The solid state photo-CIDNP effect

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SUMMARY

Photochemically induced dynamic nuclear polarization (photo-CIDNP) is non-Boltzmann nuclear magnetization which can be observed by NMR spectroscopy as enhanced absorptive (positive) or emissive (negative) signals. In solids, photo-CIDNP has been observed since its discovery in 1994 in various photosynthetic reaction centers by magic angle spinning solid-state NMR. Chapter 1 discusses how the photo-CIDNP effect in solids can be explained by a combination of coherent and relaxation mechanisms, *e.g.*, three-spin mixing and differential decay, which produce nuclear spin polarization from the initial electronic state via hyperfine interaction. Therefore, photo-CIDNP MAS NMR allows to study the electronic structure of the electronic ground-state after the photo-cycle by chemical shifts, and of the radical pair state from NMR intensities, allowing insight into the photochemical machinery of RCs at the molecular level with atomic resolution. Recently, nuclear polarizations up to a factor of 10000 above the Boltzmann equilibrium have been observed, opening new experimental possibilities for solid-state NMR.

In Chapter 2 it is shown that in nanosecond-laser flash photo-CIDNP MAS NMR, polarization generation (PG) proceeds much faster than longitudinal spin relaxation. With a nanosecond laser setup linked to the NMR console the repetition time of the experiment is limited by the minimum recycle delay of the NMR spectrometer and the maximum repetition rate of laser flashes. These limits can only be reached if polarization left after the NMR experiment is completely cancelled before the next laser flash. I introduce a presaturation pulse sequence, based on three ($\pi/2$) ^{13}C pulses and optimized timing and phase cycling that allows for such efficient polarization extinction (PE). This technique is demonstrated on selectively isotope labeled bacterial reaction centers (RCs) of *Rhodobacter sphaeroides* wild type. High-quality ^{13}C photo-CIDNP MAS NMR spectra are obtained using cycle rates up to 4 Hz. The PE-PG strategy proposed here provides a general experimental scheme for reduction of measurement time in magnetic resonance experiments based on fast PG.

In natural photosynthetic charge separation, electron-electron interactions are fine-tuned to lead to highly efficient ET. Nanosecond laser-flash photo-CIDNP magic-angle spinning NMR allows for determination of the nuclear polarizations and hyperfine interactions with atomic selectivity and with a resolution of a few microseconds. In Chapter 3, the build-up of nuclear polarization in reaction centers of *Rhodobacter sphaeroides* is found to depend on the presence and lifetimes of the molecular triplet states of the donor and carotenoid. Analysis of the data reveals that up to three electron-nuclear spin-coupling

mechanisms and two transient effects are working concomitantly in the spin-chemical machinery of RCs. Knowledge of these processes may be crucial to optimize electron-nuclear interactions in artificial photosynthetic devices.

The primary electron donor in bacterial photosynthetic reaction centers consists of two BChl cofactors, P_L and P_M. In Chapter 4 time-resolved ^{13}C photo-CIDNP MAS NMR spectroscopy is used to map the electronic structure of the donor. In the dark state, maximum electron density is localized in the center of the special pair. In contrast, in the light state, the maximum of the electron spin density is localized at the periphery of the two cofactors. The balance of electron spin density between the two BChl cofactors is shifted in favor of P_L by the ratio of 7:3. We show that the asymmetry is induced by both geometric differences between the two cofactors and non-covalent interactions with the protein to similar extents.

Finally, in Chapter 5 a general discussion of the results of this thesis and a future outlook for ns-flash photo-CIDNP MAS NMR are presented. It is shown how the photo-CIDNP intensities depend on the light wavelength and how ns-flash photo-CIDNP MAS NMR can help to elucidate the electronic structure of the whole primary radical pair. Furthermore, liquid state photo-CIDNP NMR intensities in photosynthetic RCs have been observed. In addition, new time-resolved ns-flash photo-CIDNP 2-dimensional MAS NMR experiments, a possible biosynthetic path to label with ^{13}C the carotenoid in the RCs of *Rb. sphaeroides* WT and an imaging experiment using microstrips able to localize RCs in photosynthetic membranes are proposed.