STM detection of the precession of surface spins (spin?) ESR-STM:

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- Contributers:
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- Sasha Balatsky (Los Alamos)
- Colm Durkan (Cambridge)
- Yishay Manassen

- Funded by: GIF, ISF.

The beginning:

Modulation of the tunneling current at the Larmor frequency. An rf component. The sample: thermally oxidized Si(111)7x7.

VOLUME 62, NUMBER 21 PHYSICAL REVIEW LETTERS 22 MAY 1989

Direct Observation of the Precession of Individual Paramagnetic Spins on Oxidized Silicon Surfaces

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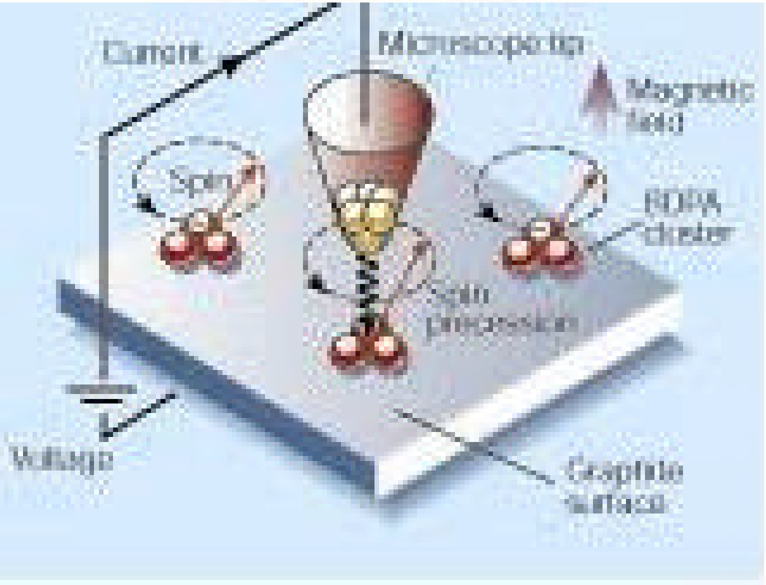
(Received 12 December 1988)

The precession of indi ... een detected using a scanning tunneling micro ... luces a modulation in the tunneling current at t ... n to be localized over distances less than 10 Å ...



The experimental setup

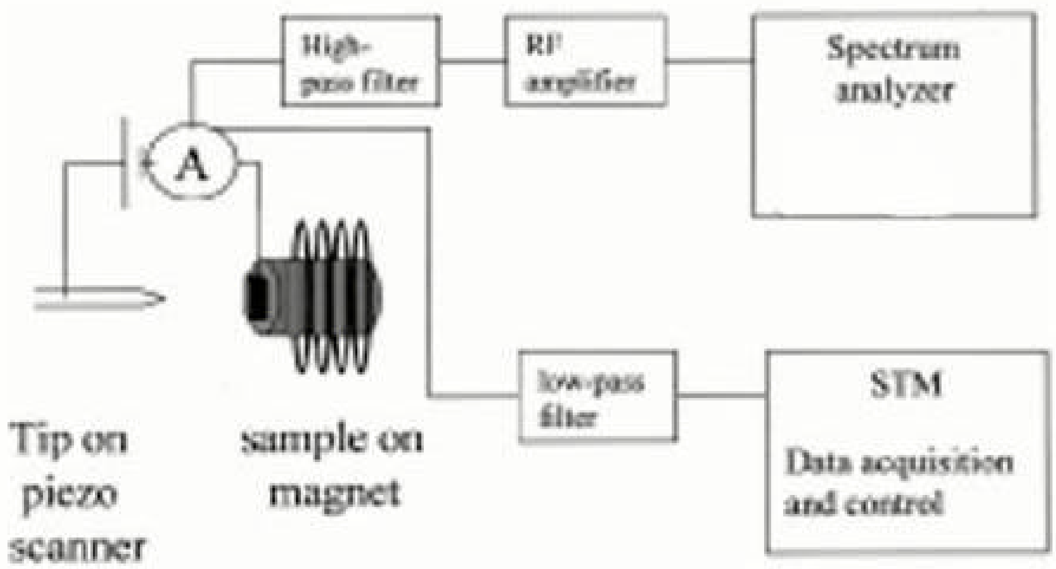


FIG. 1. Schematic of the electronics used in STM-ESR.

- Additional component: Impedance matching circuit.
- With phase sensitive detection: modulation coils and a lock in amplifier.

Main results:

- Spectra depends on a magnetic fields.
- Spectra are spatially localized

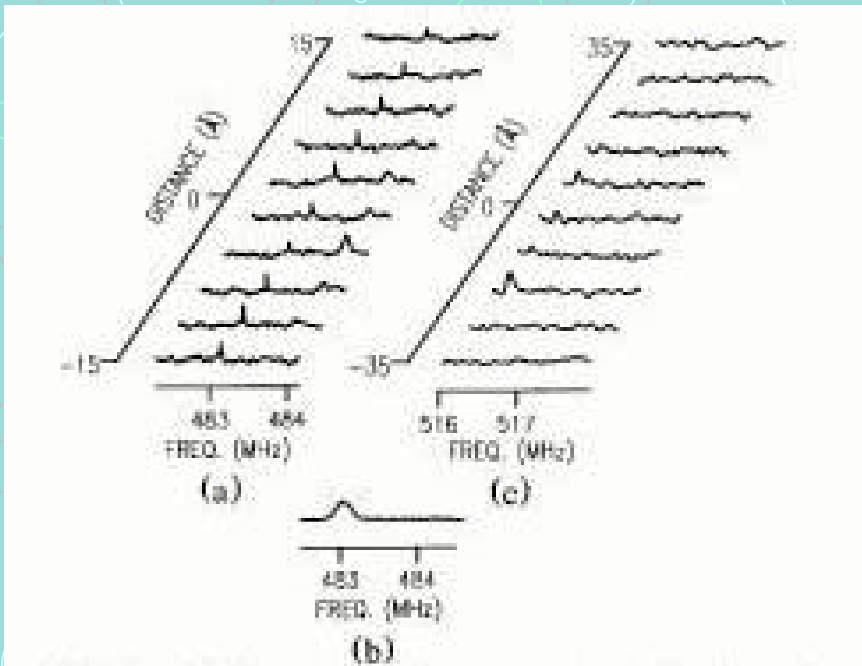
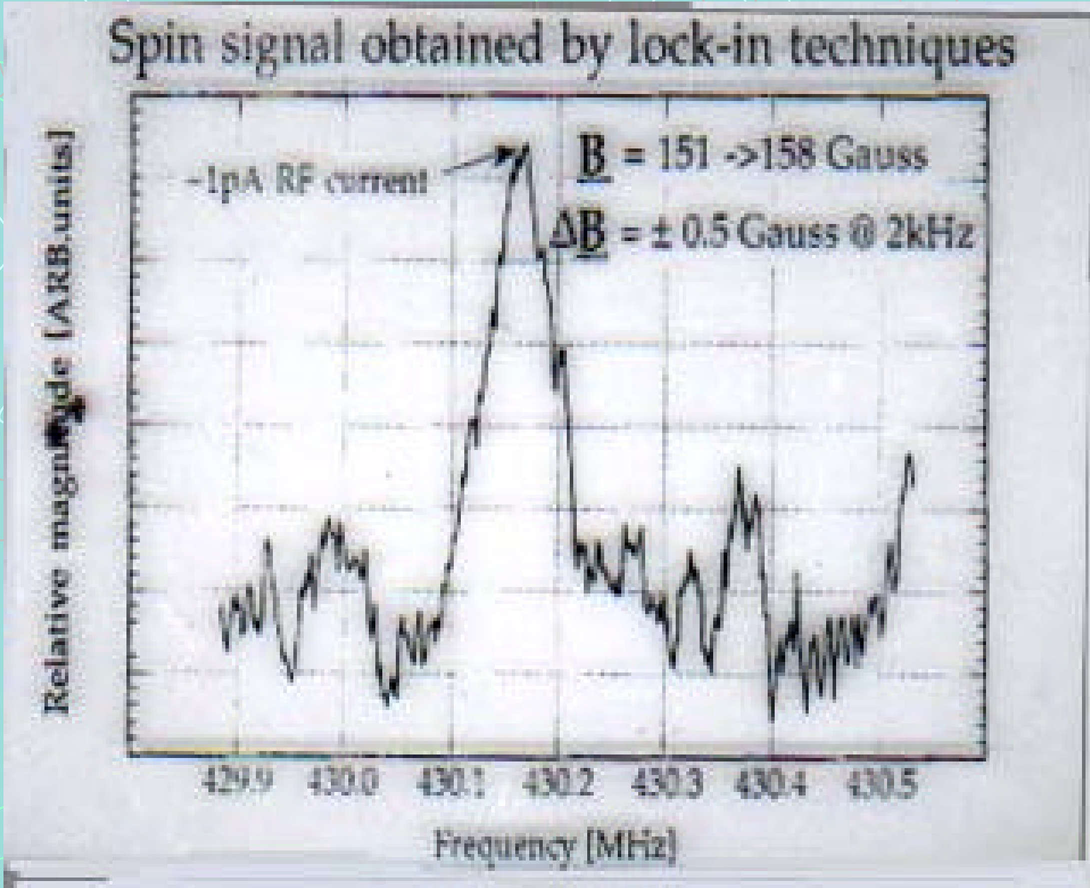


