The decay pattern is unaffected by an external magnetic field of 8.5 T; i.e., neither amplitudes nor time constants are subject to magnetic field modulation.

[Ni]-BChl in Pyridine. The transient absorption of [Ni]-BChl in pyridine after photoexcitation at 780 nm partially decays with

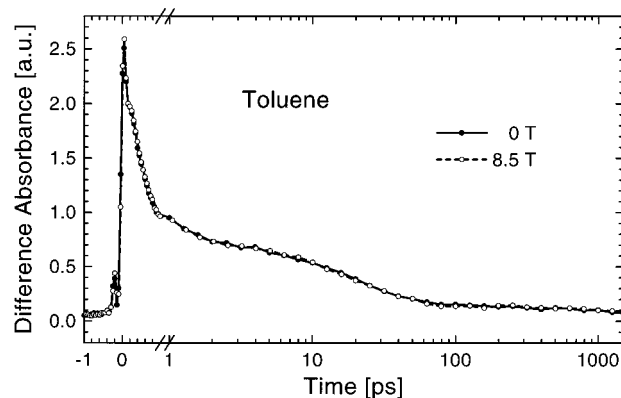


Figure 1. Transient absorption decay of [Ni]-BChl in toluene at 290 K, excited at 780 nm and probed at 680 nm without (●) and with (○) applied magnetic field of 8.5 T.

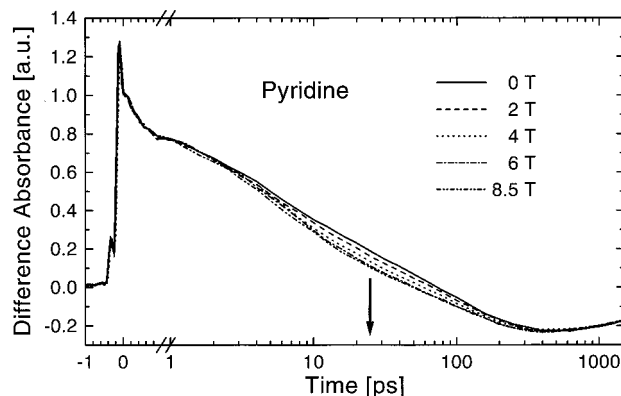


Figure 2. Transient absorption changes of [Ni]-BChl in pyridine at 290 K, excited at 780 nm and probed at 680 nm without magnetic field (—) and with applied magnetic fields of 2 (---), 4 (···), 6 (- · -), and 8.5 T (- · · -). The arrow indicates the direction of change of the signal with increasing field.

a characteristic time of 150–200 fs¹⁴ (Figure 2). A decay that is followed by an intermediate multiexponential process has been approximated by a biexponential with time constants of 6 and 90 ps.⁷ Contrary to the toluene sample, a long-lived component is observed in pyridine solution with a characteristic time which is larger than 2 ns and gives rise to a residual bleaching in our experiment.

Magnetic fields in the range of teslas leave the ultrafast 150-fs process unchanged but affect the intermediate components. With increasing magnetic field, the decay speeds up without any effect on the overall yield of the residual bleaching; i.e., the time traces at different fields coalesce at ca. 1 ns. For a closer inspection of this effect, the field dependence of the difference absorption was measured at a constant delay time. This delay time was set to 25 ps, which is the maximum of the absolute field effect (Figure 3). The effect shows an onset at 1 T and grows almost linearly until it reaches its saturation value around 7 T.

To give a more quantitative account of the field effect, the time-dependent data were fitted to a multiexponential function. In this analysis, the amplitudes and the time constants of the ultrafast and the nanosecond components were kept constant for all time traces in Figure 2. Modeling the intermediate

(14) Because of the temporal form of the pump-pulse, time constants on the order of 100 fs are difficult to extract from the data presented here. However, the value given is in agreement with the result of the study in ref 7. In this study, presumably due to a slightly different compressor setting, the temporal behavior of the pump-pulse was free of the wings seen here.

