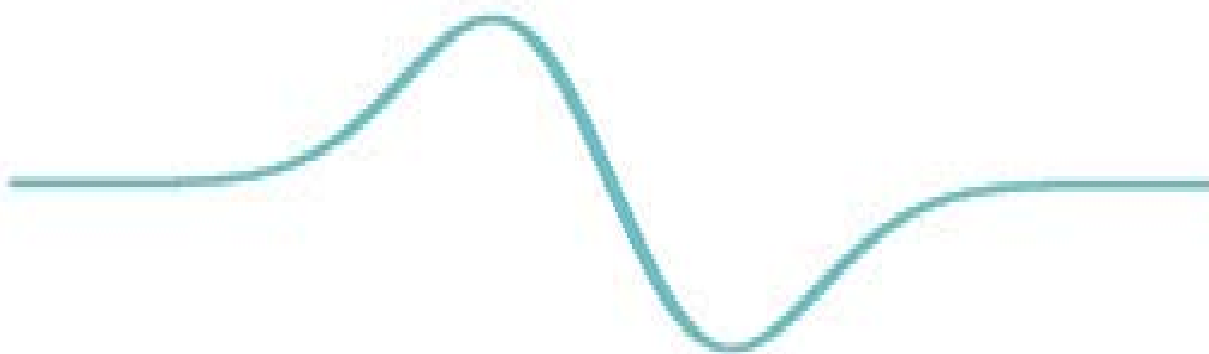


TEL-Atomic Incorporated

PO BOX 924 • JACKSON • MI 49204
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1-800-622-2866

NMR and ESR Continuous Wave Spectrometer **CWS 12-50**



**operating and experimental
manual**



**TEL_Atomic
I n c o r p o r a t e d
P O B O X 9 2 4 • J a c k s o n • M I 4 9 2 0 4
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1-800-622-2866**

Operating and experimental manual

NMR and ESR Continuous Wave Spectrometer
Model CWS 12-50

Version 2.0

Updated: 06.26.2006

File: CWS 12_50 manual v2.1

Compatible with serial #57 and up



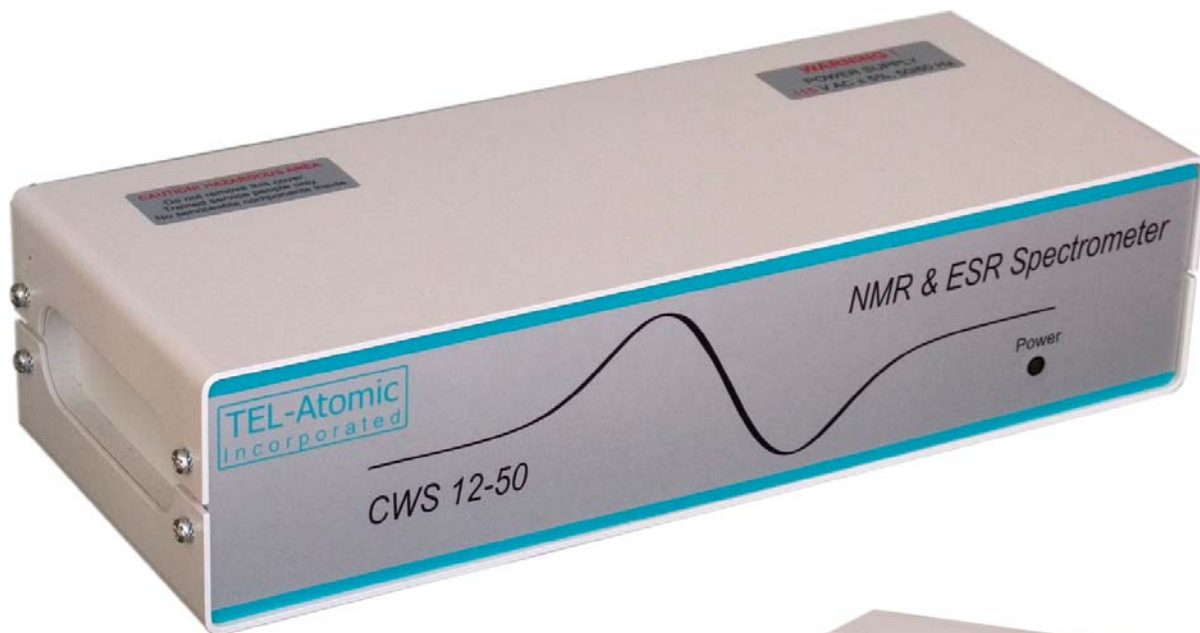




TABLE OF CONTENTS

1	INTRODUCTION	9
2	SPECTROMETER MAIN FEATURES	11
2.1	Console	11
2.2	Spectrometer control and data acquisition.....	11
2.3	Data processing.....	11
3	INSTALLATION	13
3.1	Shipment check	13
3.2	Spectrometer location and environmental requirements	13
3.3	Electrical requirements	14
3.4	Computer requirements and software installation.....	15
3.4.1	Computer considerations.....	15
3.4.2	Using program with LCD monitor.....	15
3.4.3	Using computer USB port.....	15
3.4.4	Software installation	16
4	HARDWARE CONNECTION.....	17
4.1	Unit connections	17
4.2	Configuration for NMR and ESR experiments	18
4.3	Swapping probehead between electromagnet (NMR) and Helmholtz coils (ESR)	19
5	SHIPPING ITEMS.....	21
5.1	Picture tour	21
5.2	Itemized Shipping List	23
6	SPECTROMETER BLOCK DIAGRAM	25
7	SPECTROMETER SPECIFICATIONS	27
8	SOFTWARE DESCRIPTION	29
8.1	Setup and Data Acquisition Page	29
8.2	Data Processing	35
9	MISCELLANEOUS	41
9.1	Sample preparation and positioning	41
9.2	Changing configuration file	43
10	EXPERIMENTS	45
10.1	Continuous wave NMR experiment in rubber	45
10.2	Examples of other NMR spectra	48
10.2.1	Acrylic.....	48
10.2.2	Delrin	49
10.2.3	Glycerin	50
10.2.4	Fluoroboric acid (HBF ₄).....	51
10.2.5	Teflon	52
10.3	CW ESR in TCNQ	53
10.4	ESR in other samples	55
10.4.1	DPPH	55
10.5	Nuclear magnetogyric ratio measurement with CW NMR.....	56
10.5.1	Magnetogyric ratio of protons (¹ H nuclei)	58
10.5.2	Magnetogyric ratio of ¹⁹ F nuclei.....	60

10.5.3	Field/frequency factor	61
10.6	Angle dependence of ^1H NMR spectra in gypsum monocrystal	62
10.7	Determining Earth's magnetic field with ESR experiment.....	68
10.8	Measurements of a static magnetic field with a Tesla meter (Smart Magnetic Sensor)	71
10.8.1	Angle dependence of the readings of the Tesla meter.....	73
10.8.2	Measuring magnetic field remanence in an electromagnet.	75
10.8.3	Helmholtz coils	76
10.9	2 nd modulation of magnetic field and line broadening	78

1 INTRODUCTION

Historically Electron Spin Resonance¹ (ESR) and Nuclear Magnetic Resonance² (NMR) were discovered in a series of simple experiments in which a magnetic field was swept over the sample containing uncompensated magnetic dipoles (electron and nuclear spins) exposed to electromagnetic radiation. Absorption of this radiation was detected at a certain resonant field, as predicted by earlier theories. Because the source of electromagnetic radiation (electromagnetic wave) was operating in a continuous, uninterrupted way, this kind of technique was named continuous wave (CW) to distinguish it from pulsed techniques which apply short bursts of powerful pulses to excite spins polarized by a constant magnetic field.

As technology and experimental techniques developed, continuous wave methods were later replaced by pulsed NMR and partially by pulsed ESR. However, continuous wave spectroscopy is perfectly suited for teaching purposes. Students witness the same original experiment - product of human ingenuity from the forties. This more simple technique which is not encumbered by elaborate instrumentation or sophisticated mathematics, aids the student in learning the physical laws governing NMR.

TEL-Atomic Inc. introduces a desktop, state of the art continuous wave spectrometer the CWS 12-50 that allows for demonstrations of NMR and ESR experiments through a two-in-one integrated autodyne probehead. Although designated for teaching, the CWS 12-50 hardware and software provides a convenient means for NMR spectroscopy experiments on ¹H and ¹⁹F nuclei at a magnetic field of 320 mT and ESR spectroscopy at a field of 20 mT and frequency of 50 MHz.

This manual consists of two sections:

- operating section: Chapters 1-10
- experimental section: Chapter 11

The purpose of the operating section is to provide the user with comprehensive information about the spectrometer:

- Installation
- Hardware
- Control Program

¹ *E. K. Zavoisky*, Supplement to thesis, Kazan State University, Russia, October 1944

² *E. M. Purcell, H. C. Torrey and R. V. Pound*, "Resonance Absorption by Nuclear Magnetic Moments in Solids", *Physical Review*, **69**, 37-38 (1946).

F. Bloch, W. W. Hansen and M. E. Packard, "Nuclear Induction", *Physical Review* **69**, 127 (1946)

All experiments have been performed using an off-the-shelf CWS12-50 NMR/ESR spectrometer and only originally acquired data are presented. The list of experiments include:

- Acquiring NMR and ESR spectra from factory provided samples
- Determination of magnetogyric ratio for ^1H and ^{19}F nuclei
- Measurement of Earth's magnetic field
- Observation of NMR line split in gypsum monocrystal due to its rotation
- Mapping electromagnet and Helmholtz coil with Hall effect Tesla meter

This list is not closed. More experiments will be developed and included later.

2 SPECTROMETER MAIN FEATURES

2.1 Console

- Modes of operation:
 - ¹H NMR- electromagnet 3,200 Gs/14.0 MHz
 - ¹⁹F NMR- electromagnet 3,200 Gs/13.9 MHz
 - ESR- Helmholtz coils 20 Gs/50 MHz
- Magnetic field sweep and frequency sweep in NMR mode
- Magnetic field sweep in ESR mode
- Simultaneous connection of electromagnet and Helmholtz coils to console
- Switching current direction for reversing magnetic field direction
- Integrated NMR/ESR probe with high-sensitive autodyne generator
- Synchronous phase detection
- Adjustment of 2nd Modulation Field
- 5 mm sample holders
- Phase Lock Loop for stable frequency generation
- 10-bit signal digitizer

2.2 Spectrometer control and data acquisition

- Recognition of electromagnet or Helmholtz coils connection
- Electronic switching between electromagnet and Helmholtz coils for NMR or ESR experiments
- Multiple displays of current and previous experiments
- Accumulation to improve signal-to-noise signal
- Saving data in binary file to reduce occupied space
- Saving experimental details in a setup file
- Loading setups for designed experiments
- Alarm sounds for the status of experiment (start of sweep, end of sweep, end of accumulation)
- Vertical (amplitude and field/frequency) and horizontal (amplitude) measurement cursors
- Determination of line width
- Displayed status of hardware and of experiment

2.3 Data processing

- View acquired binary data
- Store binary data in a text format (for processing with other programs like Excel)
- 1st integration of first derivative signal to obtain absorption (spectra)
- 2nd integration to obtain value of area under absorption line
- Calculate spectra 2nd and 4th Moment

- Calculate spectra line width
- Extract experimental details from old experiments and save in a setup file (to repeat experiments under same conditions)
- Print spectra and calculated parameters

3 INSTALLATION

The installation of the CWS spectrometer requires only a #2 flat screwdriver. Please read this chapter before attempting to connect the spectrometer.

3.1 Shipment check

Check the contents of the shipment against the enclosed Itemized Shipping List. Inspect all parts for any signs of damage that may have occurred during shipment. Immediately report any visible damage or incomplete delivery to your distributor.

3.2 Spectrometer location and environmental requirements

The spectrometer should be placed on a solid table or bench, preferably wooden. Try to eliminate the presence of iron beams or any other ferrous components in the electromagnet proximity that can disturb its homogeneity. Avoid a vibrating environment: elevators, frequently used doors, etc. A clean, dust free, low humidity environment is recommended.

Warning:

The magnet is protected by a process known as “bluing”. This is the same process by which gun barrels are protected. Therefore handle the magnet only by the handles since water or skin oils can cause corrosion to occur.

Do not expose the magnet to water or high humidity. Store the magnet in a low humidity environment.!!!

At least twice a year use gun oil or WD-40 to wipe the surface of the magnet. It is important to keep oil from getting into the magnet’s coils and the probehead therefore DO NOT SPRAY OIL OR WD-40 DIRECTLY ONTO THE MAGNET, rather saturate a piece of soft cloth or patch with the oil or WD-40 and wipe the magnet’s surface thoroughly with this.

3.3 Electrical requirements

Before you turn on the console, make sure that:

- The line voltage selector label matches the voltage mains supply. The label is located on the top right corner of control unit cover. 115 V label for USA market is shown in Figure 1.
- Ensure that the AC power source meets the requirements specified in Table 1.



Figure 1. 115V label for USA market.

Note:

115/220V voltage selector is located inside the control unit and should be set by authorized personnel only!

Verify that the power cable is not damaged, and that the power source outlet provides a protective earth ground contact. The working fuse is located above the power cable receptacle on the CWS 12-50 back panel.

Nominal Setting	AC Line Power Voltage [V]	AC Line Power Frequency [Hz]	Fuse [A]
115 V	100 – 122	45-100	2.0
220 V	200-230	45-100	1.0

Table 1. CWS 12-50 power requirements and fuses.

3.4 Computer requirements and software installation

3.4.1 Computer considerations

For proper operation, data storage and display, the spectrometer **CWS** control program requires an IBM PC AT VGA or compatible computer with 1GHz clock. The program and factory created files occupy less than 1MB of hard drive total space. Average binary data files with spectra first derivative and experimental parameters need only about 3 kb of space, but expand when converted into text files.

3.4.2 Using program with LCD monitor

The control program supports displays with 4:3 aspect ratio of 1024x768 pixels resolution without distortion. To work with LCD (laptop) change display resolution to 1024x768 pixels and DPI settings to Normal size (96dpi):

- Control Panel
 - Settings
 - Screen Resolution: 1024x768pix
 - Advanced:
 - DPI setting: Normal Size (96dpi).

Users of Wide Screens: If display driver does not support this resolution or you do not see the whole program window, find the closest screen resolution that displays the whole window on the monitor with the lowest possible distortion.

3.4.3 Using computer USB port

If no COM port is available use a USB/COM port adapter. In the spectrometer control program remember to select the proper COM port number.

- Tools
 - Spectrometer
 - Communication port
 - Select one of COM1-COM4 ports

Recommended and tested USB/COM port adapter vendor/model:

Vendor: www.sewelldirect.com

Model: USB to Serial Adapter part #: SW-1301; price \$17.95

3.4.4 Software installation

To install the software copy the **CWS** file from the provided compact disk into the root directory of "c:" hard drive of your computer. Keep the directory structure as factory created. For more information about program files structure refer to Table 2.

Type	Folder	Description	Default
*.exe	c:\cws	control program	cws.exe
*.ini	c:\cws	initialization	cws.ini
*.cfg	c:\cws\setup	setup	standard.cfg
*.dcw	c:\cws\acq	acquired data	
*.txt	c:\cws\proc	data in text format	
*.wav	c:\cws\audio	audio file	
.	c:\cws\temp	temporary	

Table 2.CWS program files and files location.

After copying, check files/directories and make sure that in attributes the read-only box is unchecked.

- right click on **cws** folder
- left click on **Properties**
- left click on **General**
- uncheck **Read-only** box

4 HARDWARE CONNECTION

Arrange the electromagnet, electronic unit and the computer on the desk, according to space availability and convenience. Remember that the keyboard and monitor are the most used devices. As samples will be frequently replaced and repositioned in the probehead keep the electromagnet and Helmholtz coil close to your hand and eyes.

4.1 Unit connections

- **Connect the computer and electronic unit power supply cords to the same power line to avoid unwanted ground currents.**
- **Connect the console to the probehead.**
- **Connect the electromagnet for NMR experiments (4.2).**
- **Connect Helmholtz coils for ESR experiments using the provided cables (4.2).**
- **Insert probehead either to electromagnet or to Helmholtz coils depending on experiment to be conducted.**
- **Remove sample from the storage box and carefully insert in the probehead slot (4.3).**



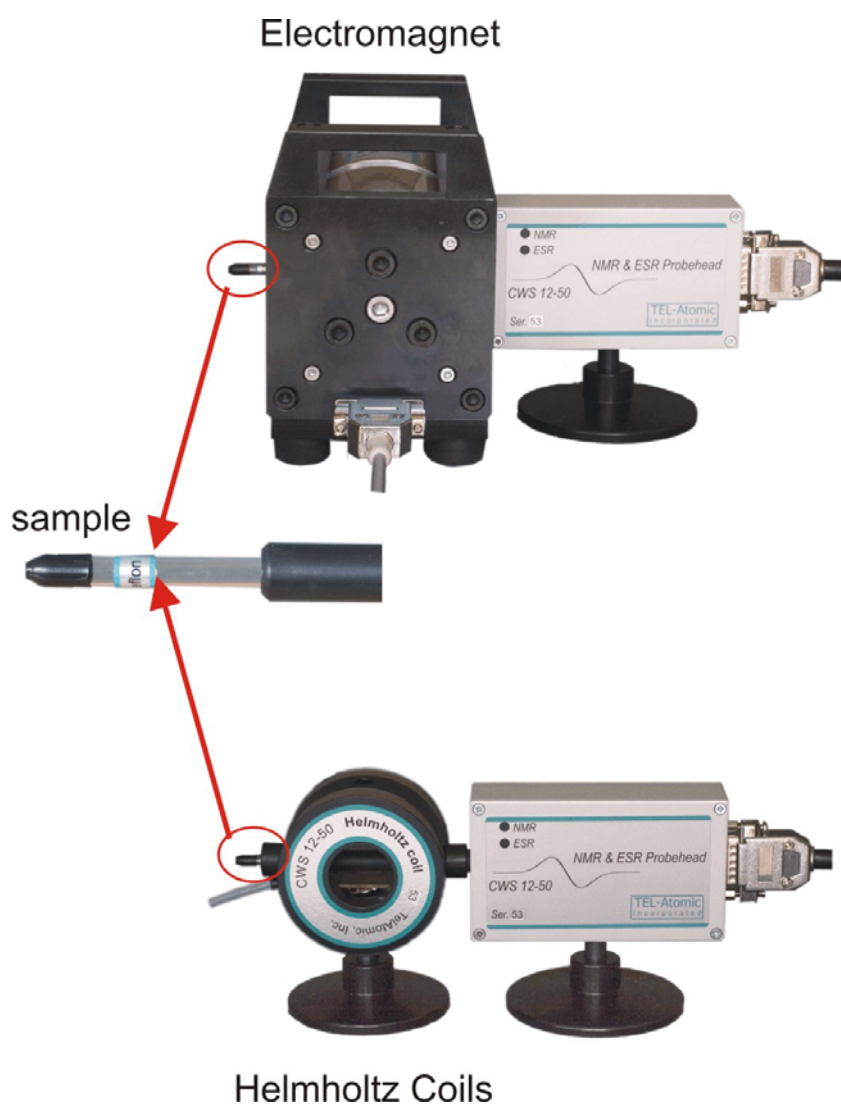
Note:

Before connecting the electromagnet and the Helmholtz coils turn off the console.