FIG. 1. (a) Consecutive rf power spectra of the tunneling current, measured at different lateral separations of the tip from a spin center in a field of 172 G. Each spectrum was taken at a point separated by 3 Å from the previous one. (b) A power spectrum near another spin center in a 172-G field, showing the nearly Gaussian line shape. (c) Same as (a), except for a field of 185 G; separation between scans = 7 Å.

1991 – In the SPM conference In Interlaken, Switzerland: ESR-STM on BDPA – with phase sensitive detection.(McKinnon and Welland, 1991).

- The problem: an
- incorrect phase
- with a phase
- sensitive
- Detetector



The phase sensitive detector is put after the spectrum analyzer.

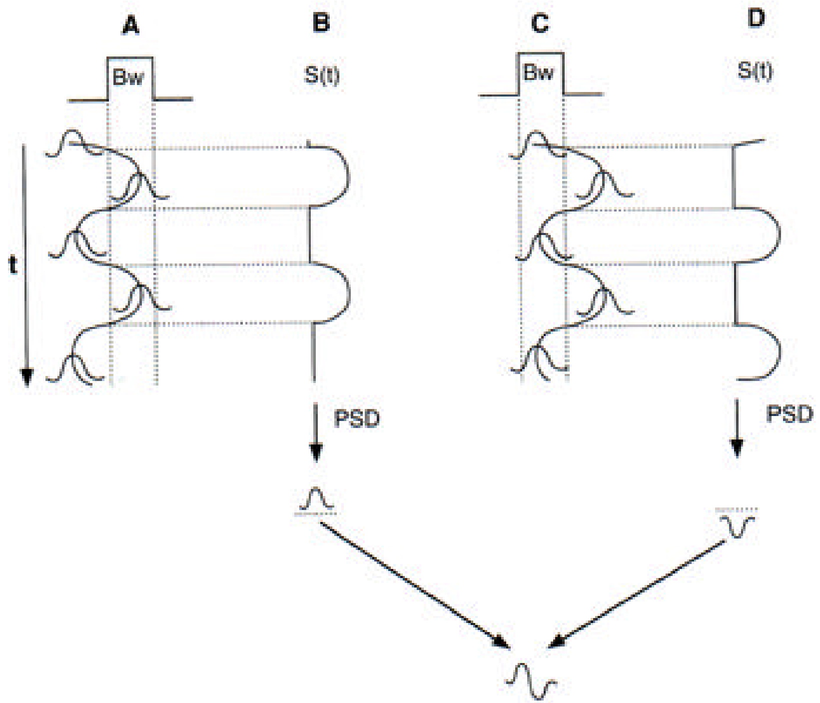


FIG. 2. A scheme of the detection mechanism with a spectrum analyzer and a lock-in amplifier. (A) The signal enters the detection band from the low-frequency side. (B) The relative phase between the output of the spectrum analyzer $S(t)$ and the field $H(t)$ creates a positive output at the PSD. (C) The signal enters the detection band from the high-frequency side. (D) This gives a negative output at the PSD. Altogether, this gives a derivative shape, as the spectrum analyzer sweeps the signal.

- A derivative signal should be observed!

Next result: Reproducible spatial localization, and tip sample interaction [Phys. Rev. B 48, 4887 (1993)]

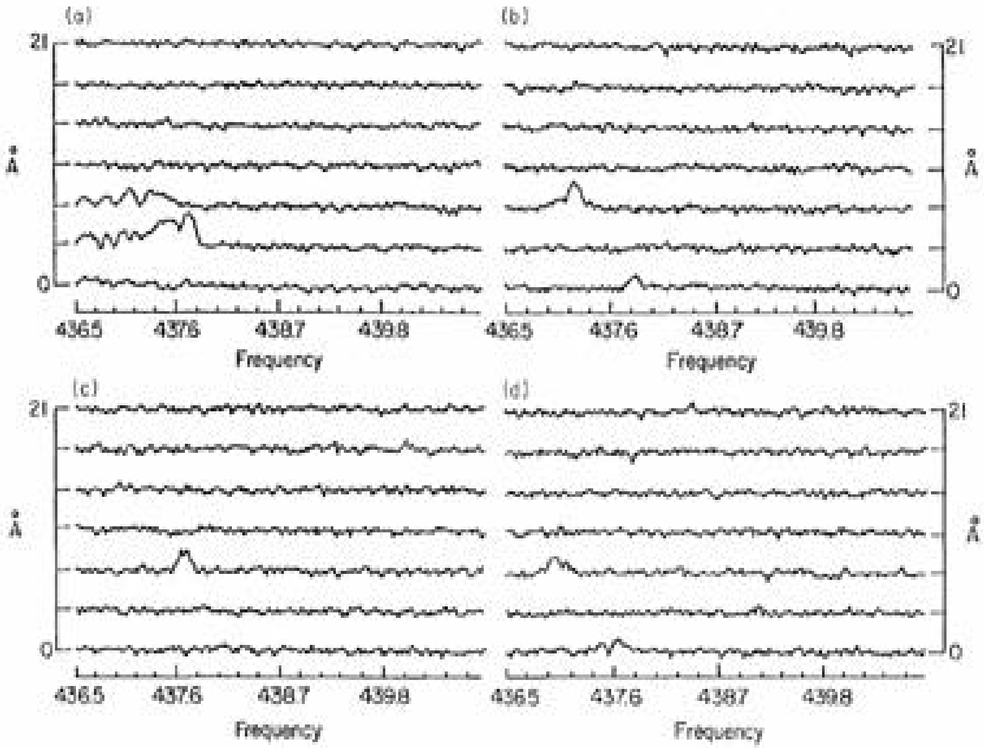


FIG. 2. rf spectra of the tunneling current at a field of 157 G. The horizontal axis displays the frequency and the vertical one the spatial location on the surface. The distance between two consecutive (vertical) spectra is 3 Å. (a)–(d) show four consecutive spatially dependent rf spectra of the tunneling current at the same locations on the surface. These spectra demonstrate the reproducibility of the spatial localization, as well as the reproducibility of the spatially dependent frequency shifts. Frequencies are measured in MHz.

