Ultrafast Photophysics and Photochemistry of [Ni]-Bacteriochlorophyll *a*

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Received: April 28, 1999; In Final Form: June 2, 1999

The ultrafast photodynamics of bacteriochlorophyll with the central Mg^{2+}-ion replaced by Ni^{2+} ([Ni]-BChl) in toluene and pyridine have been studied by femtosecond time-resolved fluorescence and absorption spectroscopy with a time resolution of 100 fs in the spectral range of 470–900 nm. Excitation of tetracoordinated [Ni]-BChl in *toluene* in its red-most absorption band leads to four transient states which decay single-exponentially with lifetimes of 100 fs, 450 fs, 4 ps, 25 ps. Except for the 4 ps component these kinetics arise from an internal conversion cascade conserving the overall multiplicity of the singlet configuration. The spectral characteristics of the intermediates indicate a deactivation process via several π- and metal-centered excited states. The 4 ps kinetic results from a relaxation within the metal d-states caused by a change of size of the central nickel ion upon electronic excitation. A different deactivation pattern is observed for [Ni]-BChl in *pyridine*, where the central metal is additionally coordinated by two axial solvent molecules. On the basis of their dynamics and their spectral positions, three different intermediates have been identified. The fastest decay with 150 fs reflects an internal conversion process. This is followed by a process that can be approximately described by time constants of 6 and 90 ps. This decay pattern, concomitant with the spectral changes, is attributed to the ejection of the axial solvent ligands accompanied by intersystem crossing. The slowest component has a characteristic time of >2 ns and is attributed to the rebinding of the pyridine ligands.

Introduction

The knowledge of the electronic properties of bacteriochlorophylls is a basic requirement for the understanding of functional modification of light-harvesting and primary charge separation processes in bacterial photosynthesis[1–7] and for their potential application as photosensitizer in PDT.[8–15] In this context, metal-substituted derivatives of bacteriochlorophyll *a* ([M]-BChl)[16–20] are of particular relevance. They have been introduced into the photosynthetic reaction center of *Rhodobacter sphaeroides* replacing the accessory pigments.[1–7] Reaction centers containing [Ni]-BChl show a significant loss channel for the ultrafast energy transfer from the excited [Ni]-BChl to the primary donor.[1] These results prompted us to investigate the photophysics of these pigments in solution, focusing on the influence of the central metal ion and its coordination state on the excited-state dynamics. The experimental results are discussed in the context of analogous studies of metal substituted porphyrins.[21–23]

In the following, we report on the excited-state dynamics upon Q_Y excitation of [Ni]-BChl in toluene and pyridine. In contrast to the central metal ions in [Mg]-, [Zn]- and [Pd]-BChl, d^8-Ni^{2+} has vacant d-orbitals at an energy well below the initially excited S_1 state of the π system.[24] The molecule is diamagnetic when the Ni^{2+} ion is coordinated only by the porphyrine macrocycle (approximately D_{4h} symmetry with an empty $d_{x^2-y^2}$ orbital). In the presence of two additional pyridine ligands the resulting paramagnetic complex[25] is of approximate

O_h-symmetry with singly occupied d_{z^2} and $d_{x^2-y^2}$ orbitals. Previous studies on the excited-state dynamics of various [Ni]-porphyrins[22,23,26–32] and (time-resolved) resonance Raman studies[33–40] indicate a decay cascade via metal centered states. Moreover, in hexacoordinated [Ni]-porphyrins, the complex deactivation kinetics were interpreted by a transient dissociation and association of the axial solvent molecules.[23,31,40]

The detailed investigation of the excited state dynamics of [Ni]-BChl profits from the possibility of selective excitation into well-defined ground-state absorption bands. In contrast to metalloporphyrins, this advantage allows to avoid constraints due to strongly overlapping bands. This opens the road to follow the details of the decay via metal centered states as well as for the transient dissociation of the axial ligands.

Materials and Methods

Sample Preparation. BChl was isolated from *Rhodobacter sphaeroides* using standard methods.[41–43] Demetalation of BChl was achieved by treatment with small amounts of glacial acetic acid to yield bacteriopheophytine (BPhe).[44] [Ni]-BChl was prepared by a transmetalation method described previously.[17] First the precursor Cd complex was prepared by refluxing BPhe in dimethylformamide with anhydrous $Cd(OAc)_2$ and subsequent purification on silica gel. Addition of nickel chloride to a solution of the resulting [Cd]-BChl in acetone resulted in transmetalation to the [Ni]-BChl. The sample was purified on silica gel.