4.2 Configuration for NMR and ESR experiments



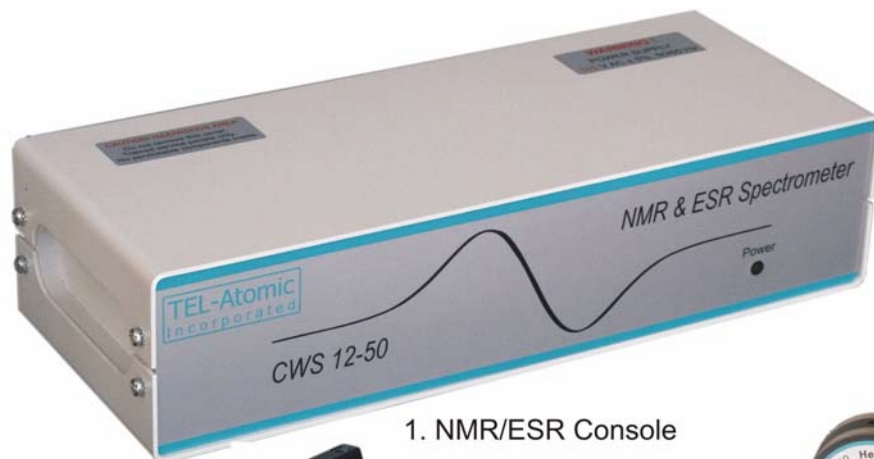
4.3 Swapping probehead between electromagnet (NMR) and Helmholtz coils (ESR)





5 SHIPPING ITEMS

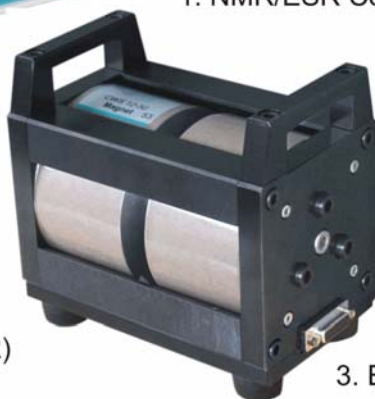
5.1 Picture tour



1. NMR/ESR Console



2. Probehead(NMR/ESR)



3. Electromagnet (NMR)



4. Helmholtz Coils (ESR)

5a. RS 232 Cable



5b. Electromagnet Cable



5c. Probehead Cable



5d. Power Cord



6. Samples



7. Hex Allen Wrench

8. Fuse



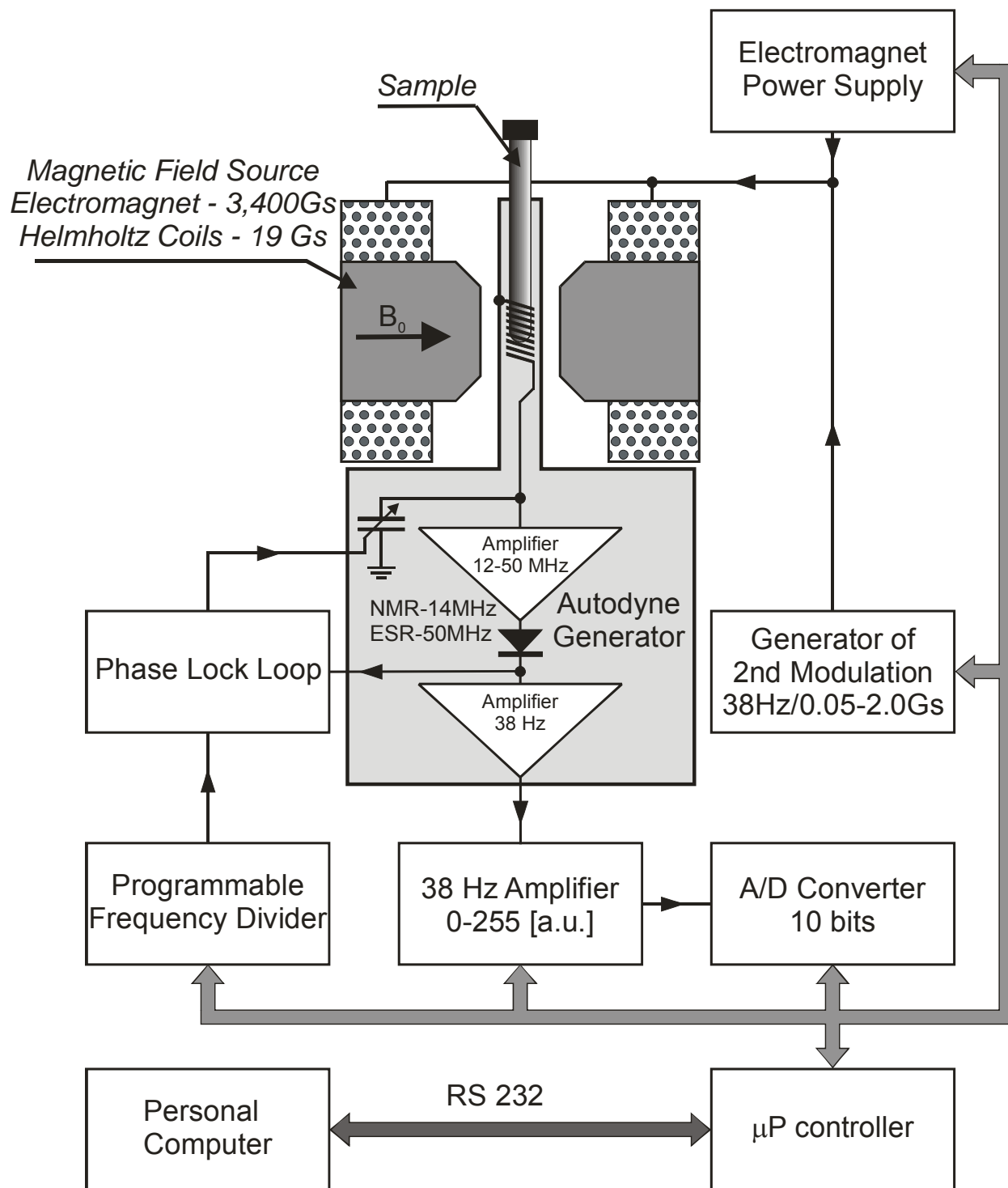


5.2 Itemized Shipping List

	Item	Shipped	Received
1	Control unit		
2	Probehead		
3	Electromagnet		
4	Helmholtz Coils		
5	Cables		
5a		RS 232	
5b		Electromagnet	
5c		Probehead	
5d		Power cord	
6	Samples		
		glycerin	
		rubber	
		acrylic	
		delrin	
		$\text{HBF}_4 + \text{H}_2\text{O}$	
		Teflon	
		TCNQ	
		DPPH	
7	Allen hex socket wrench		
8	Fuse		
9	CD with program and manual		
10	Manual		



6 SPECTROMETER BLOCK DIAGRAM





7 SPECTROMETER SPECIFICATIONS

Mode	NMR (^1H , ^{19}F), ESR
Operational Frequency	NMR ^1H -14.0MHz, NMR ^{19}F -13.2MHz, ESR-50MHz
Frequency Stability	≤ 1 PPM/ 1h
Electromagnet	
- magnetic field	320 mT
- maximum current	0.7A
- coil	2,000 turns
- gap	10.5 mm
- pole diameter	50 mm
- homogeneity	$\leq 10^{-4}$ / sample volume
- field stability	≤ 10 μT / 1hr
Helmholtz Coils	
- magnetic field	195 μT
- gap	15 mm
- coils diameter	70 mm
- homogeneity	10^{-5} /sample volume
Modulation Field	
- frequency	38 Hz
- amplitude	0.1-25 μT
Sweep of magnetic field (NMR and ESR)	
- range	0.5 mT- 10.0 mT
- time	0.5 min – 30 min
Sweep of frequency (only NMR)	
- range	20 Hz – 400kHz
- time	0.5 min – 30 min
RF Probehead	
- solenoid coil dimensions	ID= 5.8 mm; L= 12 mm
- mode	Automatically tuned for NMR or ESR
Receiver	
- gain	0-48 dB (2 dB step)
- detection	phase-sensitive
- phase adjustment	0-360 $^\circ$, step 1.5 $^\circ$
- signal filter	sweep controlled
- DC offset converter	automatic
A/D Converter	
- resolution	10 bit
- number of samples	Min 512 per sweep
Weight and dimensions WxDxH	
- electronic unit	3.5 kg, 350x135x85 mm
- probehead	0.4 kg, 35x210x70 mm
- Helmholtz coils (ESR)	0.5kg, 50x80x110 mm
- electromagnet (NMR)	10.5 kg, 175x100x160 cm
Power Consumption	110V/220 V; 50/60 Hz; 40 W
Communication Port	two way RS 232C
Computer Required	IBM PC, min 750 MHz, VGA color or compatible
Software	MS Windows operated

8 SOFTWARE DESCRIPTION

Control program for the CWS 12-50 spectrometer consists of two pages:

- **Setup and Acquisition**
- for experiment preparation and data acquisition
- **Processing**
- for acquired data processing

8.1 Setup and Data Acquisition Page

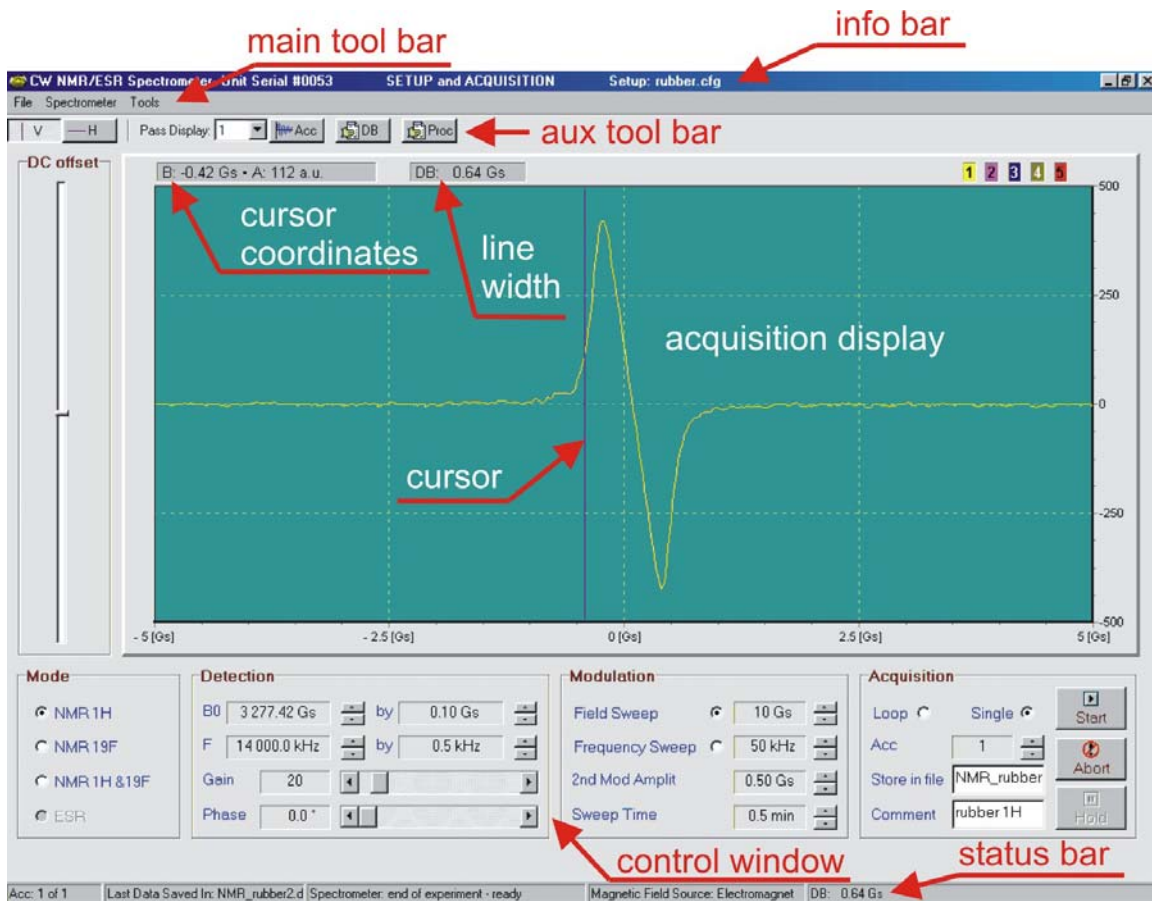


Figure 2. Setup and Acquisition page

INFORMATION BAR

- Hardware name: CW NMR/ESR Spectrometer
- Unit Serial #:
- Page Name: SETUP and ACQUISITION
- Setup Name: (default is **standard.cfg**)

MAIN TOOL BAR

File

- *Save Data As*
Saves acquired data in a file if name was not declared earlier in *Acquisition/Store in File* box
- *Open Setup*
Loads setup file with saved experimental parameters
- *Save Setup*
Saves setup file with experimental parameters with current name
- *Save Setup As*
Saves setup file under new name. Name **standard.cfg** is reserved for CWS program use. This file is loaded during program initialization along with **cws.ini**.
- *About*
Information about control program
- *Exit*
Terminates control program

Spectrometer

- *Communication Port*
Depending on availability of serial port chose between COM1, COM2, COM3, COM4 for communication between your PC and console.
- *Connect*
Connects computer to NMR/ESR console

Tools

- *Accumulation*
Shows trace of accumulated signal (white color)
- *File Location*
Defines location of different files (See Table 2 for factory created structure. Users have the freedom to create their own file names and structure)
- *Audio*
Defines location of audio files (use any *.wav format sounds)
- *Data Processing*
Links to DATA PROCESSING page
- *Service*
Only for service people use. Locked by password!
- *Current/FWD,REW*
Switches current direction effectively reversing direction of magnetic field in the electromagnet or Helmholtz coils.

AUXILIARY TOOL BAR

- *V*
Switches to vertical cursor. Returns signal amplitude and sweep values on cursor
- *H*
Switches to horizontal cursor. Returns current cursor position
- *Pass Display:*
Displays first derivative of spectrum from experimental passages
 - **1**, current pass only (yellow)
 - **2**, current pass and one before
 - **3**, current pass and two before
 - **4**, current pass and three before
 - **5**, current pass and four before
 - **off**, no signal displayed (white)
- *Acc*
Shows the trace of an accumulated signal
- *DB*
Determines acquired spectrum line width and returns this value in the box next to cursor coordinates
- *Proc*
Links to DATA PROCESSING Page

CONTROL WINDOW

Mode

- *NMR 1H*
Parameter setup for Hydrogen nuclei NMR

- *NMR 19F*
Parameter setup for Fluorine nuclei NMR
- *NMR 1H&19F*
Parameter setup to acquire signals from Hydrogen and Fluorine Nuclei
- *ESR*
Parameter setup for Electron Spin Resonance mode

Detection

- *B0*
Magnetic field magnitude [Gs]
- *F*
Autodyne generator frequency [kHz]
- *Gain*
Total gain of the receiver (0-255 [a.u.])
- *Phase*
Relative phase of the detector reference signal [deg]

Modulation

- *Field Sweep*
Select for **magnetic field sweep**
- *Frequency Sweep*
Select for **frequency sweep**
- *2nd Mod Amplit*
Amplitude of second modulation
- *Sweep Time*
Sweep time of magnetic field or frequency

Acquisition

- *Loop*
Program operates in a loop: accumulates and displays a signal, but does not store in a file
- *Single*
Program performs given number of accumulations and saves data in the chosen file name
- *Acc*
Number of accumulations
- *Store in File*
Type the name of file in which you want to store acquired data
- *Comment*
Type your comment, sample name, etc
- *Start*
Starts data acquisition
- *Abort*
Stops data acquisition and returns spectrometer to initial state

- *Hold/Continue*
Stops acquisition allowing for adjustment of certain parameters. Press again to *Continue* acquisition

STATUS BAR

- *Acc*
Shows the number of the current sweep in accumulation experiment
- *Last Data Save in:*
Displays file name of last saved data
- *Spectrometer:*
Shows status of the spectrometer and prompts an action:
 - Not Connected/Connected
 - Experiment in progress- please wait
 - Experiment Aborted- please wait.
 - Experiment Aborted- please wait
 - Experiment on Hold
- *Magnetic Field Source:*
Program automatically detects what source is connected to the console
 - Electromagnet
 - Helmholtz coil
- *DB*
Displays line width calculated from 1st derivative (min-max)

8.2 Data Processing

Data Processing page allows one to:

- **Load** a binary data file with first derivative of the absorption signal from the disk and display on the data display
- **Export** original and unchanged signal amplitudes as text for further processing with independent software: Origin, Matlab, Mathematica, Excel, etc.
- Correction of line base of first derivative
- Integration of first derivative to obtain absorption
- Calculating integral value of absorption within limits,
- Calculating 2nd moment, 4th moment and line width of first derivative and absorption lines (for NMR mode only)
- Saving processed data
- Printing data

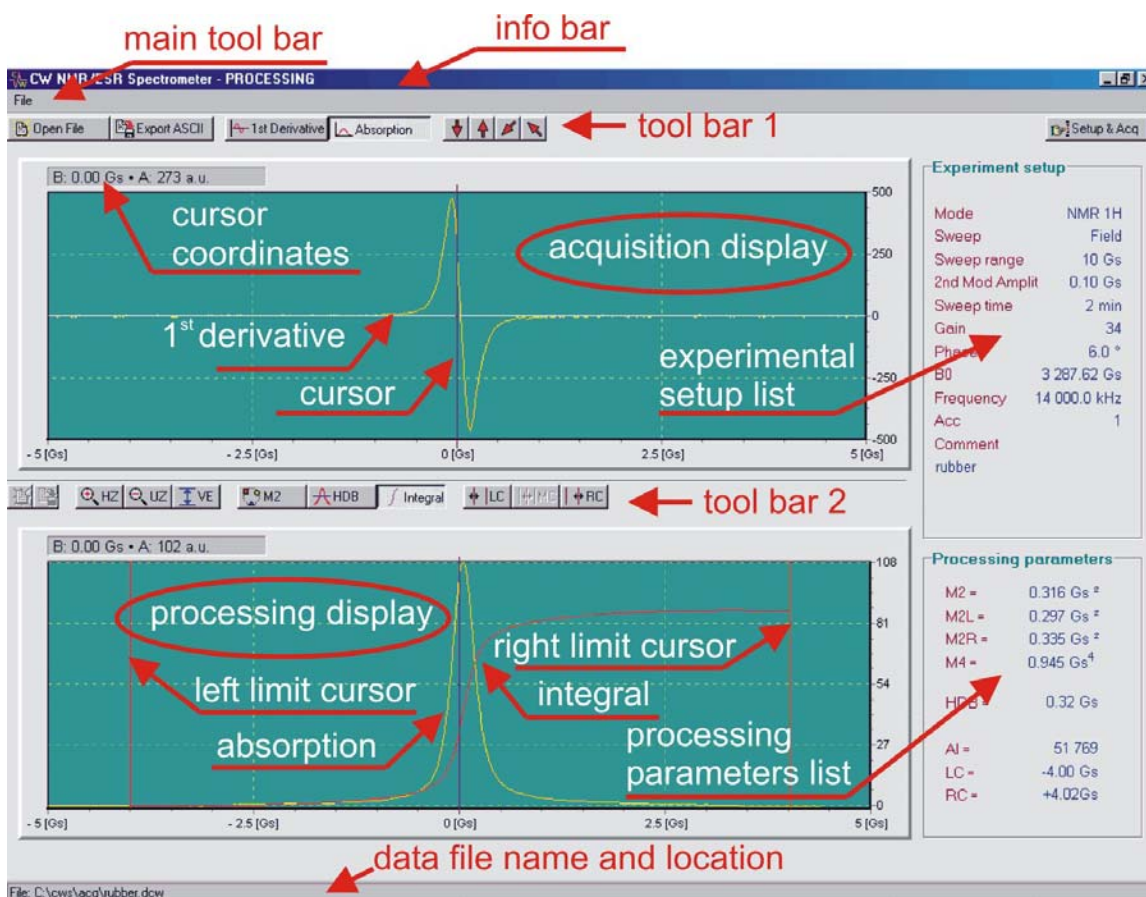


Figure 3. Data Processing page with absorption tools.