Next step: Real time response of ESR-STM signals to magnetic field modultation (J. Magn. Reson. 126, 133 (1997))

- When the field is driven by a field, (in frequency unit): $?_i = ?_c + ?? \cos(?_m t)$
- $F(t) = A\sin(?_c t + m_? \sin(?_m t)$
- Fourier expansion:
- $F(t) = A\{J_0(m_?)\sin(?_c t) + J_1(m_?)[\sin(?_c + ?_m)t - \sin(?_c - ?_m)t] + J_2(m_?)[\sin(?_c + 2?_m)t + \sin(?c - 2?m)t] + \ldots\ldots\}$
- $M_? = ??/?_m$: The modulation index.

The appearance of the frequency modulated signal:

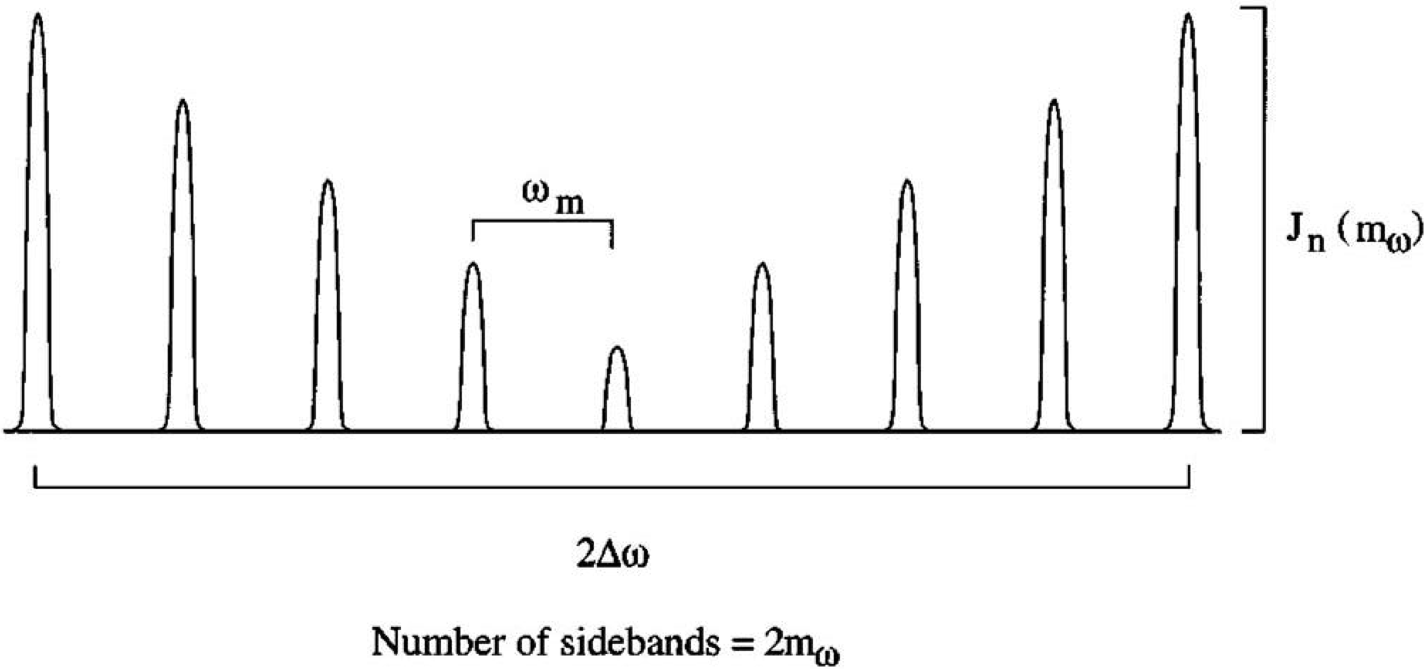


FIG. 3. A scheme of the sideband spectrum expected to be detected in the spectrum analyzer as a result of frequency modulation.

A modulated signal with the parameters: H_0=150G, ? H=27mG, ? ? =75kHz , $m_?$ =250.

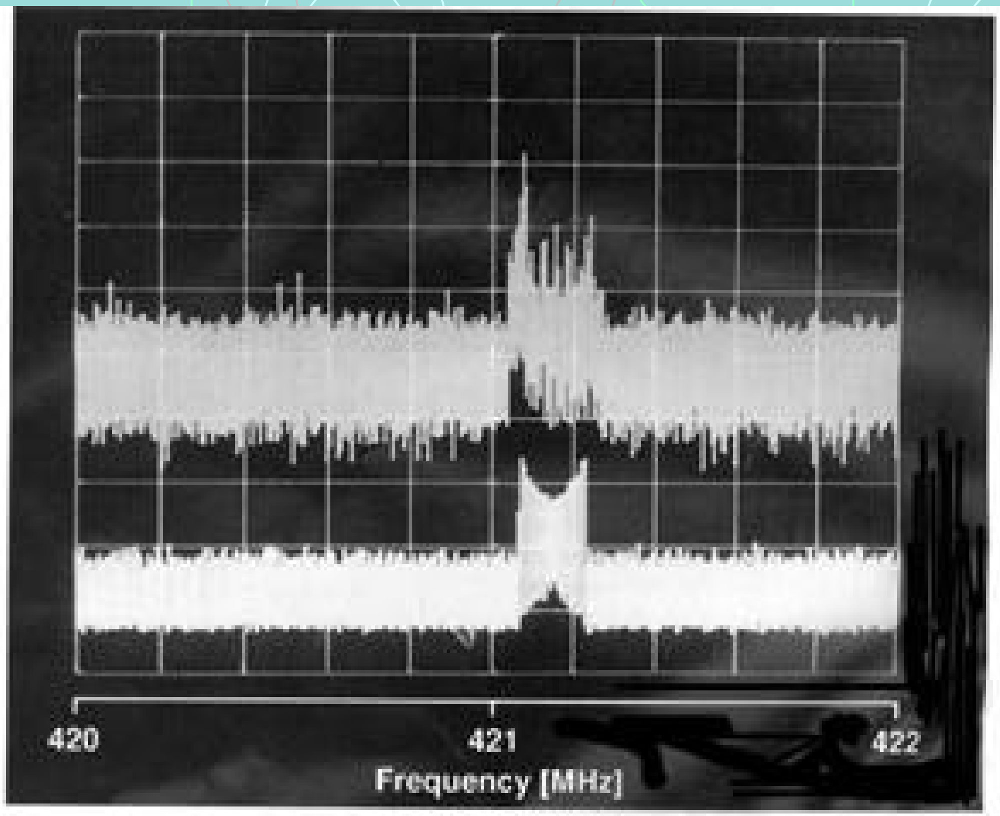
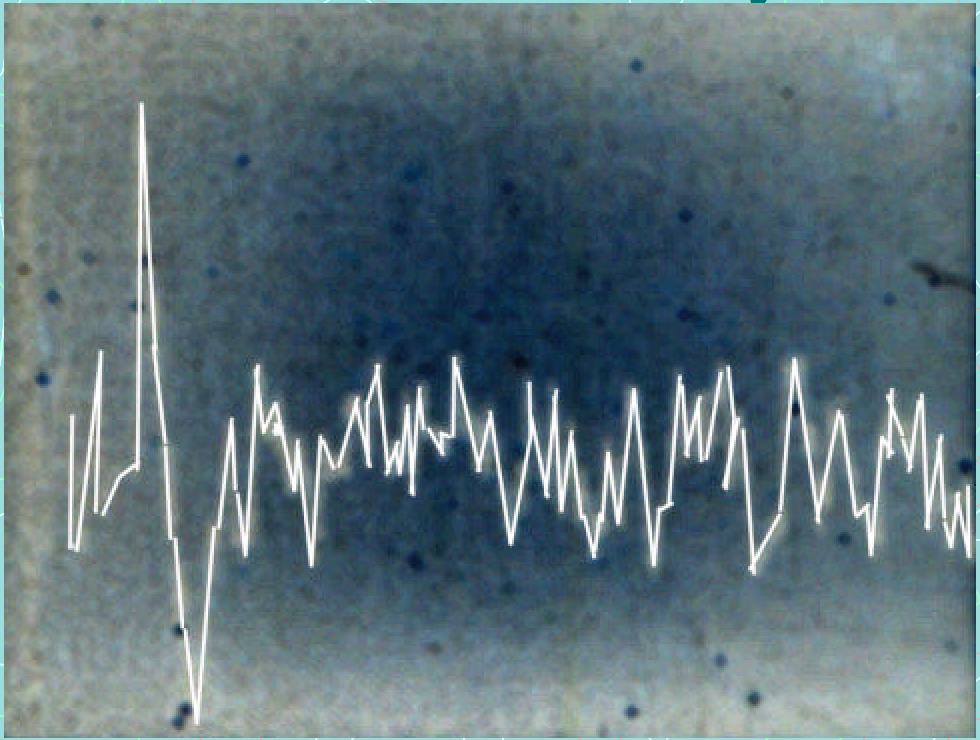


FIG. 1. (Top) A modulated ESR-STM signal detected only with a spectrum analyzer. It is observed under the conditions of field modulation described in the text. For comparison, an analogous frequency-modulated signal (bottom) from a frequency synthesizer is shown.

