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# Measurement of hyperfine coupling constants of muoniated radicals in small molecule semiconductors

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**Abstract.** We report the hyperfine coupling constants of muoniated radicals formed in a number of organic semiconductors, via transverse field measurements taken in the Paschen Back limit, and compare the results to avoided level crossing resonances. Five muoniated radicals are found in tetracene, despite there only being three potential non-equivalent bonding sites, and we suggest that this might be down to crystal packing effects. For 6,13-bis(triisopropylsilylethynyl) pentacene and 6,13-bis(trimethylsilylethynyl)-pentacene, we demonstrate that the transverse field data supports the previously published avoided level crossing resonances.

## 1. Introduction

The investigation of organic materials (OSC) is vital for the advancement of organic electronics. Owing to the ability to probe at a microscopic (local) level, the muon spin rotation/relaxation/resonance (MuSR) techniques have been extensively employed for studying this material class. In particular, it has been used to quantitatively determine the electron spin relaxation rate and the electron spin relaxation mechanisms in organic semiconductors by using the sensitivity to spin dynamics in the system at so-called avoided-level crossings (ALC) [1, 2, 3]. A more specialized technique, the low-energy muon spin rotation technique, allowed for implanting muons at buried interfaces of fully functional organic-based spintronic devices, thereby enabling the measurement of spin injection into the organic spacer layer [4]. This resulted in a better understanding of their functionality [4] and how the spintronic property of these devices can be engineered [5]. In these latter studies of spin dynamics in organic semiconductors, it is of critical importance to characterise the muoniated radicals, which are very much material specific. Here we report avoided level crossing (ALC) and transverse field (TF) measurements taken in the Paschen Back limit to determine the hyperfine coupling (HFC) constant of muoniated radicals in a number of organic semiconductors [6, 7, 8].



## 2. Theoretical background

A considerable fraction of the muons that are implanted into an organic material can usually capture an electron to form muonium, which to all intense purposes, is analogous to hydrogen in an organic semiconductor. The muon and electron spins interact via the hyperfine interaction, resulting in a four level system (one spin singlet and three spin triplet states). After a chemical reaction of the muonium with a molecule, a molecular radical (molecule with an unpaired electron) is formed, typically with a significantly lower HFC constant,  $A$ , than the vacuum value. At the time of formation, the coupled spin system can be with equal probability either in the  $|\uparrow_\mu\uparrow_e\rangle$  or  $|\uparrow_\mu\downarrow_e\rangle$  state, the latter being a combination of the triplet  $|\uparrow_\mu\downarrow_e\rangle + |\downarrow_\mu\uparrow_e\rangle$  and singlet  $|\uparrow_\mu\downarrow_e\rangle - |\downarrow_\mu\uparrow_e\rangle$  states. The four energy eigenvalues of the system, corresponding to the three spin triplets and one singlet, are [11]

$$E_{|\uparrow_\mu\uparrow_e\rangle} = E_1 = \frac{\hbar}{4} [A + 2B(\gamma_e - \gamma_\mu)] \quad (1)$$

$$E_{|\uparrow_\mu\downarrow_e\rangle + |\downarrow_\mu\uparrow_e\rangle} = E_2 = -\frac{\hbar}{4} \left[ A - 2\sqrt{A^2 + B^2(\gamma_e + \gamma_\mu)^2} \right] \quad (2)$$

$$E_{|\downarrow_\mu\downarrow_e\rangle} = E_3 = \frac{\hbar}{4} [A - 2B(\gamma_e - \gamma_\mu)] \quad (3)$$

$$E_{|\uparrow_\mu\downarrow_e\rangle - |\downarrow_\mu\uparrow_e\rangle} = E_4 = -\frac{\hbar}{4} \left[ A + 2\sqrt{A^2 + B^2(\gamma_e + \gamma_\mu)^2} \right]. \quad (4)$$

Upon application of an external transverse magnetic field,  $B$ , the muon spin in isolated muonium precesses at a frequency that corresponds to the energy difference  $E_i - E_j$ . In high transverse magnetic fields ( $B \gg A/(\gamma_e + \gamma_\mu)$ ), only the muon spin precession frequencies governed by the energy differences  $E_1 - E_2$  and  $E_3 - E_4$  are observable. The other precessions are quenched out, i.e. their amplitude is zero [9, 11]. This is the so-called Paschen-Back regime. The two observable muon spin precession frequencies are [10]

$$f_{12} = \frac{1}{2}A + \frac{1}{2}(\gamma_e - \gamma_\mu)B - \frac{1}{2}A\sqrt{1 + \left(\frac{2B(\gamma_e + \gamma_\mu)}{A}\right)^2} \quad (5)$$

and

$$f_{34} = \frac{1}{2}A - \frac{1}{2}(\gamma_e - \gamma_\mu)B + \frac{1}{2}A\sqrt{1 + \left(\frac{2B(\gamma_e + \gamma_\mu)}{A}\right)^2}. \quad (6)$$