MAIN TOOL BAR

File

- *Open*
Loads binary data file with extension *.dcw and displays first derivative of the spectrum on the data window with experimental parameters
- *Export ASCII*
Exports binary file as a text file with extension *.txt
- *Save Setup As*
Extracts and saves experimental setup to file with extension *.cfg
- *Exit*
Terminates the program

TOOL BAR 1

- *Open File*
Loads binary data file with extension *.dcw and displays on the data
- *Export ASCII*
Exports binary file as a text file with extension *.txt
- *1st Derivative*
Loads processing window with signal 1st derivative
- *Absorption*
Integrates first derivative signal and loads processing window with absorption curve (spectrum)
- *1st derivative base line correction cursor*. Any change of base line position is instantly transferred to processing window.
 - *Arrow Down*
Shifts base line down
 - *Arrow Up*
Shifts base line up
 - *Arrow Diagonal Up*
Shifts base line right limit down
 - *Arrow Diagonal Up*
Shifts base line right limit down
- *Setup & Acquisition*
Link to Setup & Acquisition Page

DATA DISPLAY

Displays loaded binary data file with 1st derivative of the resonance signal

EXPERIMENTAL SETUP

Displays complete list of experimental parameters used in the experiment

TOOL BAR 2

- **HZ**
Horizontal zoom
 - Left click on Zoom button
 - Left click on left limit and release
 - Drag courser to right limit
 - Left click to expand marked area
- **UZ**
Left click to unzoom
- *VertExp*
Vertical expansion to full screen
- **SDB**
Returns numerical value of the line width of 1st derivative
Definition: distance between line maximum and minimum

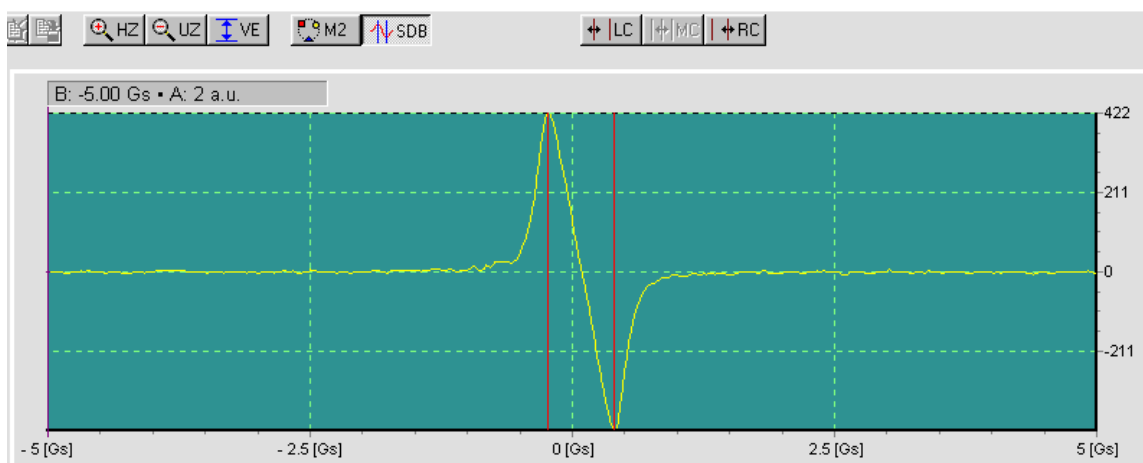


Figure 4. Calculating line width from signal of 1st derivative.

- **HDB**
Returns numerical value of the line width of absorption
Definition: line width at line half-height

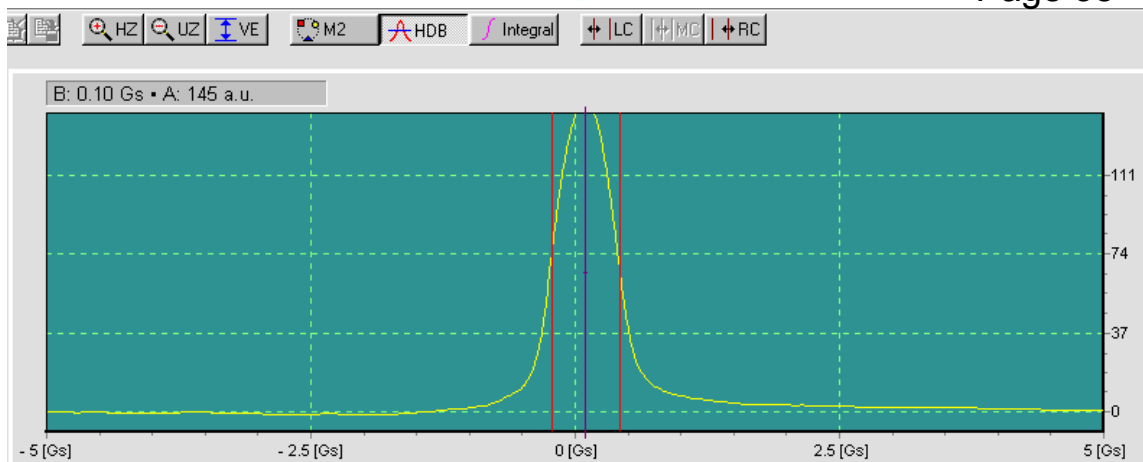


Figure 5. Calculating line width from absorption curve.

M2

Tools to calculate 2nd and 4th moment of 1st derivative and absorption (see Figure 6, note that the identical tools are used to calculate moments of 1st derivative)

- *LC*
Left cursor position for M2 limit
- *MC*
Middle cursor position for M2
- *RC*
Right cursor position for M2 limit

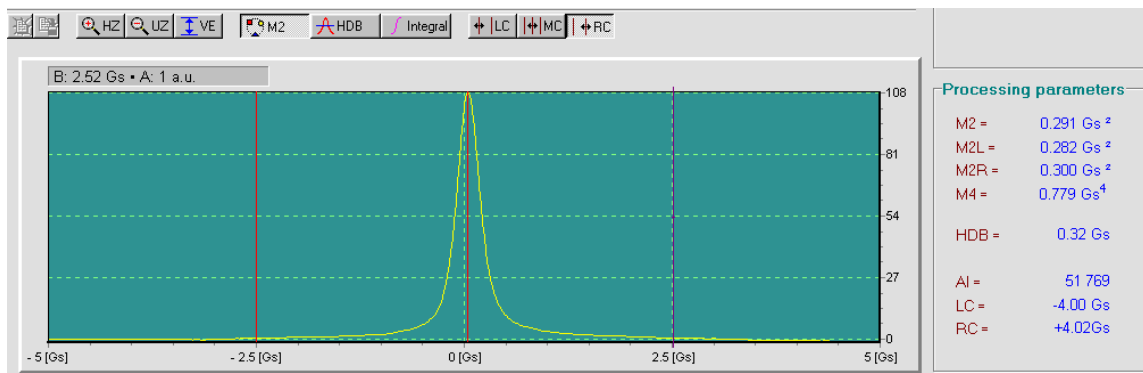


Figure 6. Calculating 2nd (M2) and 4th (M4) moments of absorption line. M2L and M2R are 2nd moments of left and right part of the absorption line, respectively, $M2 = 1/2(M2L + M2R)$.

Numerical values of 2nd and 4th moments are calculated on the fly and displayed in processing parameters window on the right.

2nd Integration tools

Tools to calculate integral value of absorption line (**AI**=absolute integral) within given limits

- *LC*
Left cursor position for spectrum integration
- *RC*
Right cursor position for spectrum integration

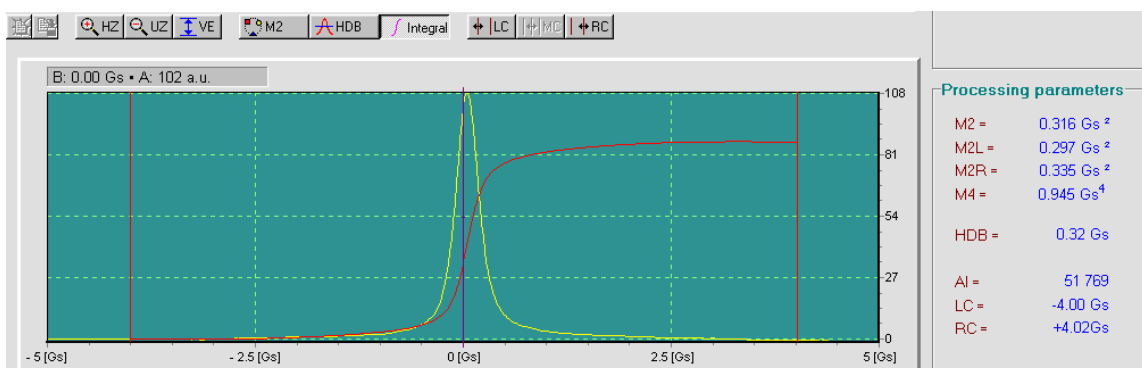


Figure 7. Calculating integral of absorption.

PROCESSING DISPLAY

Displays 1st derivative of the resonance signal or its 1st integral, depending on the action taken in TOOL BOX 1.

PROCESSING PARAMETERS LIST

Displays list of calculated parameters (M2, M4, integral value, line widths, limit cursors positions)



9 MISCELLANEOUS

9.1 Sample preparation and positioning

Introduction

The NMR/ESR signal originates from a sample located between poles of the electromagnet or inside Helmholtz coils. To avoid magnet/coils contamination and possible field homogeneity degradation due to corrosion of iron alloy and the poles use only glass vials to keep liquid samples isolated.

The spectrometer probehead incorporates an ID=5.5 mm sample holder that safely accepts standard OD=5 mm NMR tubes. We recommend glass NMR tubes from WILMAD³. The important dimensions of the sample holder design are shown in Figure 8.

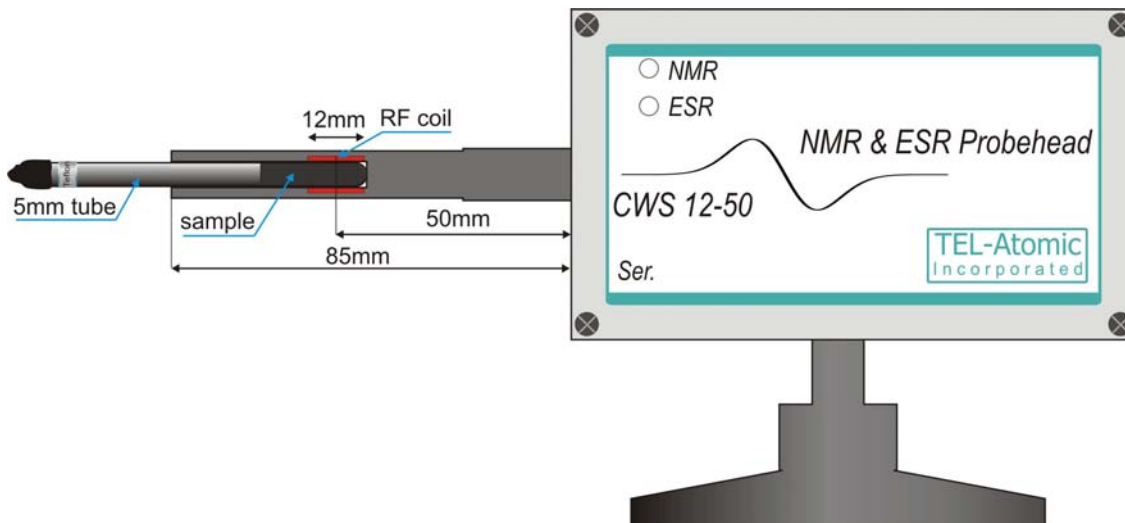


Figure 8. Probehead and sample

Liquid samples should be torch sealed. For routine studies make the sample 15-20 mm long so that it will fill the whole volume of the 12 mm long RF coil. For higher resolution NMR studies only small samples of 2-3 mm length are recommended, but expect the Signal-to-Noise to drop dramatically. As dimensions slightly vary from probehead to probehead individually adjust the sample position by observing the NMR resonance signal.

³ WILMAD/Lab Glass, PO Box 688, 1002 Harding Highway, Buena, NJ 08310-0688, USA, tel. 856-697-3000, for order 800-220-5171, www.wilmad.com, cs@wilmad.com. We suggest 5 mm student NMR tube: borosilicate WG-5mm Thrift

Solid samples like rubber, acrylic or wood can be placed directly in sample holder. They should be cylindrically shaped and no more than 5 mm OD and a minimum 20 mm length. Glue sample to glass or plastic rod for easy sample insertion and removal .

 **Note:**

Do not use samples that fit sample holder too tight!

Sample positioning

Carefully insert the tube into the probehead and gently push it to feel resistance. The center of the sample should be in the area of the most homogeneous constant magnetic field and oscillating RF field. This area is the magnet isocenter. In this particular design the center of the RF coil is about 35 mm from the holder entrance.

Since during experiments samples are held in a horizontal position, low viscosity liquids have a tendency to leave the bottom of the vial and stick to the vial wall. This will significantly lower the signal!!! For storage keep all liquid samples in an upright position and check to assure that the sample is at the bottom of the glass. If adhesive forces are too small to keep sample on the bottom, use of a larger amount of the substance is appropriate. An alternative is to “lock” the liquid on the bottom with little plug. WILMAD offers so called vortex plugs that can be used for this purpose. They are made of Teflon, which does not contain a proton, so the proton spectra are not contaminated with an extra signal from Teflon. Unfortunately Teflon contains a lot of fluorine nuclei, that can contribute to ^{19}F NMR signal so do not use this Teflon as plug with ^{19}F NMR spectroscopy

9.2 Changing configuration file

The control program can be started without any initialization and configuration files.

Follow instructions if you want to create a new **standard.cfg** setup file or change parameters in an existing **standard.cfg** file.

- Start the **control** program.
- Establish communication with the spectrometer by **Spectrometer/Connect**.
- Modify elements of the **Setup and Acquisition** page that you want to appear when the program starts.
- Save setup by **File>Save As** with new name (**new.cfg**).
- Exit program.
- Rename **standard.cfg** as **standard. old**, delete or move to another directory.
- Rename previously saved setup **new.cfg** as **standard.cfg**.
- Start program again and check if these changes you introduced appear on the Setup page.

Notes:

Any stored ***.cfg** can later be used for fast experimental setup modification by selecting **File/Open Setup**.

If you suspect that **cwne.ini** or **standard.cfg** are for some reason corrupt delete them before starting the control program. File **cwne.ini** will be recreated with current parameters after the control program is closed. Configuration file can be created following the above procedure.



10 EXPERIMENTS

10.1 Continuous wave NMR experiment in rubber

Objective

Preparation and execution of a field sweep and a frequency sweep NMR continuous wave experiment. This will serve as a template for other NMR experiments and will produce the 1st derivative of an NMR absorption signal.

Experimental setup

- Check if electromagnet is connected to console.
- Slide probehead into electromagnet and then insert a rubber sample in the probehead.
- Start control program.
- Activate console connection to the computer by **Spectrometer/Connect**
- Select **Mode/NMR 1H**. Program automatically activates connections with an electromagnet.

Procedures

Field sweep

- Fill parameter boxes with values shown in Figure 9.

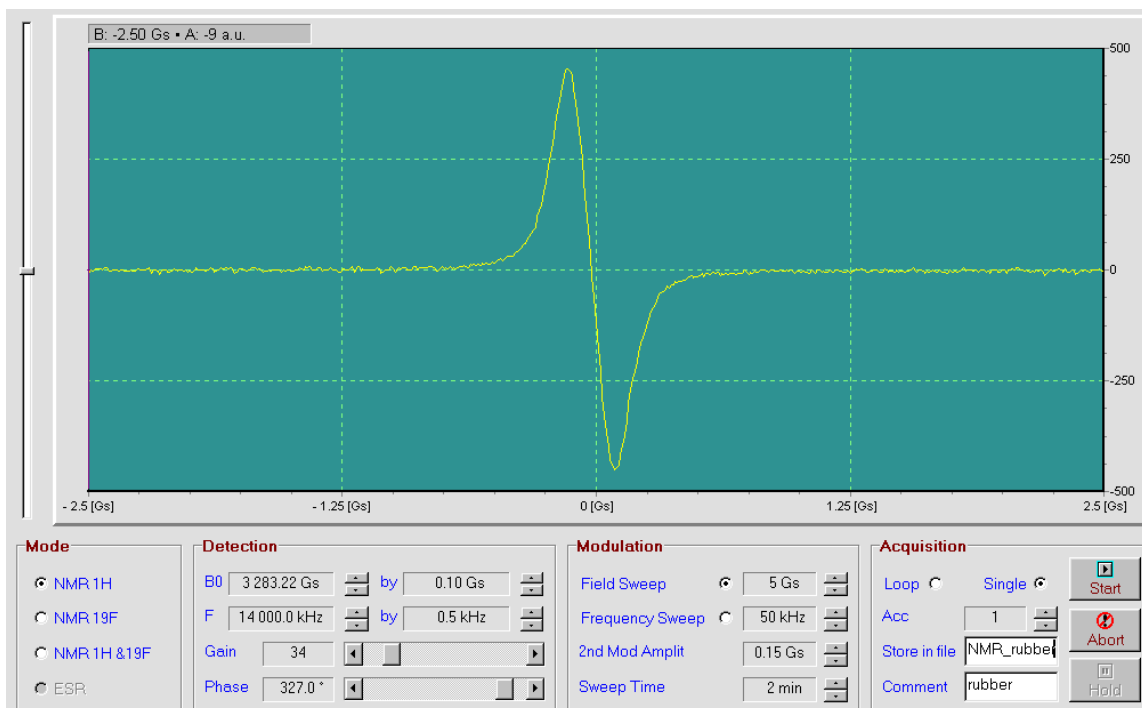


Figure 9. Experimental setup for acquiring NMR signal in rubber by magnetic field sweep.

