Single spin NMR (NMR1)

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ABSTRACT

Sequential Ionization by Scanning Tunnelling Microscope (STM) bias voltage pulses of a molecule with anisotropic hyperfine interaction, results in a temporal transformation from diamagnetic to paramagnetic. The effective magnetic field on the nucleus (in the diamagnetic state) and on the electron (in the paramagnetic state) are not parallel. The precession of the nucleus in the diamagnetic state is modulating the population and the hyperfine states and the matrix elements for the hyperfine transitions as observed in tempo with the ^{14}N nucleus. A preliminary model is presented. The technique can work on magnetic and non-magnetic molecules and can yield an STM image with atomic identification.

Keywords: NMR; Single spin; STM.

1. INTRODUCTION

- Macroscopic NMR (Nuclear Magnetic Resonance) is by far the most comprehensive technique for chemical analysis. Each nucleus has a gyromagnetic ratio that is giving resonance at a very narrow frequency range. The only element that does not have a stable NMR detectable isotope is Ar. Thus, single spin NMR will give the STM an ability to identify the atom under the tip. Moreover, it might be possible to get a detailed NMR spectrum for distinguishing the chemical environment of the same atom.
- The best way to detect a single spin nuclear resonance is through a single spin electron resonance (if the electron is coupled to the nucleus). There are today many STM studies on single spin electron spin resonance (ESR) [1-5]. An experiment was reported in the 2019 APS meeting in which spin polarized current was used for NMR detection [6]. The technique reported here, does not require spin polarized tunnelling (and as a consequence a high magnetic field), cryogenic temperature and a uniform rf irradiation at a broad frequency range. The present technique is shown to work at room temperature, low magnetic fields with a normal STM tip and without external rf irradiation, and can be generalized for all atoms and molecules.
- The main results indicate that the project have achieved a proof of concept. A bias voltage modulation for temporary ionization while recording the ESR-STM hyperfine peak as a function of time was applied. Due to the anisotropy of the hyperfine coupling together with the small size of the external magnetic field, the effective magnetic field in the paramagnetic and the diamagnetic states are not in the same direction. The amplitude of the single spin hyperfine peak is modulated in time, at the nuclear Larmor frequency of (^{14}N). The observed spectrum shows a peak in this frequency. The results are showing also a peak at half of this frequency for reasons not completely clear.

2. STATE OF THE ART

Several experiments for single spin NMR were performed: The sensitivity of NV centers [7] as a sensor for very small changes in a magnetic field, have reached to the level that single spin NMR was detectable. However, the position of the NV center is random, and no information is provided on the single spin environment. We proposed the current research in order to address three main issues: randomity of the detected position, simplicity of the detection technique and fast detection. Indeed, our results show that the single spin NMR technique with the STM has the advantage that the particular atom or molecule under the tip can provide an NMR spectrum, and in parallel, the surface is seen with atomic resolution. Comparing the present reported technique with existing spin polarized techniques shows an advantage of simplicity. An additional advantage is that by using a time domain scope, and analysing the data with a digital spectrum analyser, it is possible to observe a detectable single spin ESR and NMR within 1 second or less (Fig. 3 right).

By changing the ratio between the external magnetic field and the anisotropic hyperfine interaction; the ratio between the NMR period of time (diamagnetic) and the ESR period of time (paramagnetic) and by using the temperature as a tool to change the relaxation times, the spectral resolution has been and will be further improved.

A measurement of 1 second can be used to take a spectrum from each pixel in the STM image. This adds to the STM the significant ability not only to see the atom under the tip but also to identify it.

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The breakthrough of the project is the successful proof of concept that shows that a microscope that identifies an atom in its precise location, identifies its environment and does all in a fast and simple manner, is feasible. The concept is both revolutionary and simple. When there is a single molecule hyperfine coupling between an electron and a nucleus, the ESR can be a detector to the NMR [8]: When the population of the nuclear levels is modified, the intensity of the hyperfine peaks is modified as well [9]. Thus, as a result of ionization, when the electron (in the paramagnetic phase) and the nucleus (in the diamagnetic phase) do not precess around a magnetic field with the same direction, (Fig. 1), the population of the nuclear state when the ESR is detected, is modified. When the anisotropy of the hyperfine coupling is in the same order of magnitude as the external magnetic field, the directions of the effective field in the diamagnetic state and the paramagnetic state are naturally different.

