Force detected electron spin resonance at 94 GHz

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(Received 10 July 2006; accepted 23 October 2006; published online 5 January 2007)

Force detected electron spin resonance (FDESR) detects the presence of unpaired electrons in a sample by measuring the change in force on a mechanical resonator as the magnetization of the sample is modulated under magnetic resonance conditions. The magnetization is coupled to the resonator via a magnetic field gradient. It has been used to both detect and image distributions of electron spins, and it offers both extremely high absolute sensitivity and high spatial imaging resolution. However, compared to conventional induction mode ESR the technique also has a comparatively poor concentration sensitivity and it introduces complications in interpreting and combining both spectroscopy and imaging. One method to improve both sensitivity and spectral resolution is to operate in high magnetic fields in order to increase the sample magnetization and \( g\)-factor resolution. In this article we present FDESR measurements on the organic conductor \((\text{fluoranthene})_2\text{PF}_6\) at 3.2 T, with a corresponding millimeter-wave frequency of 93.5 GHz, which we believe are the highest field results for FDESR reported in the literature to date. A magnet-on-cantilever approach was used, with a high-anisotropy microwave ferrite as the gradient source and employing cyclic saturation to modulate the magnetization at the cantilever fundamental frequency. © 2007 American Institute of Physics. [DOI: 10.1063/1.2424452]

I. INTRODUCTION

Magnetic resonance force microscopy (MRFM) is a new measurement technique, which combines scanning probe microscopy with magnetic resonance spectroscopy to offer subsurface detection of nuclear and unpaired electron spins on a local scale. Since the original proposal in 1991 by Sidles, the area has seen rapid development and a number of comprehensive reviews have been published. MRFM is based on the principle of force detection of magnetic resonance in which the magnetization of a sample in a magnetic field is coupled via a field gradient to a mechanical oscillator, usually a microcantilever. The magnetization of the sample is modulated via magnetic resonance and the resulting force, or force gradient, is detected by monitoring the effect on the cantilever. In principle this approach is capable of extremely high sensitivity and spatial resolution, and recently the extraordinary achievement of single electron sensitivity has been demonstrated by Rugar et al. Such sensitivity opens up new experimental possibilities, and MRFM has now been clearly demonstrated using nuclear magnetic resonance (NMR), electron spin resonance (ESR), and ferromagnetic resonance (FMR). Considerable interest has been attached to NMR based MRFM for applications related to the direct imaging of biological molecules and to ESR for possible application to quantum computing and electronic device imaging. However, there are many technical challenges to be overcome before these visions become a practical reality. Most of the technical advances that have led to single electron spin sensitivity have come about through advances in cantilever technology and control. However, there are distinct differences in the approaches likely to be required for the detection of single spins and the approaches required for imaging (and identifying) spins on the scale of a few tens of nanometers. In particular, it may be desirable in practical scanning applications to use more robust cantilevers and, in spectroscopy applications, to reduce the very high field gradients necessary for maximum sensitivity in order to maximize the interaction volume of the sample with the field gradient. A number of interesting and effective strategies have been suggested to improve sensitivity such as the Boomerang technique, which operates without field gradients. However, one clear and obvious way to achieve an improvement in sensitivity for FDESR is to move to higher magnetic fields and higher sample magnetizations. Magnetization should scale linearly with applied field, at least until the electron magnetic energy \(\mu_B B\) approaches the thermal energy \(k_B T\), which, for fields of a few tesla, occurs at liquid helium temperatures. While increased magnetization at lower fields can also be obtained by operating at very low temperatures, it is likely that future force detected ESR (FDESR) strategies will revolve around choosing an operating temperature to optimize the \(T_1\) relaxation time for a given paramagnetic center for maximum sensitivity and potentially species discrimination. Another reason for interest in high field operation is that future advanced force detected NMR strategies—aiming at detecting and imaging a single nuclear spin—are highly likely to require extremely high nuclear polarizations. One potential strategy to achieve this would be through dynamic nuclear polarization (DNP) techniques, where extremely high nuclear polarizations have recently been demonstrated at low temperatures, by transferring polarization from electron spins to the nuclei of interest.