- To find NMR signal quickly in **Modulation** change:
 - **Field Sweep**=300Gs; to cover widest sweep range,
 - **2nd Mod Amplit**=1Gs; to obtain strong signal,
 - **Sweep Time select**=0.5min; to acquire preliminary result fast.
- Begin an experiment by clicking on **Start**. Look at the acquired signal and adjust the following:
 - Magnetic field **B₀** to position signal on the display window center,
 - Receiver **Gain** to fill at least half of the display window vertical scale,
 - Reduce **Field Sweep** to cover about ¼ of horizontal scale by resonance signal,
 - Detector **Phase** to get maximum signal or to chose between +/- or -/+ pass,
 - Measure line width by **DB** function available on **auxiliary tool** bar and lower **2nd Mod Amplit** to reduce line broadening. Higher value of 2nd modulation increases signal-to-noise, but broadens the line. Find compromise between low line broadening and low noise amplitude,
 - Increase **Sweep Time** to find if signal increases. Samples with long relaxation times may require longer sweep time.
- If signal is still weak, select number of accumulation **Acc** higher than 1. Note that signal-to-noise ratio increases as square root of number of accumulations.
- Repeat adjustments to obtain satisfying results.
- Store experiment in the file by **File/Save Data As**, or fill **Acquisition/Store in file** with file name and repeat experiment to store data automatically

Frequency sweep

For frequency sweep experiment in **Modulation**, select **Frequency Sweep** with widest **Frequency Sweep** available 1,000 KHz and repeat whole procedure described above. Remember to reduce **Frequency Sweep** to conduct final experiment. Usually 50-100kHz sweep is enough. Follow parameters' setting from Figure 10.

Note that the signal acquired with frequency sweep is affected by limited frequency sweep resolution (frequency synthesizer limit) and therefore is less smooth than the signal acquired with field sweep.

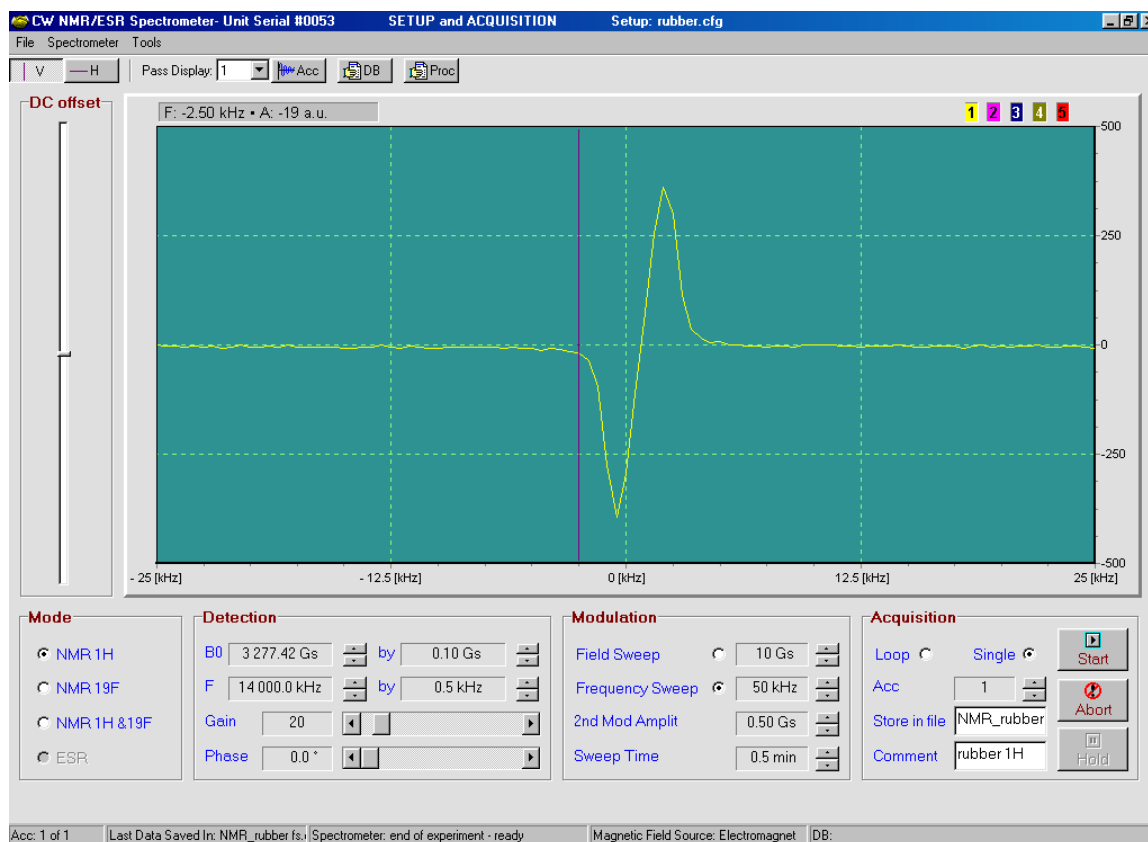


Figure 10. Experimental setup for acquiring NMR signal in rubber by frequency sweep.

10.2 Examples of other NMR spectra

10.2.1 Acrylic

Objective

Finding ^1H NMR resonance in solid-like sample characterized by wide line width.

Experimental setup and analysis

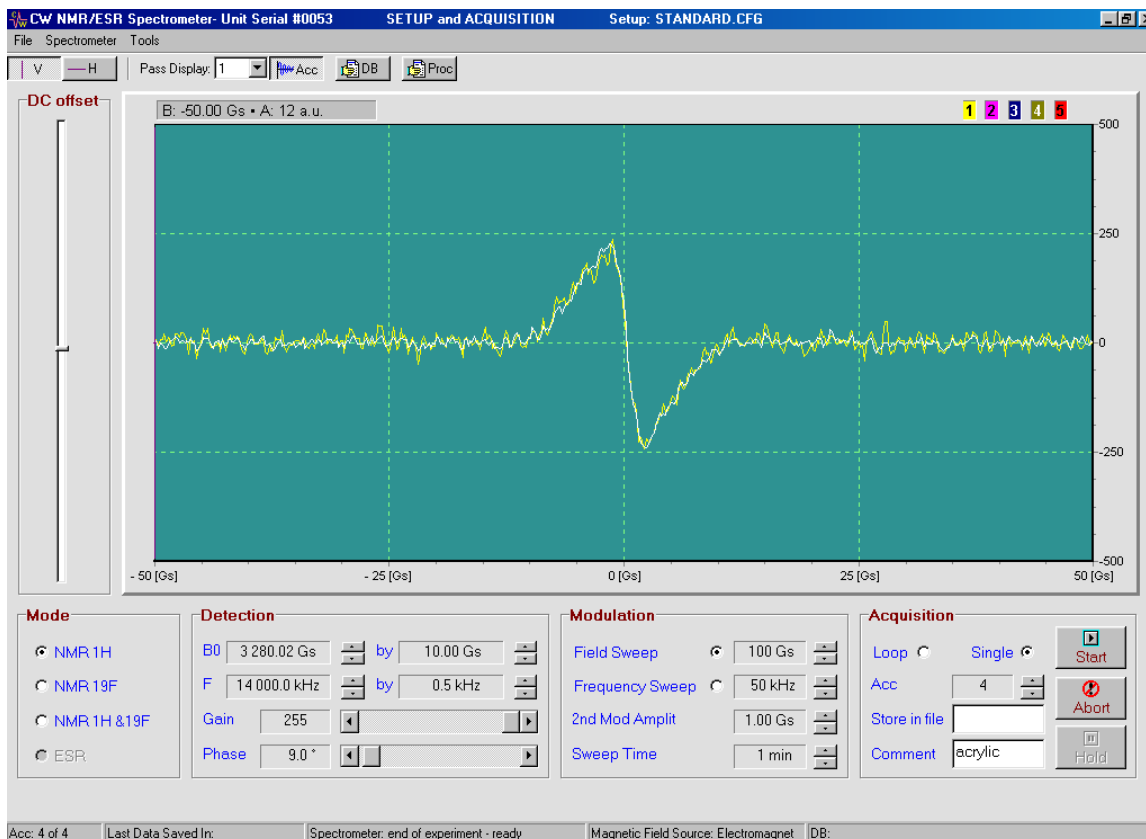


Figure 11. Experimental setup for ^1H NMR in an acrylic sample.

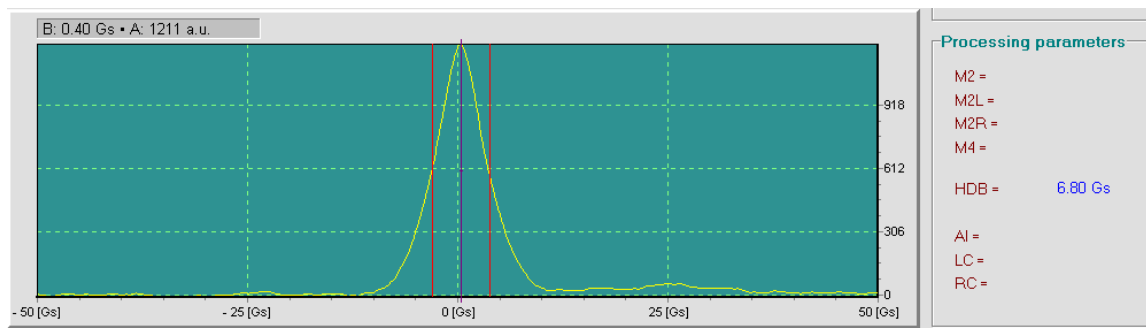


Figure 12. Absorption line and its line width at half-height in acrylic.

10.2.2 Delrin

Objective

Collecting ^1H NMR spectra containing narrow and wide components.

Setup and analysis

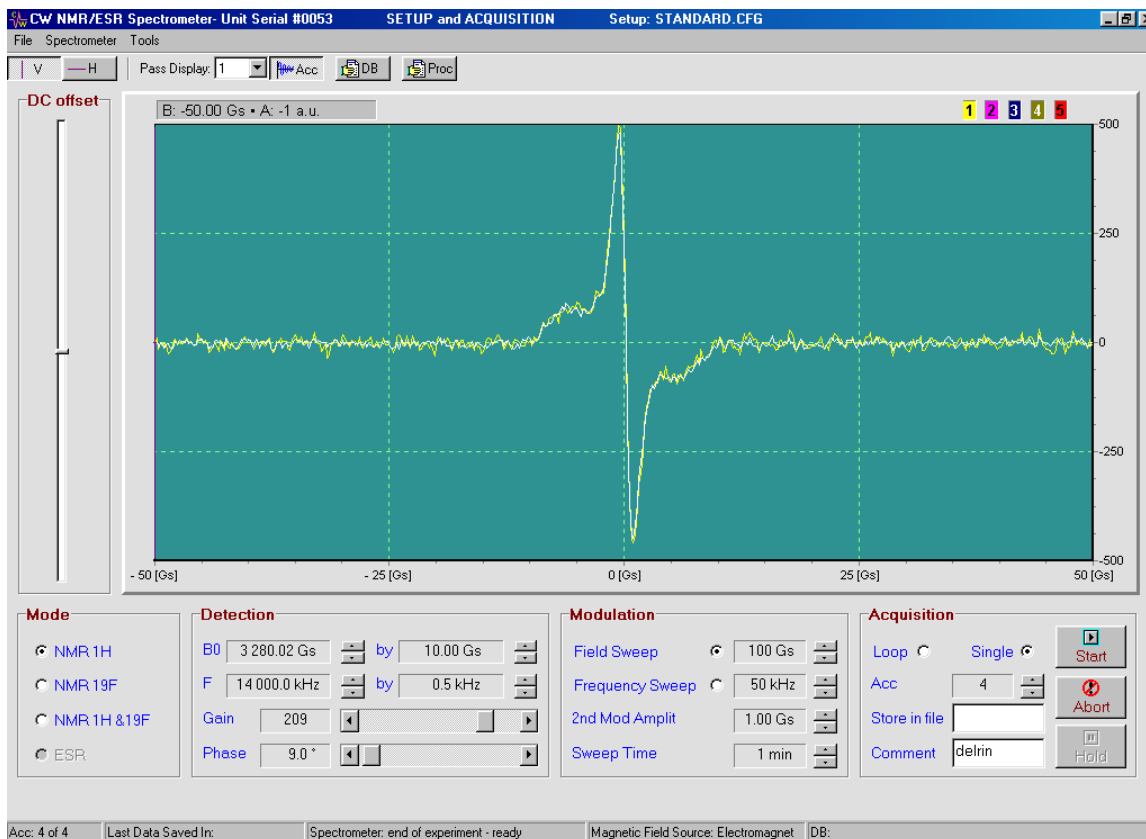


Figure 13. Experimental setup for ^1H NMR in delrin sample

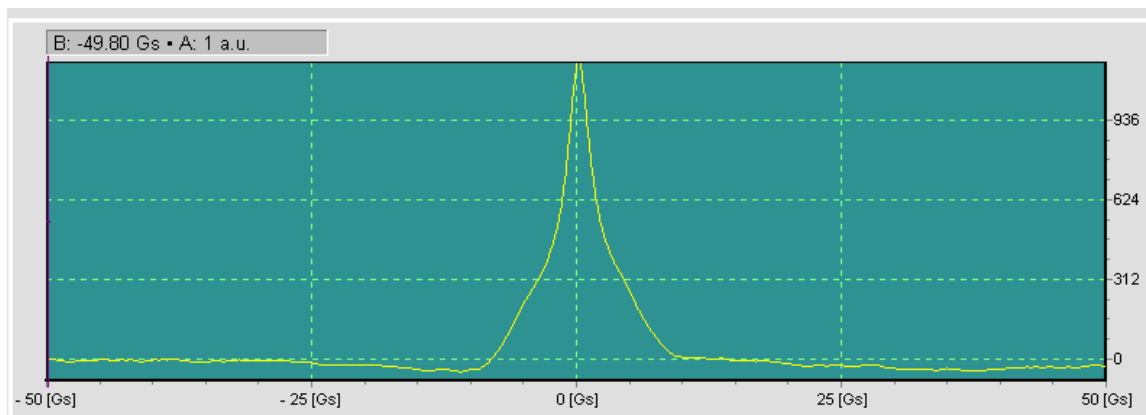


Figure 14. NMR absorption line in delrin showing two components: narrow and wide.

10.2.3 Glycerin

Objective

Collecting ^1H NMR spectra in liquid-like sample.

Setup

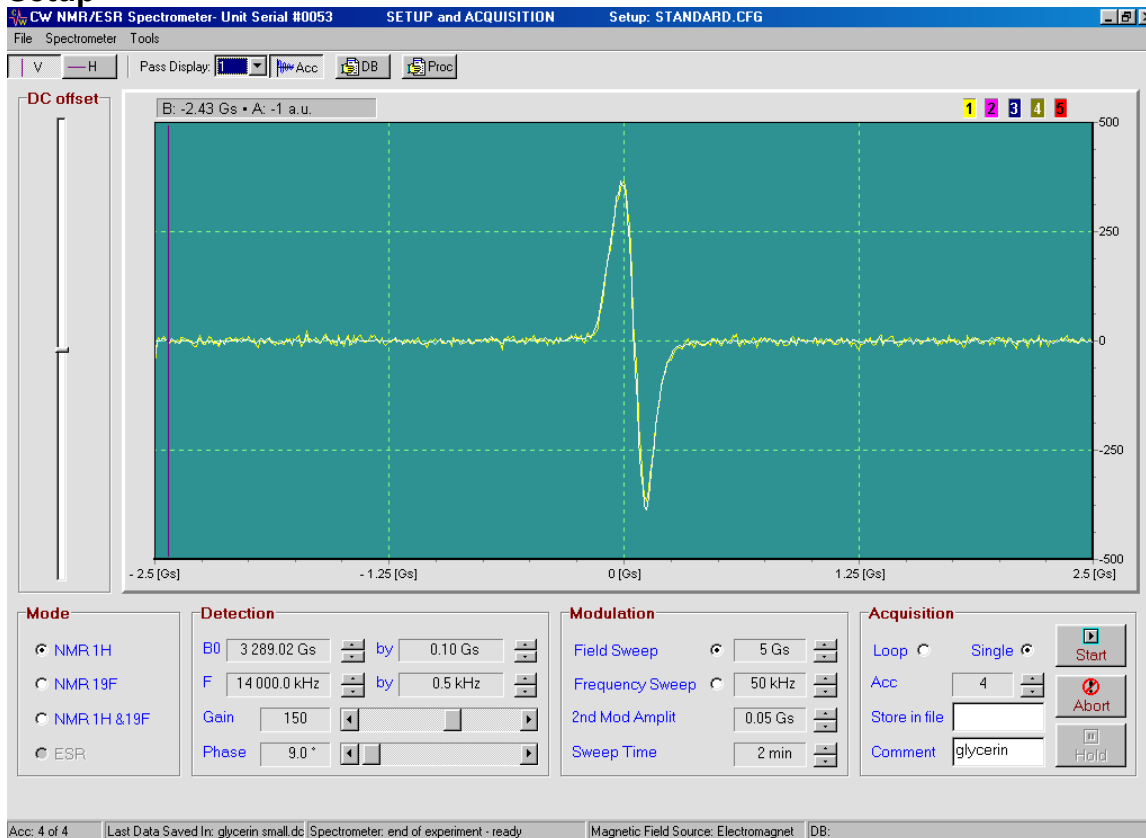


Figure 15. Experimental setup for ^1H NMR in glycerin sample

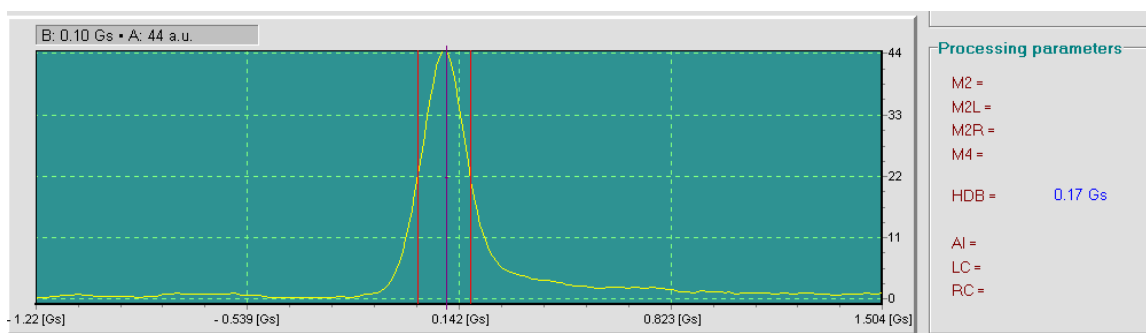


Figure 16. Absorption line in glycerin and its line width at half-height. Notice that line is only 0.17Gs or 723Hz wide.

