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Supplementary Information: A Study of the Dynamics and Structure of the Dielectric Anomaly within the Molecular Solid TEA(TCNQ)$_2$

Adam Berlie, Ian Terry, Marek Szablewski, Mark Telling, David Apperley, Paul Hodgkinson and Dominik Zeller

Muon Spin Spectroscopy

Within a typical μSR experiment, spin-polarised positive-muons are implanted within the sample and the decay of the muon polarisation is measured over many lifetimes of the muon half-life (2.2 μs). This is achieved as the decay product of the positive-muon, a positron, is preferentially emitted along the direction of the spin-direction of the muon at the time of decay, and detector arrays or banks measure the asymmetry of this decay. The positive-muon is a local probe sampling a radius of ~2 nm and it is an effective probe of local nuclear and electronic magnetism. The gyromagnetic ratio of the muon, $\gamma_\mu/2\pi$ is 135.5 MHz T^{-1}, and one can relate the precessional frequency of the muon to a static applied or internal field using the formula, $B_{\mathrm{int/ext}} = (2\pi/\gamma_\mu)\nu$, where $B_{\mathrm{int/ext}}$ is the internal or external magnetic field and ν is the precessional frequency. If the static field at the muon site becomes more inhomogeneous, one sees a broadening of the precessional frequency and a field distribution can be extracted from the spectra. For dynamic magnetic behaviour, be it electronic or nuclear, the μSR technique allows one to probe the variations within the MHz time window, where one sees a modulation of the static field distribution.

The muon is an exceptionally sensitive probe of weak magnetic fields in zero applied field and is a local probe sampling approximately a 2 nm radius mainly through a dipolar interaction that varies as $1/r^3$. Within TCNQ-based systems, it is believed that the muon forms a sigma bond with a nitrogen atom on a single TCNQ molecule [1, 2]. The result is a diamagnetic muonium state with the muon spin being most sensitive to the nuclear moment of the nitrogen atom and resulting TCNQ molecule. One particular advantage of the μSR technique is that as you are probing on the MHz time scale, one doesn't detect higher frequency processes such as soft phonon modes, which are generally observed at GHz-THz frequencies. Therefore the muon is able to selectively probe molecular and electronic dynamics in the MHz window. From previous work, the electronic moment on the TCNQ dimer is shown to be motionally narrowed at these high temperatures [3].

The time spectra associated with the decay of the muon polarisation were fitted using a dynamical Kubo-Toyabe function [4]. The static form of the Kubo-Toyabe function in zero field can be described by

$$P(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2) \exp\left(\frac{-\Delta^2 t^2}{2}\right), \tag{1}$$

where Δ is the width of the field distribution at the muon site and describes a static array of randomly orientated moments; these can be either electronic or nuclear. The 1/3 and 2/3 factors are due to the averaging over all 3 Cartesian coordinates, where 1/3 of the moments are aligned along the initial muon polarisation and therefore one observes no depolarisation of the muon spin at these sites. If the moments are not static and fluctuating within the time scale of the muon, this will modulate the field distribution and one enters a scenario, where the polarisation of the muon ensemble samples the field distribution, Δ, but also a fluctuation rate, ν. The increase in the fluctuation rate causes the 1/3 tail of the muon polarisation to relax and eventually, when $\nu > \Delta$, the muon spin relaxation will be exponential in nature.