Compared to lower microwave frequencies, resonators at millimeter-wave frequencies have dimensions more compat-
ible with existing probe heads and provide a much larger $B_z$ field per unit power input. Thus it is easier to sat-urate samples or manipulate polarization states at lower power levels with pulsed ESR techniques. Another potential advantage offered by high field ESR is the better $g$-factor reso-nant field of 3.2 T. Spectra were obtained for the organic conducted at a frequency of 93.5 GHz, corresponding to a

In this article we present preliminary FDESR ex-periments previously published were by Alzetta $et al.$ who described torque detected and force detected ESR at 23 GHz. However, there are a number of technical challenges associated with operating with magnets on cantilevers in high magnetic fields and illuminating the sample and cantilever with millimeter-wave frequencies in the centers of large superconducting magnets.

Most of the FDESR experiments previously reported employed frequencies of the order of a few gigahertz. To the best of our knowledge the highest frequency FDESR ex-periments previously published were by Alzetta $et al.$ who described torque detected and force detected ESR at 23 GHz. In this article we present preliminary FDESR experiments conduced at a frequency of 93.5 GHz, corresponding to a resonant field of 3.2 T. Spectra were obtained for the organic conductor (fluoranthenyl)$_2$PF$_6$ using both amplitude and fre-quency modulation of the illuminating millimeter-wave field to modulate the sample magnetization.

II. THEORY OF FORCE DETECTED ELECTRON SPIN RESONANCE

When a sample containing unpaired electron spins is placed in a magnetic field $B_z$, there is a net magnetization $M_0$ along the field direction, which defines the $z$ axis. This magnetization is given by

$$M_0 = n\mu_e \tanh \left( \frac{\mu_e B_z}{k_b T} \right),$$

where $k_b$ is the Boltzmann constant, $n$ is the spin density, and $\mu_e$ is the moment of a single electron spin, which is equal to the Bohr magneton for systems where the Landé $g$ factor is equal to 2. When $\mu_e B < k_b T$, the magnetization scales approximately with magnetic applied field and is approximated by

$$M_0 \approx \frac{n\mu_e^2 B_z}{k_b T},$$

which is a good approximation down to temperatures of around 10 K at 3.2 T. When a rotating magnetic field of amplitude $B_z$ and angular frequency $\omega$ is applied in a direction perpendicular to $B_z$, the magnetization along the field direction is given by the Bloch equations as

$$M_z = M_0 \left[ \frac{1 + (\omega_0 - \omega)^2 T_2}{1 + (\omega_0 - \omega)^2 T_2 + \gamma^2 B_z^2 T_1 T_2} \right],$$

where $T_1$ and $T_2$ are the longitudinal and transverse relaxa-tion times, respectively, $\gamma$ is the gyromagnetic ratio, and $\omega_0$ is the magnetic resonance frequency at the field $B_z$, given by $\omega_0 = \gamma B_z$. When the resonance condition is met, $\omega = \omega_0$, and the magnetization is reduced by

$$\delta M_z = M_0 \frac{\gamma^2 B_z^2 T_1 T_2}{1 + \gamma^2 B_z^2 T_1 T_2}. \quad (4)$$

By modulating either the amplitude or the frequency of the perpendicular field $B_z$, the sample magnetization is modulated. If $\gamma^2 B_z^2 T_1 T_2$ is large compared to unity and $T_1$ is less than the period of the cantilever resonance, then in principle an almost perfect modulation of the magnetization can be achieved. Modulation of the magnetization results in an oscillating force between the sample and a local magnetic field gradient source. This may be detected with high absolute sensitivity using microcantilevers if the modulating signal is chosen to be at the cantilever resonant frequency. More sophisticated techniques have been reported to reduce noise from spurious excitations, especially in experiments that modulate the polarizing field $B_z$.