However, a derivative signal should be and is observed many times.



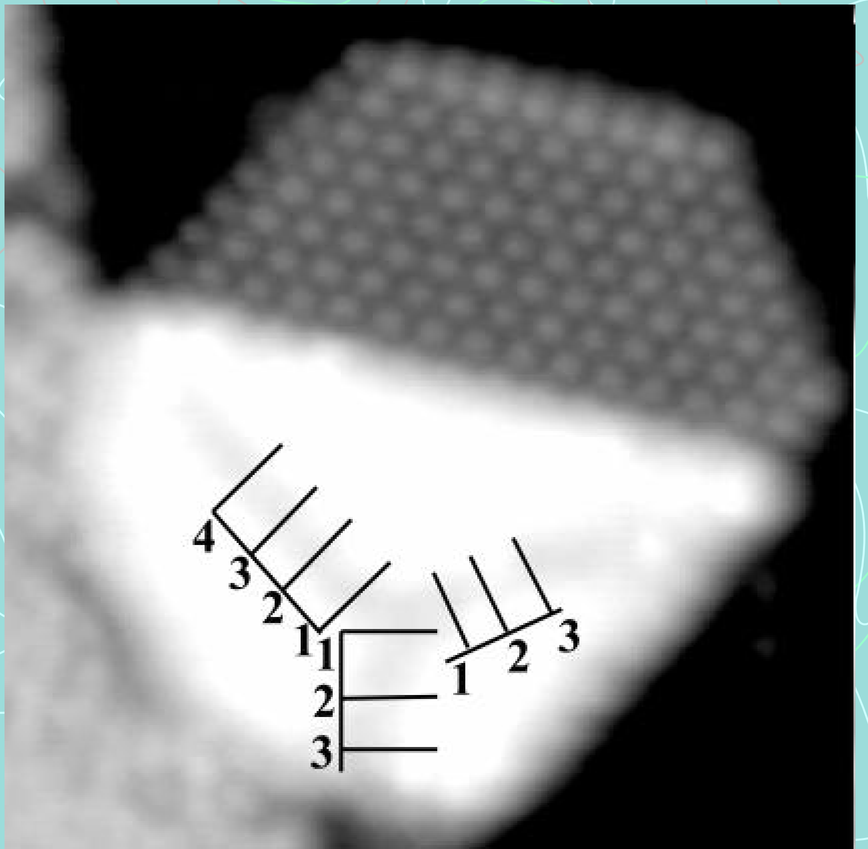
- However, the derivative is asymmetric!

This question (among others) is answered in the subsequent work: *Phys Rev B* **61** 16223 (2000)

- ESR studies of silicon surfaces (Nishi, 1971).
- 3 spin centers were identified:
- P_a – trapped electrons.
- P_b Si radical at the silicon – silicon dioxide interface.
- P_c interstitial iron in a tetrahedral site: characterized by g=2.07.
- In our case: preparation by evaporation of iron – on a silicon surface.

The spin center: a neutral iron: a d^8 atoms: effective spin S=1. In sillicides: Fe atoms – near the surface.

- Upon evaporation: we observed:
- –ß-$FeSi_2$ and ?-$FeSi_2$.
- The top part of the
- island is ? and the
- bottom ß.
- In sillicides: the Fe atom
- In a tetrahedral site in
- The subsurface layer.



ESR-STM of Fe atoms in Si (g=2.07).

- Real time response is observed also for these spin centers (? ? =120 kHz, $?_{m}$=20kHz, $m_{?}$ =6)
- Span width
- = 5 MHz.

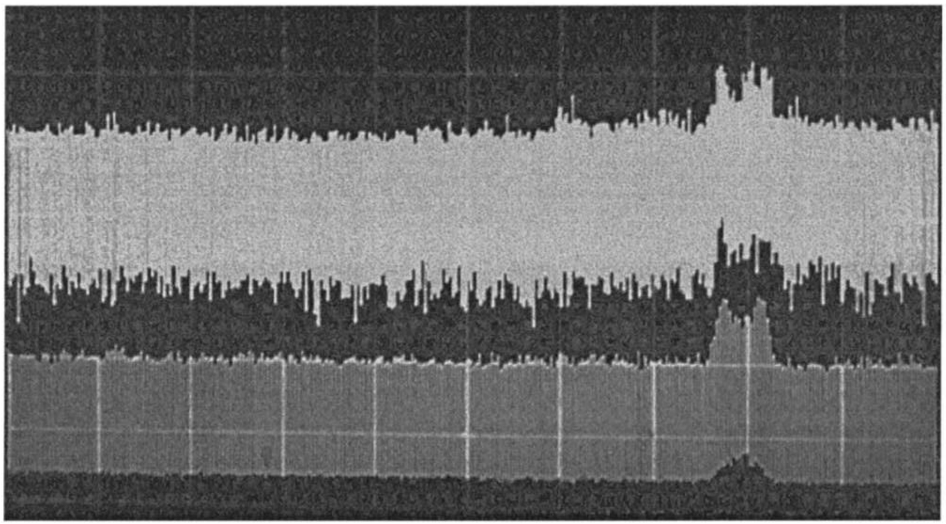


FIG. 4. An electron-spin-resonance (ESR)-STM spectrum taken with the spectrum analyzer alone. The analyzer total frequency scan was 5 MHz centered at 441 MHz. The trace in the top shows a line shape observed from the STM under conditions of field modulation. The bottom trace is the corresponding frequency modulated signal from a frequency synthesizer.

Also in Fe: a (slightly distorted) absorption lineshape with phase sensitive detection. ESR-STM-Also with atomic resolution.

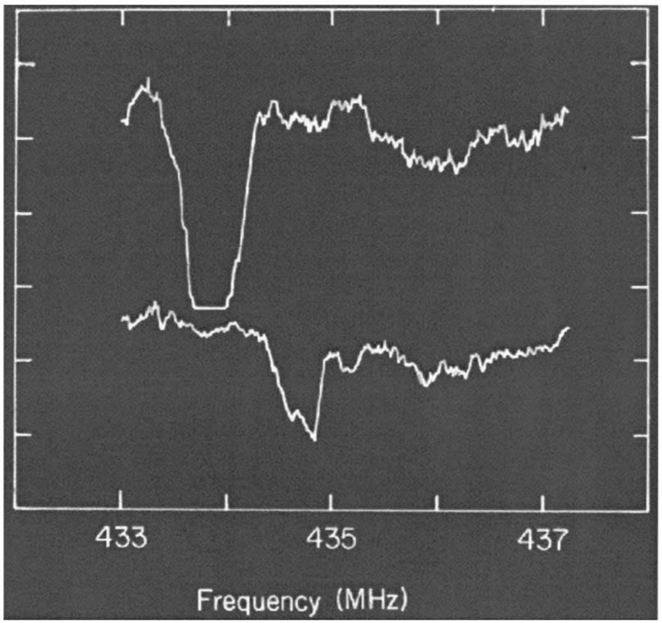


FIG. 5. Two electron-spin-resonance (ESR)-STM spectra at a frequency corresponding to $g = 2.07$ with an absorption line shape as observed with a lock-in amplifier.