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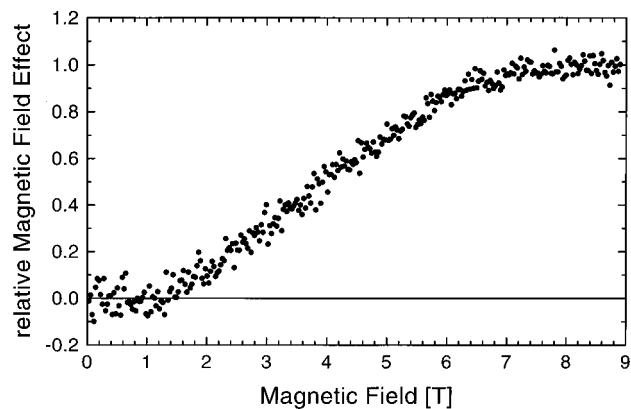


Figure 3. Relative magnetic field effect on the transient absorption at 650 nm of [Ni]-BChl in pyridine at 290 K, probed 25 ps after excitation at 780 nm.

component with only two time constants resulted in systematic deviations between the experimental data points and the fitting curve. Employing a triexponential function gave satisfactory results. Without restrictions on the amplitudes and the time constants, the magnetic field mainly affected the amplitudes and not the time constants. Therefore, we used the time constants determined by fitting the zero-field time trace for all time traces, i.e., restricting the optimization to the amplitudes. The three resulting time constants are 3.7, 13, and 110 ps. The respective amplitudes are 32.4%, 23.1%, and 44.5% in zero-field. With increasing magnetic field, the amplitude of the 13-ps component increases from 23% to 32%, whereas the amplitude of the longest component (110 ps) decreases from 45% to 34%; the 3.7-ps component is only affected by the highest field applied.

Discussion

In the following, we summarize the interpretation of the time-dependent spectra of Ni-BChl in toluene and pyridine,⁷ an interpretation which borrows from the work of Holten et al. on [Ni]-porphyrins.¹⁵ Then we give a brief introduction of the basic principles of MFE in solution photochemistry and examine which conclusion on the MFE reported here can be drawn from these principles. Finally, we propose a preliminary model for the observed effect in terms of a triplet mechanism¹⁶ and discuss the merits and the pitfalls of this model.

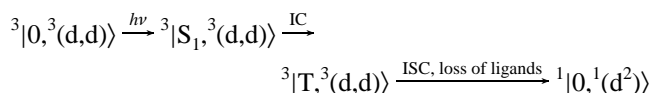
Time-Resolved Spectroscopy. For the following discussion, it is necessary to distinguish between the overall multiplicity of the molecule and the multiplicities of the two subsystems: the nickel center and the tetrapyrrole π -system. To do so, we adopt the following notation. The overall multiplicity is given by preceding superscripts, e.g., 1, 3, 5 for singlet, triplet, and quintet states, respectively; the states of the π -system are denoted 0 (the (singlet) ground state), S_1 (the first excited singlet), and T_1 (the triplet state). The quasi octahedral nickel subsystem is described by the configuration of the two d-orbitals, $d_x^2-y^2$ and d_z^2 , with e_{2g} symmetry in O_h notation. These orbitals are either both singly occupied (d,d), or the lower one, d_z^2 , is doubly occupied (d^2), depending on the axial ligand field. The multiplicity of d-states is again given by superscripts.

As already mentioned in the Introduction, optical spectroscopy gives clear information only on whether the π -system is excited (S_1 or T_1) or in its ground state (0). Information on the multiplicity of the Ni^{2+} states and hence of the total system is more difficult to obtain.