If 100% modulation of the magnetization is assumed, the amplitude of the oscillating force generated is given by

$$f_{\text{sig}} = M_0 V_{\text{slice}} G_z = M_0 A_{\text{slice}} \Delta B,$$  

where $V_{\text{slice}}$ is the volume of the resonant slice and $G_z$ is the field gradient in the $z$ direction. As the resonant slice thickness is given by the ratio of the sample intrinsic linewidth $\Delta B$ to the field gradient $G_z$, the product $V_{\text{slice}} G_z$ is approxi-mately constant and to first order given by $A_{\text{slice}} \Delta B$ where $A_{\text{slice}}$ is the effective cross-sectional area of the sample giving rise to the signal. Thus the field gradient is more important for its effects on imaging resolution, and the concentration sensitivity becomes largely probe magnet independent.

The limiting measurement noise force is dominated at high temperatures by thermal excitation of the cantilever. The equivalent noise force, in a bandwidth $b$, from thermal excitation is given by

$$f_{\text{noise}} = \sqrt{\frac{4k_b T k_c b}{\omega_c q_c}},$$

where the cantilever parameters $k_c$, $\omega_c$, and $q_c$ are the cantilever force constant, angular resonant frequency, and $Q$ respectively. By combining Eqs. (2), (5), and (6), the minimum detectable spin concentration $n_{\text{min}}$ and minimum number of detectable spins $N_{\text{min}}$ (for full magnetization modulation) are given by

$$n_{\text{min}} = \frac{1}{B_{\text{slice}} A_{\text{slice}} \Delta B} \sqrt{\frac{4 k_b T k_c b}{\omega_c q_c \mu_e^2}},$$

$$N_{\text{min}} = \frac{1}{B_c G_z} \sqrt{\frac{4 k_b T k_c b}{\omega_c q_c \mu_e^2}}.$$  

In the above it should be noted that Eq. (7) implies that the concentration sensitivity is expected to be approximately independent of field gradient, but increases in proportion to the ESR linewidth $\Delta B$ (although this will eventually be limited by the requirement to saturate or excite the ESR line). On the other hand, the absolute sensitivity can be improved substantially by moving to smaller probes and scanning distances.
III. MAGNET ON CANTILEVER SETUP

Force detection is achieved by coupling the unpaired spins in the sample to a small ferromagnet or ferrimagnet. Many previously reported experiments have used the ferromagnet to provide both the biasing field and local field gradient.\textsuperscript{15,16} Previously reported FDMR experiments in high external magnetic fields (using NMR) have usually chosen to place the sample on the cantilever, largely due to the deleterious effects of changes in cantilever $Q$ and changes in resonant frequency with field. However, practical imaging of devices using FDESR will almost certainly require a magnet-on-cantilever approach.\textsuperscript{17,18}

We have experimented with a number of different magnets including iron and neodymium iron boron particles of order 10–50 $\mu m$ diameter. These metallic magnets, however, were found to have extremely deleterious effects on cantilever $Q$ in an external field, reducing it from several thousands to a point where the thermal noise was no longer observable. More success was obtained using a barium-strontium hexaferrite. Despite a moderate saturation magnetization ($\mu_0 M \approx 0.3$ T), the high crystalline anisotropy ($2K/M \approx 2$ T) strongly reduces the effects of magnetic loss\textsuperscript{19,20} and ensures that the ferrimagnetic resonance occurs at a frequency well away from that associated with $g=2$. The low dc and microwave conductivities also ensure negligible eddy current losses. The presence of an approximately 50 $\mu m$ diameter ferrite particle on the end of a cantilever typically reduced $Q$ by a factor of 3 at 3.5 T, from a zero-field $Q$ value of around 3000. As magnetic loss should scale with particle volume, it is expected to become negligible for sufficiently small magnets.

