Room Temperature Electrical Detection of Spin Coherence in C$_{60}$

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An experimental demonstration of electrical detection of coherent spin motion of weakly coupled, localized electron spins in thin Fullerene C$_{60}$ films at room temperature is presented. Pulsed electrically detected magnetic resonance experiments on vertical photocurrents through Al/C$_{60}$/ZnO samples showed that an electron spin Rabi oscillation is reflected by transient current changes. The nature of possible microscopic mechanisms responsible for this spin to charge conversion as well as its implications for the readout of endohedral Fullerene ((N@C$_{60}$) spin qubits are discussed.

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The need for very sensitive spin measurement techniques for small electron ensembles, possibly even single spins, in organic semiconductors has grown significantly in recent years, since: (i) The development of organic spintronic devices has progressed and the possibility of spin-injection 1, spin–transport 2, and spin valves 3, 4 is increasingly investigated. (ii) Coherent spin measurements have become important for the investigation of spin-dependent processes in organic devices under operating conditions (room temperature). Examples are singlet-triplet mixing mechanisms in organic light emitting diodes 5, or spin-dependent recombination in organic solar cells, which are both relevant in order to assess the true energy efficiency limitations of these devices. (iii) Organic molecular systems such as endohedral fullerenes exhibit extremely long spin coherence times at room temperature 6 suggesting a possible use for room temperature quantum information applications 6, 7, 8, 9.

Traditional electron spin measurement techniques such as electron paramagnetic resonance (EPR) lack the sensitivity required for the minute number of spins present in the low dimensional geometries of many organic semiconductor devices. Several experimental demonstrations of much more sensitive measurement approaches based on electrical spin detection using spin to charge conversion mechanisms have been reported for various electronic or nuclear spin systems such as localized point defects of inorganic semiconductors 10, 11, 12, 13 or semiconductor quantum dots 14, 15. Most of these approaches are confined to low temperatures ($T \leq 5$ K), in part due to the short coherence times of the comparatively strongly spin-orbit-coupled spins in inorganic semiconductors at higher temperatures. In contrast, organic semiconductors are known to possess paramagnetic centers with extraordinarily long coherence times at higher temperatures and even at room temperature 6. However, to our knowledge, there have been no reports of experimental demonstrations for coherent electrical spin detection in organic semiconductors so far.

In the following, we report on the experimental demonstration of coherent spin measurements of localized paramagnetic states in Fullerene C$_{60}$ layers at room temperature by purely electrical means, namely through transient measurements of electric currents that are governed by spin-selection rules. To this end, pulsed electrically detected magnetic resonance (pEDMR) experiments were conducted on vertical photocurrents through thin C$_{60}$ films in transient nutation style experiments 13.

Several samples were prepared for this study, with 80 – 300 nm thick Fullerene films sandwiched between two Al electrodes, or between Al and ZnO. The influence of these variations on the results is minor and will be addressed elsewhere. All layers were evaporated in ultra–high vacuum and the samples were encapsulated in quartz tubes in an inert–gas glove box without intermediate exposure to air that could negatively affect the electronic properties of the thin films. The active device area was 2 mm × 2 mm and thin contact stripes were extended on a 2.6 mm × 58 mm substrate towards a region outside the resonator, in order to minimize field mode distortions in the resonator. The pEDMR measurements were carried out on a commercial pulsed ESR X–band spectrometer (Bruker E580). The sample was illuminated through the optical view port of the resonator and through one of the contact layers with a halogen lamp (110 W) and an argon ion laser (488 nm, up to 1 W power). The photo–induced bias current $I_0$ was stabilized by a current source with a long time constant, so that the transient current response (extending to $\approx 100 \mu$s) after the microwave pulses was not averaged out. The amplitude $B_1$ of the microwave field was calibrated using a 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (Tempol) standard (Sigma Aldrich).

Figure 1 shows the transient current response $\Delta I$ to microwave pulses as a function of (a) time $t$ and (c) magnetic field $B_0$. The 2D dataset (b) was modelled with a global 2D fit (d). The fit function $\Delta I(t, B_0) =$
I_{ph}(t)\Delta(B_0)\) is a product function of the time evolution of the current

\[ I_{ph}(t) = (1 - e^{-\frac{t}{\tau}}) \sum_{j=1}^{3} I_j e^{-\frac{t_0 - t_j}{\tau_j}} \]  

(1)

and the spectroscopic function

\[ \Delta(B_0) = \frac{2}{\pi} \sum_{k=1}^{4} \left( \frac{\Delta B_k}{B_0 - \frac{\Delta B_k}{\mu B g_k}} \right)^2 \]  

(2)

which is a multiple Lorentzian normalized to unit area containing Planck’s constant \( h \), Bohr’s magneton \( \mu B \), the microwave frequency \( \nu_0 \), and the Landé factor \( g_k \) and full width at half height \( \Delta B_k \) for each resonance line \( k \). The time evolution is described by the signed weights \( I_j \) and time constants \( \tau_j \) of the multi exponential decay expected from theory \([16]\), a pulse trigger delay \( t_0 \), and a saturation time \( t_s \) describing the response of the detection circuit which is due to a finite rise time.