(i) Ni-BChl in Toluene. In toluene, the ground state of [Ni]-BChl is $|^10,^1(d^2)\rangle$. Photoexcitation yields the $|^1S_1,^1(d^2)\rangle$ state. The π -excitation decays with a time constant of 450 fs. In the accompanying study presented in ref 7, it has been argued that the fast deactivation of the $\pi-\pi^*$ excitation occurs via a nickel-centered d-d state with singlet spin multiplicity, e.g., via $|^10,^1(d,d)\rangle$. The population of the d-d state forces the tetrapyrrole system to change its conformation, resulting in shifted Q_x and Q_y bands.⁷ The build-up of these shifts occurs with a time constant of 4 ps, which is also present in the data in Figure 1. The 25-ps component can be attributed to the disappearance of these shifts in response to the deactivation of the d-d state.⁷ In this interpretation, all processes in the excited-state decay conserve the overall spin state. The field independence of the excited-state deactivation of [Ni]-BChl in toluene is in accordance with this interpretation.

(ii) Ni-BChl in Pyridine. In coordinating solvents such as pyridine, two ligands occupy the axial coordination sites, which alters the approximate symmetry of the nickel center toward O_h . This makes the splitting of the two e_{2g} orbitals smaller than the spin pairing energy; thus, $^3(d,d)$ becomes the ground-state configuration of the nickel center. Combining this state with the singlet ground state of the π -system yields the triplet state $^3|^0,^3(d,d)\rangle$.

Analysis of the spectral evolution after photoexcitation into the lowest tetrapyrrole-centered $\pi-\pi^*$ state yielded the following deactivation sequence:



Photoexcitation at 780 nm takes place within the π -moiety of the molecule, generating the $^3|^S_1,^3(d,d)\rangle$ state. This state decays within 250 fs to form a state that has been assigned $^3|^T_1,^3(d,d)\rangle$. This process leaves the total multiplicity of the molecule unchanged, explaining the ultrafast rate of this process. The depopulation of the $^3|^T_1,^3(d,d)\rangle$ state does not occur single-exponentially and is accompanied with the ejection of the two pyridine ligands. This produces the tetracoordinated $^1|^0,^1(d^2)\rangle$ state, which has been identified spectroscopically. The related kinetic components have parallel spectral dependencies.⁷ This is in contrast to the behavior of the toluene sample where the two time constants in the picosecond region are associated with distinct spectral shifts. We therefore conclude that the ISC process from $^3|^T_1,^3(d,d)\rangle$ to $^1|^0,^1(d^2)\rangle$ is inherently multiexponential. It is this ISC process that is sensitive to magnetic fields.

Principles of Magnetic Field Effects. Magnetic field effects in chemistry are usually explained along the following lines (for reviews, see refs 17 and 18). The reactant state consists of a manifold of degenerate or nearly degenerate spin states. Because of the principle of spin conversion, the multiplicity of the product state defines the reactivity of the different spin states of the educt; e.g., if the product is of singlet multiplicity, then a singlet reactant state has a higher reactivity than a triplet reactant state. A magnetic field influences the transition among the spin states of the reactant and thereby the overall reactivity because the distribution among spin states with different reactivities is changed.

The magnetic field can influence transitions only among states with an energetic separation comparable to the electronic

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Zeeman splitting, which is $\sim 10 \text{ cm}^{-1}$ in the highest field applied. The energy gap of states with different multiplicity in a "medium-sized" molecule is usually much larger.¹⁹ Ake and Gouterman²⁰ calculated the energy splitting due to exchange interaction of the $^1,^3,^5|T_1,^3(d,d)\rangle$ states for Ni^{2+} -centered tetrapyrrole in pyridine, obtaining values on the order 1000 cm^{-1} . The porphyrin derivative studied here should have splittings of comparable size. The field effect should, therefore, be related to transitions among substates of the same multiplicity. If we stick to the assignment made above, these substates are the three levels of the $^3|T_1,^3(d,d)\rangle$ triplet state.

Consequently, an interpretation of the effect in terms of the triplet mechanism^{16,21–24} is close at hand. In this mechanism, the states which are mixed are the molecular triplet states T_x , T_y , and T_z , which are eigenstates of the zero-field splitting Hamiltonian. The contamination of the triplet by singlet multiplicity due to spin-orbit interaction can vary among the triplet substates. Therefore, the coupling to the (singlet) ground state is different for these substates, resulting in different ISC rate constants k_x , k_y , and k_z . In a magnetic field, the T_x , T_y , and T_z states are no longer eigenstates of the spin Hamiltonian; i.e., they are nonstationary. It is this mixing of molecular triplet states with different reactivities by an external field that gives rise to a magnetic field effect on the decay kinetics.