Toluene and pyridine solutions of the pigment were degassed (flushed with N_2) and the cuvettes were sealed in order to suppress photoinduced oxidation. The optical densities of the

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samples were adjusted to OD = 1 at 780 nm for transient absorption and to OD = 0.1 at 780 nm for transient fluorescence measurements.

Ground-State Absorption and Fluorescence. Ground-state absorption spectra were recorded on a Perkin-Elmer UV−vis spectrometer (Lambda 2S), steady-state fluorescence spectra on a SPEX fluorometer (Fluorolog SPEX DM Series). The setting of our fluorometer allows the determination of fluorescence quantum yields higher than $\Phi_F = 10^{-4}$.

Femtosecond Pump/Probe Absorption Spectroscopy. For the time-resolved absorption measurements we used a pump/probe laser system based on a 76 MHz Ti:Sapphire oscillator and a regenerative amplifier with a repetition rate of 1 kHz for excitation at 780 nm. Detailed descriptions are given in refs 16 and 45. For probing a 12 nm broad spectral window of the white-light continuum was used. The entire setup had an instrumental response function (IRF) of 120−180 fs. Pump and probe beams were focused weakly under an angle of 10° with magic angle polarization on a 1 mm cuvette. Transient absorption spectra of [Ni]-BChl were performed by extracting the signal from the decay traces at each wavelength at certain delay times.

Femtosecond Time-Resolved Fluorescence. Femtosecond time-resolved fluorescence was measured with the upconversion technique based on a 76 MHz Ti:Sapphire oscillator as described in Refs. 3, 16, and 46. After compression with a four prism chirp compensation, the pulse width was below 100 fs. To reduce the influence of long-term drifts of the laser and degradation of the samples upon the decay curves, we collected up to 32 individual time traces.

The IRF was taken before each fluorescence measurement using scattered light from the sample. The alignment was not changed except for adjusting the phase matching angle of the crystal and the detection wavelength in order to achieve an optimized signal-to-noise ratio. The full width at half-maximum (fwhm) of the IRF was about 140 fs.

Fitting Procedure. Time constants were extracted from the experimental transient absorption and fluorescence data by fitting a convolution of the experimental IRF and exponential decay functions to the data using the Levenberg−Marquardt method. The IRF of the absorption measurements was modeled by a Gaussian using time zero t_0 and the fwhm as fitting parameters. The quality of fit was judged by observing the residuals and values of the reduced χ^2.

Results and Discussion

Steady-State Absorption and Fluorescence Spectra. The absorption spectra of [Ni]-BChl in toluene and pyridine exhibit the resolved B_Y, B_X, Q_X, and Q_Y transitions in order of decreasing energy (Figure 1, Table 1). The main solvent effect in the visible spectra is associated with the Q_X and B_Y transitions decreasing by about 2000 cm^{-1} in transition energy; in addition minor shifts of < 300 cm^{-1} of the Q_Y and B_X absorption bands were observed. These shifts can be attributed to the coordination of pyridine molecules to the central ion which was demonstrated for native BChl[47,48] and, recently, for Ni^{2+} centered BChl.[17,18,49] The band positions particularly that of the Q_X band can therefore be used as a precise marker of the coordination state. Although the extinction coefficients of [Ni]-BChl in the two solvents are comparable to those of the strongly fluorescing [Mg]- and [Zn]-BChl,[17,49] no steady-state fluorescence is detectable ($\Phi_F < 10^{-4}$), indicating fast nonradiative decay pathways.

According to the four orbital model of tetrapyrroles,[50] the four lowest allowed one electron $\pi-\pi^*$ promotions (a$_{2u}$ → e$_{gy}$, a$_{1u}$ → e$_{gx}$, y-polarized and a$_{1u}$ → e$_{gy}$, a$_{2u}$ → e$_{gx}$, x-polarized) are
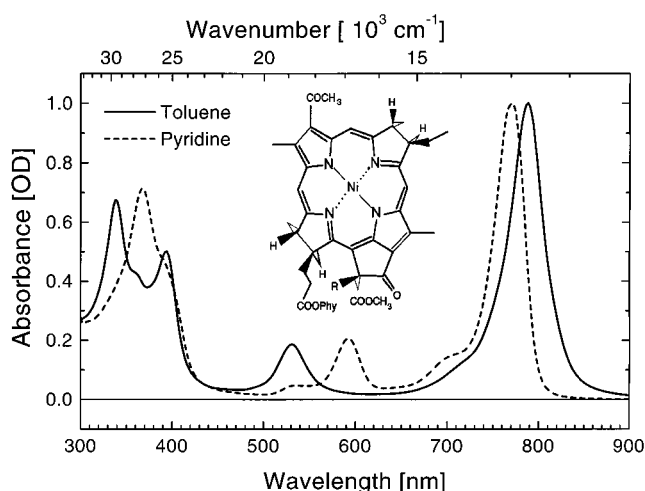