Due to the product decomposition of \( \Delta I(t, B_0) \), the spectroscopic information can be interpreted independently of the time evolution of the current if the latter is integrated out. The resulting charge-equivalent pEDMRR signal \( Q(B_0) = \int \Delta I(t, B_0) dt \) contains all spectroscopic information. In general, the integration limits are chosen to give maximal \( Q \) and the integration can be carried out using the hardware of the ESR spectrometer. Careful analysis reveals that the spectroscopic information contained in \( Q(B_0) \) does not depend on that choice. The magnitude of \( Q \) is a direct measure of the number of carriers involved in the spin–dependent process. It turns out that our room temperature pEDMRR signal is due to \( \approx 1 - 2 \times 10^4 \) elementary charges. In this small–ensemble regime, an exact model of the charge carrier dynamics is needed in order to relate the number of charges to the number of spins since the constants \( I_j \) and \( \tau_j \) depend in general on numerous parameters such as capture and emission cross sections of traps as well as carrier generation and recombination rates. Even in the best of cases, these parameters are hard to deconvolve quantitatively \([17]\), and we do not attempt this in the present paper. The spectroscopic information obtained from the data of Fig. 1 and similar data (not shown here) can be summarized as follows: (i) The signal is observed on some, but not on all samples prepared. (ii) It is observed only under illumination, and consistently absent in the dark. (iii) The initial sign of the signal is negative, corresponding to current quenching while at times \( t \gt 20 \mu s \), the sign reverses to current enhancement. (iv) The signal magnitude \( |\Delta I| \) depends on the samples investigated (by a factor of two at least), but (v) \( |\Delta I| \) depends only weakly on the illumination intensity or wavelength. (vi) The resonance condition is fulfilled at \( g = 2.0018(5) \) and (vii) the smallest observed line width is \( \Delta B_0 \leq 0.3 \text{ mT} \). (viii) Measurements at low amplitude \( B_1 < 0.2 \text{ mT} \) show a second, much broader line \( (\Delta B_0 \approx 3 \text{ mT} \) at the same \( g \) factor within our resolution.

Figure 2 shows the evolution of \( Q \) as a function of microwave pulse length \( \tau \) for three different microwave amplitudes \( B_1 \). The observed oscillatory behavior is due to transient nutation of the spins. The coherent pulses induce Rabi oscillations of angular frequency \( \omega_1 = \kappa_S \omega_1 = \kappa_S \gamma B_1 \), where \( \gamma = g \mu B / h \) is the gyromagnetic ratio. The Rabi frequency \( \omega_1 \) is indicative of the spin quantum number \( S \) via the factor \( \kappa_S \). Expected to be \( \kappa_S = 1 \) for a doublet \( S = \frac{1}{2} \), \( \kappa_S = \sqrt{2} \) for a pure triplet \( S = 1 \), and \( \kappa_S = 2 \) for a pair of coupled \( S = \frac{3}{2} \) spins when their spectroscopic separation is small: \( \Delta \omega_2 = |g_1 - g_2| / g_0 \omega_0 \ll \omega_1 \). As demonstrated in Fig. 2b by the comparison of the data to the “transient function” \( T(\alpha) \), we observe a Rabi frequency \( \omega_R = \omega_1 = \gamma B_1 \), as expected for \( S = \frac{1}{2} \). It can easily be shown that \( T(\alpha) \) is related to the Bessel function of the first kind \( J_0 \),

\[ T(\alpha) = \pi \int_0^\alpha J_0(x)dx \]  

(3)