In the remainder of this paper, we shall discuss the applicability of this mechanism for the field effects reported. Constructing a precise formalism for the situation encountered here is obstructed by the complicated nature of the triplet state we are dealing with. This triplet state is not a local (d,d) or π - π^* triplet state, but a triplet state obtained by a combination of two local triplets. In this first approach to rationalize the effect, we treat this triplet state like a normal local triplet state and ignore terms in the formalism which take account of the special nature of the triplet state.²⁵ When evaluating the physical relevance of the numerical parameters determined below, the simplified nature of the approach has to be kept in mind.

For our analysis, we used a simplified version of a stochastic Liouville formalism developed by Steiner²⁶ for the treatment of the decay of molecular triplet exciplexes:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{2} [K, \rho]_+ + \mathcal{R}\rho \quad (1)$$

Here, ρ is the spin density matrix in a basis set of three molecular triplet states, T_x , T_y , and T_z , H is the spin Hamiltonian operator, \mathcal{R} is the relaxation superoperator, and K is the reaction operator. The symbols $[\]_-$ and $[\]_+$ denote the commutator and the anticommutator, respectively. The Hamiltonian is composed of two terms, the zero-field splitting and the Zeeman term:

$$H = H_D + H_Z \quad (2)$$

The zero-field splitting term takes the following form:

$$H_D = \begin{bmatrix} \frac{D}{3} - \frac{E}{2} & 0 & 0 \\ 0 & \frac{D}{3} + \frac{E}{2} & 0 \\ 0 & 0 & -\frac{2D}{3} \end{bmatrix} \quad (3)$$

where D denotes the axial splitting parameter and E the rhombic splitting. For the field effect, only the magnitude and not the sign of these parameters is relevant.

The Zeeman term depends on the orientation of molecule with respect to the magnetic field and is given by this matrix:

$$H_Z = g\mu_B \begin{bmatrix} 0 & -iB_z & iB_y \\ iB_z & 0 & -iB_x \\ -iB_y & iB_x & 0 \end{bmatrix} \quad (4)$$

The relaxation operator \mathcal{R} accounts for transition among the triplet levels. The effect of the relaxation operator is to drive the system toward thermal equilibrium. Since the energy differences of the triplet states, i.e., the zero-field splitting and the Zeeman interaction, are small as compared to $k_B T$, the relaxation operator annihilates population differences. This relaxation is treated parametrically using a relaxation rate constant, k_{rel} , without specifying its mechanism. The reaction operator K is a diagonal matrix, with the intersystem crossing rate constants k_x , k_y , and k_z of the three triplet states as diagonal elements.

To account for the isotropic distribution of the molecules with respect to the magnetic field, the numerical solution of the differential eq 1 included orientational averaging. The tumbling of the molecules due to rotational diffusion is ignored, because anisotropy measurements indicate that this diffusion is slower than 100 ps.

Simulations. The following numerical values of the parameters involved have been used in the simulation of the MFE. The initial populations of the three $^3|T_1,^3(d,d)\rangle$ sublevels have each been set to $1/3$.²⁷ The multiexponential nature of the ISC process leads to the conclusion that at least two of the ISC rate constants are larger than relaxation rate constant k_{rel} . Otherwise, the fast relaxation would constantly retain spin equilibrium, resulting in a single-exponential decay with a rate constant of $1/3 (k_x + k_y + k_z)$. The triexponential fit of the zero-field data did yield time constants, each of which is approximately 1 order of magnitude apart from the other. Therefore, in zero-field, the eigenvalues of the differential eq 1 are very close to the rate constants. We associate the fastest process with k_x and the intermediate process with k_y , an assignment which will be justified by the magnetic field dependence. The slowest time constant could be attributed to the spin relaxation process, to the ISC process of T_z , or to a combination of relaxation and ISC. A distinction between these three possibilities is hard to make, even by considering the field dependence. However, for this analysis, the distinction is of minor importance, so we assume that the relaxation is negligible; i.e., we neglect the term $\mathcal{R}\rho$ in eq 1 ($k_{\text{rel}} = 0$) and set $k_z = 1/(110 \text{ ps})$, i.e., equal to the

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(25) For instance, the local triplet states, of which the overall triplet consists, could have different electron g -factors which would alter the Hamiltonian in the formalism.