Figure 1. Ground state absorption spectra (290 K) of [Ni]-BChl in (—) toluene and pyridine (− −). The inset shows the structural formula of the complex.

linearly combined giving rise to the B_Y, Q_Y, B_X, and Q_X absorption bands. They are pairwise degenerate in metalloporphyrins (E(Q_X) = E(Q_Y), E(B_X) = E(B_Y)) because of their D_{4h} symmetry. Compared to the porphyrins and chlorins, bacteriochlorins and bacteriochlorophylls, in particular, show four well separated $\pi-\pi^*$ absorption bands.[17,51−53]

Femtosecond Time-Resolved Spectroscopy. *1. Fluorescence.* The transient fluorescence signal upon excitation into the Q_Y band of [Ni]-BChl (Figure 2) could, in both solvents, be fit by a single-exponential decay function. The resulting lifetimes were 100 fs in toluene and 150 fs for in pyridine. This is about 3−4 orders of magnitude shorter than those of BChl and other highly fluorescent metal substituted BChls.[16]

2. Absorption. [Ni]-BChl in Toluene. The transient absorption spectra (Figure 3a) at early delay times exhibit a broad positive absorption ranging from the UV to ≈700 nm superimposed with ground-state bleaching of the Q_X and Q_Y transitions. No evidence for stimulated emission was found, indicating that the S$_1$ decay detected in fluorescence upconversion is not resolved by our transient absorption system and that the first spectral intermediate detected in transient absorption is already a successor state of S$_1$.
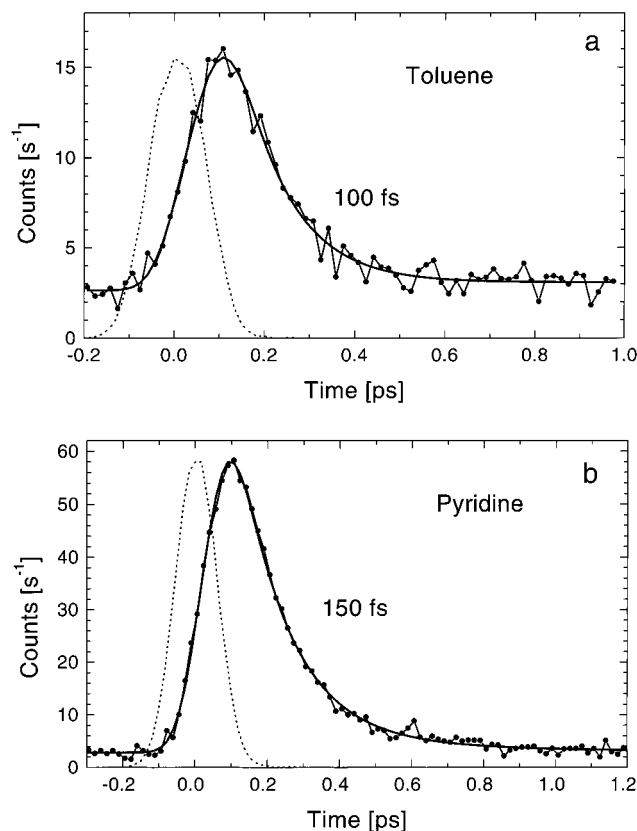
The disappearance of the broad transient absorption in the spectrum after 10 ps indicates the annihilation of the π excitation. The concomitant sigmoidal structures result from shifts of the Q_X and Q_Y Bands (≈450 cm^{-1} to the red and ≈150 cm^{-1} to the blue, respectively). After about 100 ps these sigmoidal absorption features have disappeared except for a small negative amplitude around 750 nm.

The decay traces at all probing wavelengths were analyzed in a global fitting procedure (examples are given in Figure 3b) and a minimum of three exponential decay compounds was needed for an adequate adjustment of the data. Lifetimes of 450 fs, 4 ps, and 25 ps were obtained, in addition to the 100 fs lifetime measured in time-resolved fluorescence. The corresponding amplitudes of the exponentials are displayed as a function of the probing wavelength (decay associated spectra, DAS) in Figure 3c, where each amplitude reflects the absorption change due to the transition from one excited state to its successor state.

