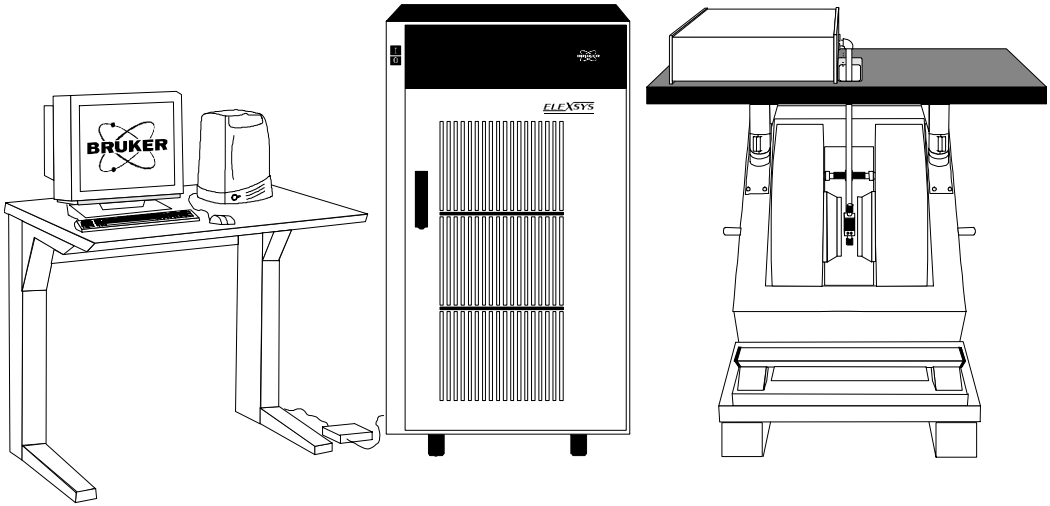
ELEXSYS E 500

EPR Spectrometer User's Manual

Basic Operations



BRUKER BIOSPIN

ELEXSYS E 500 USER'S MANUAL

Basic Operations

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ELEXSYS E 500 User's Manual: Basic Operations
Manual Version 2.0
Software Version 2.1

This manual is part of the original documentation for the Bruker ELEXSYS spectrometer.

Preface 0

Bruker strives to supply you with instructional and accurate documentation. We encourage you to tell us how we are doing. Please send us your suggestions for improvements, corrections, or bug reports. If there is anything you particularly liked, tell us as well. With your input and assistance, Bruker can continually improve its products and documentation.

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Thank you for your help.

Electrical Safety 0.1

Do not remove any of the protective covers or panels of the instrument. They are fitted to protect you and should be opened by qualified service personnel only.

Power off the instrument and disconnect the line cord before starting any cleaning work in the spectrometer. Never operate the instrument with the grounding cord disconnected or by passed. Facility wiring must include a properly grounded power receptacle.

Chemical Safety 0.2

Individuals working with hazardous chemicals, toxic substances, or enclosed liquid samples must take every precaution possible to avoid exposure to these agents. As a general rule, THINK OF THE CHEMICAL LABORATORY AS A HAZARDOUS ENVIRONMENT IN WHICH YOU MUST CONTINUALLY MAINTAIN A HIGH STANDARD OF VIGILANCE. Do not assume a cavalier attitude -- the substances with which you work present very real, and very serious threats to your health and safety.

Adhere to all currently recommended guidelines for standard laboratory safety as promulgated by governmental codes and contemporary laboratory practice. Inform yourself about the specific risks that are present when you handle actual or potential carcinogens (cancer-causing agents), explosive materials, strong acids, or any liquids that are sealed in glass containers.

Specifically:

- Be extremely careful when you handle sealed glass samples that are rapidly heated or cooled. The rapid cooling of some samples may result in the formation of a solid bolus in the sample tube that may make the tube prone to explosive rupture.
- Educate yourself about the temperature at which chemicals evaporate. When a sample gets close to the temperature at which it evaporates, it may quickly become volatile.
- In general, the safety threat posed by flying glass and violently escaping gases and liquids should not be underestimated.
- Wear safety glasses, face masks, and other protective clothing whenever there is any risk of spillage, breakage, or explosion. Protective shields should also be employed when there is any risk of explosion.
- Be sure that both storage and working areas are properly ventilated. They should be equipped with powerful blowers and fume heads.
- Store chemicals safely. Avoid integrating containers of chemicals that may result in dangerous combinations.
- Practice good housekeeping in work and storage areas. Clean up spills and refuse promptly. Do not leave volatile, combustible, or acidic liquids exposed on counters, benches, or other work areas.
- Make certain all chemical containers are properly labeled and classified, and that especially hazardous materials are appropriately designated with clearly understood decals or warnings.
- Never taste or inhale unmarked chemicals.

- All laboratories should be equipped with fire doors, fire extinguishers, fire smothering materials, and sprinkler systems or showers, as well as a detailed fire safety plan.

Microwave Safety 0.3

As long as the microwaves are contained in metal structures, microwaves can be very safe. Here are some precautions which, if followed, will eliminate the possibility of injury due to the microwaves.

- Do not have an open waveguide when the microwave power is on.
- Switch the bridge to standby when you remove or change EPR cavities.
- Never look down an open waveguide when there is microwave power. The eyes are very susceptible to damage from microwaves.

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Introduction 1

This document describes the basic operation of a Bruker Elexsys E 500 EPR (Electron Paramagnetic Resonance) spectrometer. No assumptions have been made about the background of the readers except that they have a general scientific or technical background. Many of the elementary principles necessary for following the chapters are presented in a concise form.

This manual is one of three manuals supplied with your spectrometer. In addition, there is also a second volume of this manual (Elexsys E 500 User's Manual: Advanced Operations) that describes more advanced operations and procedures of the spectrometer. Finally, there is an Xepr User's Manual describing many details of the Xepr application.

We start with a list of EPR applications. A brief description of the spectrometer and its capabilities follows. The chapter concludes with an explanation of how to use this manual.

EPR Applications 1.1

EPR has matured into a powerful, versatile, nondestructive, and nonintrusive analytical method. Unlike many other techniques, EPR yields meaningful structural and dynamical information, even from ongoing chemical or physical processes without influencing the process itself. Therefore, it is an ideal complementary technique for other methods in a wide range of studies and application areas. Here is a list of some of the EPR applications which are commonly used.

Chemistry 1.1.1

- Kinetics of radical reactions
- Polymerization reactions
- Spin trapping
- Organo-metallic compounds
- Catalysis
- Petroleum research
- Oxidation and reduction processes
- Biradicals and triplet states of molecules

Physics 1.1.2

- Measurement of magnetic susceptibility
- Transition metal, lanthanide, and actinide ions
- Conduction electrons in conductors and semiconductors
- Defects in crystals (e.g. color centers in alkali-halides)
- Optical detection of magnetic resonance, excited states of molecules
- Crystal fields in single crystals
- Recombination at low temperatures

Materials Research 1.1.3

- Degradation of paints and polymers by light
- Polymer properties
- Defects in diamond
- Defects in optical fibers
- Laser materials
- Organic conductors
- Influence of impurities and defects in semiconductors
- Properties of novel magnetic materials
- High T_C superconductors
- C_{60} compounds
- Behavior of free radicals in corrosion

Ionizing Radiation 1.1.4

- Alanine radiation dosimetry
- Control of irradiated foods
- Archaeological dating
- Short-time behavior of organic free radicals produced by radiation
- Radiation effects and damage
- Radiation effects on biological compounds

Biology and Medicine 1.1.5

- Spin label and spin probe techniques
- Spin trapping
- Dynamics of biomolecules using saturation transfer techniques
- Free radicals in living tissues and fluids
- Antioxidants, radical scavengers
- Contrast agents
- Oximetry
- Drug detection, metabolism, and toxicity
- Enzyme reactions
- Photosynthesis
- Structure and identification of metal-binding sites
- Photochemical and radiolytic generation of radicals
- Oxygen based radicals
- NO in biological systems
- Carcinogenic reactions

The Spectrometer 1.2

The Bruker Elexsys E 500 EPR spectrometer is a research grade scientific instrument. It is capable of routine measurements, as well as sophisticated and advanced experiments when equipped with the proper accessories. The modular design makes the spectrometer easy to upgrade or expand. For information and assistance in choosing and ordering accessories for your specific application, contact your local Bruker EPR sales representative.

Using this Manual 1.3

This manual is one of three manuals supplied with your Bruker Elexsys E 500 spectrometer. It describes basic operations. In addition, there is also a second volume of this manual (Elexsys E 500 User's Manual: Advanced Operations) that describes many procedures and operations in greater depth than this manual. Finally, there is the Xepr User's Manual describing many details of the Xepr application.

How to Find Things 1.3.1

Preface First, you should read the safety guide in the preface of the manual. Microwaves can be dangerous, particularly to your eyes. With normal precautions, the risk for injury can be minimized.

Chapter 2 Users who are not familiar with EPR should start by reading Chapter 2, which is a concise introduction to the theory and practice of EPR spectroscopy. It is by no means exhaustive; it gives the necessary information to follow the other chapters of the manual. A short list of references is given at the end of the chapter for more information.

Chapter 3 This chapter is a simple "how to" section describing how to acquire the spectrum of a sample. It covers turning the spectrometer on, tuning the microwave cavity and bridge, and acquiring spectra. The step by step instructions lead you through the acquisition of a strong pitch (a standard sample) EPR signal.

Chapter 4 This chapter introduces you to the essential concepts of Xepr. It describes the basic features and how to use those Xepr features.

Chapter 5 This tutorial guides you through many common data acquisition tasks. It gives you detailed examples of how to use many of the convenient and commonly used features of the spectrometer. The chapter covers both 1D and 2D spectra.

Chapter 6 This chapter gives you a tutorial on the basic operations of data processing such as data handling, baseline correction, peak picking, integration, and curve fitting.

Chapter 7 The most basic operations of the Bruker EPR spectrometer are covered in Chapter 3. This chapter introduces you to additional techniques such as manually tuning the bridge, changing cavities, and adjusting the AFC.

Chapter 8 General helpful hints for acquiring EPR spectra are presented in this chapter. Before consulting this chapter, you should be familiar with the material in Chapters 2 and 3. It gives tips on where to find EPR signals as well as how to optimize the sensitivity of the spectrometer for your particular sample.

Chapter 9 Sometimes, things go wrong. Chapter 9 gives some possible solutions to problems you may be having. Many times, problems appear to be the fault of the instrument; however, with the proper choice of operating conditions, these problems often disappear.

Chapter 10 An extensive bibliography of EPR references is given in this chapter. It includes many different EPR applications as well as educational texts. This is a good place to start a literature search.

This manual consists of two volumes. This volume is for basic operations. If you have more advanced questions please refer to volume II, Advanced Operations. All the answers to all EPR questions can not possibly fit in one manual. This manual is only part of the Elexsys E 500 documentation. It provides instructions to the essential operations of Elexsys E 500 systems. For help with software questions, consult the Xepr User's Manual. It can be accessed on-line from the Xepr program by clicking on Manual in the Help menu. If you cannot find the answer to your question, contact your nearest Bruker EPR representative. We have a team of skilled application scientists with diverse expertises. One of us will probably come up with an answer.

Fonts 1.3.2

Special fonts are used in the text to differentiate between normal manual text and the text displayed in the program.

Times — This is the font used for the normal text in the manual.

Helvetica — This is the font used for text that is displayed by the program or must be entered into the program by you.

Special notes 1.3.3

Some special notation is employed in this manual to simplify the descriptions.

< ... > The content between the brackets needs to be substituted with proper entries by the user.

> The right bracket indicates sequential selection of the menu entries. For example, Processing > Filtering > Smoothing means clicking the Processing button in the menu bar, followed by clicking Filtering in the sub-menu, and then clicking Smoothing.

Warning box.

You will see a warning box sometimes in the lefthand margin. These are meant to point out critical information. In particular, it warns you about any procedures or operations that may be dangerous to the spectrometer or you. Always read and follow this advice.

Hint box.

In addition, there are also hint boxes in the lefthand margin These are meant to be helpful hints and point out important information.

An EPR Primer 2

This chapter is an introduction to the basic theory and practice of EPR spectroscopy. It gives you sufficient background to understand the following chapters. In addition, we strongly encourage the new user to explore some of the texts and articles at the end of this chapter. You can then fully benefit from your particular EPR application or think of new ones.

Basic EPR Theory 2.1

Introduction to Spectroscopy 2.1.1

During the early part of this century, when scientists began to apply the principles of quantum mechanics to describe atoms or molecules, they found that a molecule or atom has discrete (or separate) states, each with a corresponding energy. Spectroscopy is the measurement and interpretation of the energy differences between the atomic or molecular states. With knowledge of these energy differences, you gain insight into the identity, structure, and dynamics of the sample under study.

We can measure these energy differences, ΔE, because of an important relationship between ΔE and the absorption of electromagnetic radiation. According to Planck's law, electromagnetic radiation will be absorbed if:

$$\Delta E = h\nu \,, \qquad [2\text{-}1]$$

where h is Planck's constant and ν is the frequency of the radiation.

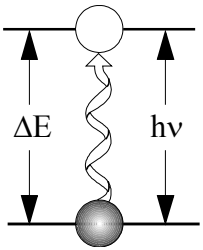


Figure 2-1 Transition associated with the absorption of electromagnetic energy.

The absorption of energy causes a transition from the lower energy state to the higher energy state. (See Figure 2-1.) In conventional spectroscopy, ν is varied or swept and the frequencies at which absorption occurs correspond to the energy differences of the states. (We shall see later that EPR differs slightly.) This record is called a spectrum. (See Figure 2-2.) Typically, the frequencies vary from the megahertz range for NMR (Nuclear Magnetic Resonance) (AM, FM, and TV transmissions use electromagnetic radiation at these frequencies), through visible light, to ultraviolet light. Radiation in the gigahertz range (the same as in your microwave oven) is used for EPR experiments.

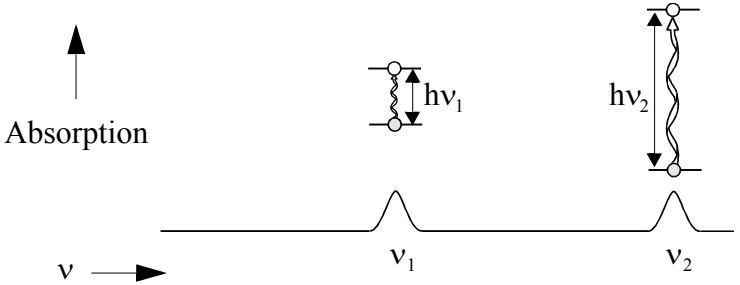


Figure 2-2 A spectrum.

The Zeeman Effect 2.1.2

The energy differences we study in EPR spectroscopy are predominately due to the interaction of unpaired electrons in the sample with a magnetic field produced by a magnet in the laboratory. This effect is called the Zeeman effect. Because the electron has a magnetic moment, it acts like a compass or a bar magnet when you place it in a magnetic field, B_0. It will have a state of lowest energy when the moment of the electron, μ, is aligned with the magnetic field and a state of highest energy when μ is aligned against the magnetic field. (See Figure 2-3.) The two states are labelled by the projection of the electron spin, M_s, on the direction of the magnetic field. Because the electron is a spin 1/2 particle, the parallel state is designated as $M_s = - 1/2$ and the antiparallel state is $M_s = + 1/2$.

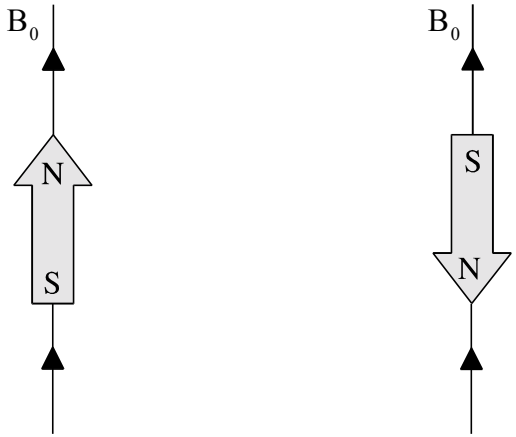


Figure 2-3 Minimum and maximum energy orientations of μ with respect to the magnetic field B_0.

From quantum mechanics, we obtain the most basic equations of EPR:

$$E = g\,\mu_B\,B_0\,M_s = \pm\,\frac{1}{2}\,g\,\mu_B\,B_0 \qquad [2\text{-}2]$$

and

$$\Delta E = h\nu = g\,\mu_B B_0. \qquad [2\text{-}3]$$

g is the g-factor, which is a proportionality constant approximately equal to 2 for most samples, but varies depending on the electronic configuration of the radical or ion. μ_B is the Bohr magneton, which is the natural unit of electronic magnetic moment.

Two facts are apparent from equations Equation [2-2] and Equation [2-3] and its graph in Figure 2-4.

- The two spin states have the same energy in the absence of a magnetic field.
- The energies of the spin states diverge linearly as the magnetic field increases.

These two facts have important consequences for spectroscopy.

- Without a magnetic field, there is no energy difference to measure.
- The measured energy difference depends linearly on the magnetic field.

Because we can change the energy differences between the two spin states by varying the magnetic field strength, we have an alternative means to obtain spectra. We could apply a constant magnetic field and scan the frequency of the electromagnetic radiation as in conventional spectroscopy. Alternatively, we could keep the electromagnetic radiation frequency constant and scan the magnetic field. (See Figure 2-4.) A peak in the absorption will occur when the magnetic field "tunes" the two spin states so that their energy difference matches the energy of the radiation. This field is called the "field for resonance". Owing to the limitations of microwave electronics, the latter method offers superior performance. This technique is used in all Bruker EPR spectrometers.