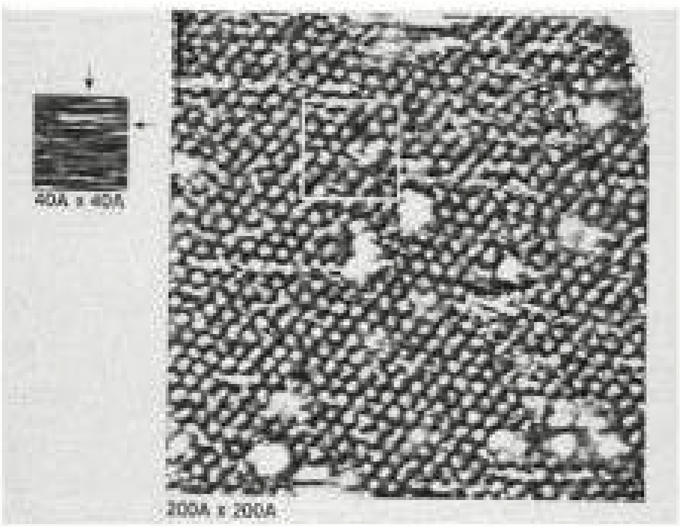


FIG. 6. A two-dimensional electron-spin-resonance (ESR)-STM image over a vacancy in a γ-$FeSi_2$ surface. The spectrum was recorded by looking at the output of the lock-in amplifier when the detection band of the spectrum analyzer is fixed at a single frequency corresponding to $g = 2.07$. The phase (in the lock-in amplifier) of this spectrum is mainly positive (which corresponds to absorption line shape).

A question left: why so many times an absorption lineshape is observed with phase sensitive detection?

- Recall: in frequency domain, a rapid passage spectrum, gives an asymmetrical lineshape [Jacobsohn and Wangness *Phys. Rev.* **73** 942 (1948).] The derivative of an asymmetric lineshape, gives a slightly distorted absorption at high time constant in the PSD. (this explains the initial results Of McKinnon and Welland 1991)

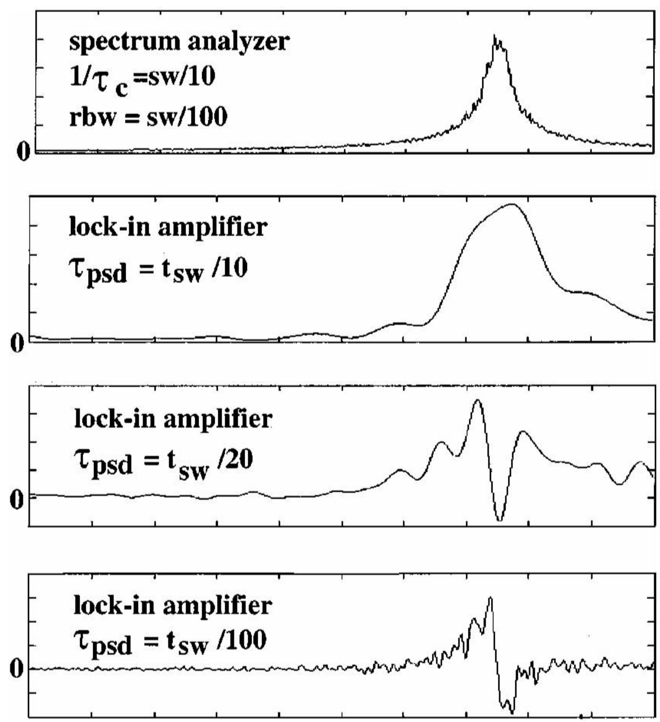


FIG. 7. A computer simulation showing the affect of increasing the integration time of the lock-in amplifier (τ_{psd}) on a signal with a finite lifetime. The upper trace shows the signal in the spectrum analyzer. The other three traces show the output in the lock-in amplifier for different values of τ_{psd}.

Another attempt of ESR-STM on a BDPA molecule:

APPLIED PHYSICS LETTERS VOLUME 80, NUMBER 3 21 JANUARY 2002

Electronic spin detection in molecules using scanning-tunneling-microscopy-assisted electron-spin resonance

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(Received 8 May 2001; accepted for publication 8 November 2001)

By combining the spatial resolution of a scanning-tunneling microscope (STM) with the electronic spin sensitivity of electron-spin resonance, we show that it is possible to detect the presence of localized spins on surfaces. The principle is that a STM is operated in a magnetic field, and the resulting component of the tunnel current at the Larmor (precession) frequency is measured. This component is nonzero whenever there is tunneling into or out of a paramagnetic entity. We have succeeded in obtaining spectra from free radical molecules from which the g factor of a spin entity may be inferred. For the molecules studied here, α,γ-bisdiphenylene-β-phenylallyl, g was found to be 2 ± 0.1. [DOI: 10.1063/1.1434301]

- The spectra are detected with a spectrum analyser only.

Summary of the results:

- ESR-STM was observed at different fields at the right frequency. Spectral diffusion is observed.

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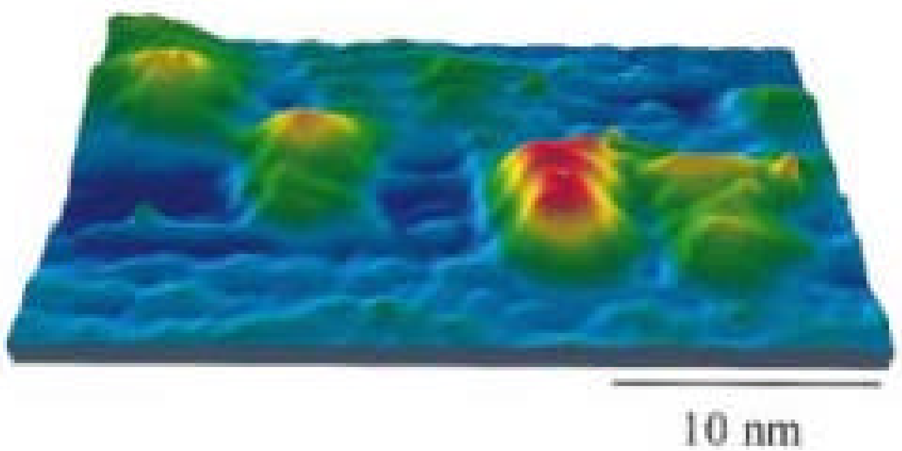

FIG. 2. (Color) STM image of a 250 Å×150 Å area of HOPG with four adsorbed BDPA molecules.

C. Durkan and M. E. Welland

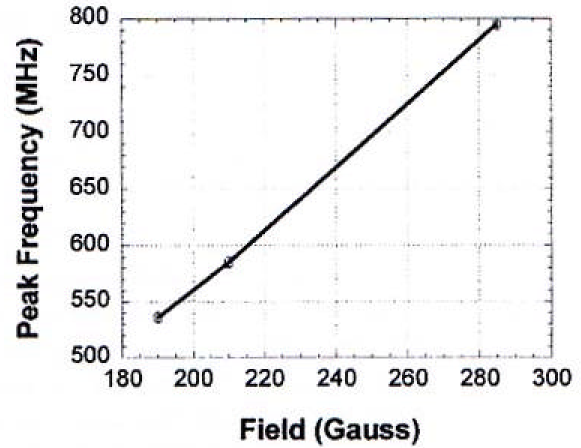

FIG. 5. Plot of the center frequency of STM-ESR peaks on clusters as a function of the applied magnetic field. From this, we obtain a value of $g=2\pm0.1$.

Important remark: An assymmtric lineshape is observed here too.