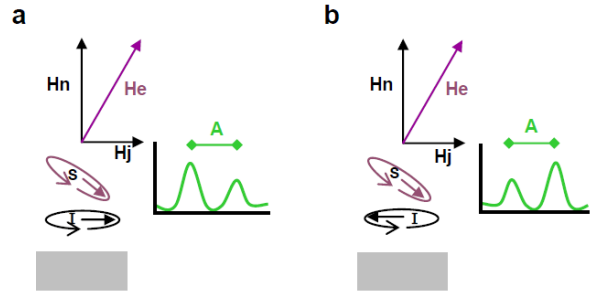


Fig. 1 The precession of the electron (S) in the quasi static orientation of the nucleus (I). In (a) the projection of I in the direction of H_e (the field that the electron feels) is positive, in (b) it is negative. The spectra in green are the expected hyperfine spectra due to the difference in nuclear polarization.

Thus, the polarization of the nuclear state and the intensity of the hyperfine peaks (Fig. 1) are dependent on the position of the nucleus. The nucleus is quasi-static in the time the electron is detected with the ESR.

Initially, in the paramagnetic state, the hyperfine peaks are equal in size. When the molecule transfers to a diamagnetic state, the precession of the nucleus (around H_n) changes the nuclear polarization (in the frame of H_e) which appears as unequal amplitude of the hyperfine peaks. At the moment when the molecule transfers back to the paramagnetic state, the nucleus precess around a field with a different direction (H_e), which is much larger than the external field. However, the accumulated longitudinal polarization of the nucleus is preserved due to the slow T_1 nuclear relaxation. Therefore, when the electron is getting out, the nuclear polarization is projected back on the original direction (H_n) and is returning to the position it was before the electron entered into the molecule. This explains how the nuclear precession and the amplitude modulation of the hyperfine peaks are continuous also with the ionization.

Although, the concept is based on known principles, no such technique has ever been tried. The experiments reported here are new and novel, and despite the simplicity, the potential impact is enormous.

4. PROJECT RESULTS

As a first example of the technique we started with a simpler experiment that is a free radical at a small bias and becomes a diamagnetic ion upon ionization with a larger bias. We have tried a Tempo molecule (Fig. 2 left) which was deposited on a Au(111) surface covered with graphene oxide. The STM image (Fig. 2 right) indicates separate molecules.

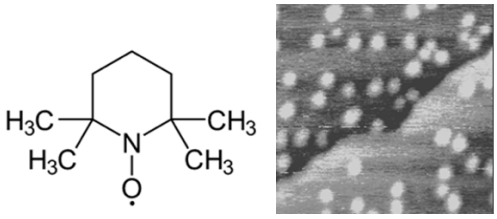
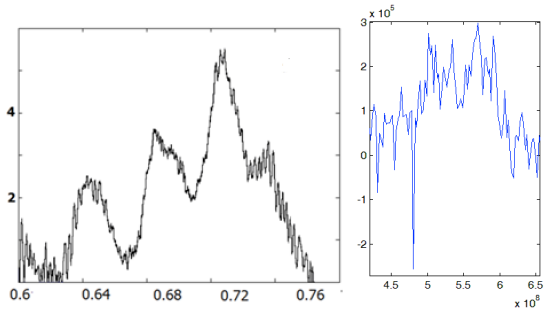


Fig. 2 left – the atomic structure of the tempo radical molecule. Right an STM image (20x20 nm^2) of tempo on Au(111)

One of these molecules yields the single molecule ESR-STM spectrum that is shown in Fig. 3. The spectrum has a clear hyperfine structure. The horizontal units are in [GHz]. In this molecule there is a shift of 30 MHz to high frequency that is a result of dipolar interaction with a neighbouring molecule.

By using time domain acquisition and digital spectrum analysis an ESR spectrum was recorded within 0.1 second (Fig. 3 right).



Fig, 3 left: An ESR-STM spectrum of a single tempo molecule accumulated at 90 seconds. The magnetic field is 230G. Right: Same molecule accumulated at 0,1 second (derivative spectrum) with a field of 186G.

The spectrum and the image were taken with a positive sample bias of 0.2V. Afterwards the NMR experiments were performed. In the experiment shown in Fig. 4, the spectrum analyser was put at a constant frequency at the center of the low frequency hyperfine peak. The video output of the analyser was recorded as a function of time with a bandwidth of 2MHz. The bias voltage was oscillating between 0.2V to 3.7 volt at a frequency of 250KHz. The diamagnetic phase is longer in time by a factor of 4 than the paramagnetic one. The video output was analyzed by a lock in amplifier, in which the reference frequency was swept from 0 to 150KHz. A significant signal was detected quite often at 70 KHz which is the Larmor frequency of the ^{14}N nucleus.