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(27) To reproduce the zero-field data, the initial populations should be equal to the respective amplitudes obtained by the triexponential fit. However, these values are roughly close to $1/3$, so for our semiquantitative purpose we assume equal population of all triplet states. It should be noted that here, contrary to the situation usually encountered in ODMR, the triplet state is populated from a triplet precursor. When a triplet state is populated from a singlet precursor, the distribution of initial population follows the ratio of the (small) singlet admixtures. For a triplet precursor, the initial population is determined by the triplet characters, which are close to 1 for all sublevels, leading to nearly equal initial population.

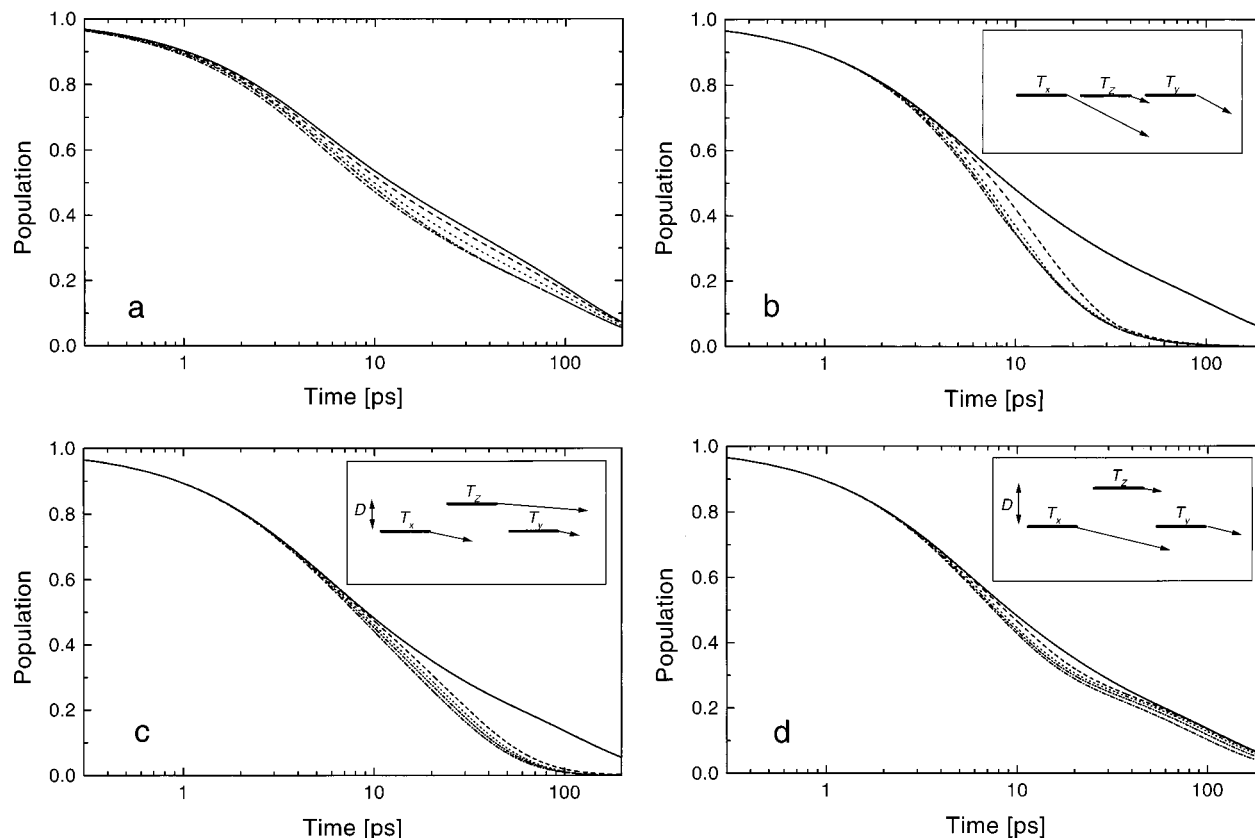


Figure 4. Simulations of the magnetic field effect using the triplet mechanism as described in the text. Magnetic field: 0 (—), 2 (---), 4 (···), 6 (— · —), and 8.5 T (— · · —). The insets illustrate the parameters used in the simulations. The magnitude of the ISC rate constants is represented by the length of the arrows. The relative energy of the states is sketched by the vertical position. (a) Experimental data represented by multiexponential fit functions. The field-independent components (200 fs and 3.7 ns) are omitted. (b) Simulation with no zero-field splitting. (c) Simulation with an axial splitting of 14 cm^{-1} and $k_z = 1/(3.7 \text{ ps})$. (d) Simulation with an axial splitting of 24 cm^{-1} and $k_z = 1/(110 \text{ ps})$.

inverse of the slowest time constant. A spin relaxation time of the order of 100 ps or longer is consistent with the value of 50 ps reported for paramagnetic Ni^{2+} -porphyrins.²⁸ However, due to the different nature of the two triplet states, this comparison can only be a first hint concerning the reliability of this value.

The postulated large differences among the three ISC rate constants can be related to the symmetry of the complex. These rate constants are nonzero because singlet multiplicity is admixed to these zero-order triplet states by spin-orbit coupling. As the complex deviates from O_h and also from D_{4h} symmetry, the energy denominator in the perturbation expression can be different, and hence the singlet contributions.²⁹

The other parameters of the formalism (eq 1) are the g -value in the Zeeman Hamiltonian and the zero-field splittings D and E . We set g equal to $g_e \approx 2$. The zero-field splitting terms were used as variables to fit the data (Figure 4).