10.2.4 Fluoroboric acid (HBF₄)

Objective

Simultaneous observance of ¹H and ¹⁹F spectra in Fluoroboric acid (known as Tetrafluoroboric acid, Hydrogen tetrafluoroborate, Hydrofluoroboric acid).

Setup

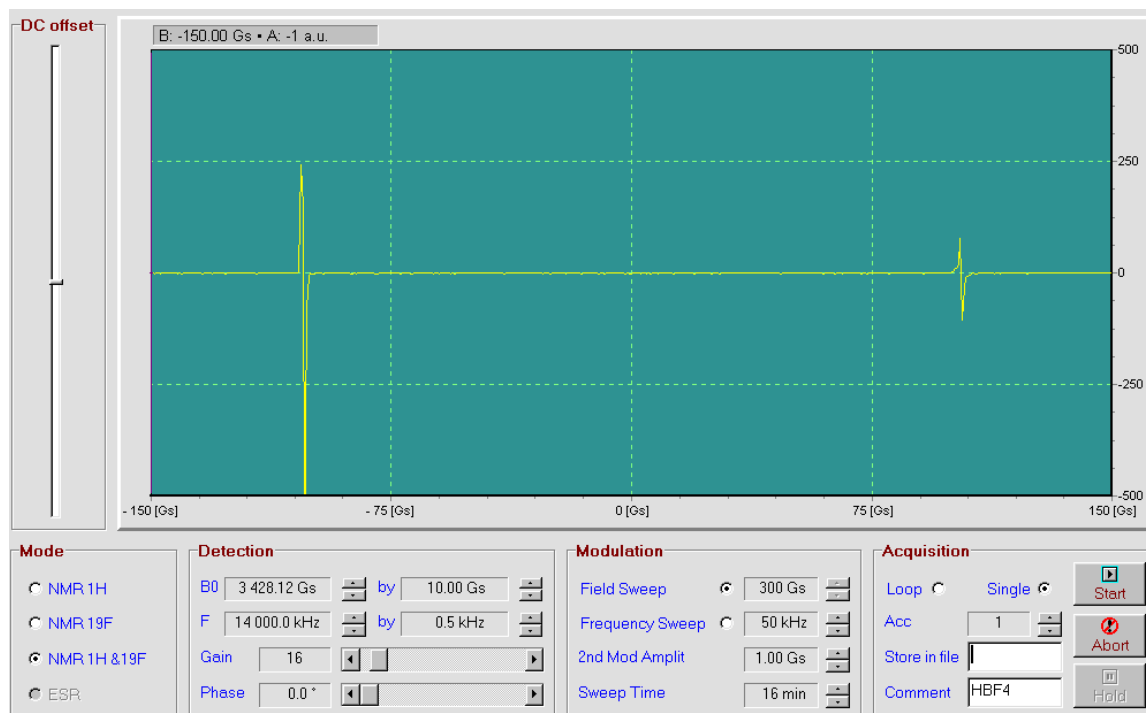


Figure 17. Setup for simultaneous observation of NMR resonances on ¹H and ¹⁹F nucleus in HBF₄

Analysis

Data from this experiment were used for calculation of γ_H/γ_F ratio. For details see Chapter 10.5.3.

10.2.5 Teflon

Objective

^{19}F NMR spectrum in solid state-like sample

Setup and analysis

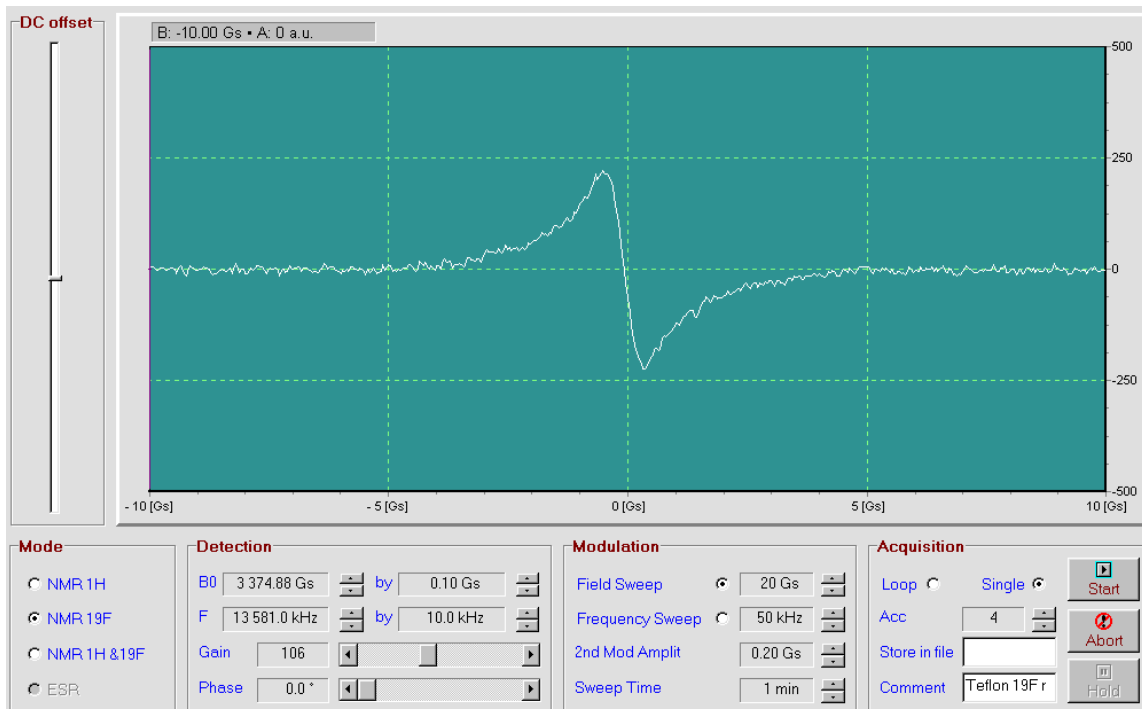


Figure 18. Experimental setup for NMR signal acquisition ^{19}F nuclei in Teflon.

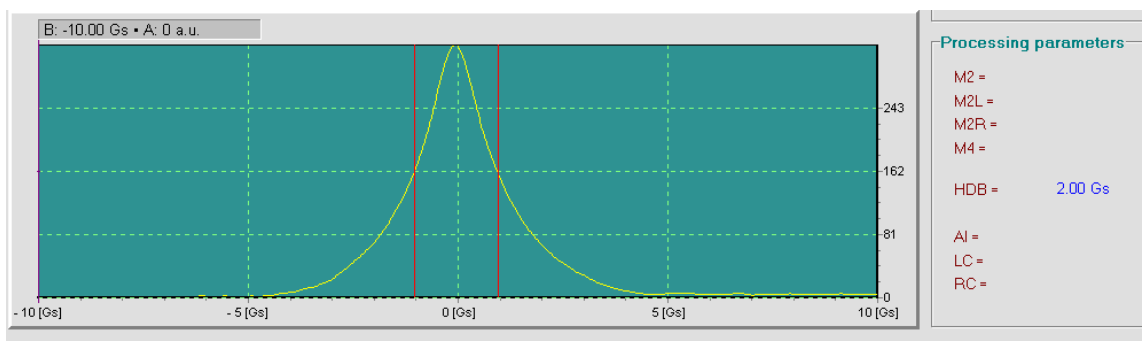


Figure 19. Absorption line and line width at half height in Teflon.

10.3 CW ESR in TCNQ

Objective

Preparation of a CW ESR experiment and data acquisition.

Introduction

TCNQ stands for 7,7,8,8-tetracyanoquinodimethane. This compound can be crystallized to the form that contains paramagnetic centers detectable as a strong and narrow line in an ESR experiment.

Experimental Setup and Procedure

- Check if Helmholtz coil is connected to console's **Coils** output.
- Slide probehead into coils (horizontal slot from the side opposite the cable) and then insert a sample in the probehead from the opposite side.
- Start control program.
- Activate console link to the computer by **Spectrometer/Connect**.
- Select **Mode/ESR**. Program automatically redirect current to Helmholtz coils.
- Follow instructions from Chapter 10.1 for CW NMR experiment. Use parameters from Figure 20 for initial settings.

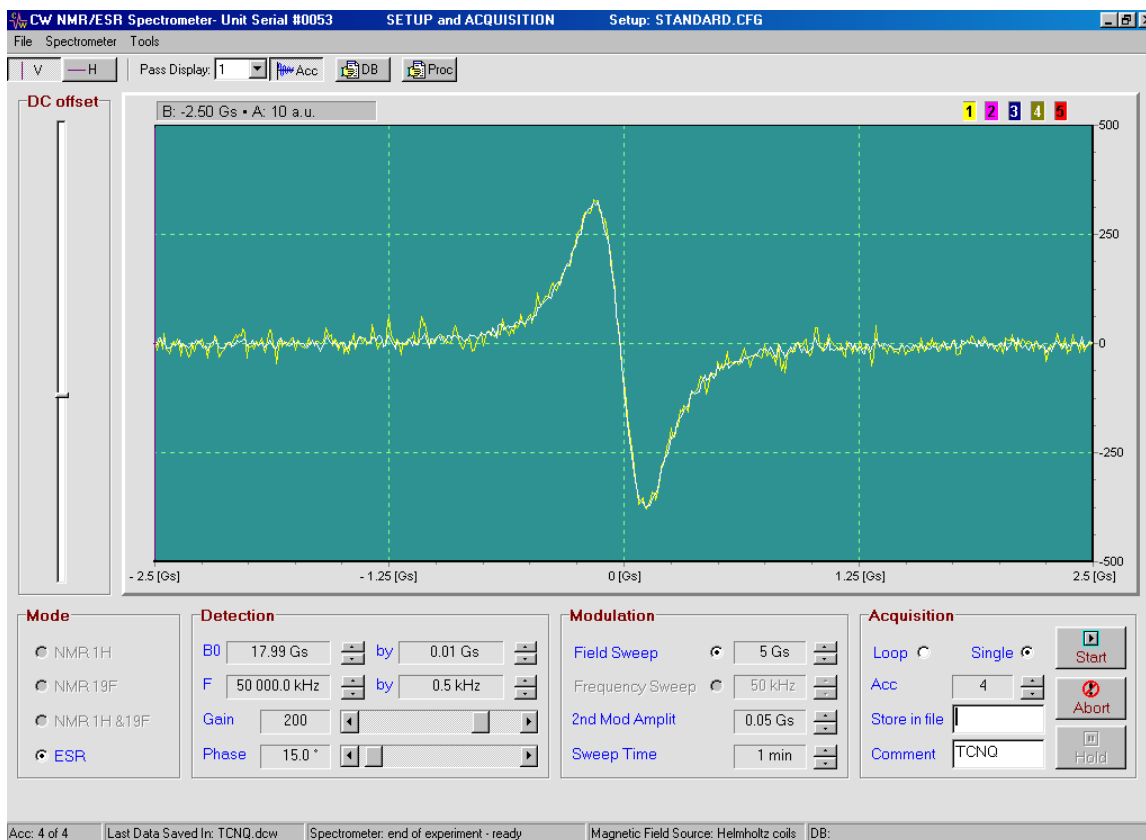


Figure 20. Setup page for ESR experiment in TCNQ.

Analysis

Analysis tools for ESR signal are limited to:

- Viewing of 1st derivative stored in binary file.
- Exporting binary data as text file.
- 1st integration of 1st derivative to obtain **absorption**
- 2nd integration to calculate absolute integral value (**AI**) under **absorption** line within given limits (**LC**- left side limit, **RC**- right side limit). Integral value is proportional to the number of spins in a sample.
- Calculation of line width: from 1st derivative (**SDB**) and from absorption (**HDB**).
- Calculation of g-factor (**G**).

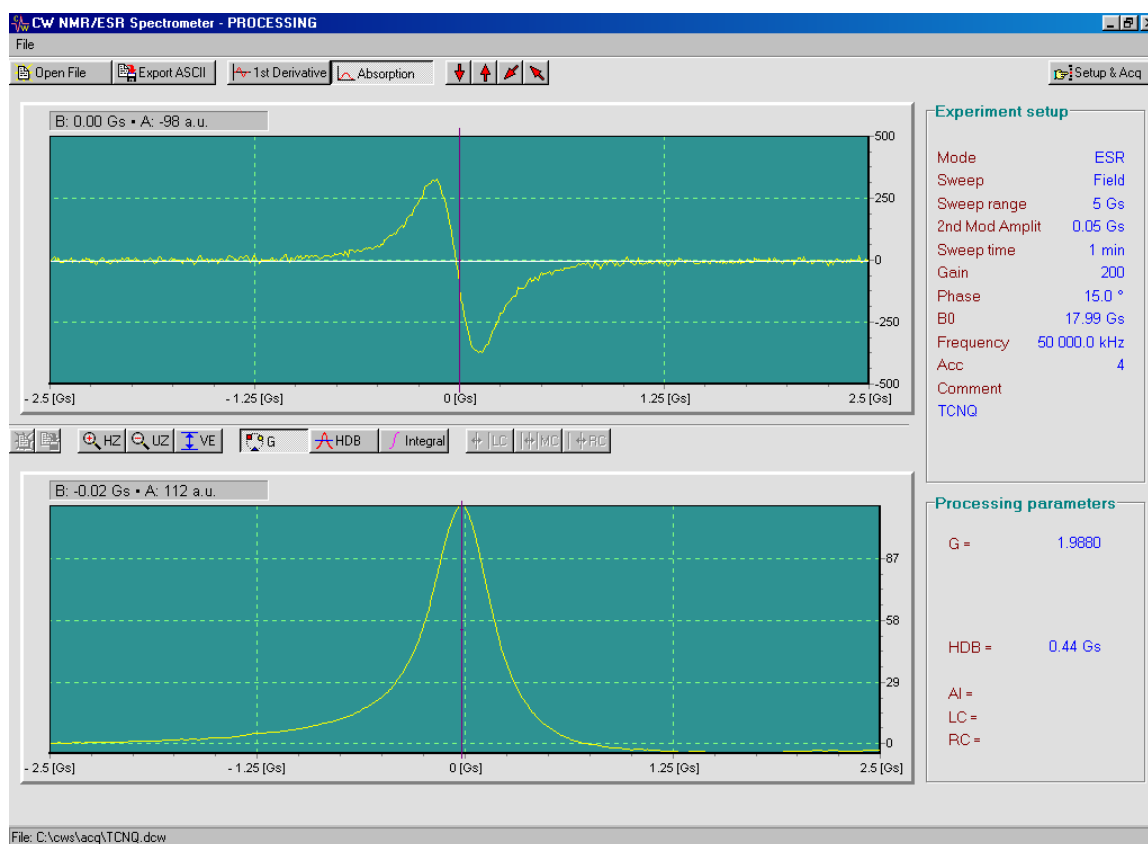


Figure 21. Processing page for data acquired in ESR experiments.

10.4 ESR in other samples

10.4.1 DPPH

DPPH (2,2-Diphenyl-1-Picrylhydrazyl) is an organic free radical that shows a strong line due to “free electrons” associated with one of the nitrogen atoms.

Setup and analysis.

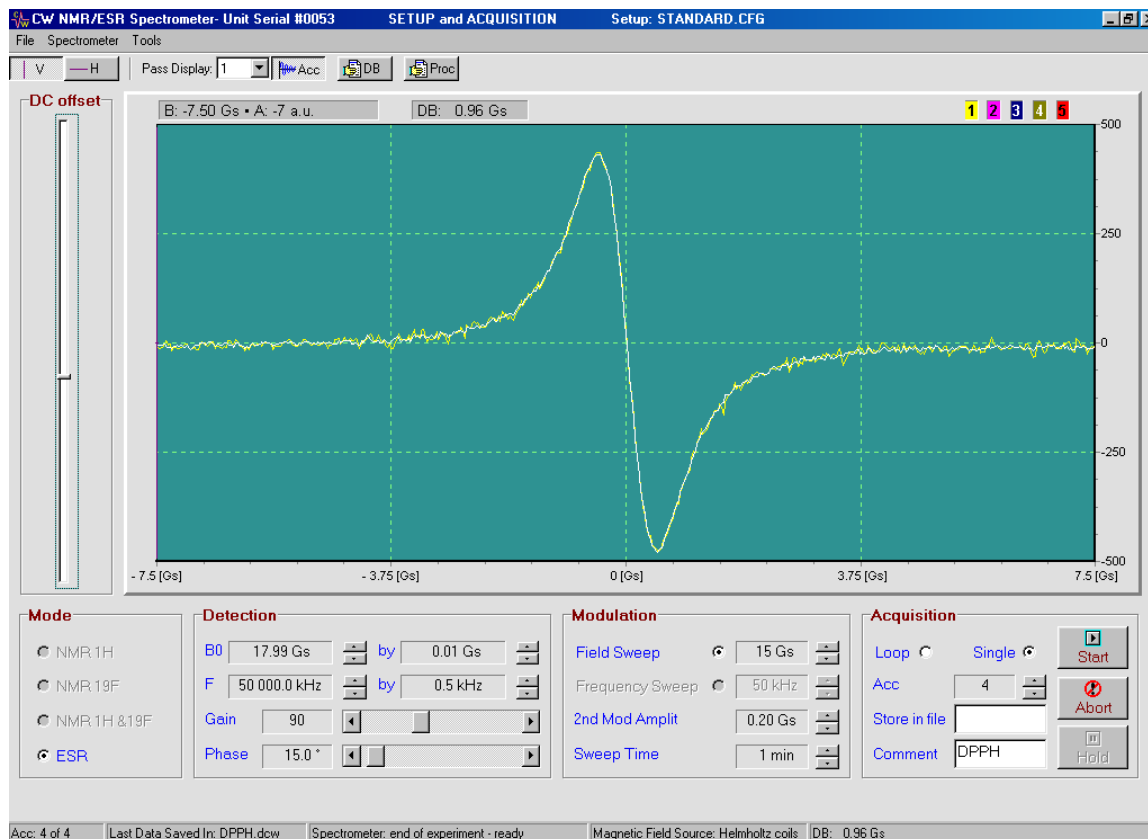


Figure 22. Setup parameters for an ESR experiment in DPPH.

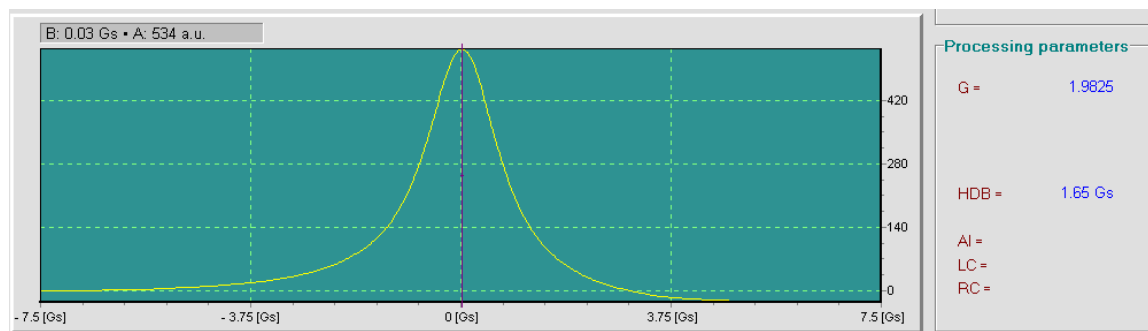


Figure 23. Absorption line and its width at half height in DPPH.