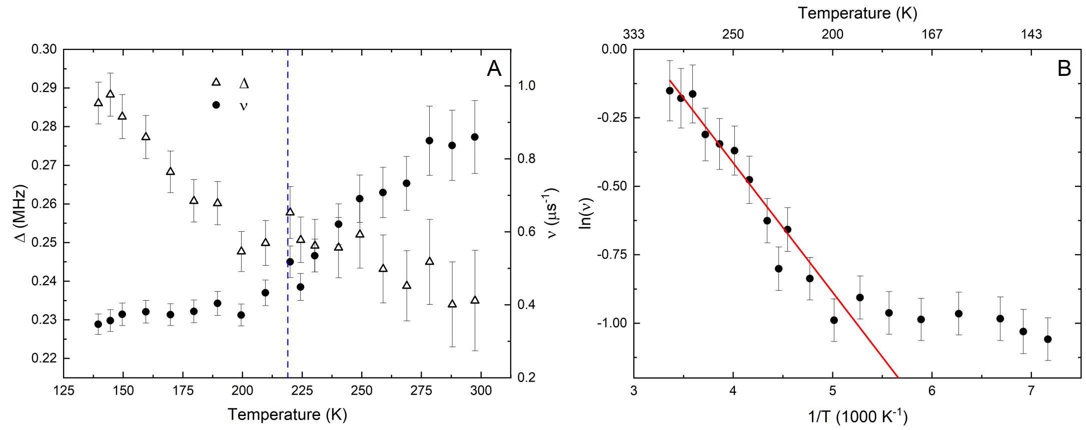

Figure 1: **A:** Parameters from the fits of the ZF muon spin time spectra to a dynamic Kubo-Toyabe function where Δ is the field distribution and ν is the fluctuation rate. The dashed line shows the temperature of the dielectric transition. **B:** An Arrhenius plot of the fluctuation rate where the solid red line is a fit to the data.

Muon spin time spectra were collected in zero applied field and between 140 and 300 K, and for the fits described above, the baseline was fixed at 2.5%. The baseline, accounts for all non-relaxing muons, such as those stopping within the sample holder. Both Δ and ν were allowed to float and the resulting parameters can be seen in Figure 1A. There is a strong temperature dependence of both parameters, with a change in both at approximately 200 to 220 K, which coincides with the onset of the dielectric anomaly of the order-disorder transition. This change in Δ is likely to be from a gradual structural phase transition within the compound, but the dynamics associated with this are outside the experimental time scale and so to the muons, appears static. The fact that ν appears fairly constant below 220 K would suggest that the modulation of this distribution from any electronic component is also constant. The intra-tetramer distances within the TCNQ stacks increase with increasing temperature, although the TEA cations are quasi-static, and the since the main relaxation channel for the muons will come from the ^{14}N nuclei, as the TCNQ molecules move further apart, Δ will change gradually. Above the dielectric transition, a different dynamic behaviour dominates.

An Arrhenius plot of ν is shown in Figure 1B, where the parameters $E_\mathrm{a}/k_\mathrm{B}$= 472(48) K and f_0 = 4.4(7) MHz were extracted. The value of the activation energy is much lower then that observed for the $T_{1\rho}$ which has been associated with the flipping of the TEA cation. Instead, the activation energy extracted from the μSR data is more in-line with the lower estimate from the Vogel-Fulcher analysis of the dielectric loss data in Ref [6]. Since the muon depolarisation is quenched within a low longitudinal field of <50 G, this confirms that the depolarisation is not caused by directly by electronic magnetism.

As mentioned, the muon is likely to believed to be directly bonded the a nitrogen on a TCNQ anion, and there is a hyperfine interaction between the muon and the quadrupole moment on the ^{14}N nuclei. It could be that μSR and the dielectric data are sensitive to one particular process that the other techniques are not. Therefore, one option is that this activated behaviour is related to or coupled to the unpaired electron across the TCNQ dimers, where there could be a gradual slowing down of this, perhaps slower than the muon measurement, that is also causing a modulation of hyperfine interaction within the time scale of the measurement between the muon and nitrogen nuclei. Given the anomaly observed within the magnetic susceptibility data by Takagi [5], the modulation caused by the change in spin dynamics might have a dramatic effect on the μSR data, even if the electronic fluctuations are outside of the time window of the measurement.Thus the resulting modulation of the field distribution at the muon site leads to the change from the static to the dynamic Kubo-Toyabe form of muon spin relaxation.

References

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