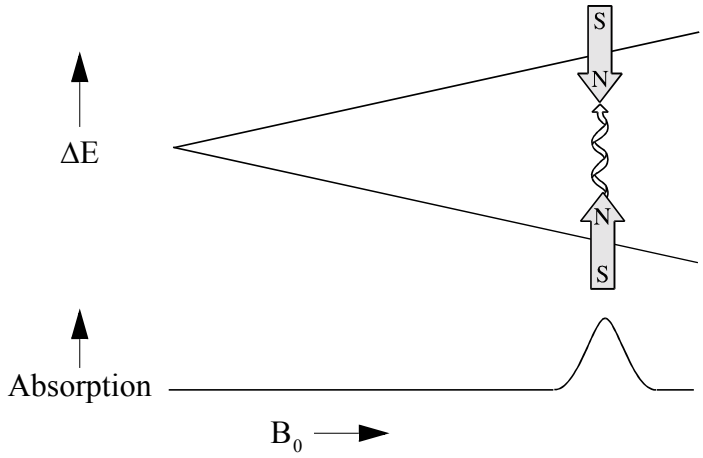


Figure 2-4 Variation of the spin state energies as a function of the applied magnetic field.

The field for resonance is not a unique “fingerprint” for identification of a compound because spectra can be acquired at several different frequencies. The g-factor,

$$g = \frac{h\nu}{\mu_B B_0} \quad , \qquad [2\text{-}4]$$

being independent of the microwave frequency, is much better for that purpose. Notice that high values of g occur at low magnetic fields and vice versa. A list of fields for resonance for a g = 2 signal at microwave frequencies commonly available in EPR spectrometers is presented in Table 2-1.

Microwave Band	Frequency (GHz)	B_{res} (G)
L	1.1	390
S	4.0	1430
X	9.75	3480
Q	34.0	12100
W	94.0	33500

Table 2-1 Field for resonance, B_{res}, for a g = 2 signal at selected microwave frequencies.

Hyperfine Interactions 2.1.3

Measurement of g-factors can give us some useful information; however, it does not tell us much about the molecular structure of our sample. Fortunately, the unpaired electron, which gives us the EPR spectrum, is very sensitive to its local surroundings. The nuclei of the atoms in a molecule or complex often have a magnetic moment, which produces a local magnetic field at the electron. The interaction between the electron and the nuclei is called the hyperfine interaction. It gives us a wealth of information about our sample such as the identity and number of atoms which make up a molecule or complex as well as their distances from the unpaired electron.

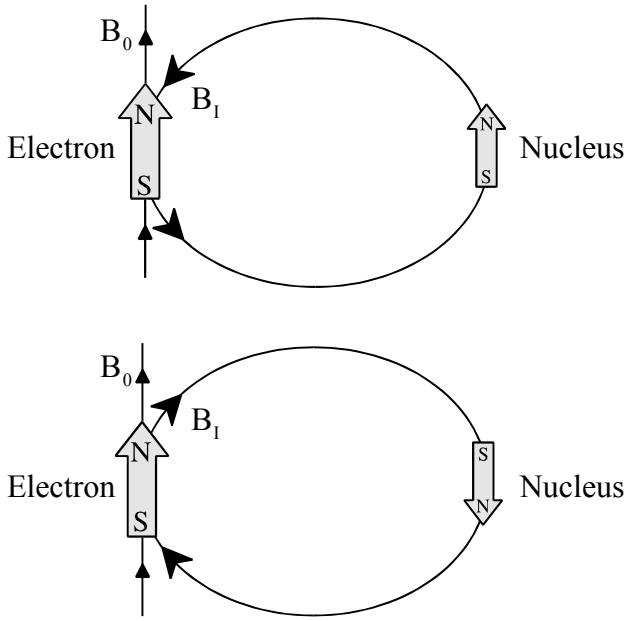


Figure 2-5 Local magnetic field at the electron, B_I, due to a nearby nucleus.

Figure 2-5 depicts the origin of the hyperfine interaction. The magnetic moment of the nucleus acts like a bar magnet (albeit a weaker magnet than the electron) and produces a magnetic field at the electron, B_I. This magnetic field opposes or adds to the magnetic field from the laboratory magnet, depending on the alignment of the moment of the nucleus. When B_I adds to the magnetic field, we need less magnetic field from our laboratory magnet and therefore the field for resonance is lowered by B_I. The opposite is true when B_I opposes the laboratory field.

For a spin 1/2 nucleus such as a hydrogen nucleus, we observe that our single EPR absorption signal splits into two signals which are each B_I away from the original signal. (See Figure 2-6.)

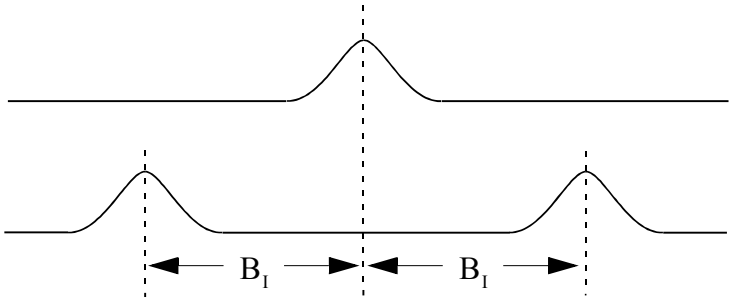


Figure 2-6 Splitting in an EPR signal due to the local magnetic field of a nearby nucleus.

If there is a second nucleus, each of the signals is further split into a pair, resulting in four signals. For N spin 1/2 nuclei, we will generally observe 2^N EPR signals. As the number of nuclei gets larger, the number of signals increases exponentially. Sometimes there are so many signals that they overlap and we only observe one broad signal.

Signal Intensity 2.1.4

So far, we have concerned ourselves with where the EPR signal is, but the size of the EPR signal is also important if we want to measure the concentration of the EPR active species in our sample. In the language of spectroscopy, the size of a signal is defined as the integrated intensity, i.e., the area beneath the absorption curve. (See Figure 2-7.) The integrated intensity of an EPR signal is proportional to the concentration.

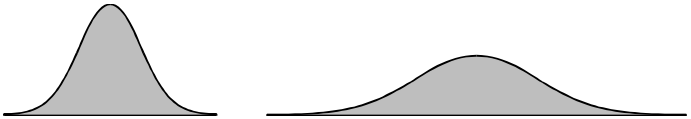


Figure 2-7 Integrated intensity of absorption signals. Both signals have the same intensity.

Signal intensities do not depend solely on concentrations. They also depend on the microwave power. If you do not use too much microwave power, the signal intensity grows as the square root of the power. At higher power levels, the signal diminishes as well as broadens with increasing microwave power levels. This effect is called saturation. If you want to measure accurate linewidths, lineshapes, and closely spaced hyperfine splittings, you should avoid saturation by using low microwave power. A quick means of checking for the absence of saturation is to decrease the microwave power and verify that the signal intensity also decreases by the square root of the microwave power.

Basic EPR Practice 2.2

Introduction to Spectrometers 2.2.1

In the first half of this chapter, we discussed the theory of EPR spectroscopy. Now we need to consider the practical aspects of EPR spectroscopy. Theory and practice have always been strongly interdependent in the development and growth of EPR. A good example of this point is the first detection of an EPR signal by Zavoisky in 1945. The Zeeman effect had been known in optical spectroscopy for many years, but the first direct detection of EPR had to wait until the development of radar during World War II. Only then, did scientists have the necessary components to build sufficiently sensitive spectrometers (scientific instruments designed to acquire spectra). The same is true today with the development of advanced techniques in EPR such as Fourier Transform and high frequency EPR.

The simplest possible spectrometer has three essential components: a source of electromagnetic radiation, a sample, and a detector. (See Figure 2-8.) To acquire a spectrum, we change the frequency of the electromagnetic radiation and measure the amount of radiation which passes through the sample with a detector to observe the spectroscopic absorptions. Despite the apparent complexities of any spectrometer you may encounter, it can always be simplified to the block diagram shown in Figure 2-8.

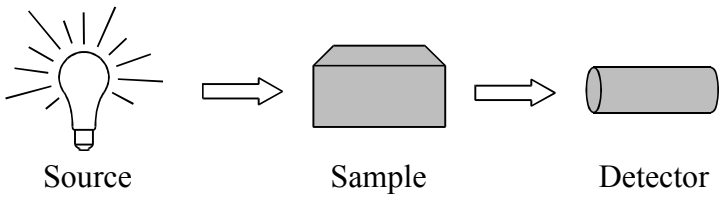


Figure 2-8 The simplest spectrometer.

Figure 2-9 shows the general layout of a Bruker EPR spectrometer. The electromagnetic radiation source and the detector are in a box called the “microwave bridge”. The sample is in a microwave cavity, which is a metal box that helps to amplify weak signals from the sample. As mentioned in Section 2.1.2, there is a magnet to “tune” the electronic energy levels. In addition, we have a console, which contains signal processing and control electronics and a computer. The computer is used for analyzing data as well as coordinating all the units for acquiring a spectrum. In the following sections you will become acquainted with how these different parts of the spectrometer function and interact.

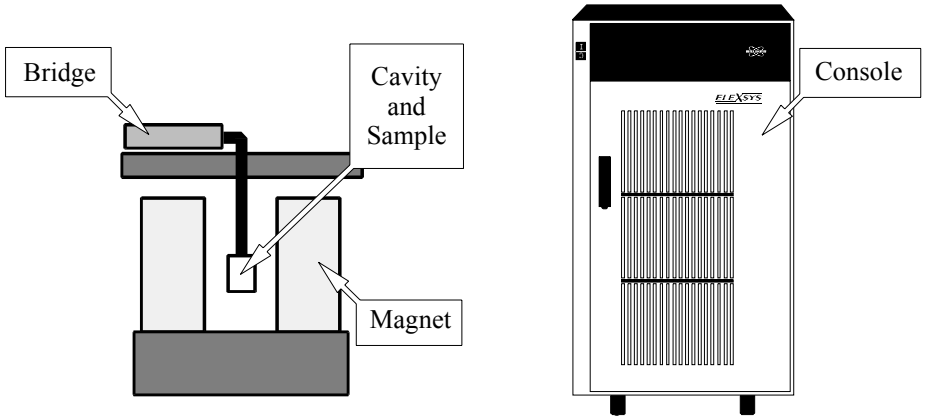


Figure 2-9 The general outlay of an EPR spectrometer.

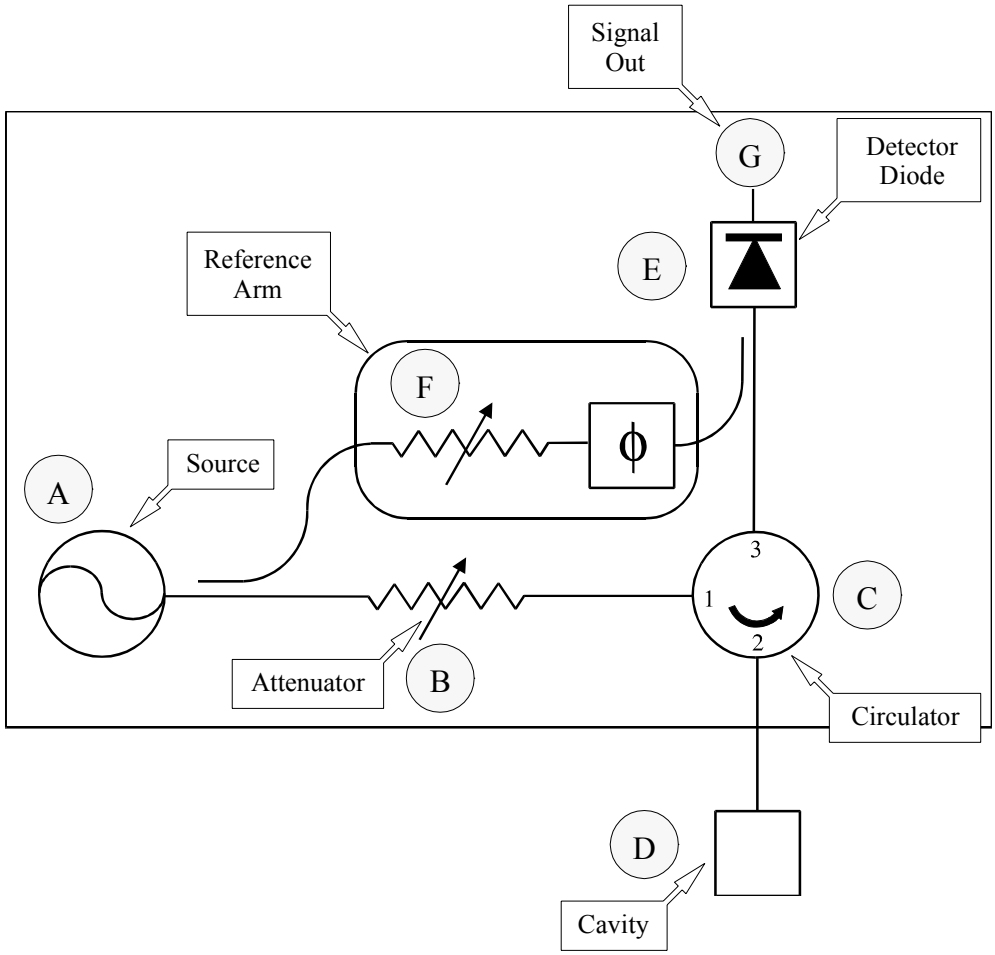


Figure 2-10 Block diagram of a microwave bridge.

The Microwave Bridge 2.2.2

The microwave bridge houses the microwave source and the detector. There are more parts in a bridge than shown in Figure 2-10, but most of them are control, power supply, and security electronics and are not necessary for understanding the basic operation of the bridge. We shall now follow the path of the microwaves from the source to the detector.

We start our tour of the microwave bridge at point A, the microwave source. The output power of the microwave source cannot be varied easily, however in our discussion of signal intensity, we stressed the importance of changing the power level. Therefore, the next component, at point B, after the microwave source is a variable attenuator, a device which blocks the flow of microwave radiation. With the attenuator, we can precisely and accurately control the microwave power which the sample sees.

Bruker EPR spectrometers operate slightly differently than the simple spectrometer shown in the block diagram, Figure 2-8. The diagram depicts a transmission spectrometer (It measures the amount of radiation transmitted through the sample.) and most EPR spectrometers are reflection spectrometers. They measure the changes (due to spectroscopic transitions) in the amount of radiation reflected back from the microwave cavity containing the sample (point D in the figure). We therefore want our detector to see only the microwave radiation coming back from the cavity. The circulator at point C is a microwave device which allows us to do this. Microwaves coming in port 1 of the circulator only go to the cavity through port 2 and not directly to the detector through port 3. Reflected microwaves are directed only to the detector and not back to the microwave source.

We use a Schottky barrier diode to detect the reflected microwaves (point E in the figure). It converts the microwave power to an electrical current. At low power levels, (less than 1 microwatt) the diode current is proportional to the microwave power and the detector is called a square law detector. (Remember that

electrical power is proportional to the square of the voltage or current.) At higher power levels, (greater than 1 milliwatt) the diode current is proportional to the square root of the microwave power and the detector is called a linear detector. The transition between the two regions is very gradual.

For quantitative signal intensity measurements as well as optimal sensitivity, the diode should operate in the linear region. The best results are attained with a detector current of approximately 200 microamperes. To insure that the detector operates at that level, there is a reference arm (point F in the figure) which supplies the detector with some extra microwave power or “bias”. Some of the source power is tapped off into the reference arm, where a second attenuator controls the power level (and consequently the diode current) for optimal performance. There is also a phase shifter to insure that the reference arm microwaves are in phase with the reflected signal microwaves when the two signals combine at the detector diode.

The detector diodes are very sensitive to damage from excessive microwave power and will slowly lose their sensitivity. To prevent this from happening, there is protection circuitry in the bridge which monitors the current from the diode. When the current exceeds 400 microamperes, the bridge automatically protects the diode by lowering the microwave power level. This reduces the risk of damage due to accidents or improper operating procedures. However, it is good lab practice to follow correct procedures and not rely on the protection circuitry.

The EPR Cavity 2.2.3

In this section, we shall discuss the properties of microwave (EPR) cavities and how changes in these properties due to absorption result in an EPR signal. We use microwave cavities to amplify weak signals from the sample. A microwave cavity is simply a metal box with a rectangular or cylindrical shape which resonates with microwaves much as an organ pipe resonates with sound waves. Resonance means that the cavity stores the microwave energy; therefore, at the resonance frequency of the cavity, no microwaves will be reflected back, but will remain inside the cavity. (See Figure 2-11.)

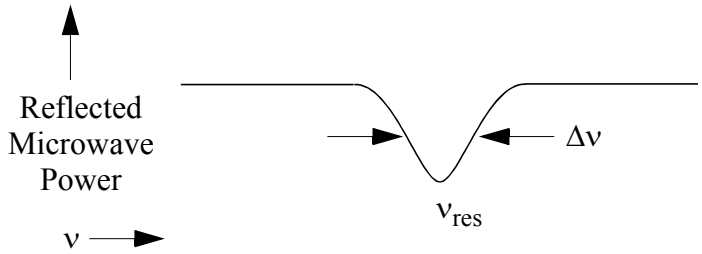


Figure 2-11 Reflected microwave power from a resonant cavity.

