

## Spectral editing through laser-flash excitation in two-dimensional photo-CIDNP MAS NMR experiments



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### ABSTRACT

In solid-state photochemically induced dynamic nuclear polarization (photo-CIDNP) MAS NMR experiments, strong signal enhancement is observed from molecules forming a spin-correlated radical pair in a rigid matrix. Two-dimensional  $^{13}\text{C}$ - $^{13}\text{C}$  dipolar-assisted rotational resonance (DARR) photo-CIDNP MAS NMR experiments have been applied to obtain exact chemical shift assignments from those cofactors. Under continuous illumination, the signals are enhanced via three-spin mixing (TSM) and differential decay (DD) and their intensity corresponds to the electron spin density in  $p_z$  orbitals. In multiple- $^{13}\text{C}$  labelled samples, spin diffusion leads to propagation of signal enhancement to all  $^{13}\text{C}$  spins. Under steady-state conditions, direct signal assignment is possible due to the uniform signal intensity. The original intensities, however, are inaccessible and the information of the local electron spin density is lost. Upon laser-flash illumination, the signal is enhanced via the classical radical pair mechanism (RPM). The obtained intensities are related to isotropic hyperfine interactions  $a_{\text{iso}}$  and both enhanced absorptive and emissive lines can be observed due to differences in the sign of the local isotropic hyperfine interaction. Exploiting the mechanism of the polarization, selectivity can be increased by the novel time-resolved two-dimensional dipolar-assisted rotational resonance (DARR) MAS NMR experiment which simplifies the signal assignment compared to complex spectra of the same RCs obtained by continuous illumination. Here we present two-dimensional time-resolved photo-CIDNP MAS NMR experiments providing both directly: signal assignment and spectral editing by sign and strength of  $a_{\text{iso}}$ . Hence, this experiment provides a direct key to the electronic structure of the correlated radical pair.

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### 1. Introduction

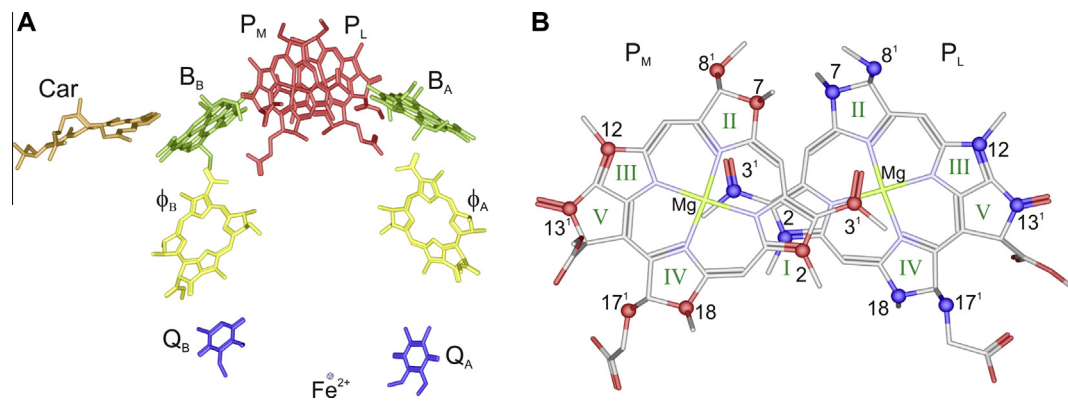
The discovery of the solid-state photo-CIDNP (photochemically induced dynamic nuclear polarization) effect (for reviews: [1,2]) by Zysmilich and McDermott in 1994 in frozen and quinone-blocked bacterial reaction centers (RCs) of *Rhodobacter (R.) sphaeroides* R26 by  $^{15}\text{N}$  magic-angle spinning (MAS) NMR under continuous illumination with white light offered a new experimental access to electron–nuclear processes during charge separation [3]. By induction of a non-Boltzmann nuclear spin polarization, enhancement of signals of a factor of more than 80,000 has been observed from the nuclei of the cofactors forming the light-induced radical

pair [4–7]. In recent years, the solid-state photo-CIDNP effect has also been observed in several photosynthetic RCs, as those obtained from the purple bacteria *R. sphaeroides* wildtype (WT) [4] and R26 [3,5,7], *Rhodospseudomonas acidiphila* [8], the green sulfur bacterium *Chlorobium tepidum* [9], the heliobacterium *Heliobacillus mobilis* [6] as well as of the photosystems I and II of plants [10–12] and algae [13]. The occurrence of the solid-state photo-CIDNP effect appears to be an intrinsic property of natural photosynthetic RCs [14]. Recent observation of the effect in a blue-light photoreceptor [15] demonstrates that the effect is not limited to natural photosynthesis.