Operating in an external magnetic field also means that the cantilever resonant frequency changes with applied field due to the increasing torque on the probe moment. This can be included as an extra field dependent contribution, $k_{\text{mag}}$, added to the cantilever force constant, and the resulting change in frequency is given by

$$\omega_c = \omega_0 \sqrt{\frac{k_0 + k_{\text{mag}}}{k_0}}. \quad (9)$$

By considering the energy of the probe magnet as a function of the cantilever angle $\theta$ and assuming that the probe moment starts off parallel to the field and perpendicular to the cantilever plane, it may be shown that $k_{\text{mag}}$, the magnetic part of the force constant, is given by

$$k_{\text{mag}} = \frac{\alpha^2}{2} \left[ m B_z (2K/M) + \mu_0 M (N_x - N_z) \right], \quad (10)$$

in which $m$ is the moment of the magnet on the cantilever, $B_z$ is the applied external magnetic field, $2K/M$ is a first order approximation to the crystalline anisotropy, $M$ is the magnetization of the ferrite, $N_x$ and $N_z$ are the demagnetization factors in the respective directions, $l$ is the length of the cantilever, and $\alpha$ is a constant depending on the cantilever mode (1.37 for a beam-shaped device in the fundamental mode).\textsuperscript{21} If there is assumed to be no crystalline anisotropy, then the equation becomes the same as given in Ref. 21. From Eqs. (9) and (10) it can be seen that the change in resonant frequency should initially scale with the square root of the field but should become independent of field when the applied field is significantly greater than the combined shape and crystalline anisotropy fields.

This behavior is shown in Fig. 1, which shows a typical variation of cantilever frequency with field, with a 10 $\mu m$ radius ferrite particle whose moment is initially aligned with the field. Such curves can be used to estimate the shape and crystalline anisotropies and the moment $m$ of the magnet on the cantilever. Assuming negligible shape anisotropy, fitting the data to Eq. (10) gives the expected value for $2K/M$ of 1.95 T and a probe moment of $9 \times 10^{-11}$ A m$^2$ (which is about an order of magnitude smaller than expected). The shape of the curve was also used to indicate how well the anisotropy field is aligned with the applied field. In contrast, if the moment is initially confined to the plane of the cantilever and perpendicular to the field, the field is seen to initially drop before increasing again at higher fields.\textsuperscript{22}

IV. EXPERIMENTAL ARRANGEMENT

The magnet-on-cantilever approach featured the sample fixed above the cantilever at the field center of a vertical bore superconducting magnet. The cantilever and sample arrangement is shown in Fig. 2. The cantilever motion was detected using a fiber optic interferometer,\textsuperscript{23} using angled fiber connectors and a low coherence length ($\sim 50$ $\mu m$) superluminescent LED (SLED) (OptoSpeed SA, Switzerland) to reduce unwanted reflections and their deleterious effects.

The cantilever used in the FDESR experiments was a beam-shaped silicon device, with dimensions of $450 \times 50 \times 2$ $\mu m^3$ and a nominal force constant of 0.2 N m$^{-1}$ (Nanosensors GmbH, now part of Nanoworld AG, Switzerland). Using the interferometer, it was possible to see the room temperature thermal excitation of the cantilever with a signal to noise ratio of up to 15 dB in air.

The experimental arrangement for the FDESR measurements was based around an existing quasioptical highfield electron spin resonance spectrometer, operating in nonresonant induction mode.\textsuperscript{24} The bulk of the signal processing is carried out in the quasioptical circuit shown in Fig. 3. This

![Graph](image-url)
approach allowed us to monitor the bulk ESR signal \textit{in situ}, as well as the signal from the FDES.

The chosen fields and corresponding frequencies mean that different approaches are required compared to lower frequency experiments. Single mode waveguide becomes lossy (\(>3\) dB/m), so we used a combination of quasioptics and a corrugated pipe to transmit the millimeter waves to the sample. Such an approach is commonly used in high field ESR systems.\textsuperscript{24–26}

The corrugated pipe was 27 mm in diameter with 0.3 mm thick walls. The corrugations were designed to be a quarter wavelength deep at 94 GHz and to effectively act as quarter wavelength shorts to eliminate currents at the walls. The propagating mode is the hybrid HE\(_{11}\) mode, which couples well to the fundamental Gaussian mode produced by the feedhorns in the optical system and has a well defined polarization. The pipe was made of nickel silver, which is easy to machine and has good cryogenic properties. The measured loss of the straight section was less than 0.01 dB/m,\textsuperscript{24} despite the relatively poor conductivity of nickel silver.