Cavities are characterized by their Q or quality factor, which indicates how efficiently the cavity stores microwave energy. As Q increases, the sensitivity of the spectrometer increases. The Q factor is defined as

$$Q = \frac{2\pi \text{ (energy stored)}}{\text{energy dissipated per cycle}}, \qquad [2\text{-}5]$$

where the energy dissipated per cycle is the amount of energy lost during one microwave period. Energy can be lost to the side walls of the cavity because the microwaves generate electrical currents in the side walls of the cavity which in turn generates

heat. We can measure Q factors easily because there is another way of expressing Q:

$$Q = \frac{\nu_{res}}{\Delta\nu} \ , \qquad [2\text{-}6]$$

where ν_{res} is the resonant frequency of the cavity and $\Delta\nu$ is the width at half height of the resonance.

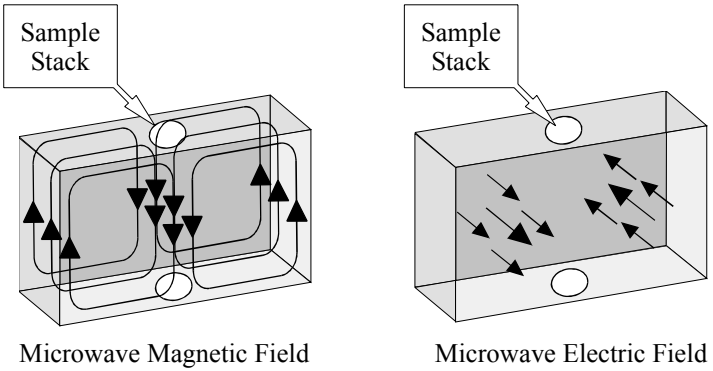


Figure 2-12 Magnetic and electric field patterns in a standard EPR cavity.

A consequence of resonance is that there will be a standing wave inside the cavity. Standing electromagnetic waves have their electric and magnetic field components exactly out of phase, i.e. where the magnetic field is maximum, the electric field is minimum and vice versa. The spatial distribution of the amplitudes of the electric and magnetic fields in the most commonly used EPR cavity is shown in Figure 2-12. We can use the spatial separation of the electric and magnetic fields in a cavity to great advantage. Most samples have non-resonant absorption of the microwaves via the electric field (this is how a microwave oven works) and the Q will be degraded by an increase in the dissipated energy. It is the magnetic field that drives the absorption in

EPR. Therefore, if we place our sample in the electric field minimum and the magnetic field maximum, we obtain the biggest signals and the highest sensitivity. The cavities are designed for optimal placement of the sample.

We couple the microwaves into the cavity via a hole called an iris. The size of the iris controls the amount of microwaves which will be reflected back from the cavity and how much will enter the cavity. The iris accomplishes this by carefully matching or transforming the impedances (the resistance to the waves) of the cavity and the waveguide (a rectangular pipe used to carry microwaves). There is an iris screw in front of the iris which allows us to adjust the “matching”. This adjustment can be visualized by noting that as the screw moves up and down, it effectively changes the size of the iris. (See Figure 2-13.)

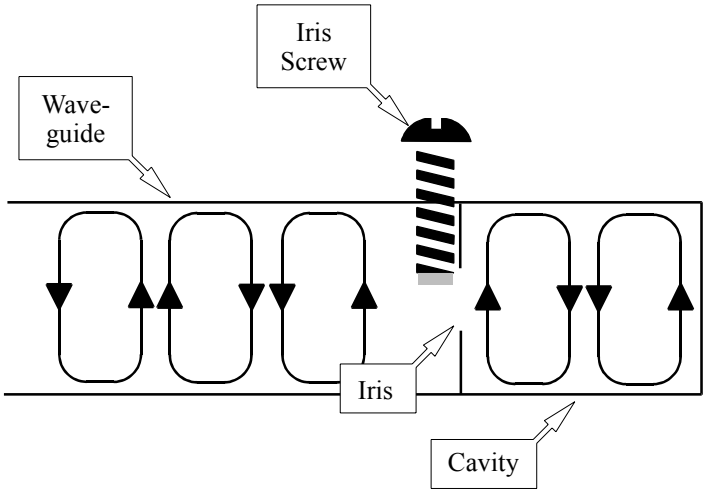


Figure 2-13 The matching of a microwave cavity to waveguide.

How do all of these properties of a cavity give rise to an EPR signal? When the sample absorbs the microwave energy, the Q is lowered because of the increased losses and the coupling

changes because the absorbing sample changes the impedance of the cavity. The cavity is therefore no longer critically coupled and microwave will be reflected back to the bridge, resulting in an EPR signal.

The Signal Channel 2.2.4

EPR spectroscopists use a technique known as phase sensitive detection to enhance the sensitivity of the spectrometer. The advantages include less noise from the detection diode and the elimination of baseline instabilities due to the drift in DC electronics. A further advantage is that it encodes the EPR signals to make it distinguishable from sources of noise or interference which are almost always present in a laboratory. The signal channel, a unit which fits in the spectrometer console, contains the required electronics for the phase sensitive detection.

The detection scheme works as follows. The magnetic field strength which the sample sees is modulated (varied) sinusoidally at the modulation frequency. If there is an EPR signal, the field modulation quickly sweeps through part of the signal and the microwaves reflected from the cavity are amplitude modulated at the same frequency. For an EPR signal which is approximately linear over an interval as wide as the modulation amplitude, the EPR signal is transformed into a sine wave with an amplitude proportional to the slope of the signal (See Figure 2-14.)

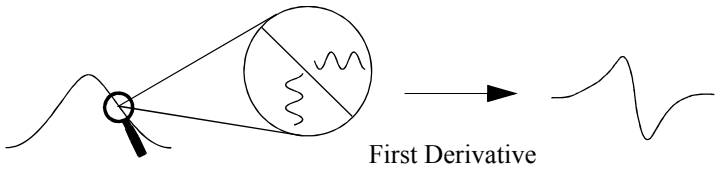


Figure 2-14 Field modulation and phase sensitive detection.

The signal channel (more commonly known as a lock-in amplifier or phase sensitive detector) produces a DC signal proportional to the amplitude of the modulated EPR signal. It compares the modulated signal with a reference signal having the same frequency as the field modulation and it is only sensitive to signals which have the same frequency and phase as the field modulation. Any signals which do not fulfill these requirements (i.e., noise and electrical interference) are suppressed. To further improve the sensitivity, a time constant is used to filter out more of the noise.

Phase sensitive detection with magnetic field modulation can increase our sensitivity by several orders of magnitude; however, we must be careful in choosing the appropriate modulation amplitude, frequency, and time constant. All three variables can distort our EPR signals and make interpretation of our results difficult.

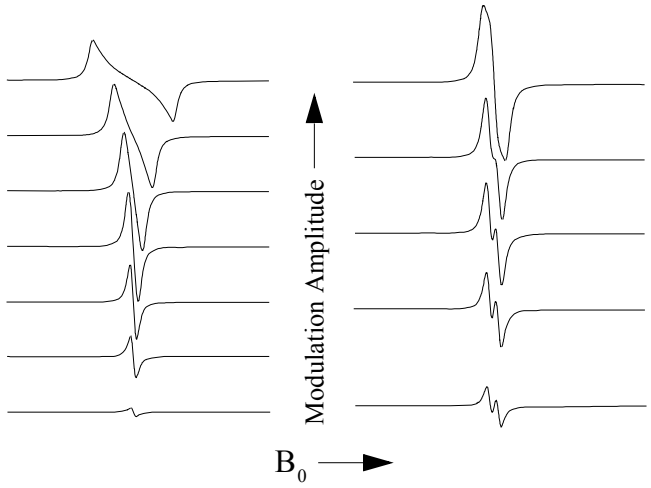


Figure 2-15 Signal distortions due to excessive field modulation.

As we apply more magnetic field modulation, the intensity of the detected EPR signals increases; however, if the modulation amplitude is too large (larger than the linewidths of the EPR signal), the detected EPR signal broadens and becomes distorted. (See Figure 2-15.) A good compromise between signal intensity and signal distortion occurs when the amplitude of the magnetic field modulation is equal to the width of the EPR signal. Also, if we use a modulation amplitude greater than the splitting between two EPR signals, we can no longer resolve the two signals.

Time constants filter out noise by slowing down the response time of the spectrometer. As the time constant is increased, the noise levels will drop. If we choose a time constant which is too long for the rate at which we scan the magnetic field, we can distort or even filter out the very signal which we are trying to extract from the noise. Also, the apparent field for resonance will shift. Figure 2-16 shows the distortion and disappearance of a signal as the time constant is increased. If you need to use a long time constant to see a weak signal, you must use a slower scan rate. A safe rule of thumb is to make sure that the time needed to scan through a single EPR signal should be ten times greater than the length of the time constant.

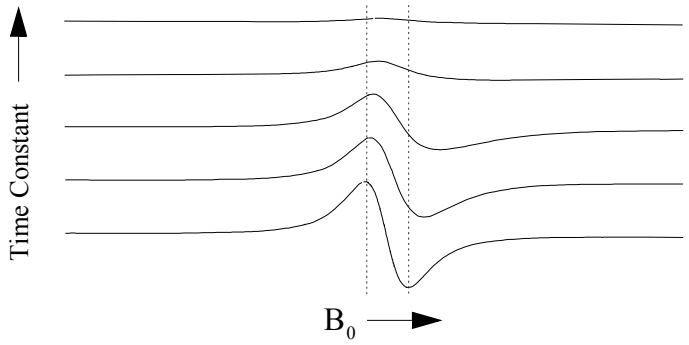


Figure 2-16 Signal distortion and shift due to excessive time constants.

For samples with very narrow or closely spaced EPR signals, (~ 50 milligauss. This usually only happens for organic radicals in dilute solutions.) we can get a broadening of the signals if our modulation frequency is too high (See Figure 2-17.) The broadening is a consequence of the Heisenberg uncertainty principle.

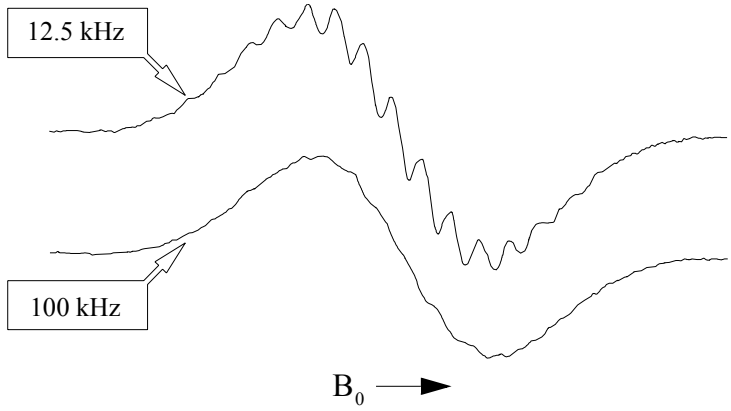


Figure 2-17 Loss of resolution due to high modulation frequency.

The Magnetic Field Controller 2.2.5

The magnetic field controller allows us to sweep the magnetic field in a controlled and precise manner for our EPR experiment. It consists of two parts; a part which sets the field values and the timing of the field sweep and a part which regulates the current in the windings of the magnet to attain the requested magnetic field value.

The magnetic field values and the timing of the magnetic field sweep are controlled by a microprocessor in the controller. A field sweep is divided into a maximum of 4096 discrete steps called sweep addresses. At each step, a reference voltage corresponding to the magnetic field value is sent to the part of the controller that regulates the magnetic field. The sweep rate is

controlled by varying the waiting time between the individual steps.

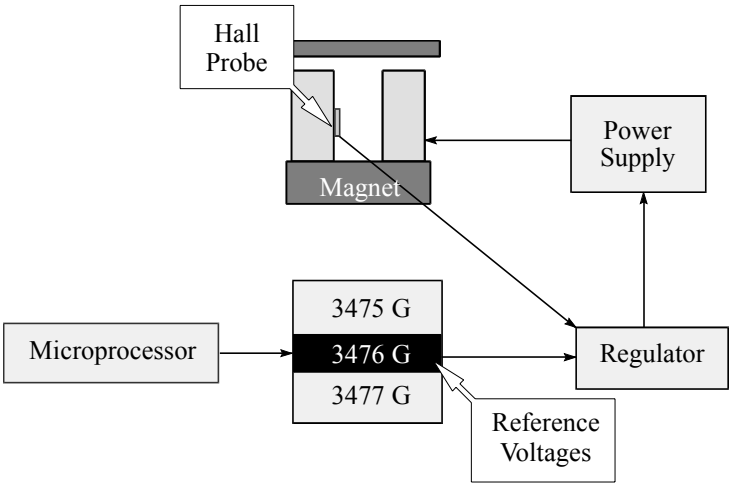


Figure 2-18 A block diagram of the field controller and associated components.

The magnetic field regulation occurs via a Hall probe placed in the gap of the magnet. It produces a voltage which is dependent on the magnetic field perpendicular to the probe. The relationship is not linear and the voltage changes with temperature; however, this is easily compensated for by keeping the probe at a constant temperature slightly above room temperature and characterizing the nonlinearities so that the microprocessor in the controller can make the appropriate corrections. Regulation is accomplished by comparing the voltage from the Hall probe with the reference voltage given by the other part of the controller. When there is a difference between the two voltages, a correction voltage is sent to the magnet power supply which changes the amount of current flowing through the magnet windings and hence the magnetic field. Eventually the error

voltage drops to zero and the field is “stable” or “locked”. This occurs at each discrete step of a magnetic field scan.

The Spectrum 2.2.6

We have seen how the individual components of the spectrometer work. Figure 2-19 shows how they work together to produce a spectrum.

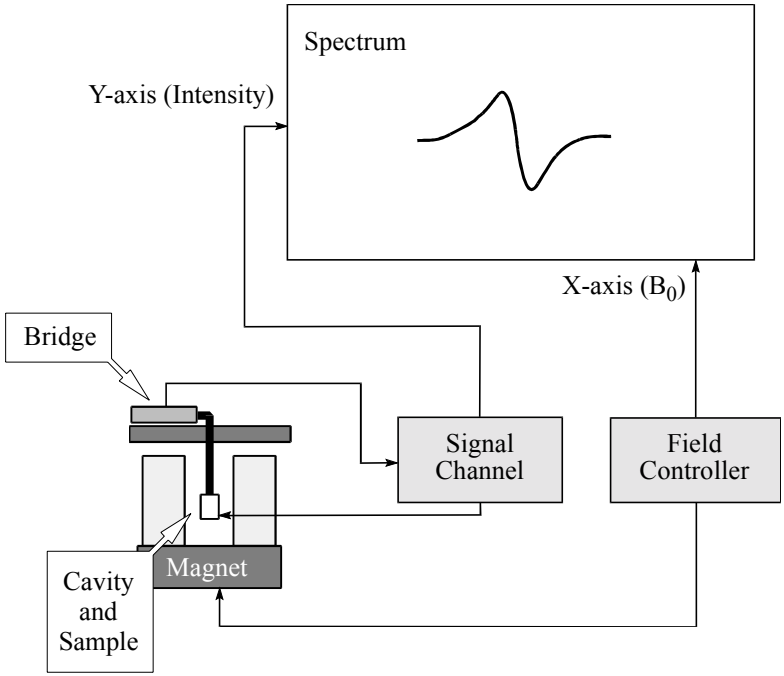


Figure 2-19 Block diagram of an EPR spectrometer.

Suggested Reading 2.3

This chapter is a brief overview of the basic theory and practice of EPR spectroscopy. If you would like to learn more, there are many good books and articles that have been written on these subjects. We recommend the following:

Instrumentation:

Poole, C. *Electron Spin Resonance a Comprehensive Treatise on Experimental Techniques, Editions 1,2:* Interscience Publishers, New York, (1967), (1983).

Feher, G. *Sensitivity Considerations in Microwave Paramagnetic Resonance Absorption Techniques:* Bell System Tech. J. 36, 449 (1957).

Theory:

Knowles, P.F., D. Marsh and H.W.E. Rattle. *Magnetic Resonance of Biomolecules:* J. Wiley, New York, (1976).

Weil, John A., J.R. Bolton, and Wertz, J.E., *Electron Paramagnetic Resonance, Elementary Theory and Practical Applications:* Wiley-Interscience, New York, (1994).

A more extensive bibliography is found in last chapter of this manual.

Getting Started 3

This chapter contains basic operating instructions for first time users of a Bruker Elexsys E 500 spectrometer. It describes basic spectrometer operation with an X-band bridge (9.2-9.9 GHz). This chapter guides you from a completely shut down spectrometer to a hardcopy of your spectrum on a printer. You will learn to acquire an EPR spectrum of a standard sample with the Xepr software. There are also recommended precautions to prevent damage to the instrument. All the components have self-protecting features; however, it is good lab practice to follow correct operating procedures and not rely on the protection circuitry. No in-depth knowledge of EPR is required; however we recommend that you familiarize yourself with some of the material in Chapter 2. To help you in the following sections, Figure 3-1 assists you in identifying the various units which comprise the EPR spectrometer.