10.5 Nuclear magnetogyric ratio measurement with CW NMR

Objective

To determine nuclear magnetogyric ratio of protons (^1H) and ^{19}F nuclei.

Introduction

The nuclei possess a magnetic moment μ which is proportional to its spin I

$$\mu = \gamma \frac{I\hbar}{2\pi} \quad \text{Eq. 1}$$

The constant γ is called the magnetogyric ratio and is a fundamental nuclear constant which has a different value for every nucleus, \hbar is Planck's constant.

Magnetogyric ratio can easily be determined by measurement of the resonant frequency for different magnetic field magnitudes and performing a linear regression analysis knowing that γ is slope in the Bloch equation:

$$\omega_0 = \gamma B_0 \quad \text{Eq. 2}$$

Experimental setup

There are many ways to conduct this experiment. The basic idea is to get several (10-20) data points of NMR resonances at different magnetic fields with corresponding frequencies.

Examples:

- Operate in a narrow frequency and field range to see changes of resonances on the same screen (Figure 24). Method used to determine magnetogyric ratio of ^1H in glycerin sample as described on page 58.
 - Keep the **Field Sweep** of 50 Gs and set **B_0** field to see resonance signal on the right margin of the screen
 - Decrease **Frequency** by 10.0 kHz and perform field sweep.
 - With **Pass Display** set for 5 observe how resonance moves towards lower magnetic field (left side of the screen). Record **f_0** and corresponding **B_0** at which resonance occur.

- Operate in wider frequency and field range. Method used to determine magnetogyric ratio of ^{19}F in HBF_4 sample (see page 60).
 - With **Sweep** of only 10 Gs (helps to measure magnetic field very accurately) change field by about 25 Gs
 - Adjust frequency to see signal visible on the screen. If necessary, temporarily expand **Sweep Width** to localize the line. Change frequency to shift the line to the center of the screen and reduce **Sweep Width**.
 - Perform final experiment without saving to the file. Record f_0 and corresponding B_0 at which resonance occurs.

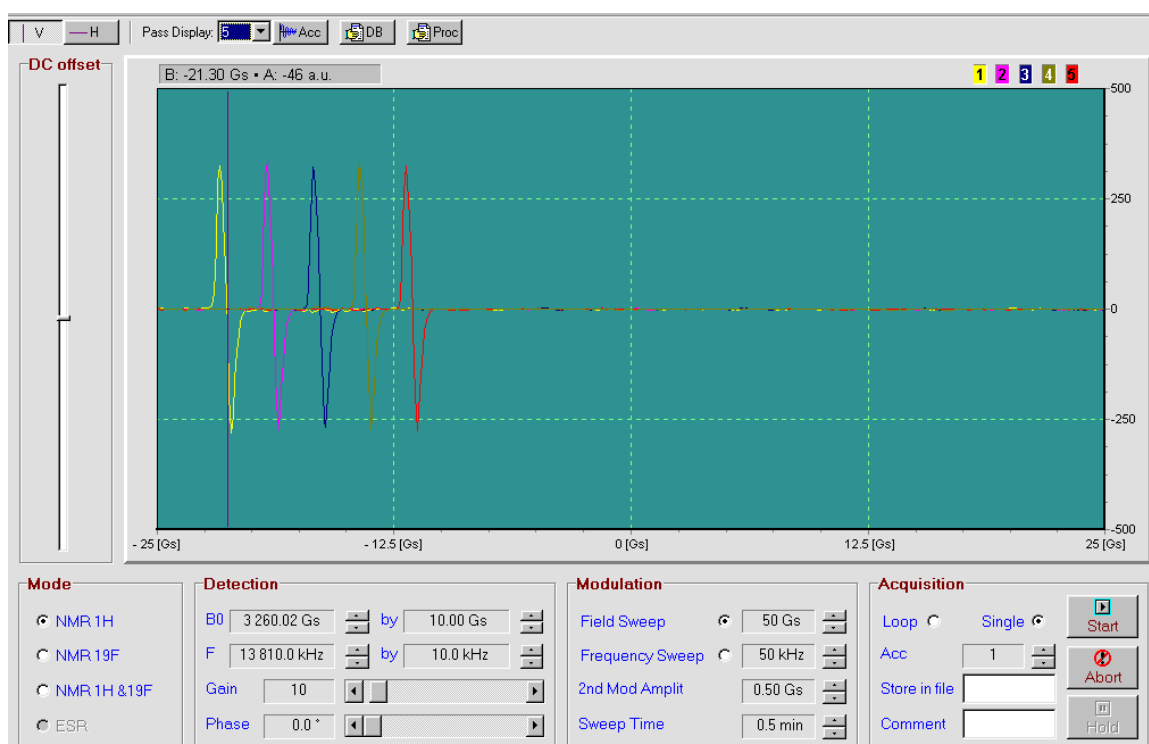


Figure 24. Experimental setup for determination of ^1H NMR resonance frequencies for different magnitudes of magnetic field in glycerin sample.

10.5.1 Magnetogyric ratio of protons (^1H nuclei)

Analysis

Linear regression analysis (using Excel statistic tools) of experimental data (see Figure 25) returns following:

- intercept = -268.9 [Gs]
- slope = 4.3464
- f_0 [kHz] = $(4.3464B_0 - 268.9)$ [Gs]

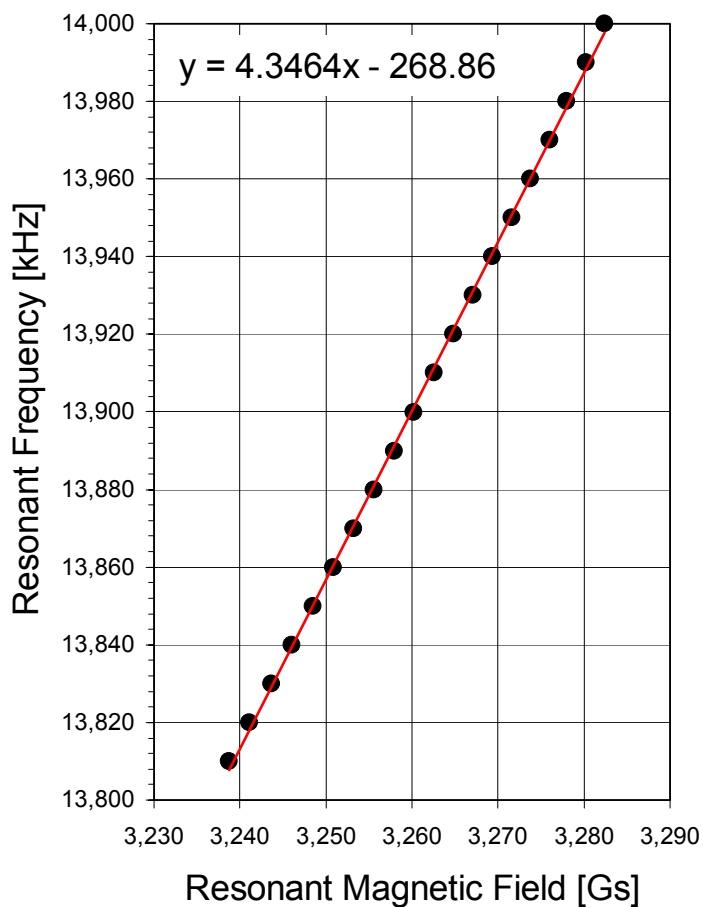


Figure 25. Plot of resonant frequency versus resonant magnetic field

Using formula $\omega_0 = 2\pi f_0$ and knowing that $1[\text{T}] = 10^4[\text{Gs}]$ one can calculate that experimental value of magnetogyric ratio for proton is:

$$\gamma_p = 2.731 [\text{s}^{-1}\text{T}^{-1}]^4.$$

This value differs from more accurate measurements available in literature⁵:

$$\gamma_p = 2.675 [\text{s}^{-1}\text{T}^{-1}]$$

2% relative error originates from limited accuracy of the reading of the magnetic field magnitude due to magnetic properties of the magnet yoke like magnetic hysteresis and magnetic remanence (see remanence measurement in electromagnet on page 75)

Accuracy of calculation can be significantly improved if in regression analysis the intercept value is set for zero:

- slope = 4.2639
- $\gamma_p = 2,679 [\text{s}^{-1}\text{T}^{-1}]$.
- relative error = 0.15%

⁴ $[\text{s}^{-1}\text{T}^{-1}] = [\text{kg}^{-1}\text{sA}]$

⁵ CODATA Bull., 1986, 63, 1

10.5.2 Magnetogyric ratio of ^{19}F nuclei Analysis

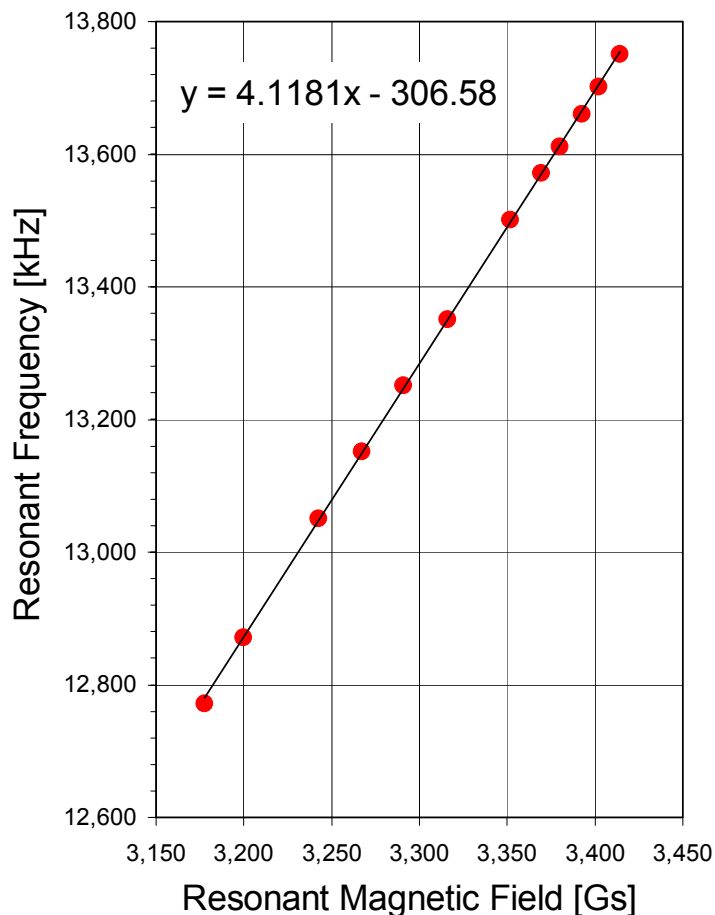


Figure 26. Data points and linear regression of resonant magnetic fields and corresponding resonant frequencies on ^{19}F in HBF_4 .

Regression analysis of data from Figure 26 returns:

- intercept = -306.6 [Gs]
- slope = 4.118
- f_0 [kHz] = $(4.1181B_0 - 306.6)$ [Gs]

Source	γ [$\text{s}^{-1}\text{T}^{-1}$]	Relative error [%]
$f_0 = 4.1181B_0 - 306.6$	2.588	2.8
$f_0 = 4.0257B_0$	2,529	0.44
Literature	2.518	

Table 3. Calculated magnetogyric ratios for ^{19}F nuclei and literature comparison.

10.5.3 Field/frequency factor

Measurements performed on resonance signals acquired during the same magnetic field sweep are not tinted with a hysteresis effect and can provide a very accurate value of the field factor- the relative parameter describing rate of magnetic field amplitudes at which resonances occur.

Assuming constant operating frequency of spectrometer ω_0 , NMR resonances for ^1H and ^{19}F nuclei will occur at B_0^{H} and B_0^{F} : $\omega_0 = \gamma_{\text{H}}B_0^{\text{H}} = \gamma_{\text{F}}B_0^{\text{F}}$.

Setup

- Refer to Chapter 10.2.4 which describes how to acquire simultaneously resonances on ^1H and ^{19}F nuclei in water solution of fluoroboric acid.
- Load saved data on **Processing** page.
- Zoom area around particular resonance and using vertical cursor read field magnitude for resonance (when 1st derivative crosses zero)

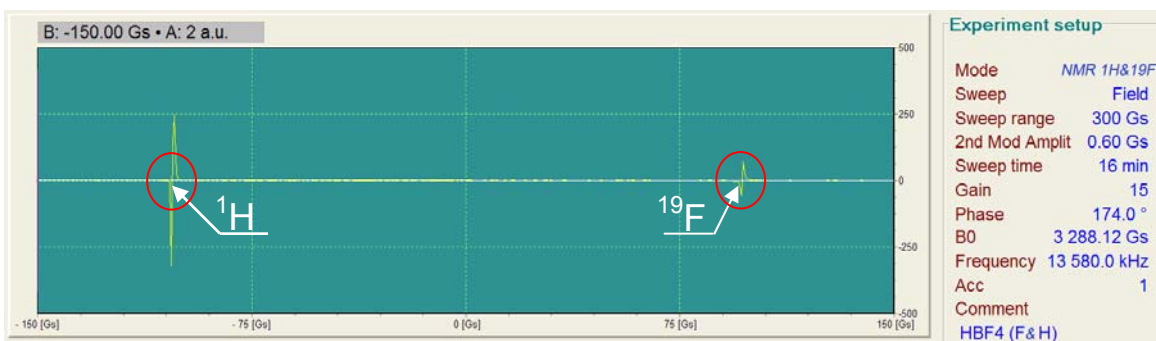


Figure 27. Simultaneously acquired NMR resonances in ^1H (left) and in ^{19}F (right) in water solution sample of HBF_4 .

Analysis

Table 4 shows summary of calculated field $B_0^{\text{H}}/B_0^{\text{F}}$ and frequency $\omega_0^{\text{H}}/\omega_0^{\text{F}}$ factors. Frequency factor is reciprocal of field factor and is equal $\gamma_{\text{H}}/\gamma_{\text{F}}$. Note very low relative error of field factor measurement.

B_0^{H} [Gs]	B_0^{F} [Gs]	$B_0^{\text{H}}/B_0^{\text{F}}$	$\omega_0^{\text{H}}/\omega_0^{\text{F}}$	Lit $B_0^{\text{H}}/B_0^{\text{F}}$ ⁶	Relative error [%]
3,186.12	3,385.02	0.9412	1.0624	0.9409	0.04

Table 4. Resonant magnetic fields of ^1H and ^{19}F nuclei at constant frequency $f_0=13,580.0$ KHz and literature comparison (in red) of field and frequency factors.

⁶ BRUKER Almanach, 2000

10.6 Angle dependence of ^1H NMR spectra in gypsum monocrystal

Introduction

It has been seen from the study of oriented crystals, that ^1H NMR spectra of solid samples can give structural information that X-ray crystallography cannot deliver due to poor X-ray scattering on the hydrogen single electron.

This observation was first published by G. E. Pake in the early years of NMR⁷. He observed the **splitting** of the NMR line from water protons in a hydrated gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) monocrystal and powdered samples. The splitting originates from the interacting of magnetic dipoles μ in a static magnetic field \mathbf{B}_0 . In crystalline solids these interactions produce an additional local magnetic field \mathbf{B}_{loc} which contributes to the effective magnetic field acting on each spin. In less rigid substances, (mostly gases and liquids) fast molecular motion averages this local magnetic field to zero.

Since **dipole-dipole** interactions decrease as the **inverse cube** of the dipoles distance, nuclear moments of protons in water molecules of hydrations are predominantly in the local field of its neighbor. Thus protons in water (spin $\frac{1}{2}$) can achieve two positions with regard to the static magnetic field \mathbf{B}_0 . Some spins will be located in higher fields (when the neighboring spin is parallel to \mathbf{B}_0) and some will be in lower fields (when the neighboring spin is anti-parallel to \mathbf{B}_0). In this simplified model, two NMR lines appear symmetrically located along the resonance at \mathbf{B}_0 .

Of the hydrous sulphates, hydrous calcium sulphate, of the chemical formula $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, known as gypsum, is the most important. (The average American house contains around 5 tons of gypsum construction material!).

The gypsum structure consists of parallel layers of $(\text{SO}_4)^{-2}$ groups bonded to Ca^{+2} . Sheets of water molecules separate consecutive layers of strongly bonded ions. The bonds between water molecules in neighboring sheets are rather weak causing the crystal to break when it is subjected to stress on a plane parallel to the sheets. This property is known as perfect cleavage in the (010) plane.

One can determine proton-proton distance in a water molecule by Pake's method, that is from the angle dependence of NMR line splitting. Assuming a certain angle of H-O-H obtained from crystallographic analysis the value of proton-oxygen distance can be calculated (Figure 28).

7 G.E. Pake, The Journal of Chemical Physics vol.16, p. 327-336, 1948, "Nuclear Resonance Absorption in Hydrated Crystals: Fine Structure of the Proton Line"

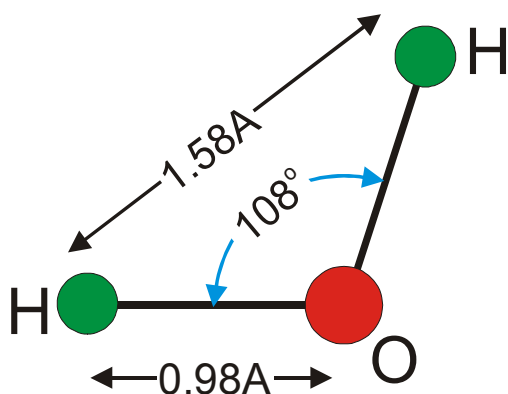


Figure 28. Atoms distances and angle in a water molecule according to Pake. H-H distance of 1.58Å was calculated from spectra splitting. H-O distance was calculated from assumption of 108° angle of H-O-H bond.

Objective

The purpose of this experiment is the **observation of the splitting** of the NMR line originating from water protons located in different local magnetic fields of the gypsum monocrystal. This experiment can illustrate high-resolution NMR spectra in solids.

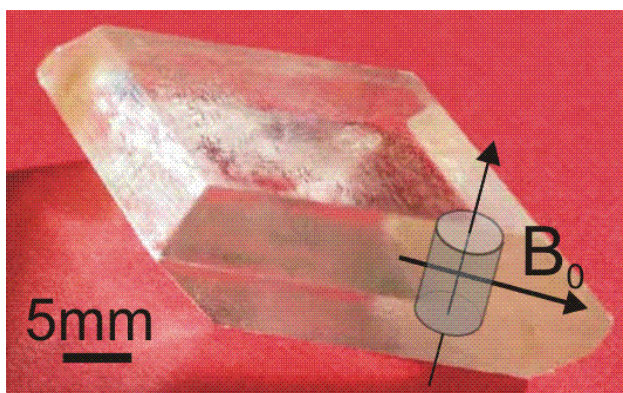


Figure 29. Sample cut from gypsum monocrystal and its orientation with regard to external magnetic field B_0 .