An overall schematic of the whole experiment is shown in Fig. 4. The magnet is an Oxford Teslatron H system with permanent leads, capable of being swept from 0 to 12 T and with a homogeneity of one part in \(10^5\) over 1 cm\(^3\) at field center.

To modulate the sample magnetization, cyclic saturation was used by modulating the applied millimeter waves. The source was a second harmonic Gunn oscillator, made in house based on a design by Calstrom.\textsuperscript{27} Amplitude modulation used an electronically driven millimeter wave modulator (ELVA 1 Ltd., Russia), and frequency modulation was achieved by modulating the oscillator bias voltage.

The input polarization of the millimeter waves was defined by the quasioptics, but the sample and cantilever holder could be rotated to an arbitrary angle with respect to the input polarization. This proved necessary as absorption of the radiation by the (highly doped) silicon cantilever was found to result in spurious excitation of the cantilever. As expected, it was found that this effect was worst when the long axis of the cantilever was parallel to the electric field polarization direction, and was at its lowest when the cantilever was perpendicular to the electric field. The effects were largest when amplitude modulation was employed. With frequency modulation, the problem was much smaller, and we believe that this was due to small variations in oscillator output power with bias voltage, as well as to the ferromagnetic (FM) to antiferromagnetic (AM) conversion due to standing waves in the system. These could be minimized by adjusting the distance between the optics system and the top of the corrugated pipe. The spurious excitation was also subsequently observed (although at a much lower level) in gold coated silicon nitride cantilevers, but the effect was seen to largely disappear with uncoated silicon nitride cantilevers.

The test sample used was a crystal of the organic conductor (fluoranthene)\(_2\)PF\(_6\). This was chosen as it has relatively long \(T_1\) and \(T_2\) (both the order of 8 \(\mu\)s)\textsuperscript{28} at room temperature which give a narrow line (\(<50\) mG at 3 T) but are short enough to allow the magnetization to be modulated at the cantilever frequency. It has been proposed as a stan-

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FIG. 2. (a) Schematic of the cantilever and fiber arrangement; (b) the cantilever and sample relative to the flange of the corrugated feedhorn. Not to scale.

FIG. 3. Simplified diagram of the quasioptical ESR system with focusing elements omitted.

FIG. 4. Overall schematic of high field FDMR experiment. The magnet is omitted for clarity.
dard field marker in high field ESR measurements. The irregularly shaped sample, approximately 0.5 mm to a side, was glued to a 5 mm square of 0.5 mm thick polyester (PET), which at this thickness is relatively transparent to millimeter waves. The cantilever on a manufacturer supplied alignment chip was positioned on a sliding insert within a nickel silver holder. The fiber was glued with an epoxy adhesive to the face of the chip holder, but varnish was sufficient to fix the alignment chip in place and to fix the cantilever into the chip. The hole pattern drilled in the top of the sample and probe holder allowed it to mate with the flange of the corrugated feedhorn used to deliver the millimeter wave field, and the PET sheet with the sample attached was gripped between the two flanges, with the sample facing the cantilever.

The sample was illuminated with ~5 mW at 93.5 GHz. Assuming that the linearly polarized millimeter wave radiation couples predominantly into a fundamental free-space Gaussian mode, this corresponds to a linear $B$ field of 52 mG or a rotating component $B_1$ of 36.5 mG. This field should reduce the magnetization by 96% in the steady state. The skin effect due to the conductivity of the sample will mean that this is an upper limit, but the ESR spectra indicated that the sample was strongly saturated.

