Advancements in Modulated MARY Spectroscopy

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MARY spectroscopy is a technique used for the detection of Magnetically Altered Reaction Yields. A variety of methods, most commonly based on optical detection, are used for probing the response of the chemical system to an applied magnetic field. Systems which exhibit a Magnetic Field Effect (MFE) comprise a spin correlated radical pair which undergoes coherent evolution between electron spin states with different magnetic moments (S↔T).

Modulated MARY [1] is a fluorescence experiment in which the applied magnetic field has both a static and a single frequency component. The fluorescence emitted by a field dependent participant in the radical pair reaction scheme is demodulated in a Lock-In Amplifier and measured.

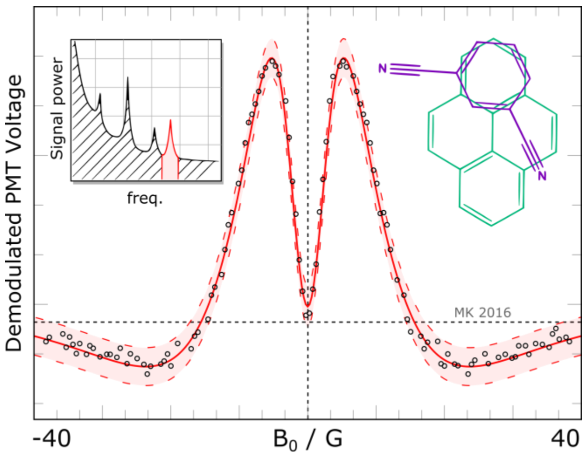

Figure 1 – Overtone MFE signal on the fluorescence of pyrene/1,3-dicyanobenzene exciplex (top right). The signal is detected by field modulation and demodulation (top left) which leads to increased sensitivity.

Here we present recent improvements of the experimental technique and application of the overtone detection for measurements of MFEs at low field. Low-field effects are especially important in the context of Flavin-based biological systems implicated in the mechanism of the avian magnetoreception. In this work, a proof-of-principle study has been conducted on a well-characterised, exciplex-forming pyrene / 1,3-dicyanobenzene system [2].

We also introduce a novel data analysis method – inverse convolution of the data with the theoretical modulation kernel by means of curve fitting. This technique aims to reconstruct the underlying MFE curve, taking into consideration the field modulation broadening effects resulting from large modulation amplitude.

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References:

[1] C. A. Hamilton, J. P. Hewitt, K. A. McLauchlan, and U. E. Steiner, *"High resolution studies of the effects of magnetic fields on chemical reactions"* Mol. Phys., vol. 65, no. 2, pp. 423–438, 1988.

[2] D. R. Kattnig, A. Rosspeintner, and G. Grampp, *"Magnetic field effects on exciplex-forming systems: the effect on the locally excited fluorophore and its dependence on free energy"* Phys. Chem. Chem. Phys., vol. 13, no. 8, pp. 3446–60, Feb. 2011.