Without its initial part (\( \alpha < \pi/4 \), \( T(\alpha) \) is a quasi \( 2\pi \) periodic function of the mutation or “turning” angle \( \alpha = \omega_R \tau \) resembling a damped sinusoid. This “built-in” damping is due to the fact that selective excitation of an inhomogeneously broadened line was assumed for the derivation of \( T(\alpha) \) and is not indicative of spin relaxation in itself, it reflects a coherent dephasing process amenable to refocussing techniques \([18]\). Figure 2b shows the fast Fourier transform of the data displayed in Fig. 2a, to-
The experimental data presented in Figs. 1 and 2 show that the magnetic resonant current imprint of the paramagnetic centers with Landé factor around $g = 2.0018(5)$ and with weakly coupled ($S = \frac{1}{2}$) systems can be observed by means of transient measurements of the photocurrent changes after coherent spin excitations at room temperature. The magnetic field spectra of the current response suggest that two different resonances are present with linewidths of $\approx 3\, \text{mT}$ and $\approx 0.3\, \text{mT}$ respectively. With the given accuracies, an undisputable association of the Landé factors with particular spin systems is difficult since various paramagnetic states in C$_{60}$ are known [10], such as the corresponding Fullerene radical states and other impurity states, as they may occur in the used device system. With the given experimental data, it is possible that the current is governed by spin–dependent recombination of excess charge carriers similar to the model described for inorganic semiconductors [16] assuming that the observed spins are due to localized defect levels which enhance recombination. It is also possible that the currents are controlled by polaron pair quenching upon polaron pair encounter with radicals. The latter has been referred to as the radical–triplet pair mechanism in the literature [20]. Thus, while the experimental data presented here cannot conclusively rule out any of these different explanations for the observed signals, there is strong evidence for a spin–dependent recombination mechanism of weakly coupled spin pairs ubiquitous in Fullerenes [19] since: (i) The nature and spectroscopic properties of these pairs are in accordance with the two observed resonances. (ii) The mechanism requires the detection of spin $S = \frac{1}{2}$ pair partners which have been confirmed by the data. (iii) The theoretically well investigated dynamical nature of such pairs after coherent spin excitations [16, 21] is entirely consistent with the current transients observed here. The well understood current quenching followed by current enhancement is characteristic for such mechanisms: It is due to the electronic relaxation of first singlet and then triplet pair densities. In spite of this strong agreement, we want to point out nevertheless that in absence of theoretical predictions for pEDMR transients due to the other spin–dependent mechanisms described in the literature, the microscopic nature of the observed signals cannot be verified with certainty.

The process responsible for the signals discussed above represents a spin to charge conversion for weakly coupled, localized spin states in a C$_{60}$ solid at room temperature. We believe that this finding may have important implications for the development of highly sensitive spin quantum readout schemes for endohedral Fullerene (N@C$_{60}$) based electron spin qubits [3]. For spin–dependent recombination through weakly coupled spin pairs as assumed above, an identification of the integrated current (corresponding to the number of detected charge carriers and therefore the number of detected spin–dependent

FIG. 2: (a) Oscillatory part of the observable $Q$ as a function of microwave pulse length at different pulse amplitudes $B_1$ for a C$_{60}$ film illuminated with an argon ion laser ($< 100 \, \text{mW/cm}^2$, $I_0 = 50 \, \mu\text{A}$). The lines are fits using the theoretical curve $T(\alpha = \gamma B_1 t)$ given in Eq. (3). (b) Fast Fourier transforms of the data in (a) and Lorentzian fits. (c) Rabi frequencies $f_R$ (open symbols) and resonance widths $\Delta f_R$ (closed symbols) extracted from the fits in (b). The full line in (c) is $f_R = \gamma B_1/2\pi$, the expected behavior of a spin $S = \frac{1}{2}$. The dotted line is the prediction of the line width as a function of $B_1$ based on the assumption of an $\approx 15\%$ field inhomogeneity. Together with Lorentzian fits. A priori, the width of the Lorentzian $\Delta f_R$ should not depend on the microwave field strength $B_1$. The observed slight increase in width, reported together with the Rabi frequency in Fig. 2c, may be due to an inhomogeneity in the $B_1$ microwave field. In a simple model, the detected FFT width can be described by $\Delta f_R^2 = \Delta f_{\text{int}}^2 + (\Delta \omega_1/2\pi)^2$ where $\Delta f_{\text{int}} \approx 1.7\, \text{MHz}$ is due to the built–in damping and a relative $B_1$ field inhomogeneity which turns out to be $\Delta \omega_1/\omega_1 \approx 15\%$ for the data presented in Figure 2. To summarize the coherent properties at room temperature, Rabi oscillation experiments similar to those reported in Fig. 2 reveal (i) a $B_1$ dependence of the Rabi frequency consistent with $S = \frac{1}{2}$ character of the signal, (ii) a damping behavior consistent with an inhomogeneously broadened “partner line", which is visible in the spectra only at low $B_1$ amplitudes, and (iii) coherent oscillations with a damping time $\Delta f_{\text{int}}^{-1} \approx 0.6\, \mu\text{s}$, which is limited by the inhomogeneity of the spin ensemble and not by the intrinsic $T_2$ decoherence time. An estimate for $T_2$ may be obtained using Rabi echoes and other refocussing techniques [18].
localized spin involved in spin-dependent transitions, marked by a surrounding sphere, is dipolarly coupled to the adjacent N@C state in C_60. For details, see text.