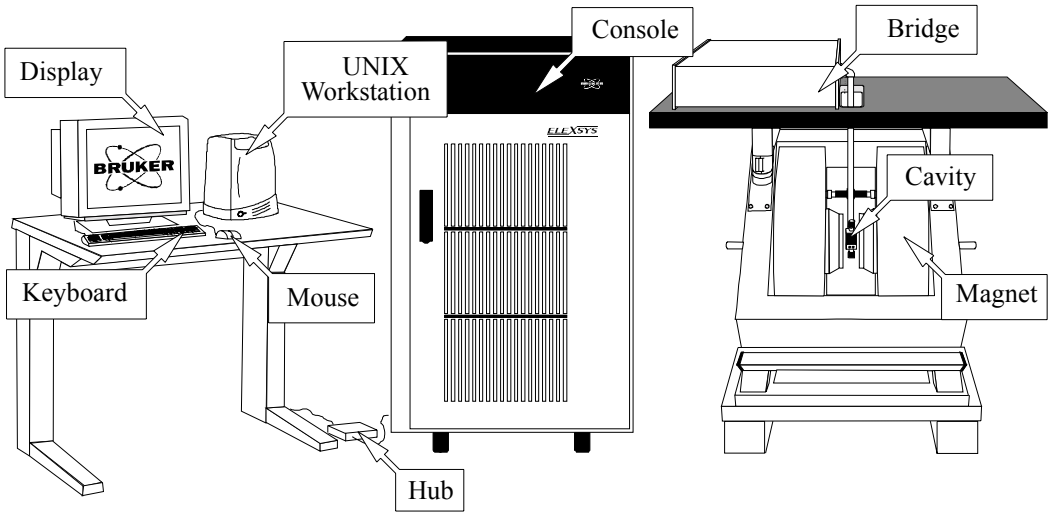


Figure 3-1 The modules and components of the Elexsys E 500 spectrometer.

Turning the Spectrometer On 3.1

If you are not sure how the electric power or water is connected, consult your local instrument or facilities manager.

1. **Turn on the power for the system.** How you do this depends on how the electric power was hooked up when the spectrometer was installed. Most likely you will activate the switch on the breaker box for the spectrometer. Breaker boxes are usually mounted on the wall. Consult the local instrument or facilities manager if you are not sure where the breaker box is.

2. **Turn on the tap water for cooling.** There are usually two valves, one for the supply and one for the return (or drain). Consult the local instrument or facilities manager if you are not sure where the valves are.

3. **Start the Xepr Program.** Log onto the UNIX workstation. If you are unfamiliar with UNIX, please refer to Appendix A or Appendix B for UNIX tips. We recommend using the xuser user account which is set up by the Bruker service engineer when the spectrometer is installed. The initial password for this account is user@xepr. Double-click the Xepr icon on the desktop to launch the program. (See Figure 3-2.)

Figure 3-2 The Xepr program desktop icon.

4. **Turn on the power for the console.** The power switch (green button) for the console is located in the upper left front corner of the console. (See Figure 3-3.) The acquisition server will boot and initialize all the modules of the Elexsys E 500 spectrometer. This process may take 30 seconds or longer: meanwhile you can continue with the next steps.

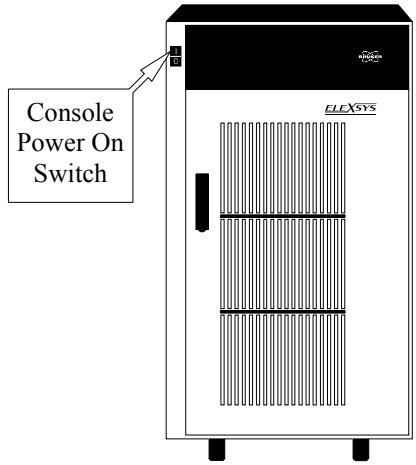


Figure 3-3 The location of the console power switch.

5. **Turn on the heat exchanger and magnet power supply. (Instructions for Small Power Supplies.)** Follow this step if your power supply looks like the power supply in Figure 3-4. You must first turn the heat exchanger on by activating the power switch. The location of the power switch may vary depending on your heat exchanger. To turn the power supply on, push its POWER ON/OFF button. Go to Step 7.

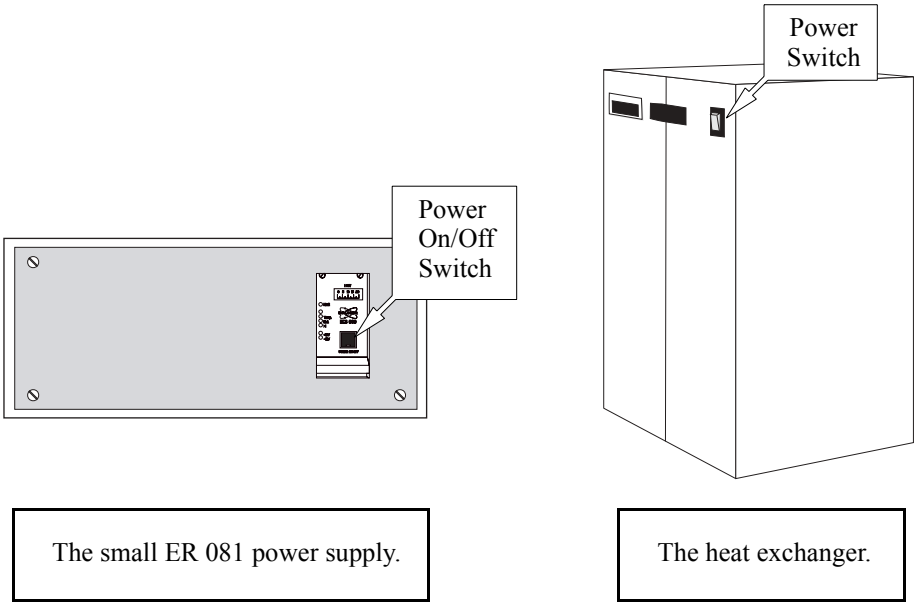


Figure 3-4 The small ER 081 power supply and the heat exchanger.

6. **Turn on the heat exchanger and magnet power supply. (Instructions for Large Power Supplies)** Follow this step if your power supply looks like the power supply in Figure 3-5. On systems with large power supplies, you need to first press the ELECTR. ON button and then the POWER ON button. Pressing the POWER ON button also starts the heat exchanger. If not, make sure that the power switch on the heat exchanger is activated.

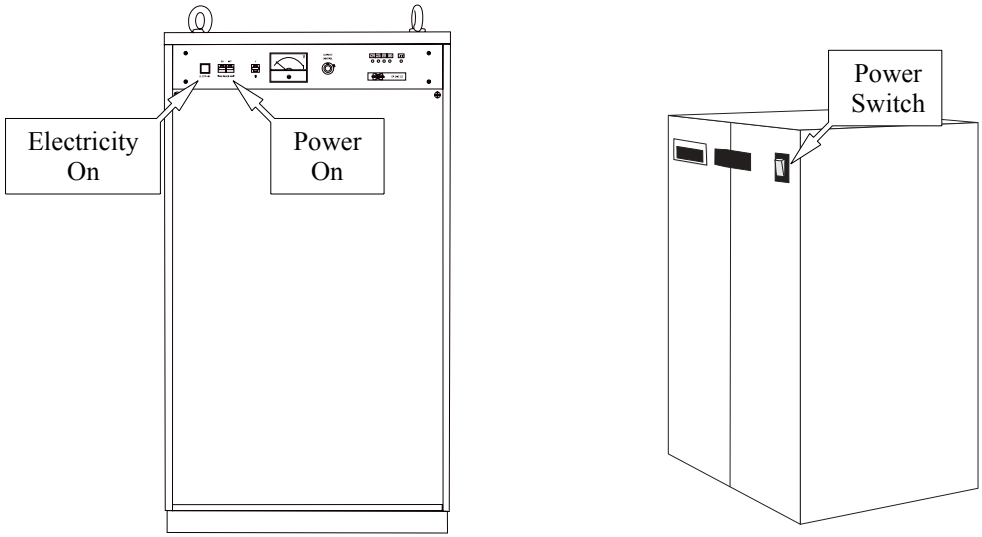


Figure 3-5 The large power supply and the heat exchanger.

7. **Connect to the spectrometer.** To control the spectrometer from the Xepr program you need to connect the workstation to the spectrometer. Click the Acquisition menu bar and then Connect to Spectrometer. A dialog box will appear with the Server Name: click OK. (See Figure 3-6.)

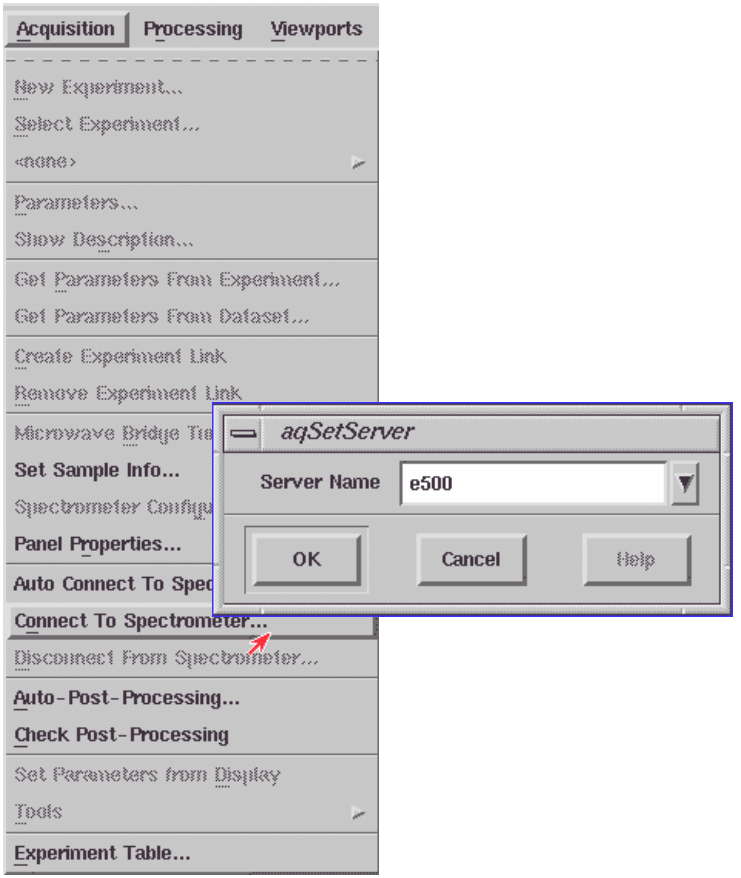


Figure 3-6 Connecting to the spectrometer.

If you were not successful in connecting to the acquisition server, consult Chapter 17 of the Elexsys E 500 User's Manual: Advanced Operations.

When the connection is complete a monitoring panel will appear in the Xepr window. (See Figure 3-7.) The monitoring panel may appear on top of the viewport or at the bottom of the viewport depending on your default settings.

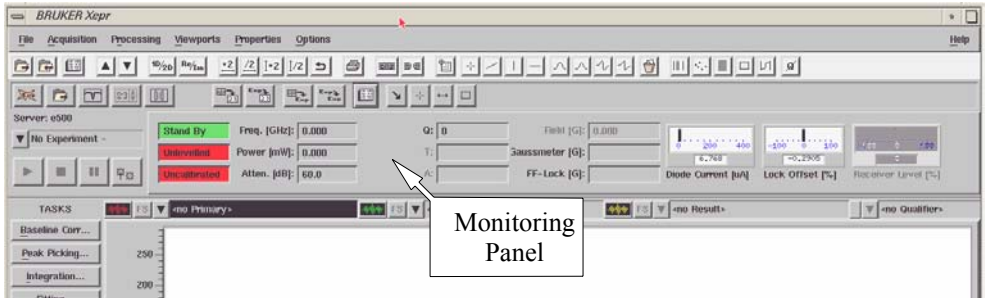


Figure 3-7 The Xepr window after connecting to the spectrometer.

8. **Install an EPR cavity if there is not one presently installed.** The instructions in this chapter assume you are using a properly installed Bruker ER 4122SHQ or ER 4102ST cavity. If there is no cavity installed or the installed cavity is not one of them, seek the assistance of a knowledgeable EPR colleague or refer to Section 7.2 to learn how to install a cavity.

9. **Proceed to Section 3.2**.

Tuning the Microwave Cavity and Bridge 3.2

1. **Open the Microwave Bridge Tuning dialog box.** Click the Tuning button in the monitoring panel. The Microwave Bridge Tuning dialog box will then appear. (See Figure 3-8.)

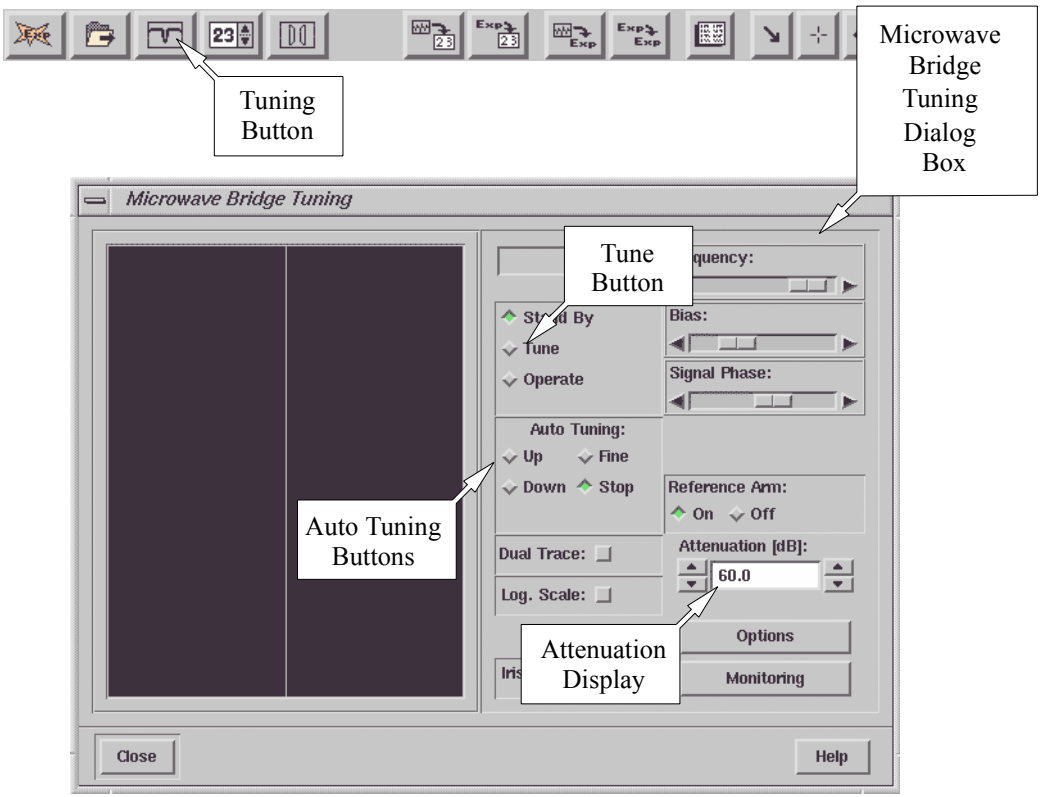


Figure 3-8 The Microwave Bridge Tuning dialog box.

There are three states or modes for the microwave bridge: StandBy, Tune, and Operate. When you connect to your spectrometer, the bridge is in Stand By, indicated by a green Stand By button. (See Figure 3-8.) If you have been acquiring spectra already, your bridge will probably be in Operate.

2. **Switch the microwave bridge to Tune.** Click the Tune button in the dialog box to change to Tune.

3. **Set the microwave attenuator to 30 dB.** The microwave attenuation is set by clicking the arrows on either side of the attenuation display in the dialog box. (See Figure 3-8.) The arrows on the left change the attenuator in 10 dB steps; those on the right in 1 dB steps.

4. **Remove the sample.** If there already is a sample in the cavity, remove it. Loosen the top collet nut (You do not need to remove the collet nut.) and carefully remove the sample from the cavity. Pulling the sample tube out as straight as possible prevents you from breaking the sample tube thereby destroying your valuable samples. (See Figure 3-9 and Figure 3-10 for details.) The ER 4122SHQ cavity is shown in the figures; however, the procedure of removing and inserting a sample is the same for ER 4102ST, ER 4122SHQ, and ER 4122SHQE cavities.

Take care if you are wearing an analog (mechanical) watch. The magnetic field in the air gap of the magnet is sufficiently strong to magnetize your watch! Therefore, to avoid damage to your watch, remove your watch before putting your hands in the magnet air gap.

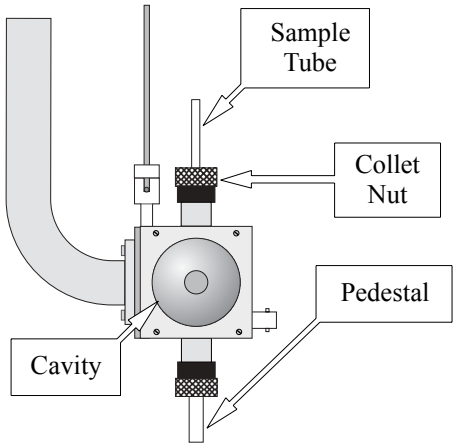


Figure 3-9 A Bruker ER 4122SHQ cavity.

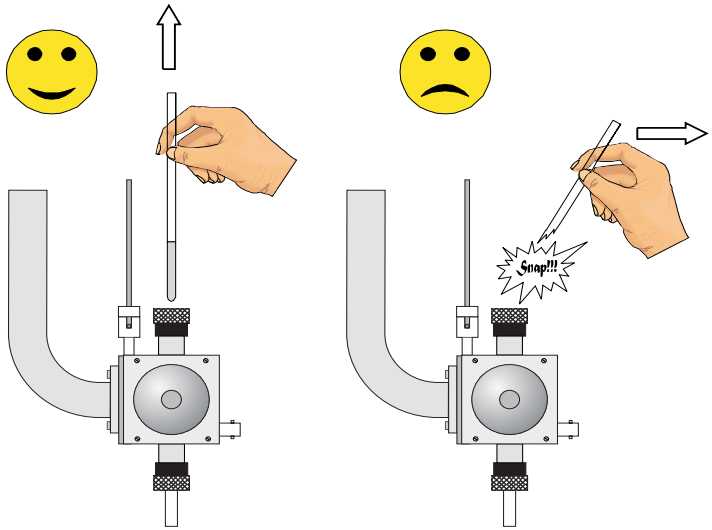


Figure 3-10 The right and wrong technique for removing a sample.