In Figure 4b, the calculated field effect is shown for negligible zero-field splitting ($D, E = 0$). It can be seen that the model reproduces the sign of the field effect, i.e., an acceleration of the decay with increasing field, but the field effect is far too large. This can easily be rationalized. The field-induced transitions occur with an angular frequency ω which is determined by the following relation:

$$\omega = \frac{g\mu_B}{\hbar} B_0 \quad (5)$$

For a field of 8.5 T, this yields transitions with an angular frequency of $1.1 \times 10^{12} \text{ s}^{-1}$, which is faster than the highest ISC rate constant, so that the decay becomes single-exponential with an effective rate constant of $\sim 1/3 k_x$. The field effect becomes smaller if the relaxation rate is larger. However, a faster relaxation is excluded by the zero-field kinetics (see above).

This leaves us with the two zero-field splitting parameters which do not affect the kinetics in zero-field, but which change the field dependence of the decay kinetics. The differences of the Ni^{2+} -N bond lengths among the four tetrapyrrole bonds should be smaller than the difference between these bonds and the axial Ni^{2+} -pyridine bonds.³⁰ This renders a large axial splitting D and a small rhombic splitting E likely. For the sake of simplicity, we will ignore the rhombic splitting, although the three different ISC rate constants, necessary to explain the zero-field data, indicate a sizable rhombic distortion of the complex. The discussion of the influence of the zero-field splittings has to take into account that, with nonzero splitting values, the assignment of the ISC rate constants k_x , k_y , and k_z is no longer only a question of nomenclature but gains physical relevance. The axial parameter D lifts the degeneracy of the T_z state with the T_x and the T_y states. Thus, it suppresses transitions between these two sets of states but leaves the transitions between the T_x and the T_y states (nearly) unchanged. Obviously,

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(29) ISC rate constants differing by more than an order of magnitude are by no means extraordinary and have, for instance, been observed for the local $\pi-\pi^*$ triplet states of free base tetrapyrrole. van Drop, W. G.; et al. *Mol. Phys.* **1975**, *30*, 1701–1721.