The broad positive feature in the DAS of the 450 fs component is comparable to the S$_1$ absorption detected in the [Mg]-, [Zn]-, and [Pd]-BChl;[16] however, it cannot be the initially excited S$_1$ state of [Ni]-BChl (vide supra). It is therefore

TABLE 1: Ultrafast Photophysics and Photochemistry of [Ni]-Bacteriochlorophyll *a*

|	ground-state absorption bands				kinetic components			
	B_Y [nm] [10^3 cm^{-1}]	B_X [nm] [10^3 cm^{-1}]	Q_X [nm] [10^3 cm^{-1}]	Q_Y [nm] [10^3 cm^{-1}]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]	τ_4 [ps]
toluene	338	394	530	788	0.1	0.45	4	25
	29.59	25.38	18.87	12.69				
pyridine	368	390	592	770	0.15	6	90	>200
	27.17	25.64	16.89	12.99	(0.2)			0

Figure 2. Spontaneous fluorescence decay of [Ni]-BChl in (a) toluene and (b) pyridine at 290 K measured by fluorescence upconversion. λ_{exc} = 760 nm, and λ_{em} = 814−820 nm.

concluded that the S_1 successor state, which is populated with a 100 fs time constant and depopulated with a 450 fs time constant, is a state where the π system is still excited. This is confirmed by the negative troughs near 790 and 535 nm in the broad positive excited-state absorption in the 450 fs DAS indicating that the depopulation of the S_1 successor state leads to an annihilation of the excitation of the π system.

The ultrafast population and depopulation of the S_1 successor state highly favor an internal conversion (IC) process for formation and decay of this state excluding the lowest triplet state of the π system. Therefore, the S_1 successor state must be a combination of a $\pi-\pi^*$ and a spectroscopically almost silent excited metal state. The following state, populated with a time constant of 450 fs, shows no π-excitation, but the photocycle is not yet finished. The 4 ps and the 25 ps components with opposite amplitudes indicate the continuing decay process with the following generation and decay of an additional metal-centered configuration with slightly shifted $\pi-\pi^*$ transitions.

[Ni]-BChl in Pyridine. The spectral characteristics and the lifetimes of the decay process of the hexacoordinated [Ni]-BChl in pyridine differ considerably from those observed in toluene (Figure 4).

At early delay times the typical broad positive transient absorption superimposed by ground-state bleaching and stimu-
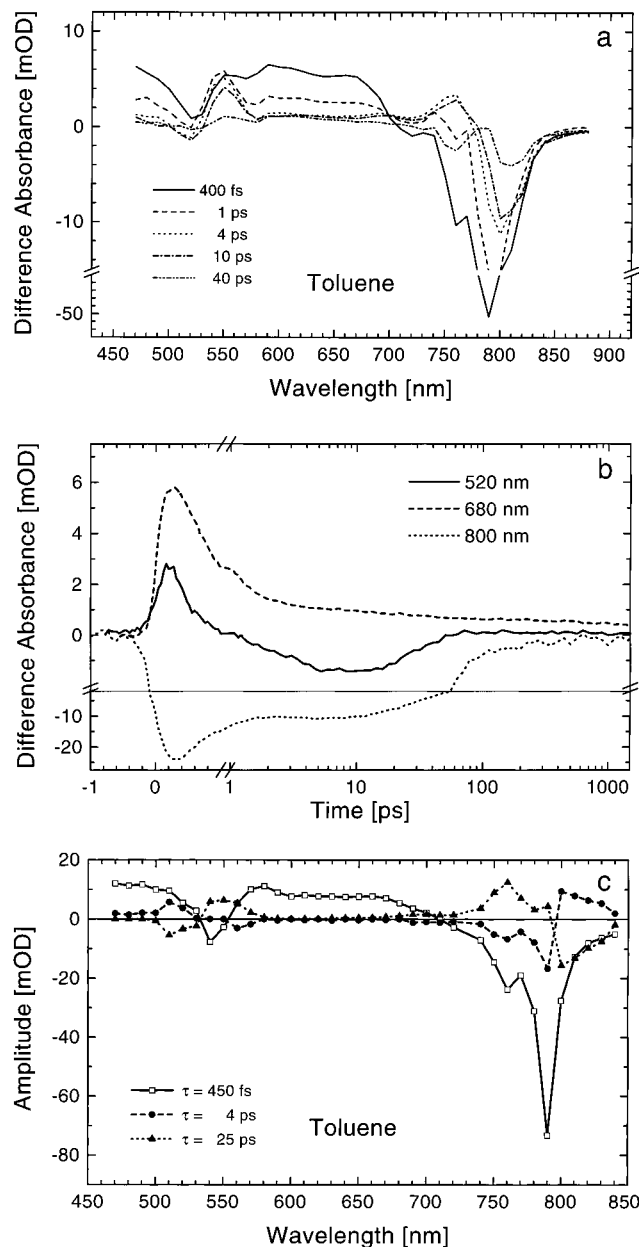
Figure 3. Transient absorption measurements of [Ni]-BChl in toluene, λ_{exc} = 780 nm at 290 K: (a) transient absorption spectra, (b) typical transient absorption decay traces at (—) λ_{pr} = 520 nm, (− −) 680 nm, and (...) 800 nm, and (c) decay associated spectra of (−□−) τ = 450 fs, (−●−) 4 ps, and (·▲·) 25 ps; amplitudes of the respective exponential decays.