If this is your first time operating an Elexsys E 500 spectrometer, we recommend that you use the strong pitch sample supplied with your instrument. Our instructions in this chapter are based on using this sample.

5. **Clean the sample tube to be inserted into the cavity.** It is vital to avoid contaminating the microwave cavity with paramagnetic contaminants that produce spurious EPR signals or distorted base lines. Wiping the outside of the sample tube with tissue paper is usually adequate.

Make sure that the pedestal is not in the cavity, as it can give an EPR signal and will also degrade the sensitivity.

6. **Insert the sample tube carefully into the cavity.** (See Figure 3-9 and Figure 3-10.) Make sure you have the appropriate collet size for your sample tube size. The tube should be slightly loose before you tighten the collet nut. The bottom of your sample should rest in the indentation on the pedestal. This ensures that your sample is centered horizontally. The height can be adjusted by loosening the bottom collet nut and moving the pedestal up and down. Tighten the top collet nut to firmly hold the sample tube in place and the bottom collet to firmly hold the pedestal.

7. **Tune the bridge and cavity.** Pressing either the Up button or Down button of Auto Tune starts the automatic tuning procedure. (See Figure 3-8.) The Up button starts by scanning the microwave frequency up in search of the cavity dip (or frequency where the cavity resonates). The Down button starts by scanning the microwave frequency down in search of the cavity dip. If you are not sure if the search should start up or down, do not worry. The frequency will be scanned until its limit is reached and then scan in the other direction until the cavity dip is found. The Auto-Tune routine adjusts the frequency, phase, and bias of the bridge and the coupling (matching) of the cavity. If there is an error message, try manual tuning described in Section 7.1. If you still have difficulty in tuning, it usually means that you have a lossy or conductive sample. Refer to Chapter 9 for trouble shooting.

8. **Close the Microwave Bridge Tuning dialog box.** Click the Close button. The Microwave Bridge Tuning dialog box will then disappear. (See Figure 3-8.)

9. **Proceed to the next section to learn how to acquire spectra.**

Acquiring Spectra 3.3

1. **Follow the instructions of Section 3.1 through Section 3.2.** You should have the spectrometer turned on, a Bruker ER 4102ST standard cavity, ER 4122SHQ or ER 4122SHQE cavity installed, a strong pitch sample inserted in it, and the microwave bridge and cavity tuned.

Figure 3-11 The New Experiment and Parameter buttons.

Some characters such as space, *, ?, / are not valid for the experiment name.

2. **Create a New Experiment.** In order to acquire a spectrum, you need to define an experiment. To create a new experiment, click the New Experiment button in the monitoring panel. (See Figure 3-11.) In the New Experiment dialog box, enter a name for the new experiment. By default the name is Experiment. Click the C.W. tab. Choose Field for Abscissa 1 and None for Abscissa 2. If the Ordinate is not Signal Channel select Signal Channel in the Ordinate drop-down list. If the buttons for Temp Unit (the variable temperature unit), Goniometer, and Gradient Unit are activated (green) click on it to deactivate it. (See Figure 3-12.) Click Create and then the dialog box will close. The spectrometer will now be configured with these settings.

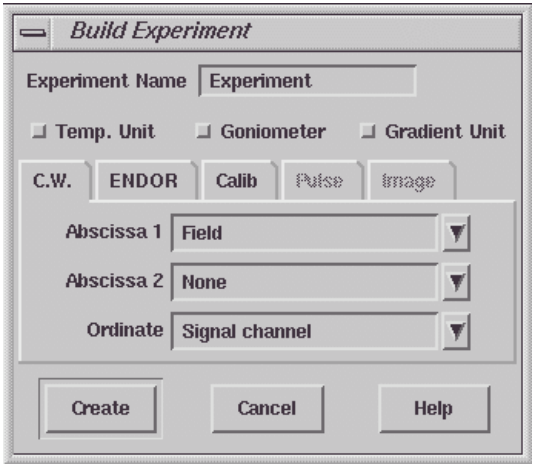


Figure 3-12 The New Experiment configuration.

It is very important to enter the sample information so that you maintain a record of the sample used to acquire the spectrum. Comments are very useful because you can keep track of such things as sample preparation details.

3. **Set Sample Information.** Click Acquisition in the menu bar, and then click Set Sample Info. A sample information dialog box opens in which you can type information regarding your sample. Enter your sample information and then click OK to close the window.

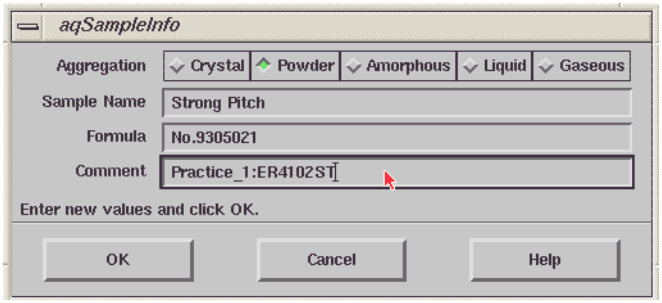


Figure 3-13 The sample information dialog box.

4. **Choose the Interactive Parameter Setting mode.** Press the Activate button. (See Figure 3-14.) This button toggles between interactive and non-interactive parameter setting modes. As you edit parameters in the parameter panel in interactive mode, the new parameters are immediately activated on the spectrometer. In the non-interactive mode, you can edit instrument parameters in the parameter panel without activating them on the instrument. In this mode, the new parameters are only activated when you click the Run button.

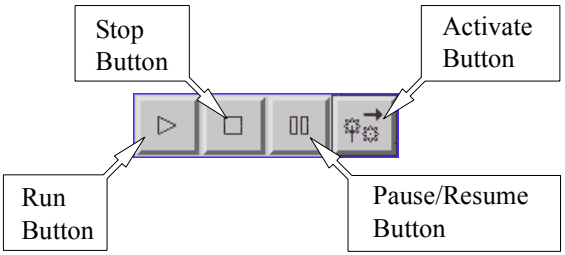


Figure 3-14 The experiment control tools.

5. **Open the Acquisition Parameters dialog box.** Click the Parameter button in the tool bar to open the dialog box. (See Figure 3-11.)

If the Calibrated button is not green (activated) you need to load a proper calibration file. Consult the local facility manager or refer to Section 7.2 to find out how to load the calibration file.

6. **Check the Signal Channel parameters.** Click the Signal Channel tab. The signal channel parameters are further split into four tabs. Click the Detection tab. Edit the parameters in the dialog box so that they match those shown in Figure 3-15. The other tabs in the Signal Channel tab are for advanced options and their default settings are OK for this experiment.

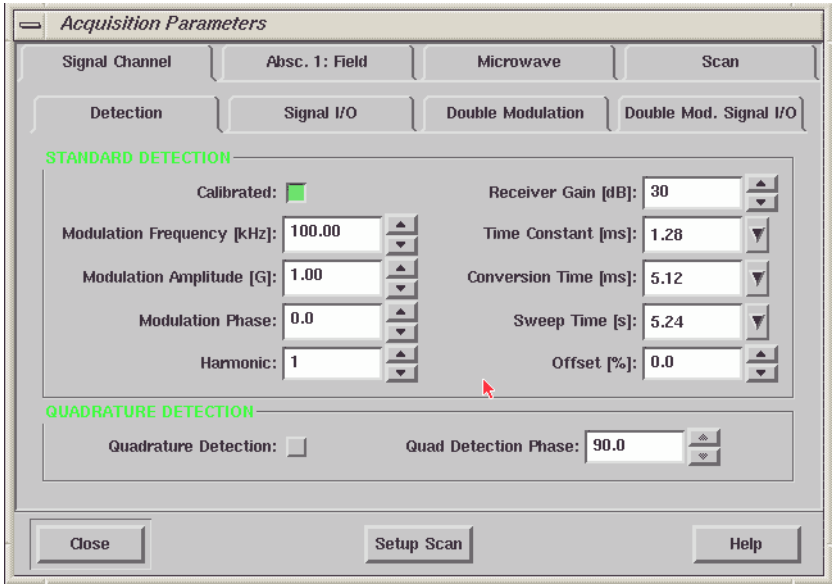


Figure 3-15 The signal channel parameters.

7. **Check the Field parameters.** Click the Absc.1: Field tab. (See Figure 3-16.) Edit the parameters in the dialog box so that they match those shown in Figure 3-16.

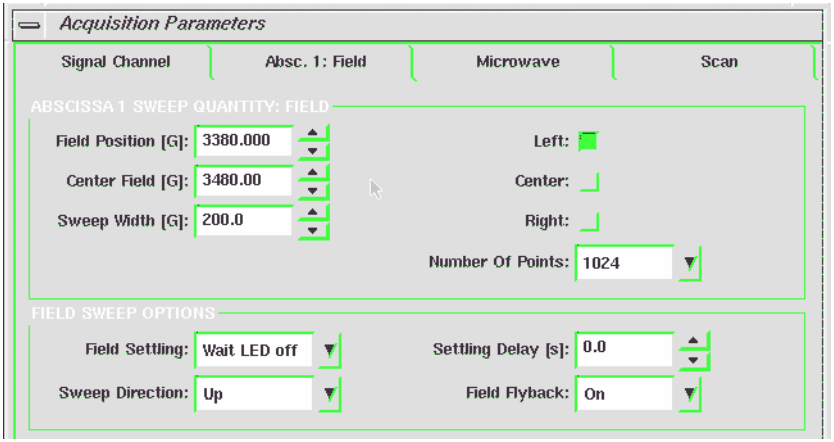


Figure 3-16 The magnetic field parameters.

8. **Check the Microwave parameters.** Click the Microwave tab. (See Figure 3-17.) Set the Attenuation to 30.0 dB.

Figure 3-17 The microwave parameters.

9. **Check the Scan parameters.** Click the Scan tab. (See Figure 3-18.) Edit the parameters in the dialog box so that they match those shown in Figure 3-18. After you have finished all the above parameter settings click the Close button.

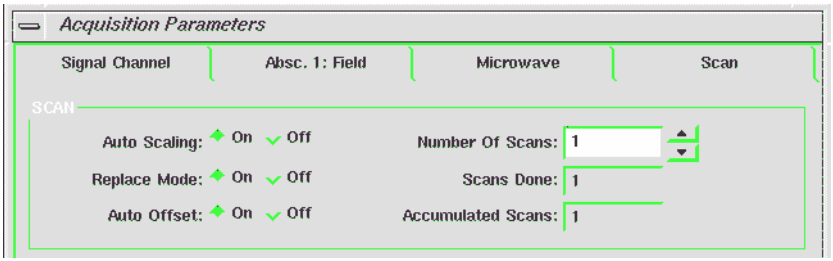


Figure 3-18 The scan parameters.

10. **Acquire a spectrum.** Click the RUN button to start an acquisition. (See Figure 3-19.) If you have a spectrum similar to the one in Figure 3-20, congratulations! You have successfully acquired an EPR spectrum.

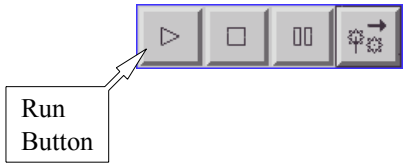


Figure 3-19 The Run button.

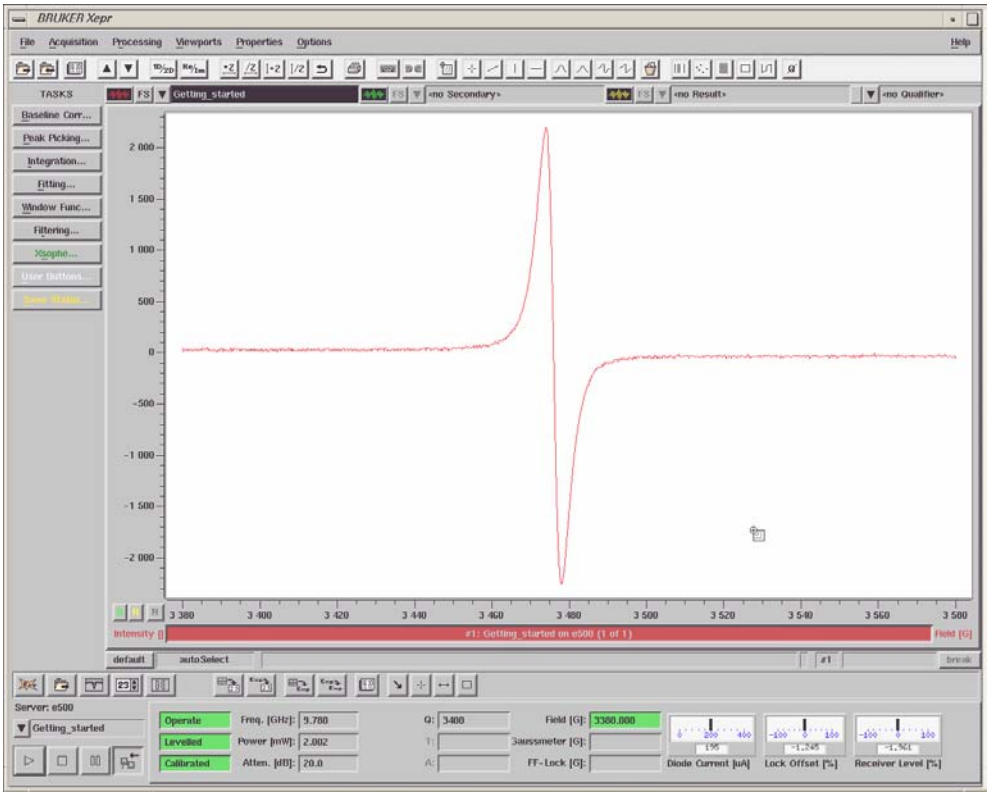


Figure 3-20 An EPR signal of strong pitch.

11. **Center the spectrum.** You may notice that the EPR line is not nicely centered. The next step will help you center your spectrum. To interactively set the center field, click Acquisition > Tools, and then the Center Tool in the menu bar. (See Figure 3-21.)

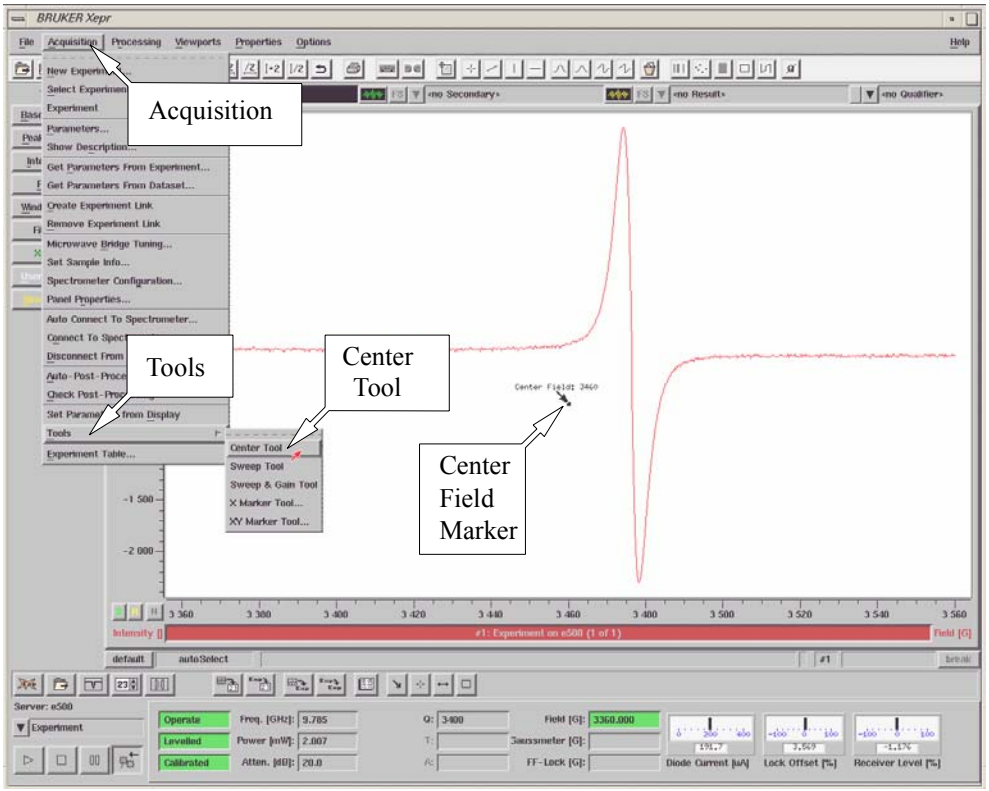


Figure 3-21 The Center Tool.

A center marker in the viewport appears. Drag the marker and place it where you would like the center field to be. (See Figure 3-22.)