In RCs of *R. sphaeroides*, light absorption induces charge separation within 3 ps from the primary donor (P) formed by 2 bacteriochlorophyll *a* (BChl) to the primary acceptor, a bacterio- pheophytin ( $\Phi_A$ ) (for review, see [16]) (Fig. 1A and B). The radical pair is initially in a singlet state (Fig. 2). From this singlet state,

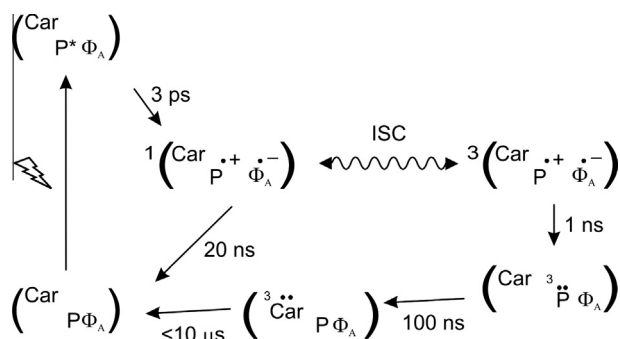
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**Fig. 1.** (A) Arrangement of cofactors in reaction centers (RCs) of *Rhodobacter (R.) sphaeroides* wildtype (WT). The primary electron donor, the special pair, is formed by the two bacteriochlorophyll *a* (BChl) molecules  $P_M$  and  $P_L$ .  $B_A$  and  $B_B$  are accessory BChl cofactors,  $\Phi_A$  and  $\Phi_B$  are bacteriopheophytin (BPhe) cofactors. On the acceptor side, two ubiquinone-10 cofactors  $Q_A$  and  $Q_B$  are located with a non-heme iron in between. The symmetry of the cofactor arrangement is broken by a carotenoid (Car) cofactor. The light-induced electron transfer occurs selectively via branch A. (B) The spatial arrangement of the two cofactors  $P_L$  (right, isotope labels in blue) and  $P_M$  (left, isotope labels in red) forming the special pair. The pyrrole rings are numbered with green Roman numerals. Both pyrrole rings I are overlapping. The isotope labelling pattern has been obtained by feeding with  $3\text{-}^{13}\text{C}_1\text{-}\delta\text{-aminolevulinic acid}$  (3-ALA, see Fig. 4). The long side chains are omitted to provide a better view on the arrangement of the active elements in the charge separation process. [pdb entry 1M3X, (Camara-Artigas et al., 2002b) the figure has been made with Accelrys Discovery Studio]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

photochemically induced dynamic electron polarization (photo-CIDEP) is observed as strongly enhanced absorptive and emissive signals in the EPR spectrum [17,18]. During the lifetime of the radical pair, the electron–spin system oscillates between the singlet state ( $S$ ) [ $^1(P^+\Phi_A^-)$ ] of the radical pair and the triplet state ( $T_0$ ) [ $^3(P^+\Phi_A^-)$ ] with a frequency that depends on both the hyperfine interaction and the difference of the electron Zeeman interaction.