lated emission around 780−790 nm is observed (Figure 4a), analogous to the behavior of other metal substituted BChl.[16] The DAS of the 200 fs component (Figure 4c) exhibits a broad, positive feature around 650 nm and the sharp negative amplitude for the stimulated emission. This demonstrates that the fastest decay process detected in transient absorption and fluorescence originate from the same excited state (S_1) and that in the S_1
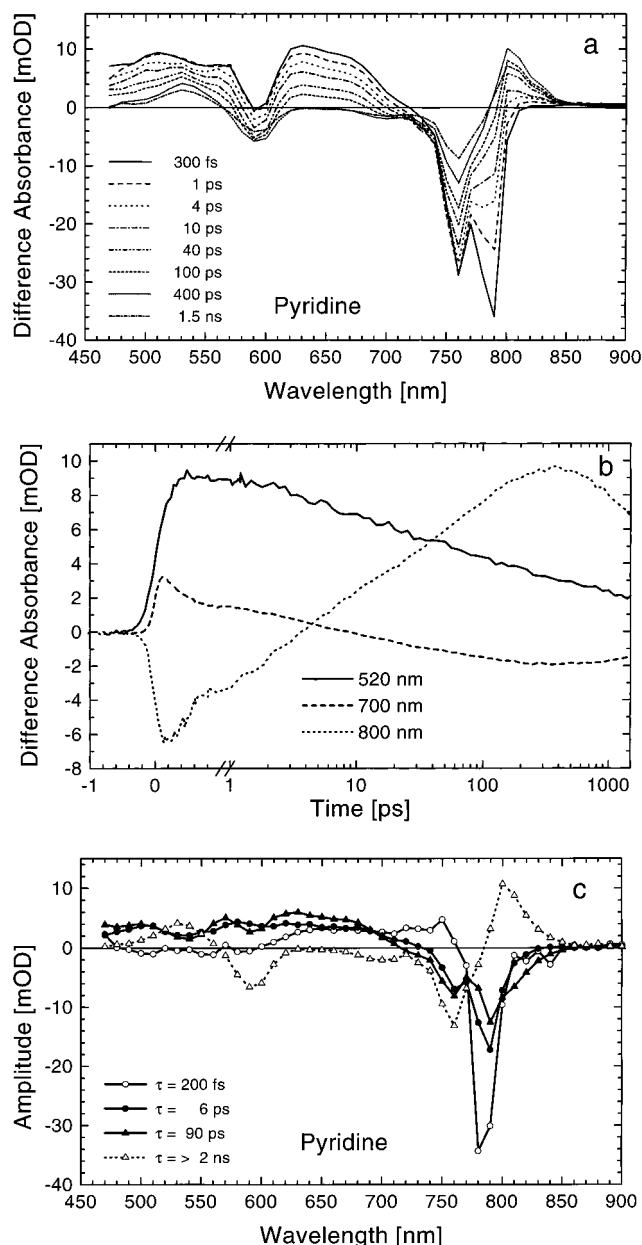
Figure 4. Transient absorption measurements of [Ni]-BChl in pyridine, $\lambda_{exc} = 780$ nm at 290 K: (a) transient absorption spectra, (b) typical transient absorption decay traces at $\lambda_{pr} = 520$ nm (—), (— — —) 700 nm, and (...) 800 nm, and (c) decay associated spectra of $\tau = 200$ fs (—○—), 6 ps (—●—), (—▲—) 90 ps, and the (·△·) >2 ns component; amplitudes of the respective exponential decays.

Figure 5. Approximation of the energy eigenvalues of (left) 4-fold and (right) 6-fold coordinated [Ni]-BChl. Black states: determined by steady-state absorption and known singlet–triplet splitting of the BChl macrocycle. Gray: estimated energy values (see text). For nomenclature see ref 54.

successor state the π system is still excited. Although the broad positive feature is similar to that typically observed for $S_1 \rightarrow T_1$ relaxation in other bacteriochlorophylls,[16] the ultrafast kinetics for the formation of the S_1 successor state again favors an IC process. Thus, also for [Ni]-BChl in pyridine the S_1 successor state must have some contribution from a metal-centered excited state.

