HIGH RESOLUTION NMR AND NUCLEAR SPIN HYPERPOLARIZATION WITH FAST FIELD CYCLING

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In this presentation, the fundamentals of spin chemistry and nuclear hyperpolarisation will be outlined concisely. Furthermore, a brief overview of the results from the past decade of research conducted within our Novosibirsk groups will be provided. The prevailing theoretical approach for the description of different types of spin hyperpolarisation has been re-formulated in terms of level crossings (LC) and level anti-crossings (LAC) of interacting spin states [1].

In order to explore the full potential of the unified approach, which addresses different types of LACs through magnetic field variation, a fully automatic, low-cost field cycling add-on was built in Novosibirsk [2]. This add-on covers the ultra-wide magnetic field range from 10 nT to 19.4 T. The shuttling device is characterised by its compact design and compatibility with commercial high-resolution NMR spectrometers. The apparatus under discussion enables the undertaking of variable heteronuclear two-dimensional nuclear magnetic resonance (2D NMR) and nuclear relaxation measurement with high resolution and high-throughput. This apparatus facilitates para-hydrogen-induced nuclear spin hyperpolarisation (PHIP) and signal amplification via reversible exchange (SABRE), as well as proton and heteronuclear photo-CIDNP and photo-SABRE [3]. It was demonstrated that the most efficient polarization transfer occurs at LACs, and that such transfer is of a coherent nature. It is evident that the utilisation of magnetic field dependence has led to the formulation of highly efficient experimental protocols for the hyperpolarisation of ^{13}C, ^{15}N, ^{19}F, ^{31}P and ^{77}Se nuclei via the implementation of adiabatic magnetic field modulation at LACs [4,5]. The proposed approach has the potential to enhance the efficiency of hyperpolarization processes at zero and ultralow magnetic fields (ZULF), as well as at weak and strong magnetic fields through the application of shaped pulses of oscillating magnetic fields.

In the domain of spin chemistry, the magnetic interactions between electrons and nuclei are encoded in the field dependence of CIDNP (Chemically Induced Dynamic Nuclear Polarisation). This process is modulated by nuclear relaxation dispersion, which plays a crucial role in the dynamics of the system. The combination of studies conducted over an ultra-wide magnetic field range facilitates the disentangling of contributions from distinct mechanisms to singlet-triplet conversion, thereby unveiling the occurrence of polarization transfer among nuclei. Photochemically active, covalently linked electron donor–bridge–acceptor triads have long been the focus of solar energy storage, due to their resemblance to photosynthetic reaction centres. A series of donor-acceptor dyads were examined through ^{13}C, ^{15}N and ^{1}H field-dependent and ^{1}H time-resolved photo-CIDNP, with theoretical calculations providing a contemporary framework. This comprehensive approach elucidated the LACs in magnetic field dependence and ascertained the sign and values of the electronic exchange interaction and detailed map of ^{13}C and ^{1}H hyperfine interactions in transient, short-lived biradicals [6].

The phenomenon of photoinduced intramolecular electron transfer (ET) is of paramount importance in the realm of charge transport in biological and synthetic systems. In the recent study, the ET was examined in peptide His-Glu-Tyr-Gly (1) and the conjugate His-Gln(BP)-Tyr-Gly (2) with benzophenone (BP) as a photoactive electron acceptor and His or Tyr as donors [7]. Time-resolved and field-dependent chemically induced dynamic nuclear polarization (CIDNP) techniques were employed to investigate electron transfer (ET) mechanisms and kinetics. Peptide 1, with benzophenone as photosensitiser, initially forms two types of radical, with a radical centre at either His or Tyr residue. Consequent to this, electron transfer (ET) occurs from Tyr residue to the His radical, both intra- and intermolecularly. Conjugate 2 forms two types of biradicals under irradiation: with radical centres at Tyr and BP across the entire pH range, and with radical centres at His and BP at slightly basic pH. Field-dependent CIDNP revealed nonzero electronic exchange interaction ($2J(ex) = -8.78$ mT) at acidic pH, indicating proximity between BP and Tyr radicals. Low-field CIDNP spectra exhibited pronounced emissive polarization patterns, accompanied by pH-dependent exchange interactions in transient biradicals.

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