The sum of the two frequencies amounts to the isotropic hyperfine coupling constant [9, 10]

$$A = f_{12} + f_{34} \quad (7)$$

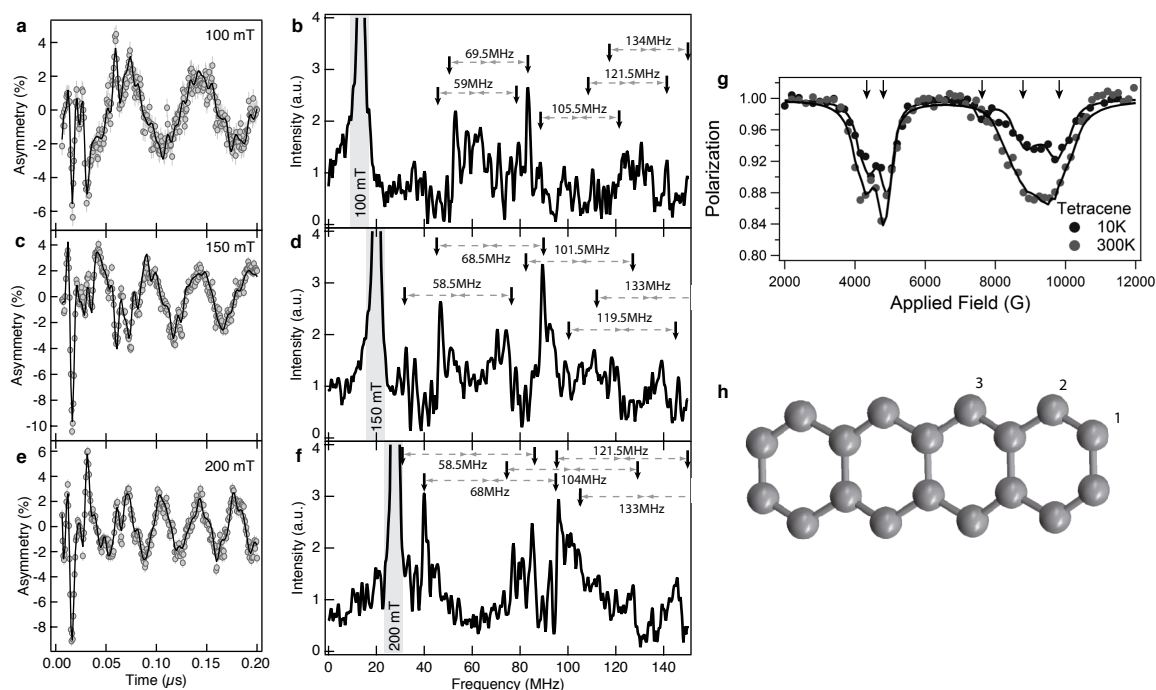
and practically in high TF experiment, these frequencies can be accessed either by conventional Fourier transforms or by fitting the time dependent asymmetry  $A_0$  directly to a sum of relaxed oscillations (two frequencies  $f_{12}$  and  $f_{34}$  per muonium site plus the diamagnetic fraction).

## 3. Results and Discussion

The MuSR experiment was performed on polycrystalline samples of the organic semiconductors tetracene, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) and 6,13-bis(trimethylsilylethynyl)-pentacene (TMS-pentacene). The transverse field (TF) measurements were taken in the Paschen-Back regime at a temperature of 10 K using the GPS spectrometer of the Paul-Scherrer-Institute, Switzerland, and the avoided level crossing (ALC) spectra were taken on the HiFi instrument at the ISIS Pulsed Muon Source, UK. For each TF data set, a total of 250 million events were measured, and we took 10 million events for each magnetic field in the ALCs.