The S_1 successor state decays in multiexponential way with characteristic times ranging from a few to 100 ps. This decay can roughly be described using biexponential trial function. Satisfactory results can be obtained when a triexponential function is used. The biexponential approach yields time constants of 6 and 90 ps, and the triexponential function 3.7, 13, and 110 ps. DAS generated using both approaches lead to the same conclusion, namely, the different components have the same spectral dependencies. For the biexponential function
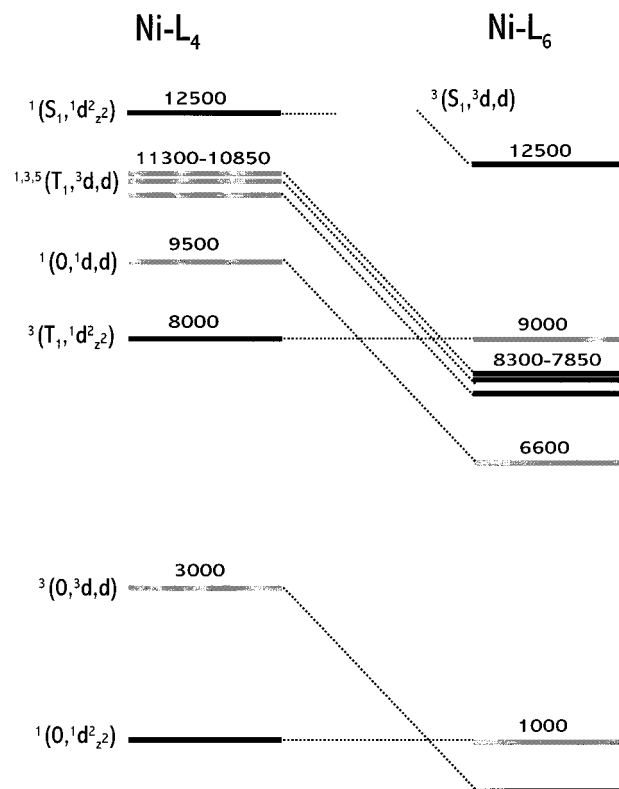
the DAS of the 6 and 90 ps components are depicted in Figure 4c illustrating these parallels in spectral behavior. Therefore, we conclude that the decay of the S_1 successor state involves only one electronic transition and this transition is intrinsically non-single-exponential.

The state formed by this process is characterized by an annihilation of the π-excitation and the appearance of shifted Q_X and Q_Y bands, as indicated by the 400 ps transient absorption spectrum (Figure 4a). These shifts disappear with a characteristic time of $\tau > 2$ ns (see sigmoidal features in the DAS in Figure 4c) indicating the end of the photocycle, i.e., the reformation of the ground state.

A more detailed discussion of the multistep relaxation process in [Ni]-BChl is presented below in combination with the energy level diagram for the lowest excited states.

Energetics and Decay Dynamics of [Ni]-Bacteriochlorophyll. The energy scheme displayed in Figure 5 is based on the following estimates: for tetracoordinated [Ni]-BChl the $^1|S_1,d^2\rangle$ state energy[54] of ≈ 12500 cm^{-1} is taken from the Q_Y absorption energy of 12800 cm^{-1} and a Stokes shift of ≈ 300 cm^{-1}.[17] The singlet triplet splitting of the π system is taken to be 4500 cm^{-1} irrespective of the actual central metal and its coordination state[17,55,56] placing the energy of the $^3|T_1,d^2\rangle$ state at 8000 cm^{-1} above the ground state. To position the metal centered excited states the procedure given in ref 24 is used, which yields a ^{3}(d,d) state ≈ 3000 cm^{-1} above the d^2 metal-ground state, thus giving rise to the $^{1,3,5}|T_1,^3$(d,d)$\rangle$ manifold at ≈ 11000 cm^{-1} for tetracoordinated [Ni]-BChl. Similarly, the singlet triplet splitting of ≈ 6500 cm^{-1} for the (d,d) configuration, again almost independent of the coordination state[24] places the $^1|0,^1$(d,d)$\rangle$ state at 9500 cm^{-1}. For hexacoordinated Ni, the paramagnetic ^{3}(d,d) state becomes the metal centered ground

state which is 1000 cm^{-1} lower in energy than the diamagnetic d^2 configuration.[24] The other states involving a (d,d) contribution are stabilized by the same energies putting the $^3|T_1,d^2\rangle$ at $\approx$9000 cm^{-1} and the $^{1,3,5}|T_1,^3(d,d)\rangle$ manifold at. 8000 cm^{-1} above the ground state.