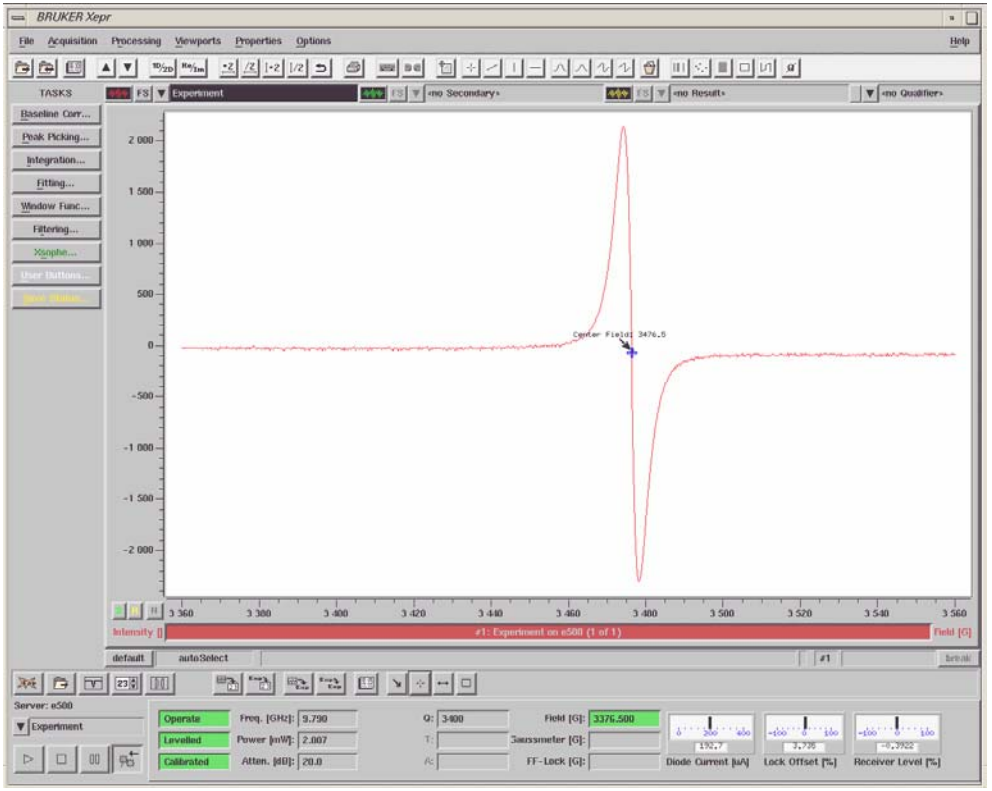


Figure 3-22 Placing the center marker.

This action replaces the center field value with the magnetic field position of the marker. To acquire the spectrum with the new center field, click the RUN button in the monitoring panel. The newly acquired spectrum will then be nicely centered. (See Figure 3-23.)

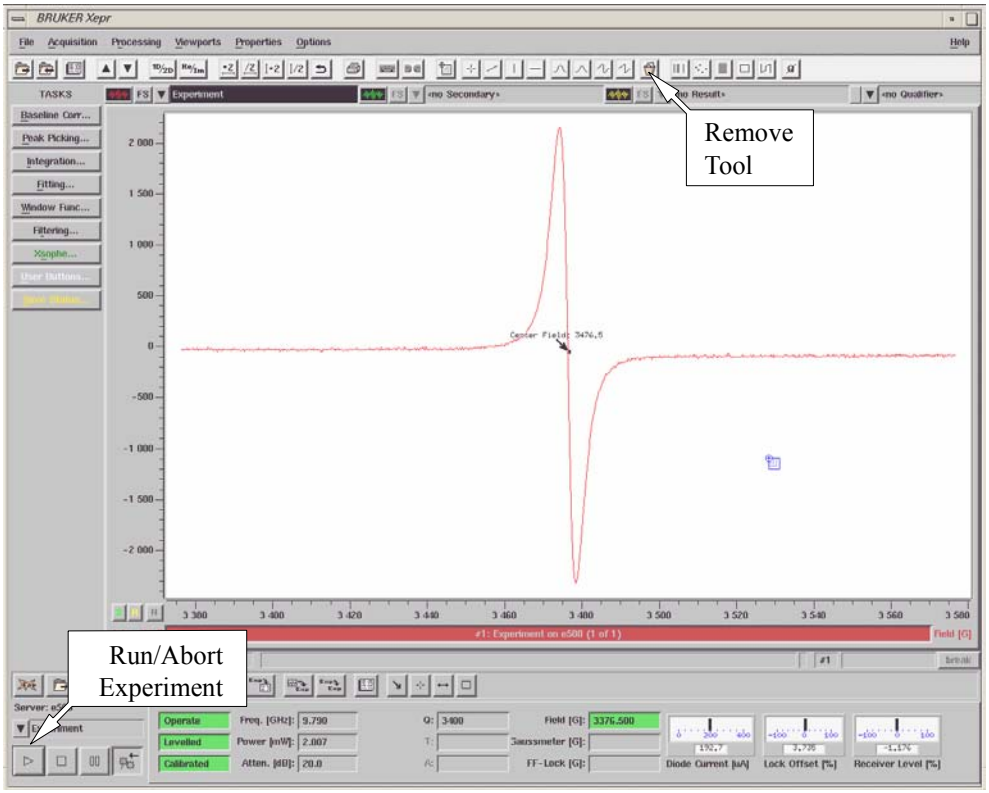


Figure 3-23 The centered spectrum.

If the tool cannot be removed in an active viewport it may be because the tool is inactive. Click the tool to activate it and then click the Remove Tool button to remove it.

12. **Remove the center marker.** You may remove the center marker by clicking the Remove Tool button in the tool bar. (See Figure 3-23.) The Remove Tool function removes the current active tool.

Storing and Saving the Spectrum 3.4

After you have acquired your spectrum, you may wish to save or store it. What is the difference between these two commands? The Store command stores the spectrum temporarily in memory which means it is lost when you exit Xepr. The Save command saves a permanent data file on your hard disk for future reference. Typically, the Store command is used to store intermediate results and the Save command is used to permanently save the results of your data processing.

1. **Store your spectrum.** Click the menu button in the viewport. Click Store in the drop-down menu. (See Figure 3-24.) The Store dialog box allows you to enter a descriptive title for the dataset. The presently active spectrum is stored in memory when you click Store.

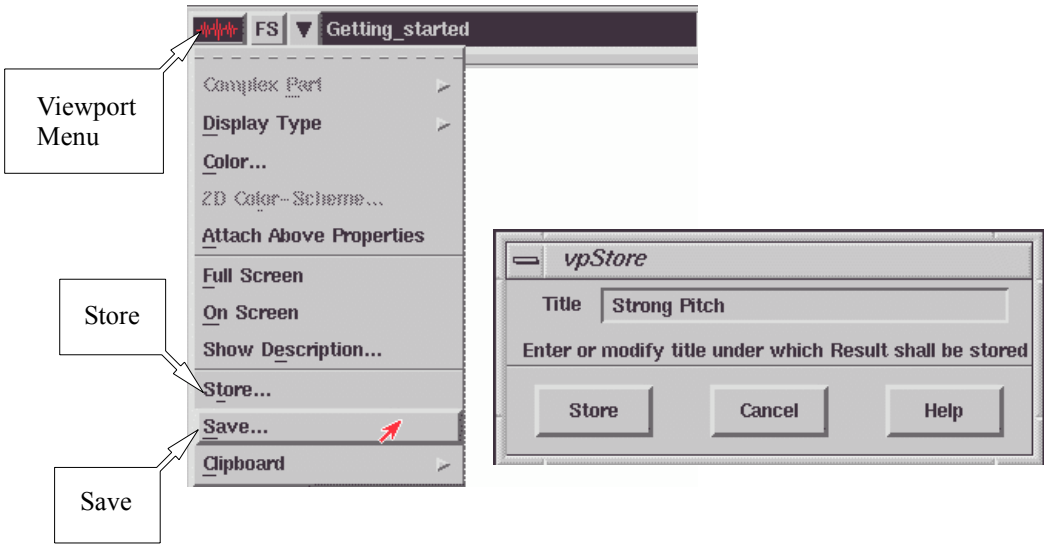


Figure 3-24 The Save, Store buttons and Store dialog box.

Do not save data in the ../xeprFiles/Data/sharedData directory. This is a protected directory and your data will not be saved. You will receive an error message.

Some characters such as space, *, ?, / are not valid for file names.

2. **Save your spectrum.** Click the menu button in the viewport. Click Save in the drop-down menu. (See Figure 3-25.) Enter a descriptive title for the dataset in the Title box. The Save dialog box lets you enter a file-name and destination directory. (See Figure 3-25.) To select the desired directory, click the appropriate paths under Group. Clicking on .. brings you to the parent directory. Enter the file name in the File box. Clicking OK saves the presently active spectrum on the hard disk. Note that the spectrum is also stored in memory when saved.

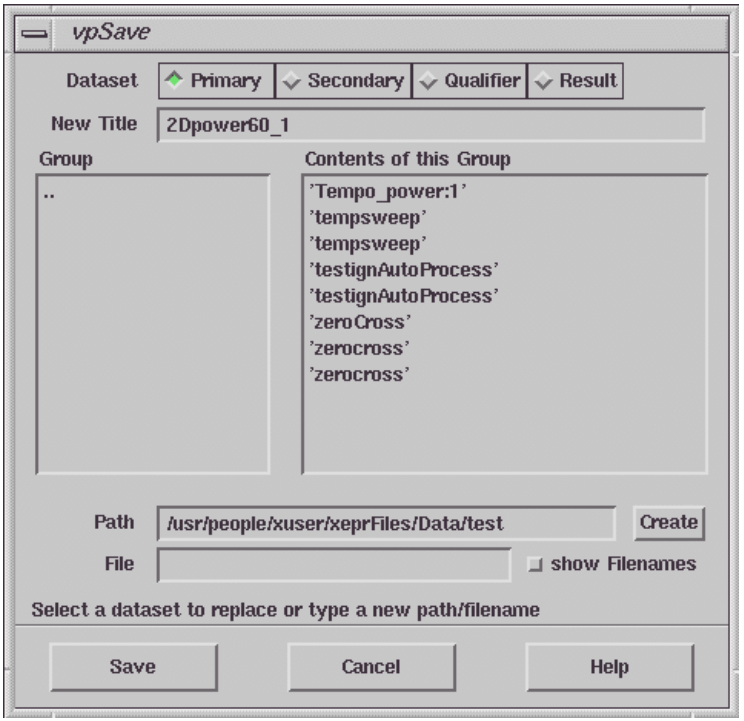


Figure 3-25 The Save dialog box.

If the chosen filename is already used for another file in the same directory, a warning box gives you the opportunity to decide whether to overwrite the existing file with the present spectrum. (See Figure 3-26.) Clicking No cancels the save process and allows you to select another name or directory.

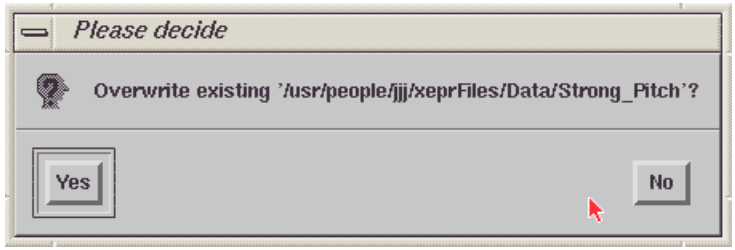


Figure 3-26 The warning dialog box for overwriting files.

Printing the Spectrum 3.5

Is your printer on line?

1. **Prepare to print the spectrum.** Turn the printer on. Make sure that the paper is loaded. Refer to your printer documentation for details. Make sure the printer is properly set up. (See Sections 15.8 or 16.8 of the Elexsys E 500 User's Manual: Advanced Operations.)

2. **Print the spectrum.** Click File in the menu bar and then Print. A dialog box will then appear in which you select desired options and print your spectrum. (See Figure 3-27.)

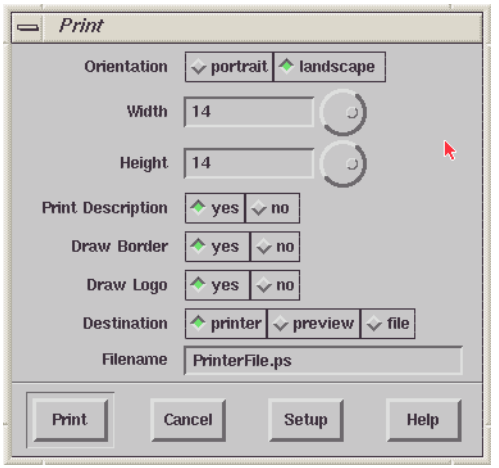


Figure 3-27 The Print dialog box.

If you experience problems printing, consult the local facility manager or refer to See Sections 15.8 or 16.8 of the Elexsys E 500 User's Manual: Advanced Operations. to find out how to setup a printer.

Select the options shown in the above figure. Clicking Print starts the document printing and closes the dialog box. The output from the printer will look similar to Figure 3-28.

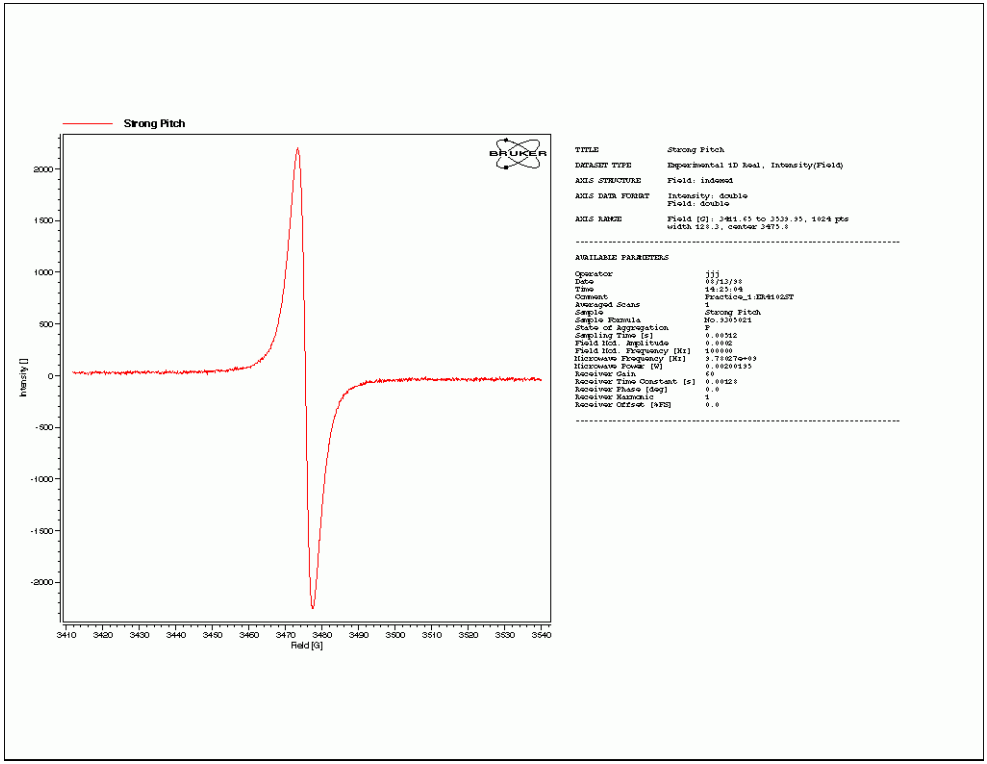


Figure 3-28 Typical output from the printer.

Turning the Spectrometer Off 3.6

1. **Open the Microwave Bridge Tuning dialog box.** If this window is not already open, click its button in the tool bar. The Microwave Bridge Tuning dialog box will then appear. (See Figure 3-29.)

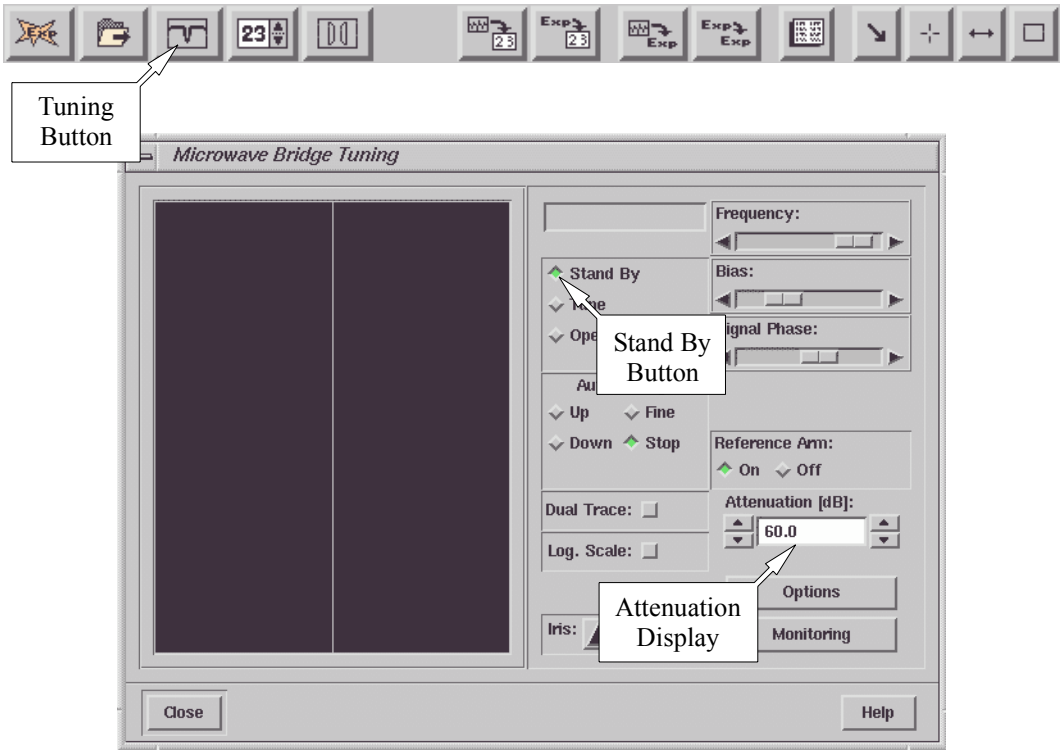


Figure 3-29 The Microwave Bridge Tuning dialog box.

It is important to exit the software in an orderly manner (*i.e.* don't just turn the computer off before disconnecting the instrument and exiting the software) because many instrument parameters are set to specific values for a safe shut-down of the spec-

Exit the software first before logging out.