### 3.1. Tetracene

Figures 1a-f shows the measured forward-backward asymmetry and Fourier transforms at 100 mT, 150 mT, and 200 mT. The Fast Fourier Transforms (FFT) were obtained by apodising the time spectra with an exponential function with a characteristic time of  $0.3 \mu\text{s}$  prior to using the FFTW routine [13]. The truncated peak at about 13.5 MHz in the 100 mT data corresponds to the interstitial free muons that precess in the externally applied magnetic field. Many satellite peaks are observable in the spectra, in pairs where the sum of the two frequencies corresponds to the HF coupling constant. The two most clear satellite peaks correspond to a HFC of  $A_{\text{TC}} = 136.3 \pm 0.3 \text{ MHz}$ . The quite complex Fourier spectra indicate there are additional components that are difficult to resolve, which is also clear in the raw time spectra. To aid in interpretation of this data, we performed an Avoided Level Crossing (ALC) measurement on the same sample using the HiFi instrument at ISIS, which is shown in Figure 1g. Multiple ALC resonances are clear, particularly at 10K, indicated by the black arrows. We modelled the spectrum using the freely available Quantum software [14] and were able to resolve five independent ALCs. Details of the hyperfine coupling constants extracted from the 10 K data are given in Table 1; further details of the ALC spectra on tetracene and other heteroacenes will be given elsewhere [15]. It is worth noting here, however, that from the molecular structure shown in Figure 1h, only three non-equivalent sites should be present in tetracene. Given that the  $\Delta_0$  ALC lines are unlikely to be large or wide enough to be observable in these spectra [2], we believe that the crystal packing breaking the equivalency of the different sites is a more likely explanation, resulting in more  $\Delta_1$  ALC lines than expected from the three sites. It is also worth noting that the various lines in the frequency spectra will be broadened by the anisotropic HFC, even in the Paschen-Back limit, making them weak and indistinct in the Fourier spectra.



**Figure 1.** Transverse magnetic field data for tetracene using a,b) 100 mT, c,d) 150 mT and e,f) 200 mT. Data is shown in the a,c,e) time domain data (points) and fits (lines). b,d,f) show frequency domain, with the black arrows indicating the peaks predicted by the time domain fits. g) An ALC spectra for tetracene at 10 and 300 K. The lines show the results of the modelling, from which the HFCs can be extracted. h) The molecular structure of tetracene with H omitted.

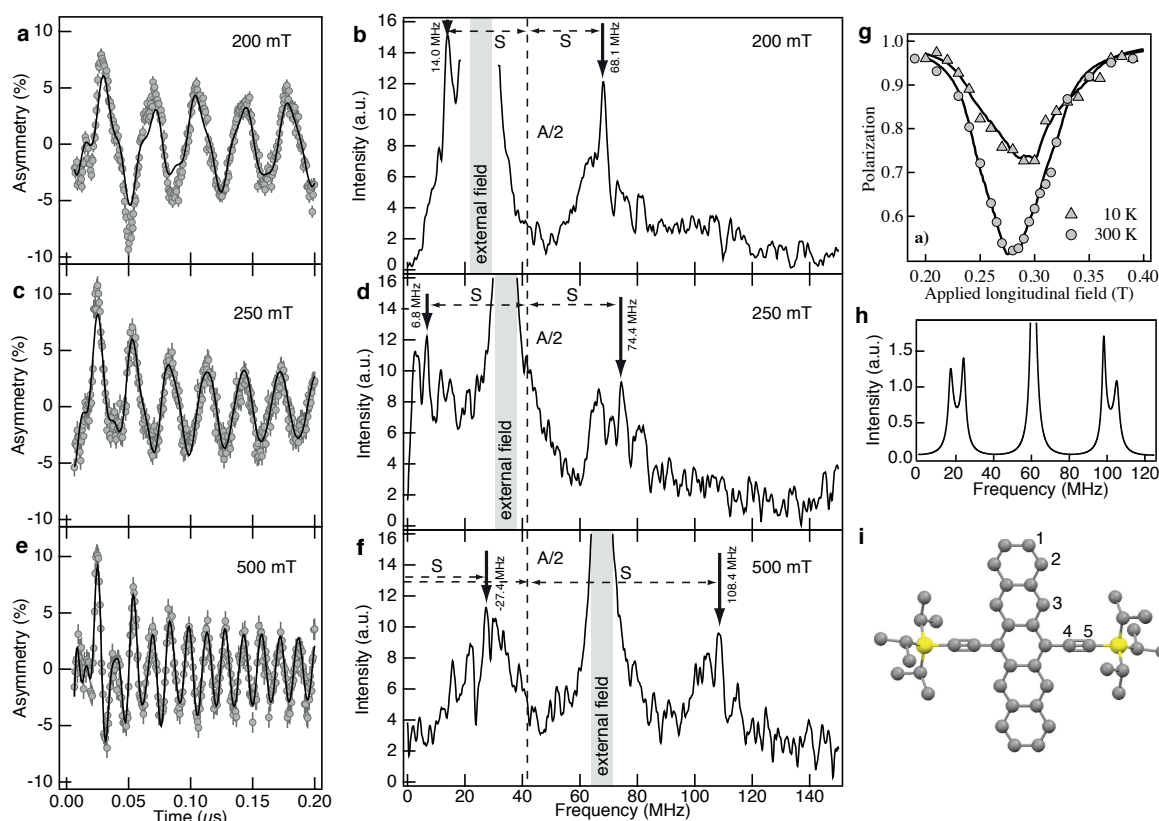
**Table 1.** Extracted hyperfine parameters for the five different muoniated radicals in tetracene, from the ALC modelling and time domain fits for the three different fields. The satellite peaks expected from the time domain fits are indicated on the frequency spectrum in Figure 1b), d) and f). Frequencies are in MHz and have been rounded to the nearest integer. Errors have been rounded up.