For *tetracoordinated* diamagnetic Ni in [Ni]-BChl ($^1|0,d^2\rangle$ ground state), excitation into the Q$_Y$ absorption at 780 nm forms the $^1|S_1,d^2\rangle$ state, which has a lifetime of 100 fs. As already mentioned, the $^1|S_1,d^2\rangle$ successor state must be a $\pi-\pi*$ state and should be formed by an IC rather than an ISC process. A pure singlet relaxation pathway favors internal conversion into $^1|T_1,^3(d,d)\rangle$ with the π system in its triplet state and an electron of the metal ion promoted into the d$_{x_2-y_2}$ orbital and metal triplet multiplicity. This intermediate state was not observed in previous transient absorption studies of [Ni]-porphyrins[22,31,32] probably due to a much slower formation than depopulation.

The second kinetic component of 450 fs (Figure 3c) is connected to an annihilation of the π-excitation yielding a "pure" metal-centered excited state. The only energetically accessible excited state with singlet multiplicity and no excitation of the π system is the $^1|0,^1(d,d)\rangle$ state. This conclusion is consistent with analogous observations of tetracoordinated [Ni]-porphyrins where a 500 fs component was attributed to the decay into a vibrationally unrelaxed (d,d) configuration.[22,32]

On the basis of the DAS (Figure 3c) the following 4 ps decay is assigned to a transient with no π-excitation, but with slightly shifted Q-absorption bands. The final 25 ps decay shows the reverse shift (Figure 3c) and forms the overall ground state. The energy level scheme (Figure 5) shows that there are only two excited states below the $^1|0,^1(d,d)\rangle$ state. The state $^3|T_1,d^2\rangle$ can be excluded because of its π-excitation, state $^3|0,^3(d,d)\rangle$ if we assume multiplicity conservation. This implies that the 4 ps decay is a vibrational and/or structural relaxation process within this electronic state.

A possible explanation for this relaxation process might be connected to the fact that in the diamagnetic [Ni]-BChl the macrocycle is in a saddle-shaped conformation. Such a conformation is the result of the small ionic radius of low-spin Ni^{2+} (60 pm) which is not compatible with the optimal Ni$^{2+}-$N bond lengths in a square$-$planar form. A S$_4$-ruffling distortion to the saddle-shaped conformation reduces these bond lengths.[17]

Upon excitation and ultrafast relaxation into the $^1|T_1,^3(d,d)\rangle$, this saddle form is conserved, but the now paramagnetic Ni^{2+} is significantly larger (70 pm) and would permit a square-planar geometry of the tetrapyrrole skeleton.[17] The response of the skeleton on the new Ni^{2+} radius is assigned to the time constant of 4 ps. This occurs while the pigment is probably in the singlet $^1|0,^1(d,d)\rangle$ state where the d system is still extended. The final 25 ps decay recovering the ground state ($^1|0,^1(d,d)\rangle \rightarrow \, ^1|0,d^2\rangle$) is again accompanied by a structural variation of the [Ni]-BChl skeleton. The attribution of the 4 ps component to a change from a ruffled to an almost planar tetrapyrrole skeleton, while in the $^1|0,^1(d,d)\rangle$> state, is consistent with the concomitant absorption changes shifting the Q$_X$ absorption band from. 530 nm in the saddle-formed molecule to. 560 nm[57] in the planar [Ni]-BChl (cf. Figure 3c). The observed shifts are in accordance with values derived from ground-state absorption studies.[17] The conclusion that all relaxation processes involved in the $^1|S_1,d^2\rangle$ decay take place under multiplicity conservation is supported by time-resolved magnetic field effect studies,[58] where none of the decay components shows a magnetic effect even at fields as high as 9 T.

Excitation into the Q$_Y$ band of the *hexacoordinated* [Ni]-BChl (paramagnetic $^3|0,^3(d,d)\rangle$ triplet ground state) leads to the
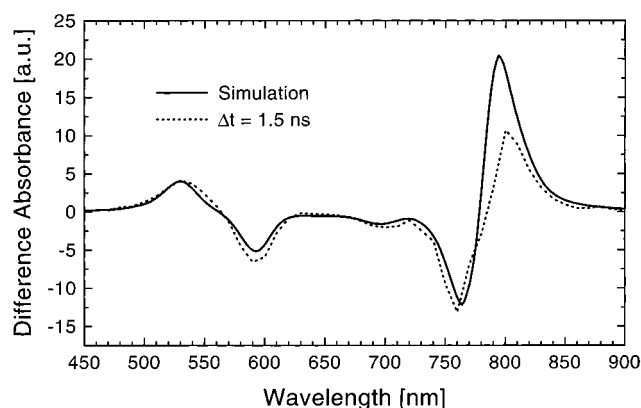