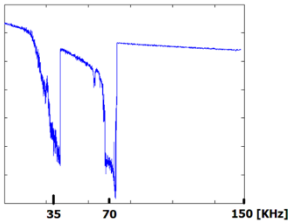


Fig. 4 ^{14}N NMR peak of the tempo molecule which was observed from frequency modulation of the low frequency hyperfine peak.

A clear peak was also observed in a frequency of half the nuclear Larmor frequency. These peaks appear in many, but not all NMR spectra. In addition, the linewidth is much broader than in the macroscopic NMR peak. The spectral resolution can be improved by optimizing the conditions of the experiment. In another experiment **(Fig. 5)**, the spectrum analyser was put on the frequency of the center of high frequency hyperfine peak. In this case a sharper NMR line, without the half frequency peak has appeared.

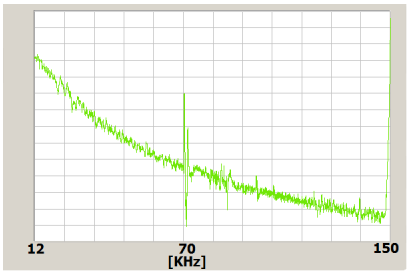


Fig. 5 ^{14}N NMR peak of the tempo molecule which was observed from frequency modulation of the high frequency hyperfine peak.

A preliminary model was developed for this phenomenon:

The basic ingredient that allows time dependent hyperfine signal is the presence of a hyperfine tensor element that is perpendicular to the external magnetic field. To demonstrate this possibility, we considered a simple model with nuclear spin ½ without relaxation, that has a hyperfine component in the z direction (direction of the external magnetic field) and another component in the x direction. We then assume that the molecule is ionized during time T, when it propagates with eigenvalues $\mp 1/2\ \nu_n$ where ν_n is the nuclear Larmor frequency, and then a period T' when the molecule is neutral, then each of the k=1,2,3,4 4-spinor states β_k at time T need to be projected on the eigenstates of the hyperfine system which thereafter propagate with λ_k . The overlap is a matrix

$$u_{kl} \equiv \beta_l^{\dagger} \cdot \beta_k(T) \mathrm{e}^{i\lambda_l T'}.$$

With N such steps we find the modulated intensity at frequency ν^*

$$I(\nu^*) = \sum_N \cos(2\pi\nu^* N) \left| \sum_{k'} [u^N]^*_{k'3} \sum_k [u^N]_{k1} \right|^2$$

Assuming that the signal is counted only during the neutral periods while the time is counted for both neutral and ionized states a peak at some ν^* means a time dependent hyperfine signal

$$\cos\left[2\pi\nu^* \frac{t}{T+T'}\right]$$

For T' $\to$0 we obtain a signal at ν_n as expected. If T' is finite, the propagation during the neutral state contributes to the overall phase and a different frequency appears. It is possible however, to evaluate ν_n from the observed frequencies.

5. FUTURE PROJECT VISION

If this project will be selected for ATTRACT phase 2 we will scale up the technology – from a preliminary

proof of concept to a fully working microscope. Figs 6a and b show the STM images we acquire today. Our work in ATTRACT Phase 1 successfully proved that the information shown in Fig. 6c is possible and reachable. By changing the ionization pulse sequence (frequency and intensity-for example – by shortening the relative "paramagnetic" period, the resolution can be improved.

The resolution can be further improved by changing the ratios between the size of the external field and the anisotropic hyperfine constant and between the nuclear Larmor frequency and the T_1 relaxation.

We will perform the experiment on different nuclei, and observe NMR on a nonmagnetic molecule (which becomes magnetic at high voltage).

The improved resolution will provide information of the environment of each nucleus (chemical shift, spin – spin coupling etc).

Pulses of external magnetic fields (perpendicular to the DC field) will be applied in synchronization with the ionization sequence. This may improve further the spectral resolution.

It is possible to record the ESR hyperfine peak (as a function of time) with a spectrum analyser and to record the modulation in time domain using a rapid scope and to use a digital spectrum analyser **AFTER** the data acquisition. A good NMR spectrum can be observed in 1 second and less. The feasibility was shown by a spectrum in the ESR case (Fig. 3 right).