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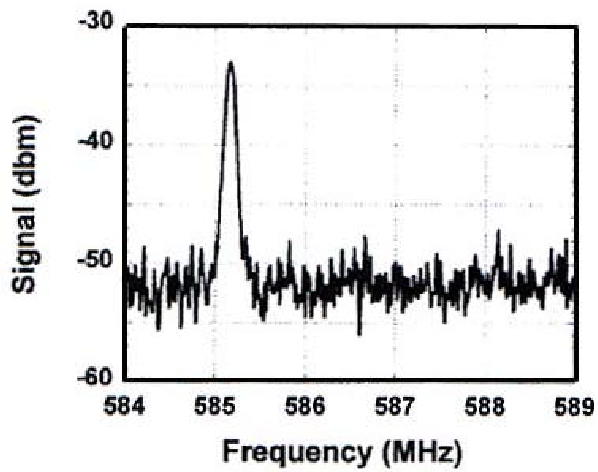


FIG. 4. STM-ESR spectra of BDPA clusters for an applied field of 210 G.

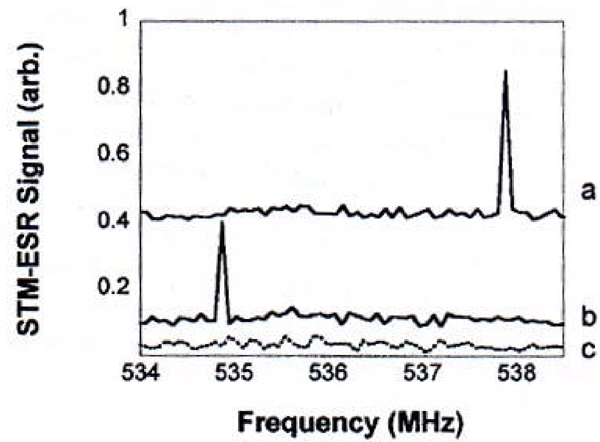
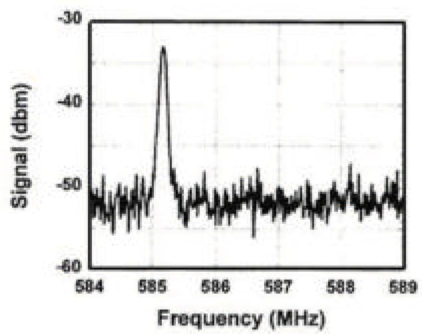
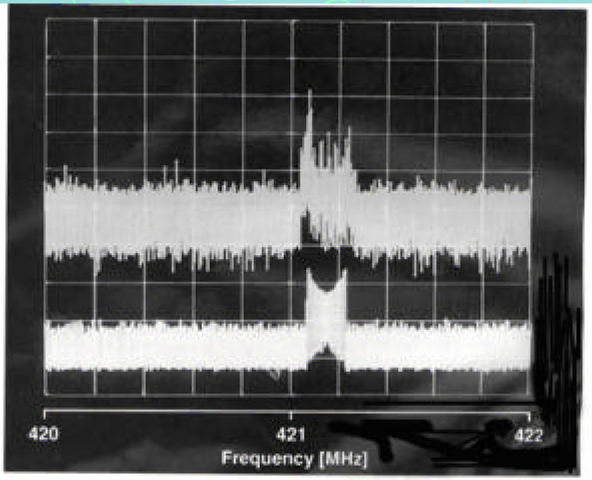


FIG. 3. STM-ESR spectra of (a), (b) two different areas (a few nm apart) of the molecule-covered sample and (c) bare HOPG. The graphs are shifted vertically for clarity.

An alternative explanation for the asymmetric lineshape: connected to the sharp increase of linewidth with the magnetic field. (with Colm Durkan).

- Recall: Two examples of an asymmetric lineshape: a paramagnetic molecule – left and a silicon radical – right.





Line width in ESR-STM :

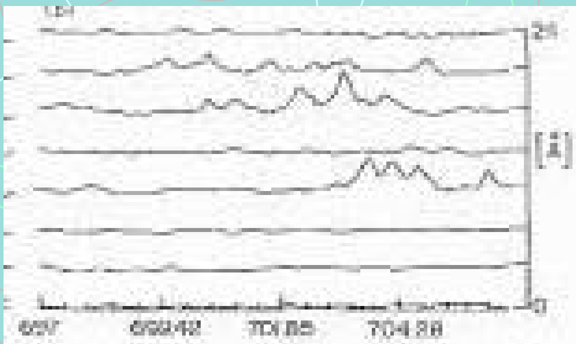
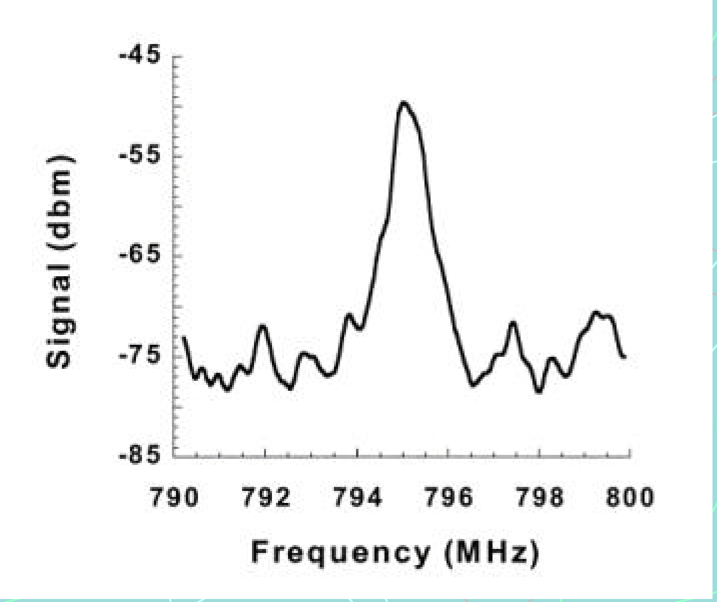
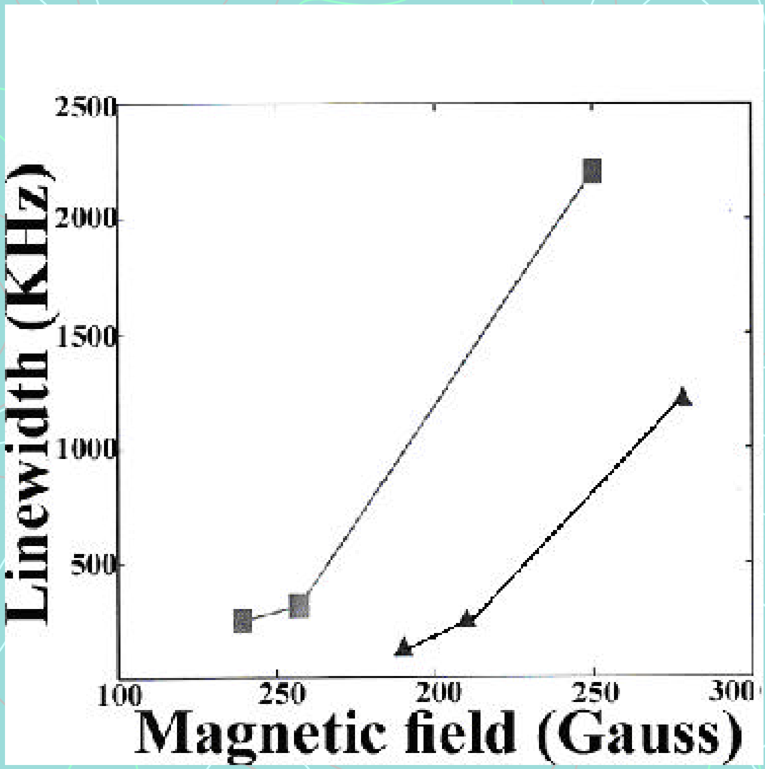


FIG. 3. Two spatially dependent rf spectra (not of the same location) showing the larger linewidths and the larger frequency shifts of the signal at higher magnetic fields (250 G). Frequencies are measured in MHz.



