

# **Specific MARY Spectrum from Radical Anion of Pentafluorobenzene**

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## **Abstract**

The paper presents the first resolved experimental MARY spectrum for a system with nonequivalent nuclei – radical anion of pentafluorobenzene. This observation dispels the common apprehension that because of rather involved energy level layout a system with not all nuclei magnetically equivalent cannot produce resolved MARY lines in nonzero fields, and greatly increases the practical scope of level-crossing techniques for studies of spin-correlated radical pairs. The experimental finding is supported by schemes of energy levels calculated for this system.

## **1. Introduction**

Spin chemistry techniques offer a valuable extension of magnetoresonance methods to short-lived paramagnetic species such as transient radicals and radical ions, which form as spin-correlated pairs and often persist for only as short as several nanoseconds [1]. However, the gain in sensitivity of an experimental technique to shorter times is invariably accompanied by a trade-off in its spectroscopic richness. Techniques employing microwave (MW) pumping, such as various implementations of Reaction Yield Detected Magnetic Resonance (RYDMR), in principle produce complete ESR spectra of pair partners, but already lack finer details of the conventional CW ESR spectra due to shorter lifetimes of the target species and usually relatively high MW power and modulation amplitude needed to obtain the spectra in the first place. Because of indirect, i.e. optical detection of resonance microwave absorption RYDMR techniques can tolerate very low stationary concentrations of the target species, but still require that they live long enough to flip their spin with available microwave power. This usually translates into about 100 ns for a typical maximum available MW power of about 1 W for a conventional CW ESR bridge and resonator. Still shorter lifetimes are accessible for level-

crossing techniques such as Magnetically Affected Reaction Yield (MARY) spectroscopy, in which the driving force is the much stronger internal hyperfine couplings (HFC) in the partners of the pair rather than the applied oscillating field. Species with lifetimes down to nanoseconds become routinely observable, but the spectrum itself is a single line in zero magnetic field bearing almost no information on magnetic parameters of the target species.

However, in 1980s it was realized that level crossing in radical pairs can in principle produce specific spectra. It is very fitting to acknowledge in this Festschrift that Kev Salikhov and colleagues demonstrated [2, 3] that systems with equivalent nuclei, such as radical anion of hexafluorobenzene, can in principle produce observable lines in nonzero fields – multiples of the single hyperfine coupling constant  $A_{\text{HF}}$ . Although much weaker than the ubiquitous zero field line, these “satellite” lines were then indeed observed experimentally [4, 5], and even richer spectra were reported later [6]. The uniqueness of systems with equivalent nuclei lies in a very regular energy level layout governed by just one parameter  $A_{\text{HF}}$ , so that the crossings for them also occur at regular, well-defined places and thus lend themselves to experimental observation. For a more complex system the crossings would spread out and become even weaker, and it was believed that there is little hope in going beyond equivalent nuclei. In this contribution we present a reliable MARY spectrum for a system with non-equivalent nuclei – radical anion of pentafluorobenzene. This observation provides a major boost to possible spectroscopic content of level-crossing techniques as applied to radical pairs in solution, and invites a further development of ideas first formulated in [2, 3].

## **2. Experimental**

A detailed description of MARY (Magnetically Affected Reaction Yield) spectroscopy as applied in this work was published recently [7, 8], and we only briefly summarise the method here. MARY spectrum is essentially a conventional stationary magnetic field effect (MFE) curve

– dependence of the yield of recombination fluorescence from radical ion pairs in irradiated solutions on external static magnetic field – with sharp lines in zero and low field due to degeneracy of the spin energy levels of the pair. Similar techniques have also been implemented by other groups [9-15]. To amplify the weak and narrow MARY lines against the slowly changing background of the MFE, magnetic field modulation with lock-in detection of the signal and symmetric passage through zero of the field is used, producing a first derivative experimental spectrum resembling CW ESR lines.

Experimentally about 1 cm<sup>3</sup> of degassed solution in a quartz cuvette is placed in the field of a Bruker ER-200D ESR spectrometer equipped with an offset coil with a separate DC power supply to provide “negative” shift of magnetic field, an X-ray tube (BSV-27Mo, 40kV x 20mA) for sample irradiation, and a photomultiplier tube assembly (FEU-130) to detect fluorescence. The external magnetic field is modulated at 12.5 kHz, and the signal from PMT is demodulated with a Stanford SR-810 Lock-In Amplifier interfaced to PC. No microwave power was ever applied to the samples. All experiments were carried out at room temperature. The purified solvents – *n*-dodecane and squalane – were provided by Mrs N.Ivanova and Dr. V. Borovkov. Pentafluorobenzene (98+%) was purchased from Avocado and used without additional purification.