Figure 6. Spectral simulation of the deligation influence on the $\pi-\pi*$ transitions of [Ni]-BChl in pyridine: ($-$) difference of the ground-state absorption spectra of [Ni]-BChl in toluene and pyridine and (...) observed signal in pyridine 1.5 ns after excitation.

state $^3|S_1,^3(d,d)\rangle$. This state decays with a time constant of $\approx$150 fs to the S$_1$ successor where the energy is still located within the π system (vide supra). The subsequent decay which is characterized by two fit components (6 and 90 ps) reflect the decay of the excited π system. The longest component of >2 ns is due to the recovery of the ground state. The DAS of this slowest kinetic component is almost identical to the calculated difference of the ground-state absorption bands of the toluene- and pyridine-dissolved samples (Figure 6). This observation indicates that the state repopulating the ground state is state where the axial ligands are dissociated from the [Ni]-BChl and ground-state formation is associated with rebinding of the axial ligands. Similar transient dissociation kinetics of axial ligands was reported for [Ni]-porphyrins in coordinating solvents.[23,31,40]

One of the interesting questions arising is, which decay pathway leads to the ligand ejection. The decay of the fluorescent state does not extinguish the $\pi-\pi*$ excitation of the macrocycle. Therefore, in a possible successor state the porphyrine substates have to be in the triplet state which is a $\pi-\pi*$ excited state and nonfluorescent. This leaves the states $^3|T_1,d^2\rangle$ and $^{1,3,5}|T_1,^3(d,d)\rangle$, which have similar energies and cannot be discriminated by absorption spectroscopy. We favor an IC pathway via $^3|T_1,^3(d,d)\rangle$ on the basis of the following arguments: (i) The formation of the $^3|T_1,^3(d,d)\rangle$ state is an one-electron process, while the formation of $^3|T_1,d^2\rangle$, is a two-electron process. (ii) The decay of $^3|T_1,d^2\rangle$ into the ligand free $^1|0,d^2\rangle$ is expected to occur on the longer nanosecond to microsecond time scale (T$_1 \rightarrow$ S$_0$ ISC in BChl[56,59]) rather than on the experimentally observed picosecond time scale.

In the $^{1,3,5}|T_1,^3(d,d)\rangle$ manifold, unpaired electrons reside in d orbitals allowing for fast ISC due to large spin$-$orbit induced multiplicity mixing. The multiexponential nature of the $^{1,3,5}|T_1,^3(d,d)\rangle \rightarrow \, ^1|0,d^2\rangle$ transition might be the consequence of different ISC rate constants of the substates of the manifold. This interpretation is strongly supported by the magnetic field effects on these kinetic components [58] which confirm that the loss of axial pyridine ligands is accompanied by intersystem crossing to a singlet state.

Conclusions

The excited-state dynamics of the [Ni]-BChl after excitation to the lowest singlet state of the porphyrine π system using femtosecond transition absorption spectroscopy showed a complex kinetic behavior with characteristic time constants ranging from 100 fs to 25 ps in toluene and 150 fs to > 2 ns in pyridine.

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The analysis of the spectral characteristics of [Ni]-BChl in *toluene* let us conclude that three excited states, two mainly π-centered and one mainly metal centered, but all of them with overall singlet character, were transiently populated. The fastest decay component involves a singlet−triplet transition in the metal d system (compensated by singlet−triplet transition in the π system), triggering a shift of the Q_X and Q_Y bands due to geometrical changes of the tetrapyrrole macrocycle.

For [Ni]-BChl in *pyridine* also three excited states (two mainly π centered, one mainly metal centered) were involved, but only the fastest decay is attributed to an IC process. Although it is impossible to observe the pure metal configuration, based solely on the optical spectra presented, there is a number of plausible arguments that the formation and the decay of the other two intermediates involves ISC processes within the metal d states. In parallel to the ISC processes, spectral shifts of the Q_X and Q_Y bands are observed which reflect the dissociation and reassociation of the axial pyridine ligands. Thus both the spectral changes induced by the diamagnetic to paramagnetic transition and the spectral changes induced by the presence and absence of axial ligands are separately observed. The detailed mechanism responsible for the multiexponential ISC has been elucidated by experiments in high external magnetic fields.[58]

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