For the case of maximal dipolar coupling (reached at an angle \( \theta = 0 \) between the qubit–probe spin axis and the direction of an applied magnetic field) and an assumed distance of \( r = 1 \) nm, a splitting of the probe spin resonance into four lines with 1.855 mT separation can be expected. Hence, if we assume a line width of 0.3 mT (see Fig. 1) for the electrically read probe spin, the given line separation should be sufficient for a distinction of the qubit eigenstates required for a readout.

In conclusion, we report on a very sensitive electrical detection of coherent spin motion of localized, weakly coupled electron spins in thin C_60 films at room temperature which has been demonstrated by means of transient photocurrent measurements after short coherent electron spin resonant excitation. The observed data reveals the presence of electron spin Rabi oscillation of paramagnetic centers at a Landé factor of \( g \approx 2.0018(5) \). The nature of the observed signals is in agreement with described spin–dependent charge carrier pair recombination models. It has been pointed out that the ability to coherently measure (read) localized electron spin states in C_60 solids with high sensitivity may be utilized as a potential read-out mechanism for endohedral N@C_60 Fullerene qubits.

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[1] V. Dediu, M. Murgia, F. C. Matacutta, C. Taliani, and S. Barbarana, Solid State Commun. 122, 181 (2002).
[2] K. Tsukagoshi, B. W. Alphenaar, and H. Ago, Nature (London) 401, 572 (1999).
[3] Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, Nature (London) 427, 821 (2004).
[4] J. R. Petta, S. K. Slater, and D. C. Ralph, Phys. Rev. Lett. 93, 136601 (2004).
[5] S. R. Forrest, Nature (London) 428, 911 (2002).
[6] W. Harneit, Phys. Rev. A 65, 032322 (2002).
[7] M. Mehring, W. Scherer, and A. Weidinger, Phys. Rev. Lett. 93, 206603 (2004).
[8] J. K. M. Morton, A. M. Tyrnyshkin, A. Ardavan, K. Porfyrakis, S. A. Lyon, and G. Andrew D. Briggs, Phys. Rev. Lett. 95, 200501 (2005).
[9] J. K. M. Morton, A. M. Tyrnyshkin, A. Ardavan, S. C. Benjamín, K. Porfyrakis, S. A. Lyon, and G. Andrew D. Briggs, Nature Physics 2, 40 (2006).
[10] C. Boehme and K. Lips, Phys. Rev. Lett. 91, 246603 (2003).
[11] M. Xia, I. Martin, E. Yablonovitch, and H. W. Jiang, Nature (London) 430, 435 (2004).
[12] A. D. Greentree, A. R. Hamilton, L. C. L. Hollenberg, and R. G. Clark, Phys. Rev. B 71, 113310 (2005).
[13] A. R. Stegner, C. Boehme, H. Huebl, M. Stutzmann, K. Lips, and M. S. Brandt, Nature Physics 2, 835 (2006).
[14] J. R. Petta, A. C. Johnson, J. M. Taylor, E. A. Laird, A. Yacoby, M. D. Lukin, C. M. Marcus, M. P. Hanson, and A. C. Gossard, Science 309, 2180 (2005).
[15] F. H. L. Koppens, C. Buizert, K. J. Tielrooij, I. T. Vink, K. C. Nowack, T. Meunier, L. P. Kouwenhoven, and L. M. K. Vandersypen, Nature (London) 442, 766 (2006).
[16] C. Boehme and K. Lips, Phys. Rev. B 68, 245105 (2003).
[17] C. Boehme and K. Lips, phys. stat. sol. (c) 1, 1255 (2004).
[18] S. Stoll, G. Jeschke, M. Willer, and A. Schweiger, J. Magn. Reson. 130, 86 (1998).
[19] C. A. Reed and R. D. Bolskar, Chem. Rev. 100, 1075 (2000).
[20] C. A. Steren, H. van Willigen, and M. Fanciulli, Chem. Phys. Lett. 245, 244 (1995).
[21] T. Eickelkamp, S. Roth, and M. Mehring, Mol. Phys. 95, 967 (1998).