### 3. Results and discussion

Fig. 1 shows experimental MARY spectra for solutions of pentafluorobenzene in alkanes. The left portion of the figure shows the spectrum for solution of 10<sup>-2</sup> M C<sub>6</sub>F<sub>5</sub>H in *n*-dodecane in field range from -50 to 550 G with modulation amplitude 10 G, total acquisition time about 20 hours (averaging over 100 repetitive scans about 10 min each). It can be seen that there is a pronounced zero field line, which is slightly overmodulated under these conditions, the wide arching background of the conventional MFE curve, and a group of lines in the vicinity of 100 G

put in the balloon – the subject of this work. The right portion of the figure shows the spectrum for solution of  $2 \cdot 10^{-2}$  M  $C_6F_5H$  in more viscous squalane in a smaller field range from -50 to 250 G and with lower modulation amplitude of 5 G – all done to improve resolution, total acquisition time about 10 hours (averaging over 100 repetitive scans about 5 min each). It can be seen that the group of lines consists of two dominant lines in higher field, at about 150 G and about 90 G, and two further, weaker shoulders can be discerned in lower fields, at about 50 G and about 30 G. The recombining pairs in both cases is radical anion of pentafluorobenzene and radical cation of solvent, and the dominating hyperfine couplings are concentrated in the radical anion, for which two sets of slightly different  $A_{HF}$  have been reported:  $A_F(2) = A_F(6) = 101$  G,  $A_F(3) = A_F(5) = 45.5$  G,  $A_F(4) = 279$  G,  $A_H = 4.0$  G [16], or  $A_F(2) = A_F(6) = 107$  G,  $A_F(3) = A_F(5) = 48.0$  G,  $A_F(4) = 295$  G [17]. The role of the luminophore is played by pentafluorobenzene.

To explain the observed experimental spectrum the energy layout of this system was analyzed theoretically. In modeling it was assumed that the pair consists of a partner with five spin  $\frac{1}{2}$  nuclei in groups 1, 2, 2 with  $A_{HF}$  279 G, 101 G, 45.5 G, respectively, and a partner without hyperfine couplings that models the radical cation of the pair. The modeled Hamiltonian has the form:

$$H = \{ \omega S_{1z} + \vec{S}_1 (a_1 \vec{I}_1 + a_2 (\vec{I}_2 + \vec{I}_3) + a_3 (\vec{I}_4 + \vec{I}_5)) \} + \{ \omega S_{2z} \},$$

where the terms in curly braces describe the two partners,  $\omega$  is the external magnetic field. Since there are 7 spins  $\frac{1}{2}$  in this system, there is a total of 128 states. However, there are three conserved quantities in this system, total nuclear spin of equivalent nuclei 2 and 3 (either 0 or 1), total nuclear spin of equivalent nuclei 4 and 5 (either 0 or 1), and total z projection of all spins in the system (electrons and nuclei). The matrix of the Hamiltonian is thus reduced into block-diagonal form, with the largest block of 18 interlocked states, which were diagonalized numerically. Fig. 2 shows thus computed eigenvalues (energy levels of the system) for two representative blocks, left with effective nuclear spins  $\frac{1}{2}$ , 1, 1 and their projections  $\frac{1}{2}$ , 0, -1,

respectively, and right with effective nuclear spins  $\frac{1}{2}$ , 1, 1 and their projections  $\frac{1}{2}$ , 1, -1, respectively. The electron projections were either  $\alpha\beta$  or  $\beta\alpha$ , as the pair in experiment is formed in its singlet electron state. It can be seen that there are multiple crossings, but, although indeed spread out, they still tend to cluster in the fields where lines are observed in experiment: about 150 G, about 90 G, about 30-50 G. There are certain crossings at other fields as well, but these were not resolved in experiment. There also are other blocks in the Hamiltonian, but the presented energy level diagrams with crossings are indeed representative, and furthermore, they are statistically most significant contributors to the overall signal from the pair.

#### **4. Conclusion and Outlook**

In this work we have obtained a reproducible resolved MARY spectrum for a system with nonequivalent nuclei. This observation leads to a paradigm shift in applied level crossing spectroscopy, demonstrating the possibility of going beyond systems with equivalent nuclei and drastically expanding the scope of systems available for experiment. Although the presented spectra required rather long acquisition times, the lines themselves are not exceedingly weak and indeed compare favorably with lines for systems with equivalent nuclei. It is now believed that for a system with a fairly good luminophore the spectra can be taken much faster, which is important for practical applications. Complete theoretical description of such systems, although rather tedious, is nevertheless possible, as was recently demonstrated numerically for a more complex nuclear configuration 4+4+2 (originally pyrene[12] and then biphenyl [18]) and analytically for two groups of equivalent nuclei [19], and is now most welcome.

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## Figure Captions

Fig. 1. Experimental MARY spectra for solution of  $10^{-2}$  M  $C_6F_5H$  in *n*-dodecane, modulation amplitude 10 G, 100 scans x 10 min (a), and solution of  $2 \cdot 10^{-2}$  M  $C_6F_5H$  in squalane, modulation amplitude 5 G, 100 scans x 5 min (b).

Fig. 2. Eigenvalues for two representative sub-blocks of Hamiltonian, both with effective nuclear spins  $\frac{1}{2}$ , 1, 1, projections  $\frac{1}{2}$ , 0, -1 (left), and  $\frac{1}{2}$ , 1, -1 (right), respectively, electron projections  $\alpha\beta / \beta\alpha$ .

Fig. 1.