This will enable the accumulation of an NMR spectrum for each pixel in the STM image within one second. The bottleneck in this case, is the necessity for rapid data storage of large files on the hard disk of the computer. A PXI national instrument oscilloscope has these abilities..

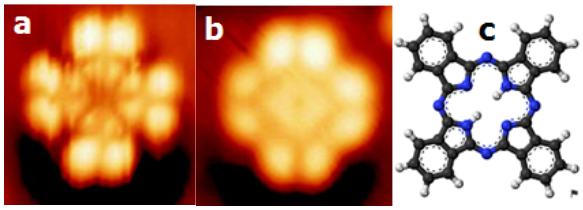


Fig. 6 STM image (a, b) of a phtalo cyanine molecule and its chemical structure (c).

5.1. Technology Scaling

The first 4 TRL levels were successfully done in the ATTRACT phase 1 stage.

In order to demonstrate general applicability for use for industrial applications (TRL 5,6), we will show that the technique is applicable for non-radical molecules that will become a radical as a result of ionization (opposite to TEMPO) and to observe of single spin NMR on different nuclei.

The observation of spectra in time scales of seconds, will make the technique relevant for industrial environments (Fig. 6).

Afterwards, we shall focus on TRL 8, 9 and in collaboration with an industrial partner we shall create a commercially available product.

5.2. Project Synergies and Outreach

We will need an expert in macroscopic NMR. and a chemist for synthesis of different large magnetic and non-magnetic molecules which have different atoms. We will add to the consortium an industrial partner with expertise in NMR and in STM machines fabrication. We will publish our results in scientific journals, present our technology in relevant conferences and will create a dedicated web page.

5.3 Technology application and demonstration cases

In pharmacology, we will show how two molecules approach each other and more specifically, how a drug molecule approaches the active site of a protein.

Mapping capability of each atom is crucial for the electronic industry. We will demonstrate it in layer by layer growth (atomic layer deposition) that is capable of fabrication of structures of a scale of 20nm. (Fig. 7).

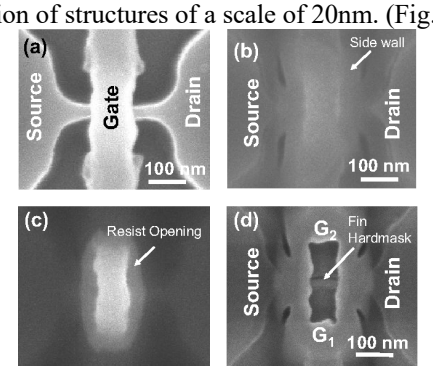


Fig. 7 SEM images of an electronic circuit made by atomic layer deposition.

In the fabrication process we will identify exact local chemical composition in situ.

5.3. Technology commercialization

Suitable investors for commercialization are manufacturers of NMR and SPM equipment. We plan to contact potential investors through BGU Negev, the technology transfer company owned by Ben Gurion University. They have in-house knowledge of the business sector.

We shall consider applying for further funding for reaching the market: Seed money, Business angels may be the first to be considered, However, as a first step, we shall try and see if a large company already working in the field of NMR or STM maybe interested to invest.

5.4. Envisioned risks

Although the technique was shown to be feasible, there are several risky factors in phase 2 project (if awarded): The technique depends on fast and smooth temporal ionization of very different species. This may depend on the specific STM substrate, the insulating layers, the vacuum and temperature conditions etc. A parallel study of ionization will be useful.

Another risk is due to the specific parameters of the different species: There are two possibilities: First to develop a detailed theoretical model that will find the optimization of the experimental conditions for each species. The second tool is to change the magnetic field's direction with an additional temporal external field which is synchronized with the ionization. This tool, can solve many of the problems associated with the dependence on the specific parameters of the spin system.

The projection of the polarization of the nucleus on H_N to restore the previous phase of the nucleus is not always precise. This is probably the reason for the large linewidth and the peak at half the Larmor frequency (because it is a projection of a one dimensional function on a two dimensional plane). It is similar to the difference in NMR between diode and quadrature detection, thus it is possible to use 2 temporary consecutive orthogonal magnetic fields.

5.5. Liaison with Student Teams and Socio-Economic Study

Unfortunately, we were not aware of this opportunity while working on ATTRACT phase 1, but we shall participate in this activity during ATTRACT phase 2. An experienced person in the lab will be responsible for the Laison.

6. ACKNOWLEDGEMENT

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7. REFERENCES

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