Towards photo-CIDNP MAS NMR as a generally applicable enhancement method

Thamarath Surendran, S.

Author: Thamarath Surendran, Smitha
Title: Towards photo-CIDNP MAS NMR as a generally applicable enhancement method
Issue Date: 2014-02-20

Summary

Solid-state photochemically induced dynamic polarization (photo-CIDNP) is one of the hyperpolarization techniques that tremendously enhances the sensitivity and selectivity of solid state NMR. This thesis addressed several new issues concerning the capacity of photo-CIDNP MAS NMR as hyperpolarization technique: The applicability to cells, the use of medium magnetic fields and its occurrence in non-photosynthetic systems. It is based on the solid-state photo-CIDNP effect which was first observed in 1994 in quinone-depleted bacterial RCs of purple bacteria *Rb. sphaeroides* under illumination and detected by enhanced MAS NMR signals as a dramatic modification of signal intensities. As shown in the Introduction (Chapter 1), the solid-state photo-CIDNP effect is based on several mechaninsms transferring the original electron spin order occurring at the birth of the radical pair to nuclear polarization. The maximum enhancement of this effect was observed at the magnetic field of 4.7 Tesla at about a factor of 10000. Over the years, this technique has proved to be very efficient in understanding the electronic structures of the RCs in several photosynthetic bacteria and plants.

The solid-state photo-CIDNP effect of heliobacterial (*Hb. mobilis*) cells is analytically used in Chapter 2. The pigment in strictly anaerobic *Hb. mobilis* cells (Braunstoff) is photoconverted with bubbling oxygen to a pigment which is very common in aerobic photosynthesis. The bacteria also change their colour to green (Grünstoff). Both forms of these *Hb. mobilis* cells are analyzed by whole-cell ^{15}N and ^{13}C photo-CIDNP MAS. The experiments on ^{15}N and ^{13}C isotope labelled *Hb. mobilis* cells reveal the identity of the radical pair in both forms of *Hb. mobilis*. Time resolved experiments on ^{15}N and 3-^{13}C-ALA labelled *Hb. mobilis* Braunstoff cells demonstrate a remarkable similarity with the photo-CIDNP response from the RC of *Rb. sphaeroides* R26. In Grünstoff, early mobility of triplet states is observed. The colour change and different spectral patterns are explained by the photoconversion of accessory cofactors. This study expands the application of the

solid-state photo-CIDNP effect to explore also natural systems in which the protein purification is impossible or difficult.

The maximum enhancement of the solid state photo-CIDNP effect was observed for a magnetic field of 4.7 Tesla in the quinone depleted RCs of *Rb. sphaeroides* WT and R26. In Chapter 3, the magnetic field dependent studies of the solid state photo-CIDNP effect are expanded to lower magnetic fields as 2.4 and 1.4 Tesla. WT and R26 RCs show different enhancement patterns in magnetic fields less than 4.7 Tesla. In WT RCS, the observed matching curve is well in agreement with the solid-state photo-CIDNP theory. In R26 RCs, the maximum enhancement factor of about 80000 is observed close to a magnetic field of 1.4 Tesla. This pure contribution of the DR mechanism allows to explore the electron spin density distribution of donor triplet state in R26 RCs.

Until now, the solid-state photo-CIDNP effect was considered to be an intrinsic property of photosynthetic RCs. The first observation of the solid-state photo-CIDNP effect for the blue-light photoreceptor phototropin LOV1-C57S is presented in Chapter 4. Magnetic field dependent studies of this protein are presented in Chapter 5. Also here a matching profile is observed that is narrower than the profile observed for WT RCs. It is assumed that the short radical pair lifetime in photosynthetic RCs leads to broad matching functions and therefore straightforward experimental observation.

We addressed several new issues concerning the capacity of photo-CIDNP MAS NMR as hyperpolarization technique: The applicability to cells, the use of medium fields and its occurrence in non-photosynthetic systems. In Chapter 6, it is assumed that photo-CIDNP effects are rather common in electron transfer systems, if the right conditions are applied. Long radical pair life times will lead to short matching windows. Hence, equipment as shuttle systems will have to be applied to operate in this regime. Upon success, photo-CIDNP MAS NMR has a chance to become an attractive generally applicable hyperpolarization method.