- At larger fields larger
- Linewidths are observed
- Both for silicon radicals
- And molecules.
- In contradiction with the
- Usual ESR situation.

Similar linewidth dependence



- Similar dependence:
- Possible explanation
- Sampling with fewer
- # of electrons when
- The field is increased.
- A calculation: linewidth
- When the sampling times
- Are determined by the
- Poisson distribution.

Simulation of Random Sampling

- Recall: It is impossible to sample a periodic function if the sampling time is larger than half of the period (Nyquist Theorem).

- A current of one Nanoamperes is $6.25x10^9$ electrons per second.

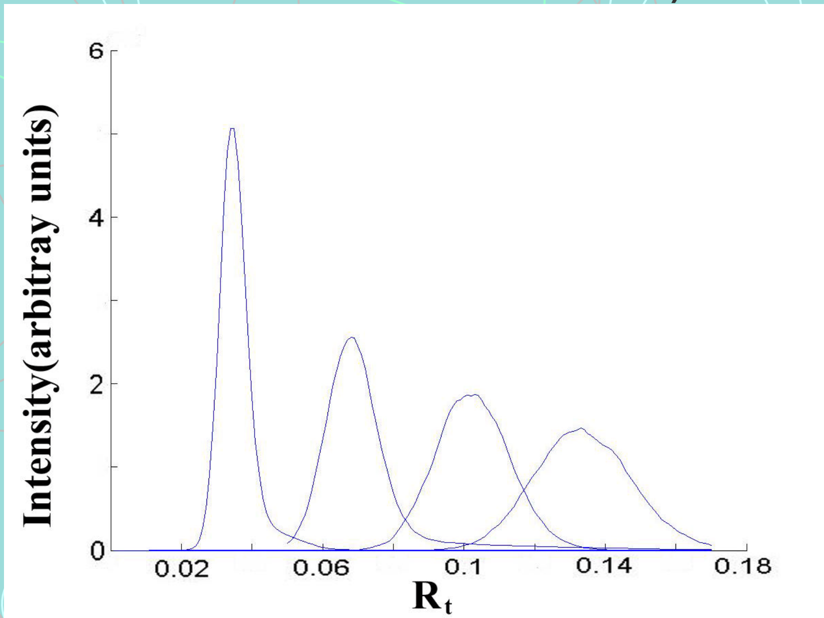
- In conditions of a constant sampling time, the largest frequency we can measure (at one nanoampere) is $3.1x10^9$ Hz

In conditions of random sampling times, as the average frequency approaches this limit, more and more sampling times will be too large. This will result in an increase of the linewidth

The simulation: An estimation of the spectrum of a periodic . function when the sampling times are according to the Poisson distribution.

Results of the Simulation:

- R_t is the ratio between the Precession time
- and the average sampling time (For a frequency of 200MHz, Rt is 0.033).



- Increase in linewidth:
- Linear with the field.
- Longer spin lifetime:
- Narrower line and slower
- Increase in linewidth.
- Lineshape: asymmetric
- as in the experiment.
- Comment: we did not take into account other causes of linewidth increase: Back-action effects.

Proposals for the mechanism:

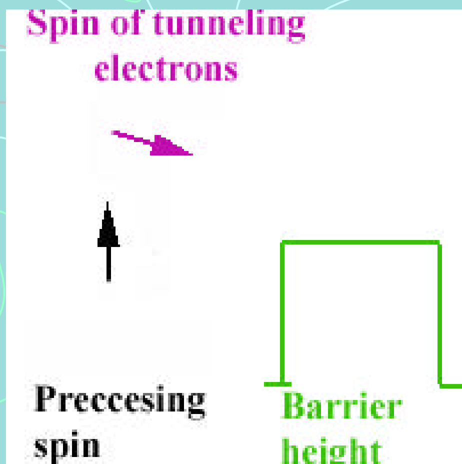
- D. Mozyrsky et.al. Phys. Rev. B, 66, 161313 (2002).
- A. V. Zhu and A. V. Balatsky, Phys. Rev. Lett. 89, 286802 (2002).
- L. Levitov and I. Rashba, Phys. Rev. B 67, 115324 (2003).
- R. Ruskov and A. N. Korotkov, Phys. Rev. B
- 67, 075303 (2003).
- L. N. Bulaevskii and G. Ortiz, Phys. Rev. Lett.
- 90, 040401 (2003).
- and more…

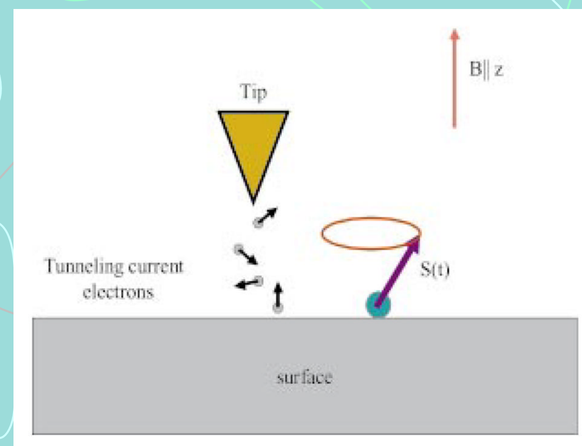
Our proposal (A. V. Balatsky, Y. Manassen and R. Salem, *Phil. Mag. B* **82**, 1291 (2002), *Phys. Rev. B*, **66**, 195416 (2002))is: spin noise because of exchange interaction between the precessing spin and the tunneling electrons.

- The random orientation of the spins of the tunneling electrons s results in a random barrier height.

- $$I=I_0 \exp\{-[(F - JS \bullet s)\backslash F_0]^{1/2}\}$$

- Upper view side view





The basic claim: In a field of 200G, the period of precession time: $1/?_L$=2ns. 20 electrons (in 1nA). The average spin polarization is 1/4th of that of the polarization of an electron (for unpolarized electron beam.

- A spin dependent tunneling matrix element:
- $G=G_0 \exp\{-(F-J \cdot S(t)s)/F_0\}^{1/2}$, $F_0=h^2/8md^2$
- Expansion of G
- $G=G_0 \exp[-(F/F_0)^{1/2}[\cosh[JS/2F\ (F/F_0)^{1/2}]+s\,n(t)$ $\sinh[JS/2F\ (F/F_0)^{1/2}]$ Namely, there is a part dependent on the localized spin: dI(t) n(t)s(t). n-unit vector of S.
- (using $\exp[-(A-B)]^{1/2}= \exp[-(A)1/2]\exp[B/(2A^{1/2})]$ and
- $\exp(i\,s\,W) = \cos|W| + i\,s\,\sin|W|$

The part which is dependent on the localized spin: $dI(t) \quad n(t)s(t)$

$n(t)s(t) = n^x(t)s^x(t) + n^y(t)s^y(t) + n^z(t)s^z(t)$ (only transverse components give a signal).

Summation over time T (period of precession).