The sample has a cylindrical form of approximately 5mm diameter and 6mm long. It was cut from a large gypsum monocrystal as shown in **Figure 29**. The long axis of the sample is perpendicular to a crystal perfect cleavage (plane (010)).

Setup

- Prepare home-made goniometer (Figure 30):
 - From thick cardboard cut two discs of 4" and 2" diameter.
 - With sharp blade cut 5mm holes in the centers of both discs.
 - Divide big disc into 16 segments $360/16=22.5^\circ$ apart and tape it to the magnet's side. It will serve as an angle marker.
 - On the small disc mark a radius with a thick pen and slide it on the end of the gypsum sample glass. It will serve as a dial. Tape or glue the dial and the glass together.

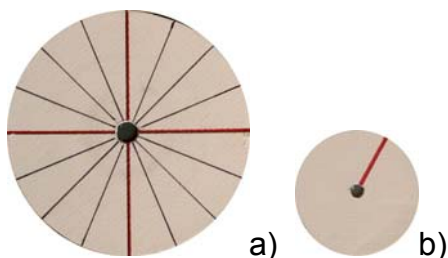


Figure 30. Cardboard angle marker (a) and dial (b) as elements of a home made goniometer.

- Carefully insert crystal with attached dial in a probehead as shown on Figure 31



Figure 31. Home-made goniometer for gypsum monocrystal study attached to the electromagnet.

- On **Setup and Acquisition** page prepare experimental setup similar to one on Figure 32. Note the large accumulation number equal to 16. It is of utmost importance to set this number at least 16 because of very weak signal from water trapped between gypsum crystal layers.
- Perform and save experiments for crystal orientations that differ at least by 90° (45° recommended).

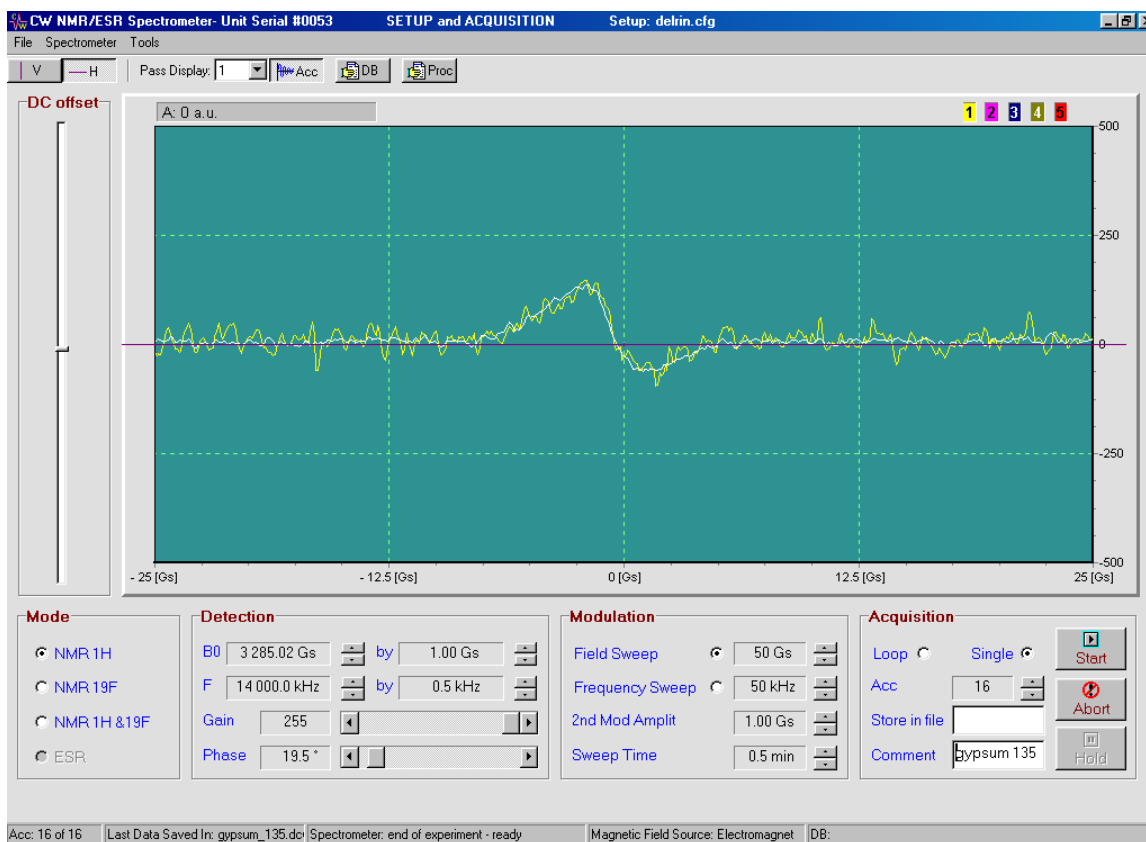


Figure 32. Setup for observation of NMR signal from gypsum monocrystal. Activate **Acc** button, that displays accumulated (white trace) signal along with currently acquired pass (yellow trace).

Analysis

On the **Processing** page load previously saved data of signal first derivative acquired with different crystal orientations. Click on **Absorption** to see spectrum. Check all orientation to find line split. Line split visible on Figure 34 is equal 3.70Gs or in frequency units 15.7 kHz.

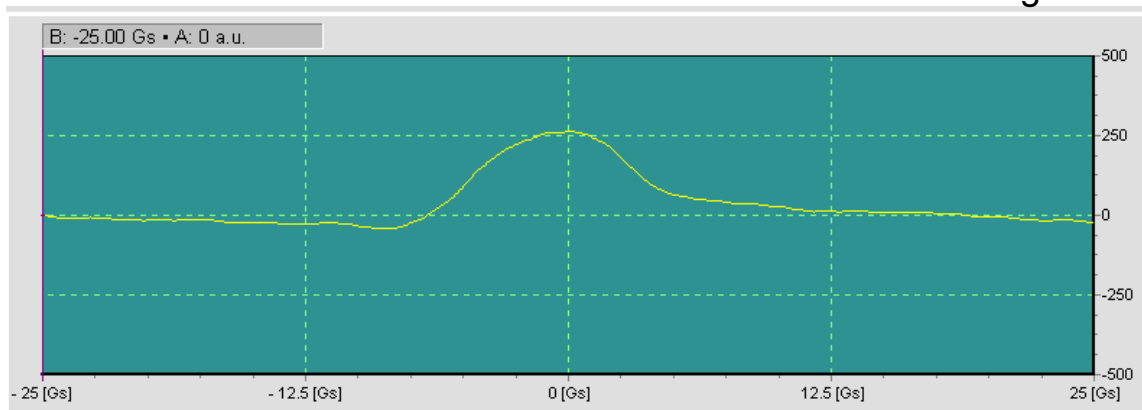


Figure 33. Absorption line in a gypsum monocrystal without splitting.

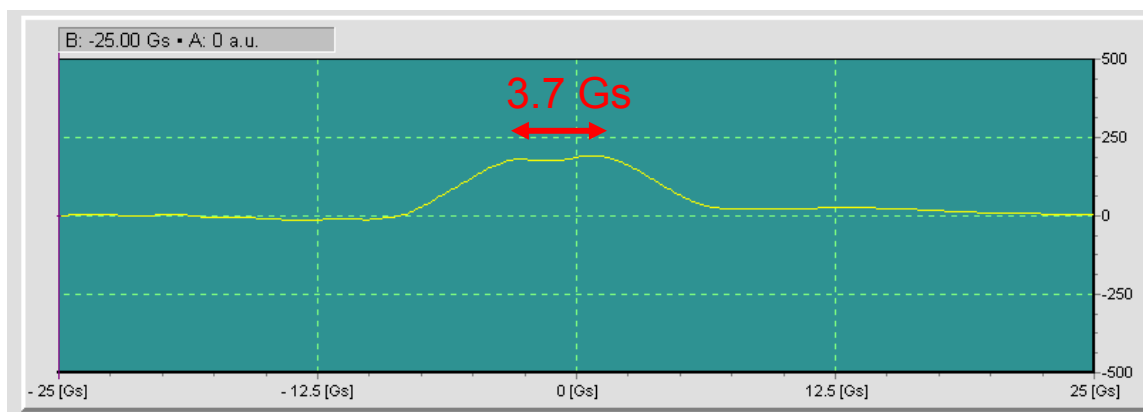


Figure 34. Split of absorption line due to rotation of crystal by 90° with regard to orientation that produced spectrum on Figure 33.

Variations:

- Acquire a large gypsum crystal, make another cut and repeat measurements.

Note

You may purchase gypsum monocrystals from:

Great South Gems & Minerals

38 Bond Drive,

Ellenwood, GA 30294

1-888-933-4367

www.greatsouth.net

- Since cutting gypsum is a difficult task, crush the monocrystal to powder and repeat measurements with a polycrystalline sample.

- Place small amount of dry plaster composition that contains predominately gypsum. Acquire NMR signal of dry powder. Then add a drop of water and repeat the experiment several times when mixture hardens.

10.7 Determining Earth's magnetic field with ESR experiment

Objective

Estimation of the magnitude of the Earth's magnetic field in different environments using Electron Spin Resonance in TCNQ sample.

Introduction

Local magnitude of the Earth's magnetic field changes with time and position. In an undisturbed environment it varies from 0.3 Gs to 0.6 Gs depending on latitude.

This small magnetic field value can be easily measured with the CWS NMR/ESR spectrometer by recording the resonance field shift in an ESR experiment caused by different orientations of the Helmholtz coils with regard to magnetic North-South direction.

When \mathbf{B}_0 field originating from the Helmholtz coil is parallel to Earth's magnetic field $\mathbf{B}_{\text{Earth}}$, both fields add and an effective magnetic field is $B_0 + B_{\text{Earth}}$. When \mathbf{B}_0 is antiparallel both fields subtract and an effective magnetic field is reduced to $B_0 - B_{\text{Earth}}$. This ESR experiment allows for easy measurement of these effective fields by determination of ESR resonant fields. The difference between resonant returns doubled value of Earth's magnetic field.

Experimental setup

- Connect Helmholtz coils to the console for ESR measurements.
- Insert probehead in the Helmholtz coil and place both on a piece of cardboard that can be easily rotated by 360° . Keep coil/probehead assembly close to console to have enough room for rotation.
- Get a standard compass for determination of magnetic directions.

Procedure

Using the compass orient the probehead-Helmholtz coil assembly to have B_0 field parallel to magnetic South-North direction⁸ (see Figure 35).

- Prepare setup to acquire ESR signal from TCNQ sample. Set **Field Sweep** to minimum value of 2Gs (follow values from Figure 36).
- Run field sweep experiment
- Rotate probehead-Helmholtz

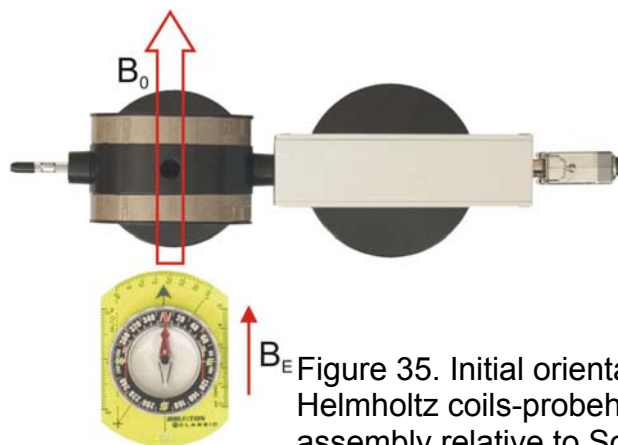


Figure 35. Initial orientation of Helmholtz coils-probehead assembly relative to South-North direction.

⁸ Helmholtz coils produce magnetic field along coils opening.

- coil assembly to have B_0 field anti-parallel to South-North.
- Run **Field Sweep** experiment
- Repeat experiments with two remaining orientations of Helmholtz coils: East-West and West East.

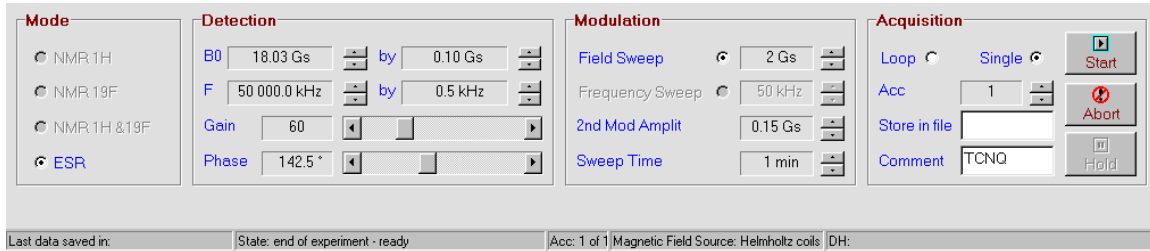


Figure 36. Experimental setup for determination of Earth magnetic field using ESR in TCNQ sample.

Analysis

- Display results of all four experiments using **Display passes/4**.
- With vertical cursor measure the field when first derivative crosses zero for orientations.

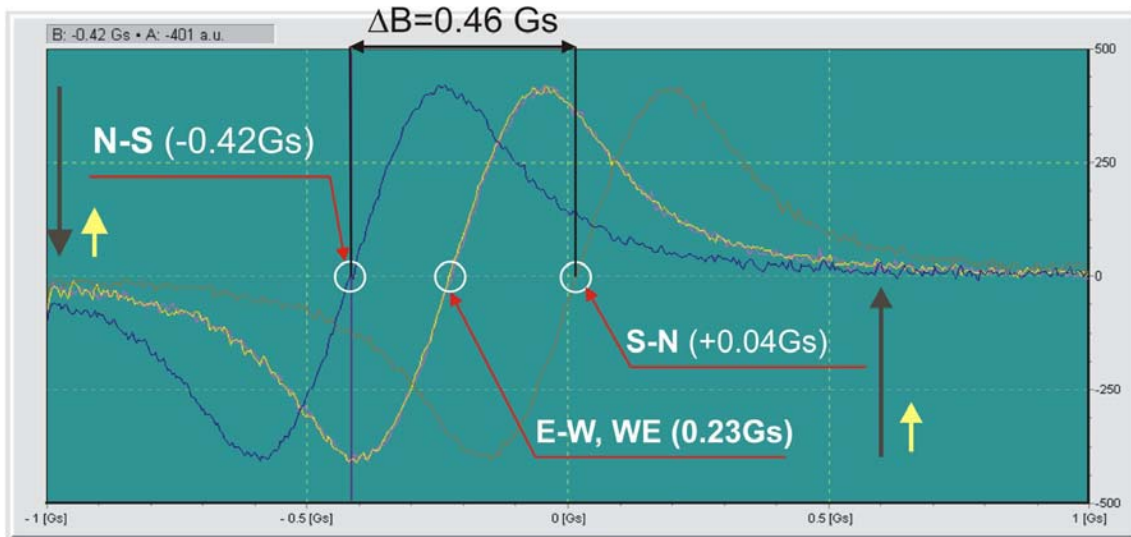


Figure 37. Shift of resonance magnetic field in an ESR experiment with free radicals in TCNQ sample for different Helmholtz coils orientation. Dark blue- B_0 and B_{Earth} anti-parallel, olive- B_0 and B_{Earth} parallel. Red- B_0 is oriented East-West and yellow- B_0 is oriented West-East. Note perfect overlapping yellow and red, showing that for these orientations Earth magnetic field is not giving any contribution to effective field acting on electron spins. Total magnetic field shift is 0.46Gs and $B_{\text{Earth}} = 0.23\text{Gs}$. B_0 is of the range of 17.8Gs.

- Calculate ΔB
- Earth magnetic field is half of the ΔB
- In the presented experiment $B_{\text{Earth}}=0.23\text{Gs}$ is significantly lower than the expected 0.5 Gs because of strong shielding originating from steel construction of the building where experiments were conducted.

Variations

- Do not use compass, but repeat field sweeps for multiple B_0 orientation while recording the resonant field B_{res} . Plot $B_{\text{res}} = f(\text{orientation})$ and find field extreme values to determine ΔB .
- Bring spectrometer to “iron free” environment (field, park) and repeat measurements. This configuration can serve as a very accurate magnetometer for extremely low magnetic field.
- Do not rotate Helmholtz coils but reverse magnetic field direction by reversing current by: **Tools/Current/FWD,REW**

10.8 Measurements of a static magnetic field with a Tesla meter (Smart Magnetic Sensor)

Introduction

TEL-Atomic Inc., sales a new pocket-sized Tesla Meter Model 2000 equipped with Hall probes that cover the measurements of a magnetic field in the range of 0.01 to 1999 mT. This Tesla meter can be used in a series of experiments with a CWS 12-50 electromagnet and Helmholtz coils to measure the magnetic field inside and outside the magnet and to illustrate properties of the Hall effect magnetic sensors.



Figure 38. TEL-Atomic Inc. Tesla Meter Model 2000

An electric current flowing through a conductor located in a magnetic field experiences a transverse force called the Lorentz F_L magnetic force. This force is defined as a vector product:

$$\vec{F}_L = q\vec{v} \times \vec{B} = qvB \sin \Theta \quad \text{Eq. 3}$$

q - carrier charge

v - velocity of the carrier

B - magnetic induction

Θ - angle between vectors v and B

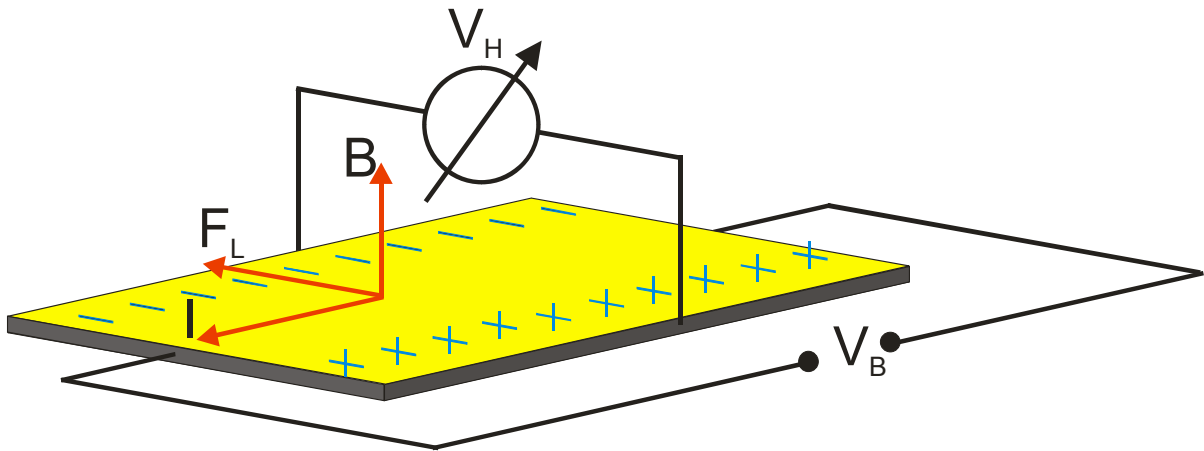


Figure 39. Lorentz force and separation of flowing electric charge (+/-) by an external magnetic field \mathbf{B} .