	<b>ALC</b> HFC	<b>TD</b> HFC	<b>0.2 T</b>		<b>TD</b> HFC	<b>0.15 T</b>		<b>TD</b> HFC	<b>0.1 T</b>	
			$f_{12}$	$f_{34}$		$f_{12}$	$f_{34}$		$f_{12}$	$f_{34}$
1	120	117±2	31±2	86±1	117±9	39±1	78±9	118±2	45±2	73±1
2	135	136±1	40±1	96±1	137±1	47±1	90±1	139±1	55±1	84±1
3	208	208±3	75±1	133±3	203±8	82±8	121±1	211±2	92±1	119±2
4	243	243±1	96±1	147±1	239±1	100±1	139±1	243±10	108±10	135±1
5	267	266±3	104±2	162±2	266±1	111±1	155±1	268 ±4	119±2	149±3

Using the information on the HFC extracted from the ALCs, we fit the time series spectra to an eleven component fit; ten frequencies from the muonium (five lots of  $f_{12}$  and  $f_{34}$  per muonium site) plus the diamagnetic fraction. The resultant fits are shown in Figure 1a,c, and e, and it is clear that the complex time domain fits are in extremely good agreement with the experimental data. The results of the fitted frequencies are shown in Table 1, and they compare very favourably to the values obtained from the ALC modelling. This indicates that the five ALC lines are all from  $\Delta_1$  transitions.

### 3.2. TIPS-Pentacene

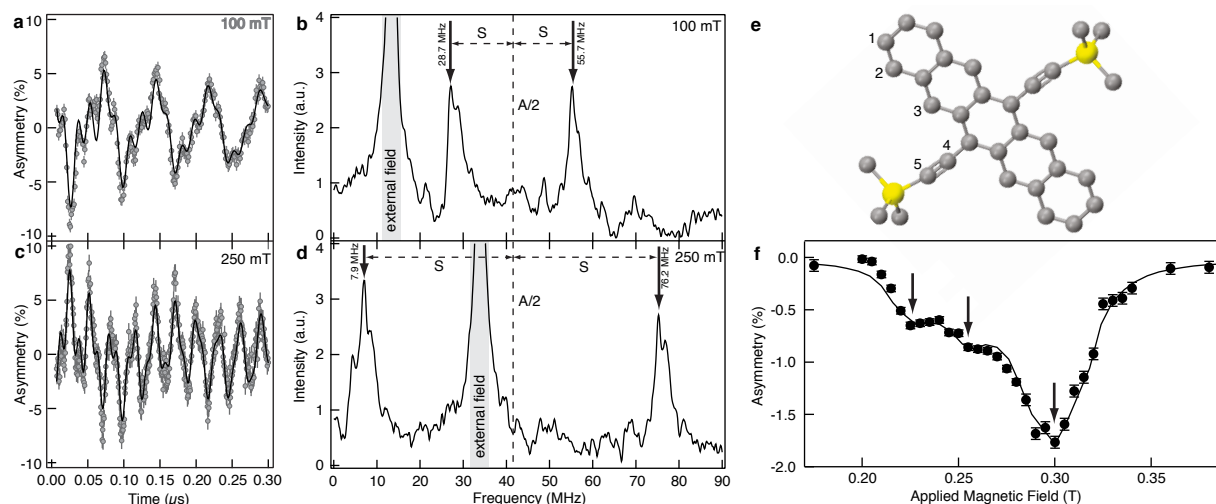
Figures 2a-f shows similar data sets for applied fields of 200, 250 and 500 mT for the case of TIPS-pentacene. The characteristic frequencies are once more indicated by the black arrows in Figures 2b,d and f. Interestingly, the spectra are significantly less noisy, or less complex, than tetracene. However, the satellite peaks appear relatively broad, which could be either from the anisotropic terms of the hyperfine tensor or from more than one site with a slightly different isotropic hyperfine coupling constant, such that the multiple satellite peaks are partially merged and difficult to unambiguously distinguish from each other. Previously, maximum entropy analysis of the ALC measurements and TF data (shown in Figure 2g and h respectively) indicated there were two muoniated radicals with similar HFCs, [5]. These two sites may originate from different muonium bonding positions (or binding angles to the same site) with a slightly different HFC constants. DFT calculations in the original work suggested that sites 3 and 5, shown in Figure 2i, have very close HFCs resulting in overlapping ALCs. The TF measurements presented here are consistent with the previously reported data. The separation of the satellite peaks,  $2S$ , increases as a function of the external field. Notice that one frequency is negative signifying a reversal of the precession direction. As negative and positive precession frequencies cannot be distinguished in a power spectrum, both appear as positive values. However, the distance,  $S$ , is reflected from the ordinate axis as can be seen in Figure 2e, thereby revealing that the value is indeed negative. The average value for the isotropic HF interaction constant extracted from a three-component fit to the time domain data is  $A_{\text{TIPS}} = 81.4 \pm 0.6$  MHz. Unfortunately, since the two HFCs are so close, it is not possible to fit a five component function to the data, although the maximum entropy, FFTs and the ALC data suggest it is present.