V. RESULTS

Amplitude and frequency modulated experiments were carried out on the fluoranthene samples near 93.5 GHz at room temperature, and the results may be seen in Fig. 5. The vertical dashed line in the figure indicates the location of the ESR signal at the high field side of the two force detected signals. The half maximum linewidth of the AM signal is 3.7 G (0.37 mT). This is more than an order of magnitude greater than the already strongly saturation broadened ESR linewidth $G$. The broadening of the force detected signal is due to the field gradient from the ferrite particle on the cantilever tip. The experiments were conducted at atmospheric pressure, with a loaded cantilever frequency of 6.3 kHz and a $Q$ of 30. The amplitude modulation was 100% and the frequency modulation was about 125 kHz p-p. A one second time constant (corresponding to 0.25 Hz bandwidth) was used for both measurements. The amplitude modulated result shows a constant offset due to the spurious polarization dependent interaction of the millimeter waves with the cantilever mentioned earlier. The signal to noise ratio is estimated at 31 dB. The signal to noise for the FM case is better, at 35 dB, and there is little obvious FM to AM conversion. For all these measurements the thermally excited spectrum of the cantilever was always clearly visible above the measurement system noise floor.

As shown in Fig. 6, the sensitivity will be considerably improved by operating in a vacuum, in order to increase the $Q$ of the cantilever. The illuminating millimeter waves were again frequency modulated, this time by 1.75 MHz p-p. The cryostat was evacuated to $10^{-2}$ mbar to give a cantilever $Q$ of 3100 at a field of 3.3 T, which led to a signal to noise ratio of around 50 dB with a 0.25 Hz bandwidth. A spurious base line is present, thought to be due to the FM to AM conversion, which is approximately constant over the whole spectrum. A smaller sample was used than in the previous figure and the line is more symmetrical than the FM line in Fig. 5, showing that the sample subtends a smaller solid angle above the probe magnet. The shallower slope between the positive and negative peaks indicate a degree of overmodulation.

VI. MODELING

The shape and field position of the FDESR signals is typical of what would be expected from measurement of an extended sample where the scan distance is comparable to the extent of the sample. This can be seen by examination of Fig. 7, which shows model AM FDESR spectra for a 350 $\mu$m thick, 350 $\mu$m cylindrical sample at two different distances from the probe, where we have summed the individual force contributions from each part of the sample at a given field.29

The form of the signals can be understood by considering the field and field gradient from the probe magnet, which is assumed to be an effective point dipole parallel to the $z$ direction. As the moment is parallel to the external field and perpendicular to the plane of the cantilever, we need only...
concern ourselves with the $z$ components of the field due to the probe magnet (the “tip field”) and the tip field gradient:

$$B_z = \frac{\mu_0 m}{8\pi r^3}(3\cos 2\theta + 1),$$

$$G_z = \frac{\partial B_z}{\partial z} = \frac{\mu_0 m}{4\pi r^3}[\cos \theta(9 - 15\cos^2 \theta)].$$

There will only be an interaction with the sample when the sum of the tip and external fields fulfills the resonance condition. The tip field, which is much smaller than the external field, will be positive up to an angle $\theta$ of 54.7°, beyond which it will subtract from the external field. Thus, Eq. (11) tells us that when the probe is relatively far from an extended sample the FDESR signal will largely appear at lower fields than the natural ESR signal. However, when the probe is close to an extended sample there can be a significant contribution from spins at angles subtended greater than 54.7°. However, it is the variation of the field gradient with angle away from the $z$ axis that is responsible for the magnitude and shape of the signal: at 39.2°, the phase of the generated signal changes by 180°. Thus, when the probe is relatively far away, virtually all the spins contribute to a repulsive force on the sample and lead to a positive going peak on the low field side of the resonance position. However, as the probe is brought closer, the positive peak will become broader and shallower due to the higher field gradient and will move to lower fields. There will also be a significant attractive force due to the contribution of spins at higher offset angles. This negative peak becomes more centered around the natural resonant field as the field contribution due to the magnet tip becomes smaller and changes sign beyond 54.7°. This negative peak is visible in the 120 $\mu$m model and is more pronounced for the 100 $\mu$m case.