2. **Switch the microwave bridge to Stand By.** Click the Stand By button in the dialog box to change to Stand By. (See Figure 3-29.) The microwave attenuator will be automatically set to 60 dB.

3. **Close the Microwave Bridge Control dialog box.** Click the Close button in the dialog box. The Microwave Bridge Tuning dialog box will then disappear.

4. **Remove the sample from the cavity.** See Section 3.2 for details on how to do this.

5. **Cover the upper collet or insert a solid collet plug.**

6. **Disconnect from the spectrometer.** Click the Acquisition menu bar and then click Disconnect From Spectrometer. The monitoring panel will disappear.

7. **Exit the Xepr program.** Click the File menu bar and then click Exit. You will be asked if you wish to save the changes.

8. **Log Out**. Click the right mouse button (for SGI O2 workstations) or click on the Gnome icon on the bottom of the screen (for the Linux workstations) and click Log Out in the drop-down menu. You need to confirm this by clicking Yes or select the proper radio button and click OK.

9. **Turn off the heat exchanger and magnet power supply. (Instructions for Small Power Supplies.)** Follow this step if your power supply looks like the power supply in Figure 3-30. To turn the power supply off, push the POWER ON/OFF button. Turn the heat exchanger off by pressing the power switch. The location of the Power ON/OFF button may vary depending on your heat exchanger. Go to Step 11.

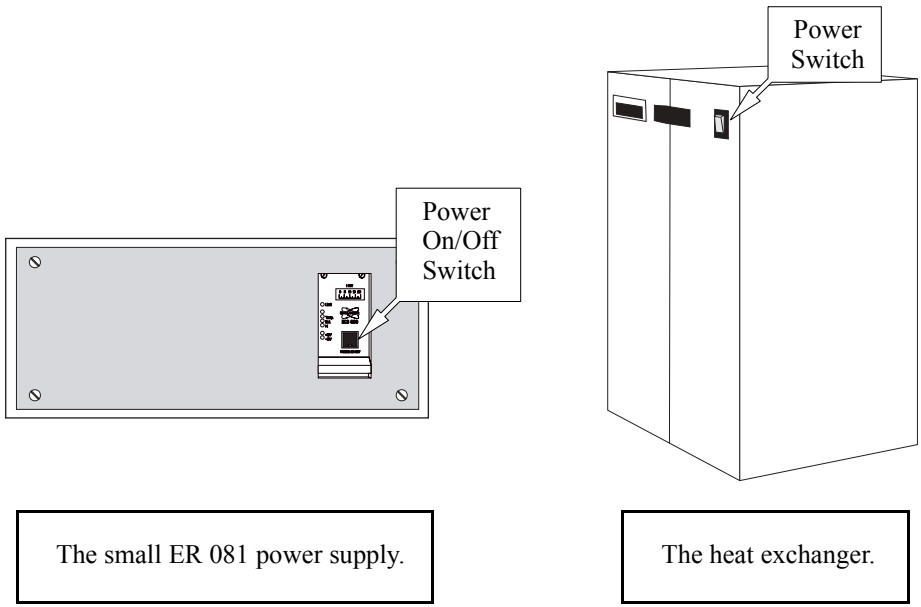
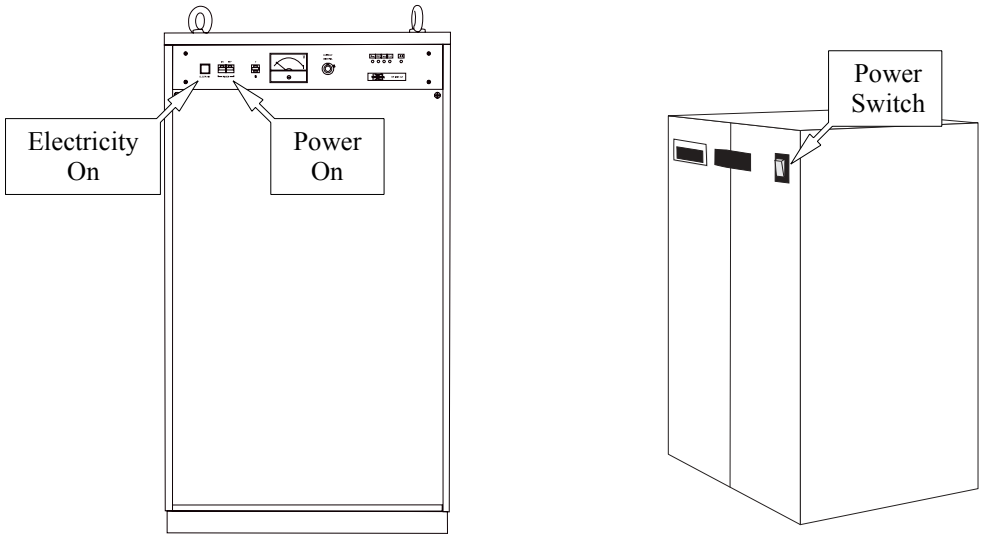


Figure 3-30 The small ER 081 power supply and the heat exchanger.

10. **Turn off the heat exchanger and magnet power supply. (Instructions for Large Power Supplies)** Follow this step if your power supply looks like the power supply in Figure 3-31. On systems with large power supplies, you need to first press the Power OFF button and then the ELECTR. ON button. Pressing the POWER OFF button also turns the heat exchanger off.



The large ER 082/083/085/086 power supplies.

The heat exchanger.

Figure 3-31 The large power supply and the heat exchanger.

11. **Turn off the tap water for cooling.** There are usually two valves, one for the supply and one for the return (or drain). Consult the local instrument or facilities manager if you are not sure where the valves are.

12. **Turn off the power for the console.** The power switch (red button) for the console is located in the upper left front corner of the console. (See Figure 3-32.)

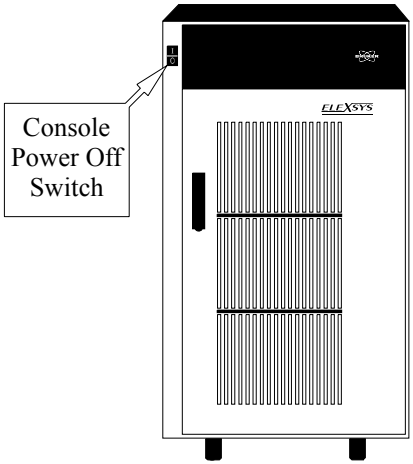


Figure 3-32 The location of the console power switch.

13. **Turn off the power for the system. (Optional)** How you do this depends on how the electric power was hooked up when the spectrometer was installed. Most likely you will deactivate the switch on the breaker box for the spectrometer. Breaker boxes are usually mounted on the wall. Consult the local instrument or facilities manager if you are not sure where the breaker box is.

To reduce wear and tear on the hardware it is best to leave the workstation on unless it is not going to be used for a long time or there will be a power outage. Consult the workstation documentation or the SGI manual to learn how to turn off the workstation.

If you have many power outages or electrical storms, it is a very good idea to shut off the power to the spectrometer.

Essential Concepts of Xepr 4

We shall explore some of the most fundamental Xepr operations in this chapter. You will need these operations for both acquiring and processing data. Therefore, we highly recommend reading this chapter before exploring the following two chapters on these two topics. This is meant to be a tutorial and not a reference for the Xepr software. For detailed explanations, please refer to the Xepr User's Manual.

Basic Components of an Xepr Window 4.1

Figure 4-1 shows the basic components of an Xepr window. It has the following basic components:

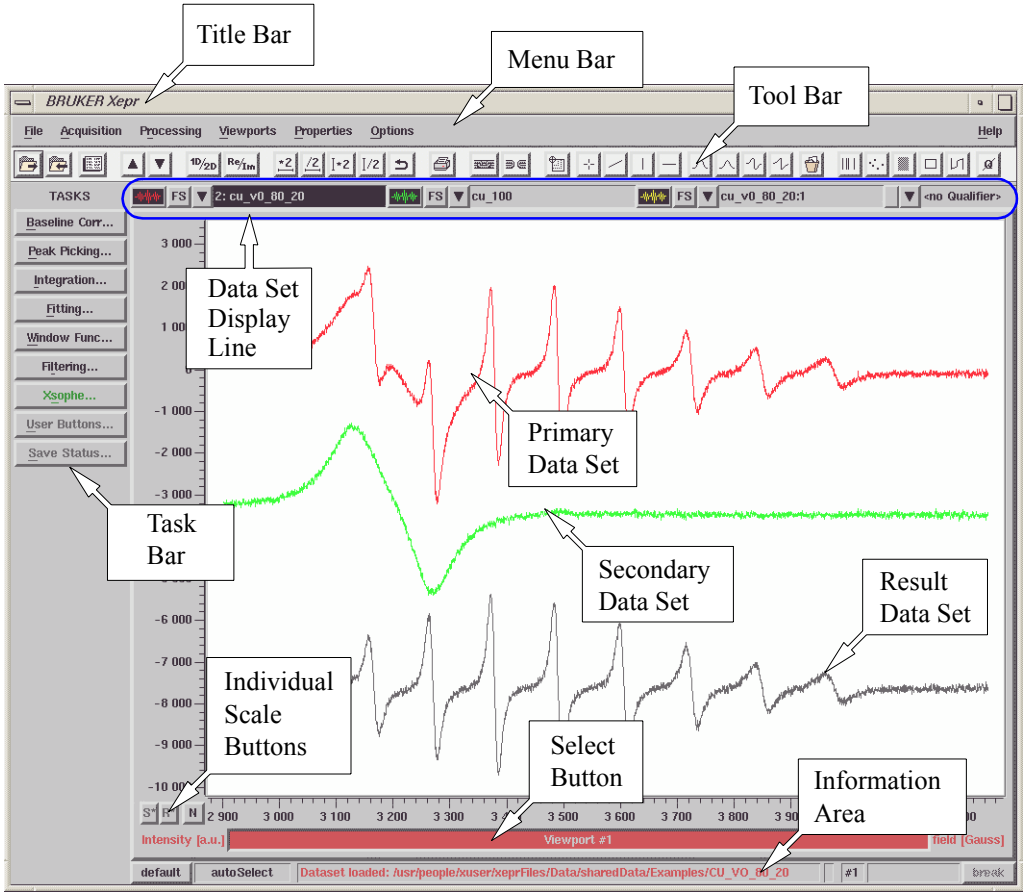


Figure 4-1 The basic components of an Xepr window.

Title Bar The title bar displays the title of the application, Bruker Xepr.

Menu Bar The menu bar groups several menus together. The File menu deals with input and output of files. The Acquisition menu lets you configure the spectrometer and setup data acquisitions. The Processing menu groups many data processing routines. The Viewports menu allows you to set various formats to display your data. The Properties menu sets up the Xepr window's features. In the Options menu you can create additional features such as macros and tools and view the history of the executed commands. Under the Help menu you can find a software manual for Xepr, a searchable data base for instructions, and information about the Xepr software. Under each menu button you will find a dotted line on top of the drop-down menu. Clicking on the dotted line opens a floating frame which contains all the submenu items. It is very useful when you need to access that menu item frequently.

Tool Bar Buttons for frequently used commands are grouped here for your convenience.

Tasks Bar Tasks are macros which organize and streamline the individual processing steps required to perform common operations such as Baseline Correction, Integration, and Peak Picking. These routines are group together in the Task Bar.

Viewports The window in the center is called the Viewport. It displays your data. We will discuss viewports in the next section.

Viewports 4.2

The viewport is the central feature of the Xepr software. All datasets are presented and processed in a viewport. When you start the Xepr software, a single viewport appears by default. A viewport can show 1D or 2D datasets in the display area with a multitude of options. (See Section 4.2.1.) You can control which data sets are displayed and their options with the dataset display line. (See Section 4.2.2.) When you have more than one spectrum in the viewport, they can be individual scaled by using the individual scale buttons. (See Section 4.2.4.)

Display Area 4.2.1

The center part of a viewport is the display area. By default, the background is black. There are four types of data sets that can be displayed:

Primary If you only have one data set, it is normally in the Primary data set. This is the spectrum which you process or analyze.

Result After you process the data set in Primary, the results of your operation are temporarily stored in the Result data set. The Result and Primary data sets appear simultaneously in the Viewport. They can be distinguished from one another by their color.

Secondary Some operations require two data sets, such as subtracting two spectra from one another. In this case, the second spectrum should be loaded into the Secondary data set. Like the Result and Primary data sets, it is identified in the display area by its color.

Qualifier The qualifier allows you to define or qualify the region of a data set which is affected when you perform an operation. By default, the whole data set is qualified.

Data Set Display Line 4.2.2

Below the tool bar is the Data Set Display Line. It is separated into four sections corresponding to the data set which it controls. Most of the sections consists of four elements which are described below.

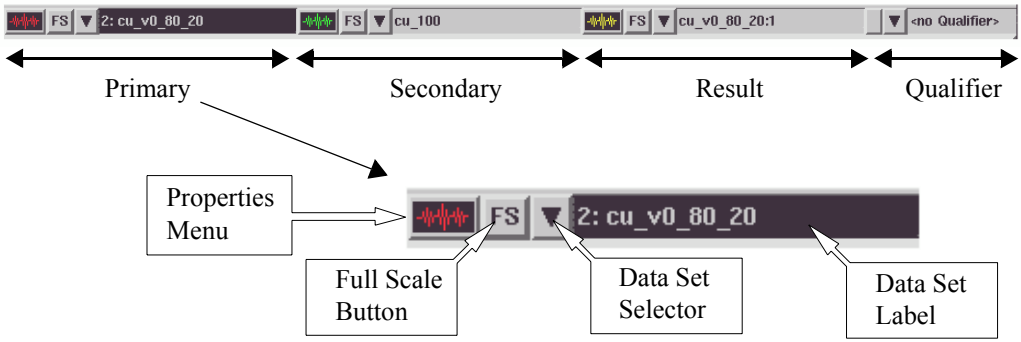


Figure 4-2 The Data Set Display Line and its elements.

Data Set Label

The Data Set Label indicates which spectrum is selected, for example cu_vO_80_20 in Figure 4-2 is selected as the Primary Data Set. The inverse video highlighting indicates that the Primary Data Set is active, *i.e.* that it is the input for any data processing. For example, if we wished to multiply the Secondary Data Set by three, we would first click the Secondary Data Set Label to make it active and then perform a multiplication. By default, the Primary Data Set is active. Each type of data set (Primary, Secondary ...) has its own Data Set Label.

Data Set Selector

In order to select a data set, click the small triangle next to the Data Set Label. A menu will drop down listing all of the spectra which are currently loaded in Xepr. (See Figure 4-3.) To select the spectrum to display in the viewport, click the desired spectrum. You can also choose not to show any spectrum in the dataset by clicking <no Primary> (or <no Secondary>...) A particularly useful feature is <Result>. When you click it, it loads the latest Result Data Set.

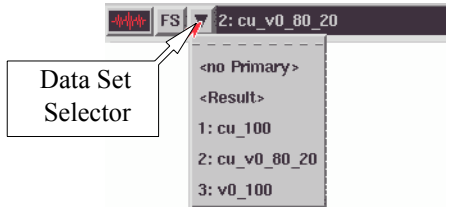


Figure 4-3 Selecting a dataset to display.

Full Scale Button

To the left of the Data Set Selector is a button labeled FS. (See Figure 4-3.) When clicked, it resizes the spectrum so that it completely fills the viewport.

Properties Menu

The Properties menu allows you to choose the Display Type. (See Figure 4-4.) 1D datasets can be presented as points, line, histogram, or numeric. For 2D datasets you can choose from density, contour, dot plot, transparent, and hidden lines.

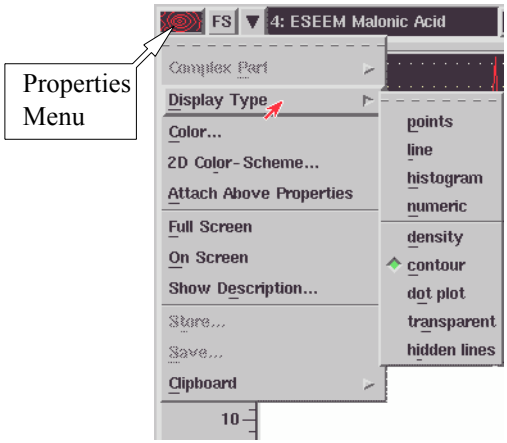


Figure 4-4 Choices for the display type of a dataset.

You can choose the color of the display to distinguish Primary, Secondary, and Result datasets. (See Figure 4-5.)

Figure 4-5 Choosing the dataset color.

Show Description allows you to view the parameters of the dataset you select.

You can store or save the currently displayed dataset. Store will temporally save the data in the memory. When you quit Xepr the data will be lost. The Save function will write the data onto the hard disk and make the data permanent.

The Result Section 4.2.3

The Result section is similar in structure to the Primary section. In the property menu most of the submenus are the same except that there is Show History to allow you to view the data processing history. (See Figure 4-6.) The FS button is the same.

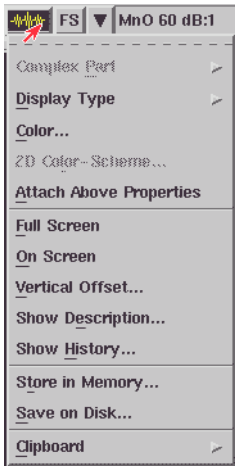


Figure 4-6 The properties menu of the Result section.

The select menu is a little different The menu lists the results of each data set processing operation. It has a <no Result> button to clear the Result from the viewport.

Sometimes when much data is processed the huge amount of data could overload the memory and slow down the computer. The Clear List button removes all the temporary result data.

(See Figure 4-7.) Store or Save the useful results and use Clear List frequently when you process data intensively.