Sum over N (number of electrons per cycle)

? $I = 1/N \, S_{i=1}^{N} n^x(t_i)s^x(t_i) + n^y(t_i)s^y(t_i)$

Since the spin wavefunctions are uncorrelated (to first order):

$(S_{i=1}^{N} n^x(t)s^x(t))^2 \quad < N>$

The relative dispersion at the Larmor frequency:

? $I^2/I_0^2 = \langle (n^x)^2 \rangle \langle N \rangle / \langle N \rangle^2 \quad 1/\langle N \rangle$

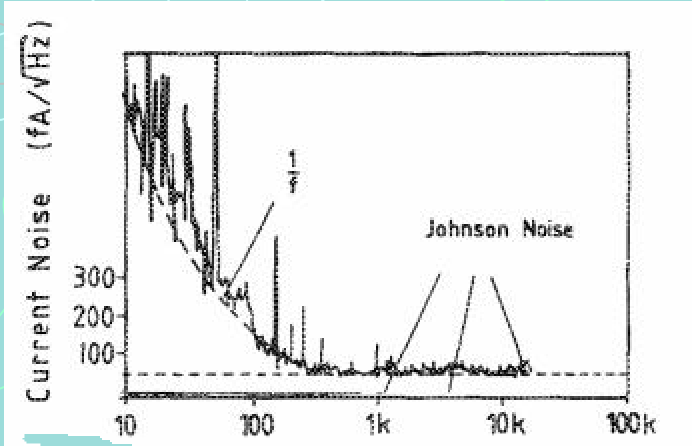
- Estimation of magnitude: $2/(N)^{1/2} \sin[\, JS/2F \ (F/F_0)^{1/2}\,]$ for d=0.4nm, F_0=0.1eV and the magnitude is 0.02 of the DC current (J=0.1eV) (much larger than the shot noise – about 1pA)
- Regarding linewidth: Observed from golden rule formula:
- Prediction: with larger spin polarization : Broader and stronger signals. A fascinating possibility a superconducting tip.
- (J.-X. Zhu et. al. Phys. Rev. B 67, 174505 (2003).)

Functional dependence of the signal

- In time domain:
- $<dI(t)dI(t')>/I_0^2 = \{\sinh[JS/2F\,(F/F_0)^{1/2}]\}^2$ $S_{i=x,y,z}<n_i(t)n_j(t')><s_i(t)\, s_j(t')>$
- In frequency domain: (Spectral density).
- $<I_?^2>/I_0^2=\{\sinh[JS/2F\,(F/F_0)^{1/2}]\}^2$ $S_{i=x,y,z}\, ?d?_1/2p <(n_i)^2_{?-?1}><(s_i)^2_{?1}>$
- $<(n_i)^2_?>=?/\{(?-?_L)^2+?^2\}$ and $<(s_i)^2_?>$ is the power spectrum of the tunneling electrons: If white noise the signal will be smeared.

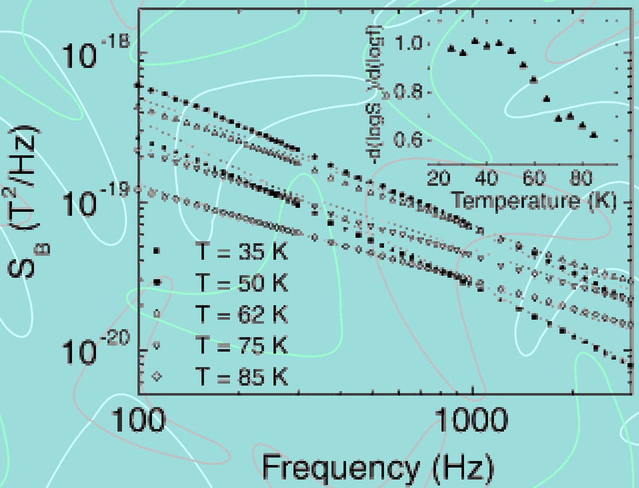
Flicker 1/f noise.

- A universal phenomenon: a large enigma
- Large correlations in low frequencies: The noise spectrum is much larger at low frequency and is proportional to 1/f
- J. B. Johnson, *Phys. Rev.* **26** 71, (1925).
- Appears in electrical components, music, ocean streams.
- Common but quite partial explanation: The noise is a result of consecutive random events of exponential relaxation. When there is a diverging relaxation time t 1/f noise is observed.
- 1/f noise in STM:
- *Appl. Phys. Lett.* **55** 2360 (1989).



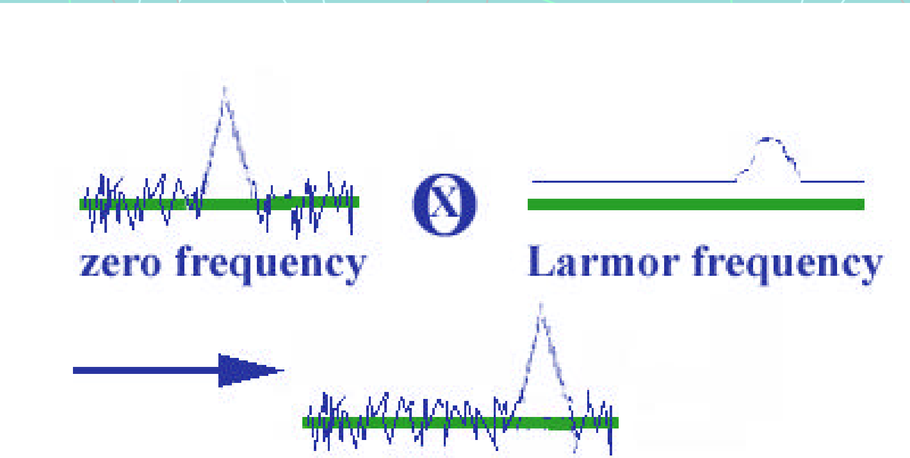
Magnetic 1/f noise:

- The 1/f fluctuations are expected to appear in all magnetic systems but are difficult to measure.
- Can be measured by SQUID of by a Hall microprobe.
- Such noise was measured in spin glasses in antiferromagnets and superparamagnets. We expect such noise also in a paramagnetic systems



- M. B. Weissman and N. E. Israeloff
- *J. Appl. Phys.* **67**, 4884 (1990).
- S. I. Woods et. Al. *Phys. Rev. Lett.*
- **87**, 137205 (2001)

Namely, the correlations in the spins of the tunneling electrons appear because of 1/f magnetic noise. This can be either due to adsorption of paramagnetic atoms on the tip or as an internal property of the tunneling electrons.



In other words: the exchange interaction with the precessing spin, transforms the 1/f peak to the Larmor frequency.

Future experiments (in low temperature): The only way to prove that we see a single spin: is through interaction with: other spins

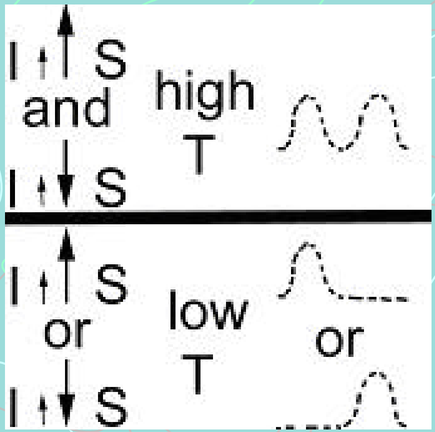
For example through hyperfine interaction AS•I neighboring nuclei:

S=1/2, I=1/2

?? ?? ?? In macroscopic hyperfine spectrum: 2 peaks.

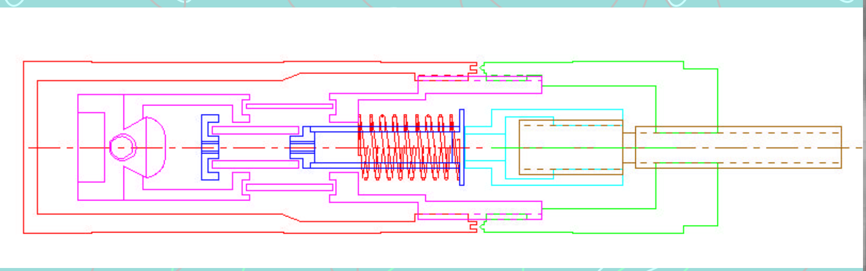
For room temperature single spin: 2 peaks.

At low temperatures: 1 jumping peak.



Our design of a UHV-LT microscope:

- The fundamental principle: sealing the STM in UHV on an indium ring. Then putting the STM in the cryostat. Putting cold He gas for thermal exchange



- Sample Au(111) on
- Mica.

STM detection of the precession of surface spins (spin?) ESR-STM:

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- Contributers:
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- Sasha Balatsky (Los Alamos)
- Colm Durkan (Cambridge)
- Yishay Manassen

- Funded by: GIF, ISF.