Eq. 3 implies the following:

- The magnetic force is perpendicular to both the current \mathbf{I} and the magnetic field \mathbf{B}
- The magnitude of the magnetic force \mathbf{F}_L is zero when charges move parallel to the magnetic field (or when the charges are stationary) and reaches a maximum $\pm(qvB)$ when the charges move perpendicular to the magnetic field

The Lorentz magnetic force separates moving charge carriers (Figure 39). The separation effect was named *Hall effect* after E.H. Hall who discovered it in 1879. The charge separation produces transverse voltage between two sides of the conductor that is linearly proportional to the magnetic field \mathbf{B} and is used to measure magnetic field.

10.8.1 Angle dependence of the readings of the Tesla meter.

Before starting experiments prepare the spectrometer electromagnet and Tesla meter probe.

- For all measurements use the Tesla meter axial probe type SMS102. The probehead should be removed to give free access to the space between electromagnet poles.
- Wrap the Tesla meter sensor in the middle 2-3 times with $\frac{1}{4}$ " paper tape.
- Cut a 1" diameter disc from cardboard $\frac{1}{8}$ " thick.
- With a sharp blade cut a rectangular shape in the center that will fit the Tesla meter probe. Draw an arrow extending from the probe.
- Slide the Tesla meter probe in the slot. The arrow will be useful in angle measurements while the edge of the paper tape gives a convenient reference in magnetic field mapping (see Figure 40a).

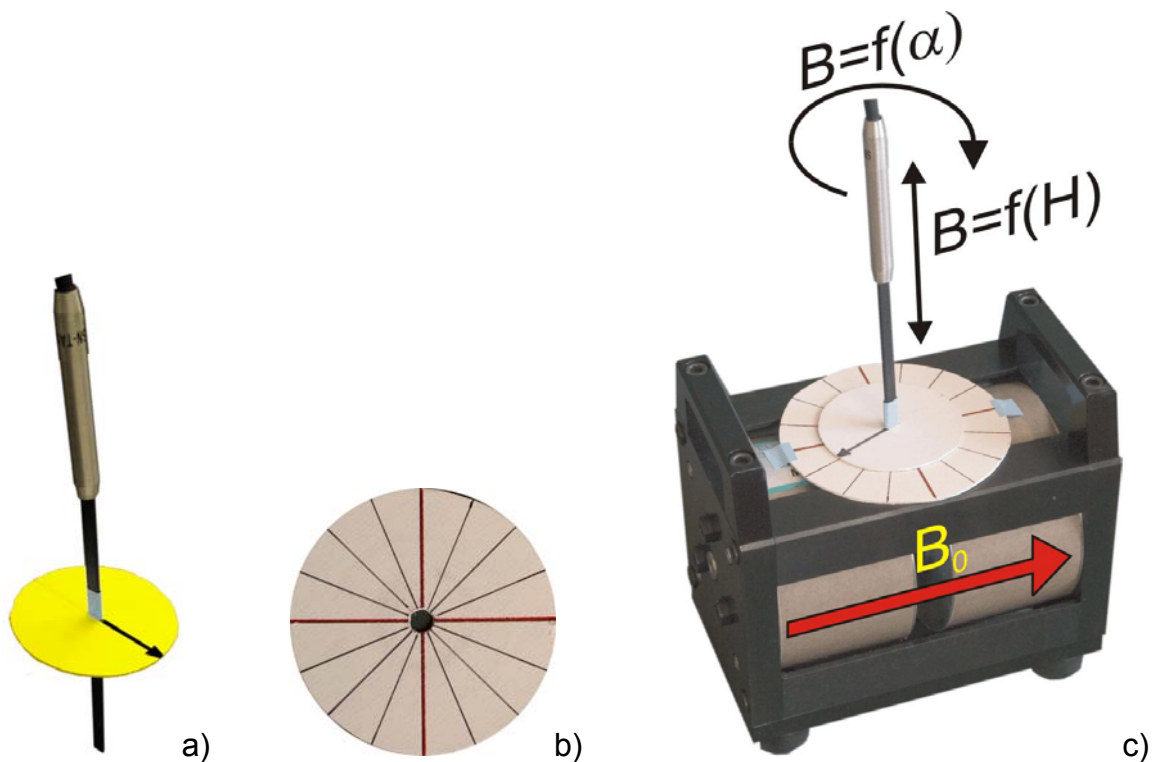


Figure 40. Measuring magnetic field in electromagnet.

- From the same cardboard material cut large 4" disc and divide it into 16 equal segments (Figure 40b). Cut 6mm hole in the disk center and tape it on the top of the magnet (Figure 40c)

- Attach probe to the Tesla meter and turn it on, zero and calibrate meter and insert probe in a magnet.
- For angle dependence of Hall sensor indications place probehead in electromagnet center and record the Tesla meter reading while rotating the probe.
- For axial mapping move the probe vertically and read field every 5 mm. For proper readings keep probehead surface parallel to electromagnet's poles.

Analysis

- Plot Tesla meter readings for different angle orientations and vertical positions of the probehead (Figure 41).

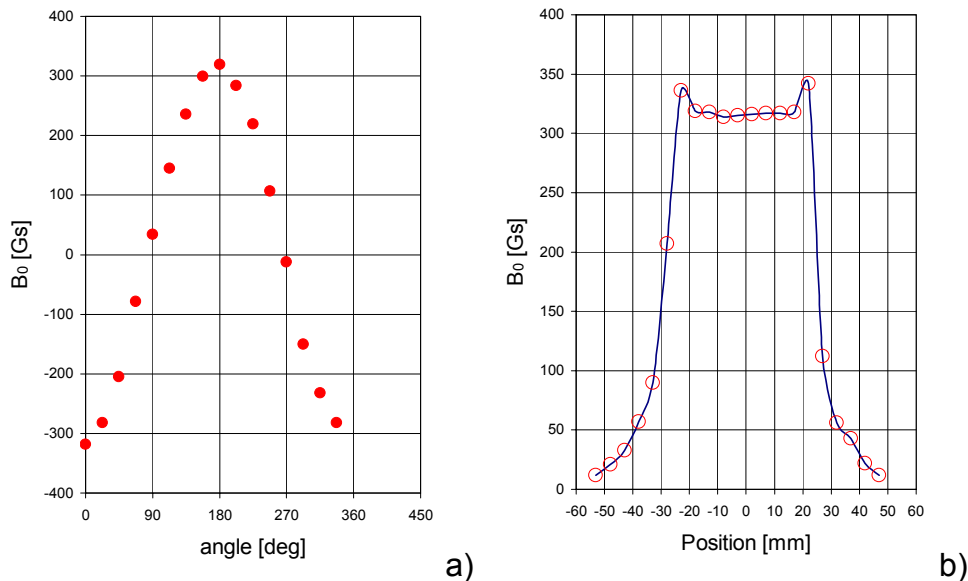


Figure 41. Angle (a) and vertical axis (b) dependence of magnetic field reading with Hall effect type Tesla meter.

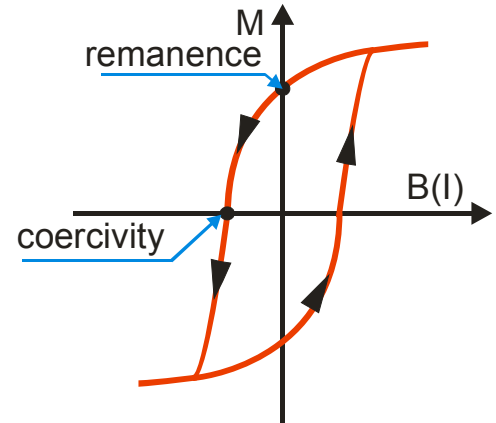
- Keeping in mind Eq. 3 fit experimental points (Figure 41a) to a sine function.
- From vertical axis dependence (Figure 41b):
 - Determine regions of most uniform (homogeneous) magnetic field.
 - Calculate magnetic field gradient close to poles' edges.
 - Explain increase of magnetic field on poles' edges.
 - Analyze influence of magnetic field uniformity on the resonance signal.

10.8.2 Measuring magnetic field remanence in an electromagnet.

A magnetic field in an electromagnet is produced by a direct current that flows through its coils. The amount of magnetization the electromagnet retains at zero driving current (field) is called **remanence**. It must be driven back to zero by a current (field) in the opposite direction.

One can see **remanence** of the CWS 12-50 magnet in the following experiment.

With the console off (no current) insert the Tesla meter probe between poles. While rotating the probe measure the magnetic field amplitude. Usually remanence varies between 2-3 mT. Note that the magnitude of the Earth's magnetic field is two orders lower and cannot significantly contribute to the measurement.



10.8.3 Helmholtz coils

Introduction

Helmholtz coils are a simple source of a relatively spatially uniform magnetic field obtained by use of a pair of circular coils on a common axis with equal currents flowing in the same sense. For a given coil radius the most uniform central field is obtained when coils separation is equal to the radius of the coils (a slightly larger separation improves the field uniformity). A cylindrical region extending between the centers of the two coils and approximately 1/5 of their diameter has a nearly homogeneous magnetic field. Helmholtz coils design is very simple and does not require a heavy or expensive yoke. Unlike electromagnets they can not produce strong magnetic field. CWS 12-50 Helmholtz coils produce a 20 Gs magnetic field, compared to the 3200 Gs produced by an electromagnet.

Axial mapping of coil's magnetic field and angle dependence of the readings of Tesla meter.

Make an experiment following instructions for electromagnet in Chapter 10.8.

Monitoring magnetic field sweep during ESR experiments.

- Wrap the Tesla meter probe with thick tape that will hold probe inside the Helmholtz coils (Figure 43).

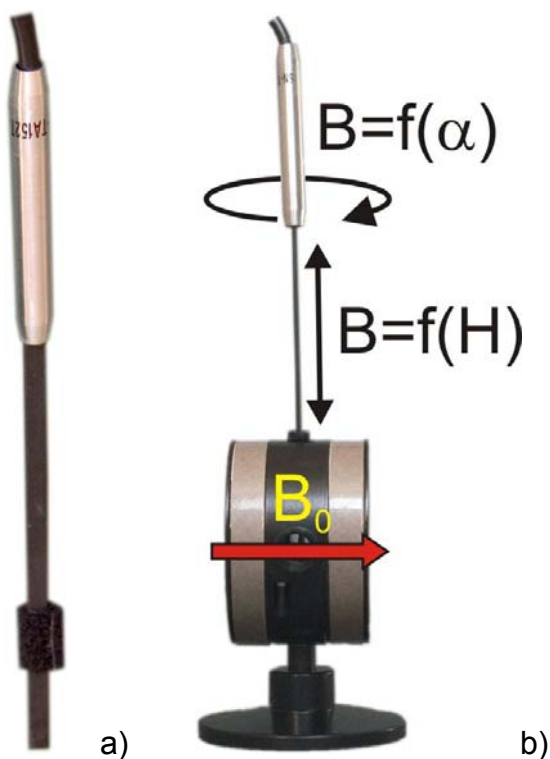


Figure 43. Measuring magnetic field in Helmholtz coil.

- Connect Helmholtz coils to console.
- Insert spectrometer probehead in Helmholtz coils.
- Place TCNQ sample in spectrometer probehead.
- From the top insert Tesla meter axial probe in the Helmholtz coils and carefully locate it as close as possible to spectrometer probehead. For high accuracy of measurements remember to keep the Tesla meter probe axis parallel to \mathbf{B}_0 axis!
- On spectrometer **Setup and Acquisition** page prepare ESR experiment as described in Chapter 10.3 .
- For the observation of magnetic field changes choose **Sweep Time=4min**.
- Run experiment and see changes of magnetic field during different phases of experiment. Perform **Hold**, **Abort** functions and check what happens.

10.92nd modulation of magnetic field and line broadening**Introduction**

Physics of magnetic resonances requires very slow passage through resonance line to fulfill the so called adiabatic conditions, when energy of nuclear spins do not change fast. Therefore the received signal is a very slowly changing alternate signal, which is almost direct current, of the amplitude of single microvolt, very difficult to amplify. Because alternate signals can be easily amplified and linearly detected in wide dynamic range, a DC-like resonance signal coming from the probehead must be somehow modulated and convert to alternate one. This is done by an additional modulation of the magnetic field (see Figure 44) during field sweep called 2nd modulation (because sweep of the magnetic field is called 1st modulation). Another benefit of applying modulation to the magnetic field is the possibility of using phase sensitive detector synchronized with 2nd modulation characterized by high linearity and for filtering of coherent noise. Look at the spectrometer block diagram at page 25 for details.

An awkward consequence of this 2nd modulation is that the signal under detection is not the absorption signal, but its 1st derivative and it is artificially broadened, depending on 2nd modulation amplitude. So properly designed experiment requires finding the right 2nd modulation amplitude as a tradeoff between the gain from the resonance signal amplitude and the deteriorating natural line shape.

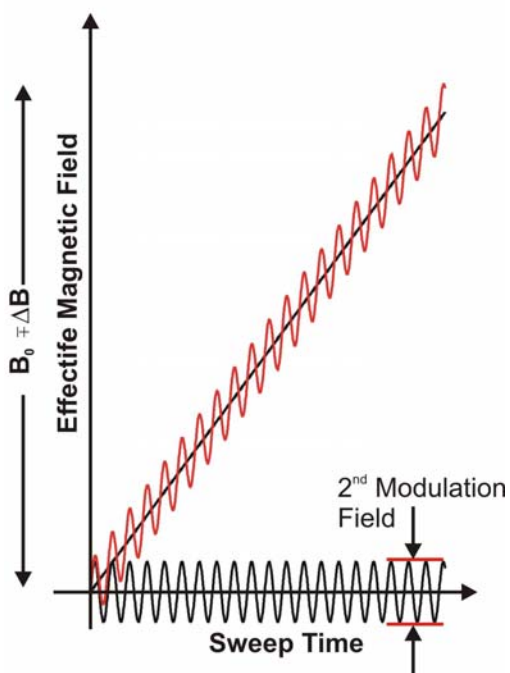


Figure 44. Modulation of the magnetic field: sweep as a 1st modulation and sinusoidal as 2nd modulation.

Objective

Studying influence of the 2nd modulation on the line width and on signal amplitude.

Setup

- Connect electromagnet to console
- Insert glycerin sample in probehead
- On **Setup and Acquisition** page prepare experimental setup similar to one on Figure 45.
- Run experiments for different **2nd Mod Amplitude**.
- Measure width of 1st derivative by pressing on DB. It calculates line width as difference between line minimum and maximum.
- For qualitative comparison display simultaneously 5 field sweeps for 5 different 2nd modulation amplitudes by **Pass Display/5**

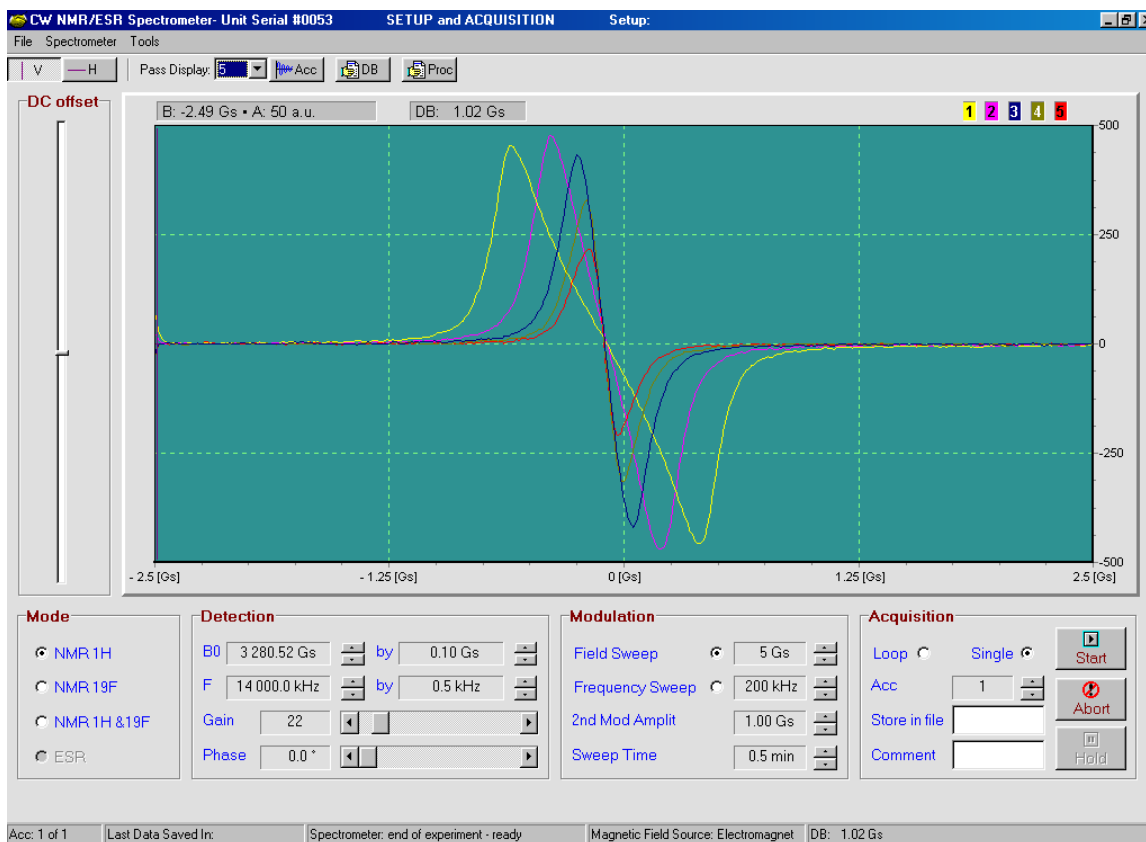


Figure 45. Experimental setup and results from the study of 2nd modulation influence on signal amplitude and line width.

Analysis

Table 5 shows summary of experiments for 5 different 2nd modulation amplitudes. Note continuous increase of line width, while signal amplitude reaches maximum for 0.50 Gs. It will be highly recommended to chose 0.10 Gs for final experiment when 50% gain in signal intensity is penalized only by 12% line broadening.

#	2 nd mod [Gs]	Line width [Gs]	Amplitude [a.u.]
1	0.05	0.17	216
2	0.10	0.19	325
3	0.20	0.30	433
4	0.50	0.58	477
5	1.00	1.02	451

Table 5 . Line width and signal amplitude for different 2nd modulations.