**Fig. 2.** Kinetics and spin dynamics of electron transport in quinone-depleted RCs of *R. sphaeroides* wild type (WT). After absorption of a photon the photochemically excited state of the primary donor  $P^*$  is formed and an electron is transferred to the primary acceptor  $\Phi_A$ , a bacteriopheophytin cofactor. Initially, the radical pair is in its singlet state  $^1(P^+\Phi_A^-)$ . It evolves into a triplet state  $^3(P^+\Phi_A^-)$  due to the electronic interactions and hyperfine coupling with nearby nuclei, a process which is known as intersystem crossing (ISC). The radical-pair mechanism (RPM) leads to sorting of nuclear spins via the isotropic hyperfine coupling, but without a net increase of the population difference of the spin up and the spin down nuclear states. In the TSM, hyperfine coupling, nuclear and electronic Zeeman interactions, and anisotropic interactions involving electrons and nuclei lead to symmetry breaking and net nuclear polarization that can be observed both in laser excitation experiments and under steady-state conditions. The lifetime for recombination from the singlet state to the ground state is 20 ns, while charge recombination from the  $^3(P^+\Phi_A^-)$  radical pair state forms a donor triplet state  $^3P$  with a time constant of 1 ns. With continuous illumination the difference in recombination rates from the singlet and triplet states to the neutral ground state also break the symmetry when they match the inverse of the pseudosecular component of the hyperfine interaction, a process that is known as the DD mechanism. For the WT, the  $^3P$  is rapidly converted (100 ns) in a carotenoid triplet ( $^3Car$ ) and followed by a much slower decay from the carotenoid triplet state to the ground state. Time-resolved experiments have shown that a large fraction of the excited state decays via  $^3Car$ , in competition with back conversion to the  $^3(P^+\Phi_A^-)$  that decays rapidly with 20 ns to establish the steady state. Before reaching this steady state, however, transient effects from RPM, TSM and DD can be observed with time-resolved photo-CIDNP, on a timescale of 10  $\mu s$  and different mechanisms can be resolved by adjusting the time between the photo-CIDNP excitation and the NMR detection scheme.

The coherent interconversion from singlet to triplet radical pairs and back gives rise to spin sorting within the scheme of the well-known radical pair mechanism (RPM) (Fig. 2) [19,20]. Under continuous illumination (CI), the RPM does not induce signal enhancement because the reaction products of both decay branches are have opposite sign and cancel exactly.

In solid-state photo-CIDNP MAS NMR experiments under CI, two additional solid-state mechanisms run in parallel to induce *net* nuclear polarization which remains under steady-state conditions (Fig. 2) [1,2]: (i) Electron–electron–nuclear three-spin mixing (TSM) breaks the balance by coherent evolution of the correlated radical pair state in interaction with the nuclear spins and the applied magnetic field, depending on the signs of the electron–electron and of the anisotropic electron–nuclear interactions [21,22]. (ii) In the electron–nuclear differential decay (DD) mechanism [23], the symmetry is broken by different lifetimes of the  $S$  [ $^1(P^+\Phi_A^-)$ ] and of the  $T_0$  [ $^3(P^+\Phi_A^-)$ ] states. The dependence of secular part of the hyperfine coupling  $A$  is the only single matching of interactions  $2|\omega_i| = |A|$  is required and the difference of singlet and triplet radical pair lifetimes must be of the order of the inverse hyperfine coupling [1]. A more detailed analysis shows [24] that  $^{13}\text{C}$  the hyperfine coupling anisotropy  $\Delta A$  required for these solid-state mechanisms scales with the local electron spin density in the  $p_z$  orbitals of the  $\pi$  system of the radical cation state. Photo-CIDNP intensities in this regime are roughly proportional to  $\Delta A^2$  [1].

In time-resolved experiments on RCs of *R. sphaeroides* WT, transient nuclear polarization has been observed long as 10  $\mu s$  [25]. The decay from the singlet state to the ground state is 20 ns, much faster than the pathway via the donor triplet state  $^3P$ , which is rate limited by the decay from the carotenoid triplet state to the ground state, i.e., 10  $\mu s$  (Fig. 1). Thus, transient nuclear polarization can be observed, originating from the nuclear polarization associated with rapid decay of the  $^1(P^+\Phi_A^-)$  state while the polarization associated with the decay of the  $^3P$  channel is hidden by the paramagnetic triplet state of the carotenoid ( $^3Car$ ) during its lifetime. As a result, the nuclear polarization of the triplet decay channel cannot be detected on the nearby nuclei in experiments with a short delay  $<10\ \mu s$  between optical excitation and NMR detection (Fig. 2) [2,25]. Hence, transiently, using time-resolved experiments, RPM nuclear polarization can be observed under solid-state conditions since the triplet decay rate differs from the singlet one [25]. The sign of the transient light-induced signals follows Kaptein's sign

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