**Figure 2.** a,c,e) Time-domain asymmetry plots of transverse field measurement of TIPS-pentacene at 200 mT, 250 mT and 500 mT. The solid lines are fits to the data. b,d,f) The corresponding power spectra in the frequency domain. The satellite peaks are pointed out by the arrows. g) Muon’s polarisation as a function of magnetic field, where two distinct ALC resonances are observable. h) Maximum entropy analysis of the TF data shown in f, where two very distinct peaks are observable. i) Molecular structure of TIPS-Pentacene, with the muonium bonding sites indicated. All data were taken at a temperature of 10 K.

### 3.3. TMS-Pentacene

An equivalent data set for TMS-pentacene for the applied fields of 100 and 250 mT are shown in Figure 3. Similar to TIPS-Pentacene, the spectra are significantly less noisy or less complex than tetracene. However, it can be seen that there is also a skewness to the satellite peaks. Previously reported ALC measurements indicated that three sites with similar isotropic HFCs exist in TMS-pentacene [3], as shown by the black arrows in Figure 3f, suggesting that the skewness observed in Figure 3 is indeed related to the multiple positions of the muonium. However, we are unable to completely rule out that it is down to anisotropy. Due to the difficulties resolving these additional peaks, the pair of satellite peaks with the highest intensity is followed in the FFTs, where it can be seen that  $S$  increases with increasing external field, while  $A$  and hence  $A/2$  remain almost constant. The isotropic HF coupling constant  $A_{\text{TMS}} = 84.0 \pm 0.6$  MHz extracted from fits to the time domain is very close to the value (82 MHz) extracted from the most intense ALC shown in Figure 3f [3]. As discussed above, only two ALC resonances were observed in TIPS-pentacene at this field, despite the similarity in molecular structure with TMS-Pentacene. The additional site in TMS-pentacene could be related to solid-state packing, as TMS-pentacene crystallises with a herringbone packing [3] whereas TIPS-pentacene crystallises with a two-dimensional brickwork arrangement, with close  $\pi - \pi$  overlap [2].



**Figure 3.** a-d) The TF data for TMS-pentacene. e) The molecular structure of TMS-Pentacene, with five potential muonium adducts shown. d) The asymmetry as a function of field, where three clear ALC resonances are observable. All data were taken at a temperature of 10 K.

#### 4. Conclusions

We have reported HFC constants for muoniated radicals in three organic semiconductors, using a combination of TF and ALC techniques. In all cases, the extracted constants from the TF and ALC measurements are within the margin of error of each other, and their values are within the expected range in molecules such as these [2]. Interestingly, in tetracene, we observe two ALC resonances more than there are unique sites on the molecule. TF data suggests these ALC resonances are not  $\Delta_0$  lines, since the data appears consistent with multiple components. The eleven component fit (five HFCs plus diamagnetic) give HFCs that are very similar to those extracted from the ALCs. We conclude these additional HFCs are related to the crystal packing, either by lifting the inequivalency of bonding sites or by enabling different bonding angles on the same site. We also observe more ALC resonances in TMS-pentacene than in TIPS-pentacene, despite a similar molecular structure. We conclude that this is also due to crystal packing.

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