(30) A X-ray structure of a similar hexacoordinated Ni^{2+} -porphyrin indeed demonstrates that there is a substantial difference between the axial and the in-plane bond lengths. Kirner, J. F.; et al. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 107–112.

the field effect will depend on whether the ISC rate constant k_z of the nondegenerate state is associated with the slowest, the intermediate, or the fastest process. Following the discussion above concerning the values of the zero-field splitting parameters, one should expect a large difference between the k_z constant and the other two. A k_z value equal to the inverse of the slowest lifetime yields the largest differences.

Nevertheless, we did perform simulations with $k_z = 1/(3.7 \text{ ps})$ and $1/(110 \text{ ps})$. In both cases, a significant effect of the parameter D on the field effect is observed only if D is larger than the Zeeman energy in the highest field, i.e., $D > 8 \text{ cm}^{-1}$.

For $k_z = 1/(3.7 \text{ ps})$, a further increase of D does not affect the field effect. In Figure 4c, the field dependence for an axial splitting of 14 cm^{-1} is shown. The discrepancy between experiment and simulation is now smaller, but the simulation still yields far too large effects. The reason is that, in this scenario, the T_x and the T_y state have very different ISC constants ($1/(13 \text{ ps})$ and $1/(110 \text{ ps})$), and coupling of the two states will give an effective decay time of $\sim 26 \text{ ps}$.

For $k_z = 1/(110 \text{ ps})$, a further increase of D above 8 cm^{-1} does affect the field effect. This is because the longer lifetime of the T_z state in this scenario leaves the relatively small off-diagonal terms in the Hamiltonian (the Zeeman terms) more time to couple the T_z state with the other states. A saturation of the influence of D on the MFE is seen for $D \approx 24 \text{ cm}^{-1}$. The simulated MFE for this value is shown in Figure 4d. Now the agreement between experiment and simulation can be regarded as satisfactory.

A splitting parameter of 24 cm^{-1} may be considered to be too high a value for a Ni^{2+} complex. However, comparison of this splitting with values of ground-state Ni^{2+} is obstructed by two particulars. On one hand, the electronic character of the ground-state Ni^{2+} triplets differs from the one encountered here, the former being a (d,d) triplet state and the latter a combination of (d,d) and $(\pi-\pi^*)$ configurations. This reduction of d-character should decrease the zero-field splitting of the $^3|T_1, ^3(d,d)\rangle$ states as compared to pure (d,d) states. On the other hand, the reported zero-field splittings usually refer to complexes where

the deviation from O_h coordination is small.³¹ For instance, Carlin et al.³² reported a value of 4 cm^{-1} for $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6]^{4-}$, a complex with six identical ligands. The larger deviation from octahedral symmetry in [Ni]-BChl should increase the splitting. Because of these two counteracting influences, the final decision on the reliability of the splitting value derived from the simulation cannot be made here.

To gain insight into the physical relevance of these splitting parameters and the order parameters derived from the simulations, a quantum chemical study of the nature of the triplet state would be very helpful. Such a study should produce relationships between the EPR parameters of a Ni^{2+} -centered (d,d) triplet and the triplet state encountered here. This would help to improve the spin Hamiltonian for the simulation of the MFE and might deliver values for couplings of triplet substates to the singlet ground state which could support the large differences in the ISC rate constants.

Conclusions

It was shown that the dynamics of an intersystem crossing process of a large molecule containing a transition metal in solution can be subject to magnetic field modulation on a time scale of 10 ps. This modulation makes it possible to distinguish between spin-conserving and nonconserving steps in the complex decay pattern of a Ni^{2+} -centered BChl. The essential features of the field effect can be rationalized using a simple triplet mechanism, if an unusually large axial zero-field splitting and an electron spin relaxation time longer than 100 ps are assumed.

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