One feature to note is that the signal variation with distance is much smaller than what the $1/r^3$ dependence of the gradient may lead one to expect for a point sample. Indeed, for extended samples, the signal magnitude can, over certain ranges, increase with increasing distance. The signal shape shown in Fig. 7 is sensitive to sample geometry due to the shape of the sensitive resonant slice$^{29,30}$ and will be modified for samples where the lateral extent of the sample is significantly greater than the probe-sample separation. The exact details of the probe magnet will have a significant effect on the observed linewidths as the probe field and gradient will scale as the cube of its radius. Thus we would expect only broad agreement between the simple model and the experimental case, where the probe-sample separation was approximately 80 $\mu$m.

VII. DISCUSSION

In line with virtually all previously reported FDESR results, it should be stressed that we are reporting measurements on highly favorable samples. Fluoranthene has a high spin concentration ($8 \times 10^{20}$ cm$^{-3}$), and very long time constants at room temperature with both $T_1$ and $T_2 \sim 8 \times 10^4$ $\mu$s, which makes the sample easy to saturate at low power levels, but still allows the magnetization to recover on a time scale that is relatively short compared to the period of the cantilever resonance. The absolute sensitivity for the AM FDESR measurements shown in Fig. 5 is estimated at $8 \times 10^{11}$ spins (or $6 \times 10^9$ polarized spins) in a 1 Hz bandwidth, and the concentration sensitivity is estimated at $4 \times 10^{15}$ spins/cm$^3$ in a 1 Hz bandwidth. The sensitivities were estimated given that the measurements were limited by thermal noise. The estimations are based on simple assumptions about the volume that contributes to the signal the shape of which depends on the magnitude of the probe moment. Using the same assumptions, we estimate that the theoretical signal to noise ratio should be between 20 and 50 dB. Given the uncertainties in the probe moment and linewidth, the experimental value is consistent with the theoretical prediction.

Compared to recent FDESR results the absolute sensitivity is relatively modest, with a large increase in performance required to approach single spin sensitivity. This sensitivity can be compared with that of a modern continuous wave 94 GHz ESR spectrometer, which, for favorable samples, can have room temperature absolute sensitivities of the order $10^7$ spins, and concentration sensitivities of order $10^{11}$ spins/cm$^3$ measured in a 1 Hz bandwidth, normalized for a 1 G linewidth. Thus, compared with induction mode ESR, the AM FDESR spectrum shown in Fig. 5 is more than three orders of magnitude worse for absolute sensitivity and more than eight orders of magnitude worse for concentration sensitivity.

In principle there are a number of straightforward means to make the FDESR measurement more sensitive. Ultrasoft cantilevers with extremely high $Q$s ($\sim 150 000$) have now been used to demonstrate attonewton sensitivity. These improvements in cantilever parameters alone might lead to improvements in both absolute and concentration sensitivities by over three orders of magnitude. A reduction in temperature will offer both lower thermal excitation of the cantilever and greater polarization, but the concentration sensitivity will still be relatively poor in comparison to induction mode ESR, implying that FDESR methodologies like Boomerang$^8$ will be required to significantly improve concentration sensitivity. However, the absolute sensitivity (i.e., the minimum
detectable number of spins) can be further significantly improved through smaller probe magnets and scanning distances leading to higher field gradients. It is under these conditions that single spin sensitivity has been reached with long averaging times.

This suggests that FDESR is likely to be at its most useful either when operating near single spin sensitivity or for performing microscopy or spectroscopy on microscopic samples of relatively high spin concentration. In either case, the extra polarization and spectral resolution provided at high fields are likely to be valuable in reducing averaging times and species discrimination.

ACKNOWLEDGMENTS

The authors would like to acknowledge the mechanical workshop at St Andrews for the construction of the probe holders and many of the quasioptical elements, particularly G. Radley, P. Aitken, and D. Steven. They would also like to thank P. Reidi, N. Poolton, D. Robertson, and N. Elejalde from St Andrews for useful advice and discussions and E. Dormann from Karlsruhe University for the fluoranthene sample. This work was supported by the U.K. Engineering and Physical Sciences Research Council.