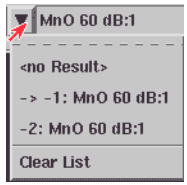


Figure 4-7 The selection menu of the Result section.

Individual Scale Buttons 4.2.4

You can set different scales for the Primary, Secondary, and Result datasets by clicking these buttons. (See Figure 4-1.) Clicking S adjusts the scale for the Secondary dataset only. Clicking R allows you to independently adjust the Result dataset scale. A * will appear next to S or R when the Secondary or Result dataset scales are different. Clicking N brings them back to the same scale as the Primary dataset.

Multiple Viewports 4.3

You can open more than one viewport to view different datasets or display the same dataset in different ways.

Opening a New Viewport 4.3.1

To open a new viewport click the Viewports button as shown in Figure 4-8. Click New 1D Viewport or New 2D Viewport in the drop-down menu and then select either the new viewport to be horizontally or vertically divided from the original viewport. A new Viewport will be created and set currently active.

Figure 4-8 Creating a new viewport.

Controlling the Viewports 4.3.2

The viewports share the same Dataset Display line to control the viewport. The Dataset Display line only controls the currently active Viewport. To activate a viewport, simply click the Select button and the color of that viewport Select button will change to red indicating that viewport is activated. (See Figure 4-1.)

Linked Viewports 4.3.3

By default each newly created viewport is “linked” to the viewport from which it was created. “Linked” means the viewports show the same dataset but in different style or representation. Figure 4-9 shows four viewports that have been created and linked together. All four viewports show the same 2D EPR spectra from a ruby crystal rotated along the **a** axis. Viewport #1 shows an individual slice of the dataset. Viewport #2 shows a 2D contour plot of the ruby crystal “road map”. Viewport #3 shows the density plot of the 2D spectra. Viewport #4 displays a small portion of Viewport #1 to show details of the spectrum. You may notice the dashed line rectangles: each rectangle indicates the display range of the other linked viewports. The number in the upper left corner identifies the linked viewport.

If you want to display different datasets in different viewports you can unlink the viewports. Click the select button to activate the viewport you want to unlink. Select Unlink Viewport under the Viewports drop-down menu or click the Unlink button in the tool bar. Select the dataset you want to display. Activate and select another viewport and load another dataset to display. You can have different datasets showing in different viewports.

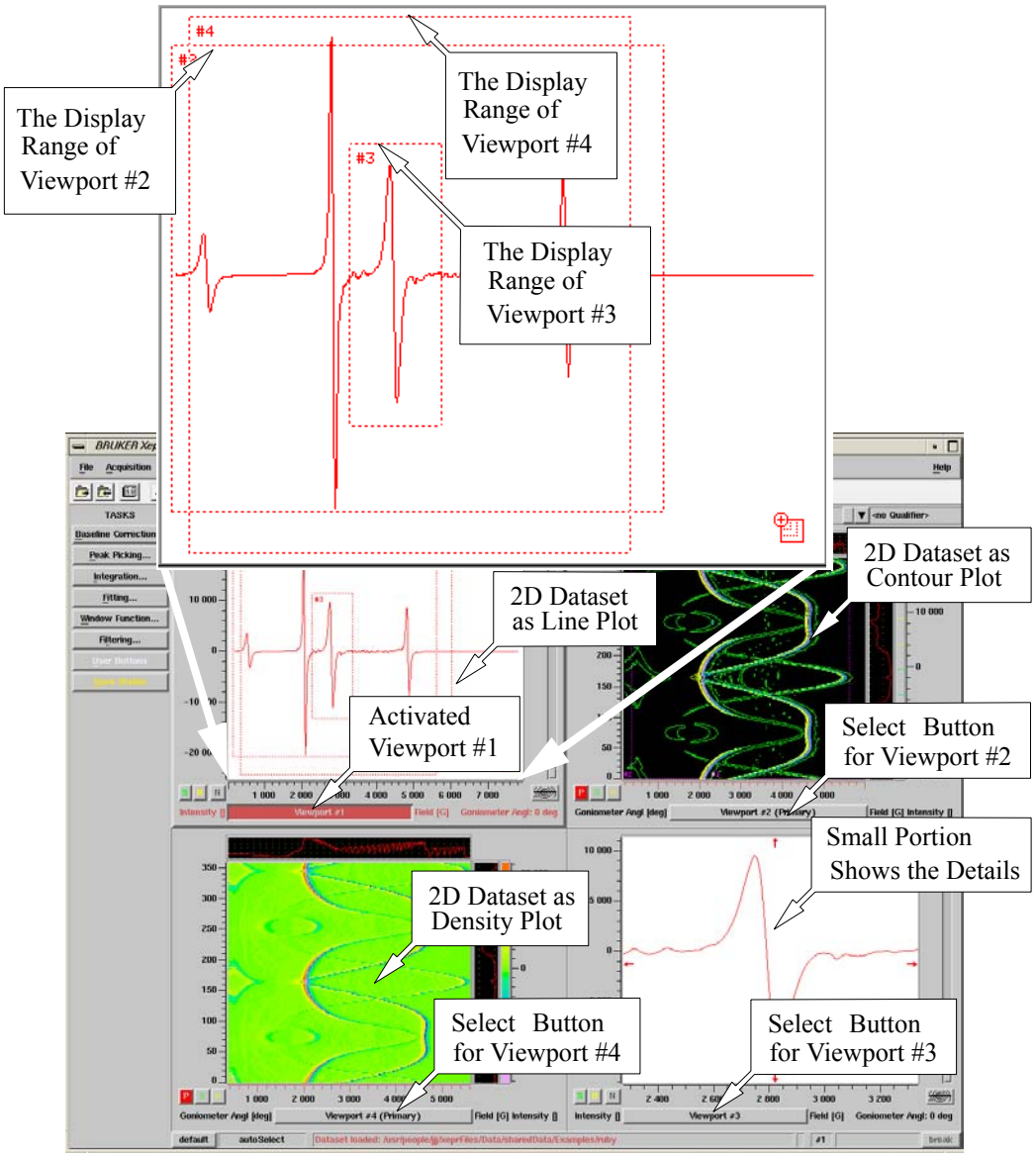


Figure 4-9 Using linked multiple viewports to view simultaneously the same dataset in a variety of different ways.

Tools 4.4

The tool bar lies underneath the menu bar. (See Figure 4-1.) It contains 31 commonly used tools arranged in eight groups. In order from left to right, we list the name and the function of each tool button.

Data Set Management 4.4.1

Load Dataset Clicking this button opens a dialog box for choosing the dataset (and its path) you want to load into Xepr. (See Figure 4-10.)

Clicking the two dots (..) in Group will bring you up one directory level.

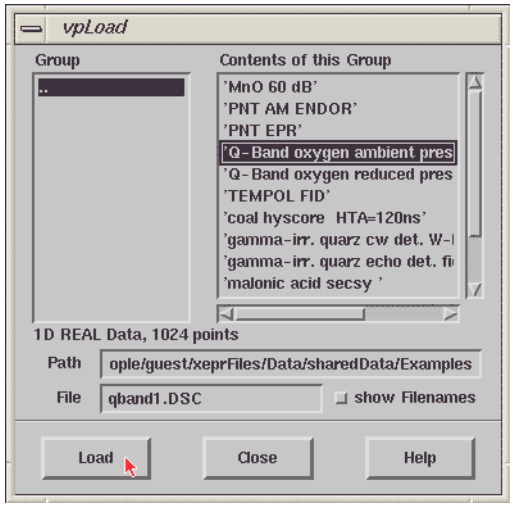


Figure 4-10 Loading datasets.

Save Dataset Clicking this button opens the save file dialog box so that you can save the dataset onto the hard drive. On top, you can select the source (*e.g.* Primary, Secondary, ...) as well as enter a title for the dataset. Below, you can choose the path and filename for the saved dataset. (See Figure 4-11.)

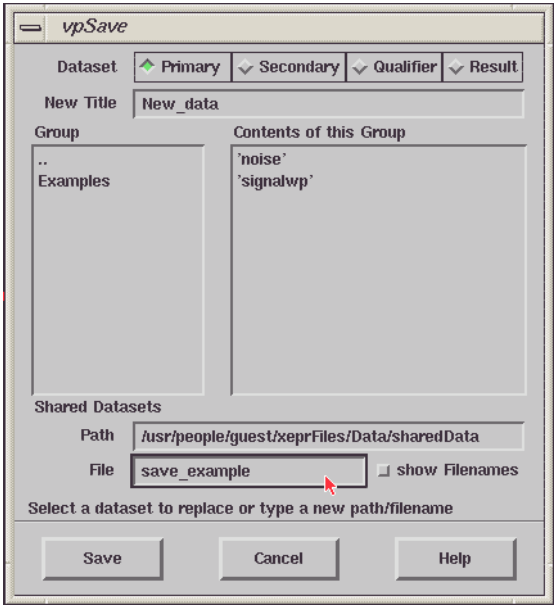


Figure 4-11 Saving a dataset.

Dataset Table This dataset table lists all the datasets loaded or currently stored in memory.

Dataset Selection 4.4.2

Previous Dataset Clicking this button displays the dataset listed before the current dataset in the dataset table.

Next Dataset Clicking this button displays the dataset listed after the current dataset in the dataset table.

Display Toggling 4.4.3

Toggle Dimension Clicking this button toggles the current active viewport between 1D and 2D formats.

Toggle Complex Part Clicking this button toggles the current display between the real and imaginary part of the dataset if the dataset is a complex dataset.

Zooming 4.4.4

X-Range ∗ 2 This button expands the X-axis by a factor of 2.

X-Range / 2 This button shrinks the X-axis by a factor of 2.

Y-Range * 2 This button expands the Y-axis by a factor of 2.

Y-Range / 2 This button shrinks the Y-axis by a factor of 2.

Previous Range Clicking this button will bring you back to the previous range.

Printing 4.4.5

Print Viewport Click this button to print the spectra in the currently active viewport.

Viewport Linking 4.4.6

Link Viewport Clicking this button opens a dialog box asking you which viewport you want to link to or warning you that the current viewport is already linked.

Unlink Viewport Clicking this button unlinks the current viewport or tells you the current viewport is unlinked already.

Graphics and Measurement Tools 4.4.7

Expand With this button selected you can select regions to zoom or expand with the mouse.

Dot Marker A point marker will appear in the current viewport when you click this button. You can use mouse to move it to where you want.

Free Line This marker provides you with a straight line of arbitrary angle and length. Both ends can be moved by dragging with the mouse.

Vertical Line This tool provides you with a vertical line. You can move it to any place and stretch it to any length with the mouse.

Horizontal Line This tool is similar to the vertical line except that it is horizontal.

Gaussian This tool provides you with a gaussian line shape. You can change its height and width by dragging its handles.

Lorentzian This tool is similar to the gaussian line shape except that it is a lorentzian line shape.

Derivative Gaussian This tool provides you with a first derivative gaussian line shape. You can change the height and width with the mouse.

Derivative Lorentzian This tool is similar to the derivative gaussian tool except that it is a first derivative lorentzian line shape.

Remove Tool If you use the mouse to select the marker and then click this remove tool button the marker will disappear.

Qualifiers 4.4.8

The last group consists of six qualifier buttons. The various types of qualifiers allow you to select certain parts of the spectrum for processing. When the qualifier is active, one or several handles appear for changing the size of the qualifier. Clicking on the qualifier will activate that qualifier.

Position Qualifier This qualifier provides you with a vertical line and allows you to select an x-axis position for processing. You can drag the qualifier to the exact position you want to select.

Point Qualifier You can select a point for processing with this tool. Using the mouse, you can precisely move the qualifier to the desired point.

Region Qualifier Using this qualifier you can select a region of the x-axis for processing. Grabbing the handles on each side, you can move the region to cover the part of dataset you want to process.

Area Qualifier This tool provides you with a rectangle to cover the area you wish to process. Dragging each corner can change the size of the square.

Integral Qualifier This tool consists of two vertical lines and a free line. The vertical lines indicate the starting and ending points respectively. The free line indicates the offset and the slope. It is designed for integration.

No Qualifier This tool removes the qualifier.

Mouse Functions 4.5

Depending on which buttons you pressed, the mouse performs many different functions such as resizing, moving, and measuring. By default, the mouse is in auto select mode and will change its function and mouse cursor according to the buttons pressed and location of the cursor. You can find the status of the display function in the info area at the left bottom corner of the viewport. The following examples illustrate the various mouse functions.

The Cursors 4.5.1

The mouse cursor indicates the current mouse function in Xepr.

Expand When this cursor is present you can click the left mouse button on the position you want to expand and drag the mouse to the place you want to end. A rectangle will show up indicating the area you want to expand. The area covered by the square will expand to fill the screen of the viewport.

Zoom This symbol indicates that the zooming function is activated. Clicking with the right mouse button in the display area of the viewport displays this symbol. Dragging the cursor upwards or downwards vertically zooms in or out the area you point to. Dragging towards the right or left horizontally zooms in or out the area you point to. Dragging at an arbitrary angle will zoom both horizontally and vertically at the same time. If you click the right mouse button in the x- or y-axis area, you zoom either horizontally or vertically.

Moving Clicking on the middle mouse button changes the cursor to this symbol. The spectrum will move in the direction you drag the mouse. When you click the middle mouse button in the axis area you only move the spectrum either up and down or to the left and right.

Read Out With this mouse function you can read out the X-, Y-, and other values of the point where the mouse is in the spectrum. See the next section for details.

Reading Out Coordinates 4.5.2

Move the mouse cursor close to the spectrum curve. The mouse cursor will change from the Expand to the Read Out cursor. Left click on a point of the spectrum: the coordinates of the cursor are displayed next to the cursor. The field value, intensity, and the g factor value are also displayed inside the Viewport Select Bar if the spectrum is an EPR field sweep spectrum. (See Figure 4-12.)

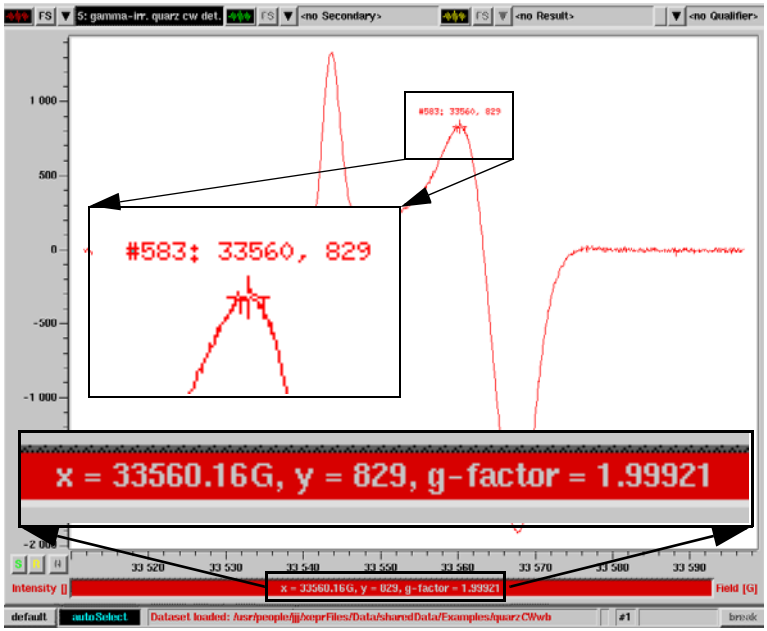


Figure 4-12 Using the Read Out mouse function.

Measuring Distances 4.5.3

Move the mouse cursor to the starting point. Press the left button and the right button simultaneously. Hold the mouse buttons and drag the cursor to the point where you want to end the measurement. The distance between the starting point and the ending points are displayed in the Viewport Select Bar. (See Figure 4-13.)

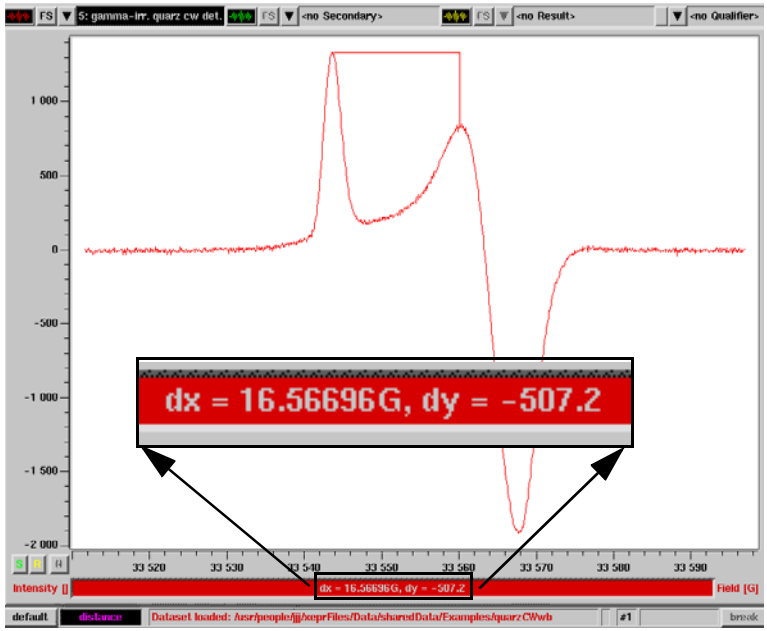


Figure 4-13 Measuring distances.

Zooming Spectra 4.5.4

You can zoom in on a specific area of a spectrum by using the rectangular scaling option. Move the mouse pointer to the display area of the viewport. The mouse pointer will change to the expand cursor. Click the left mouse button and drag the rectangle until it encompasses the region of interest. Release the mouse button and the region of interest will then expand to fill the viewport. (See Figure 4-14.)

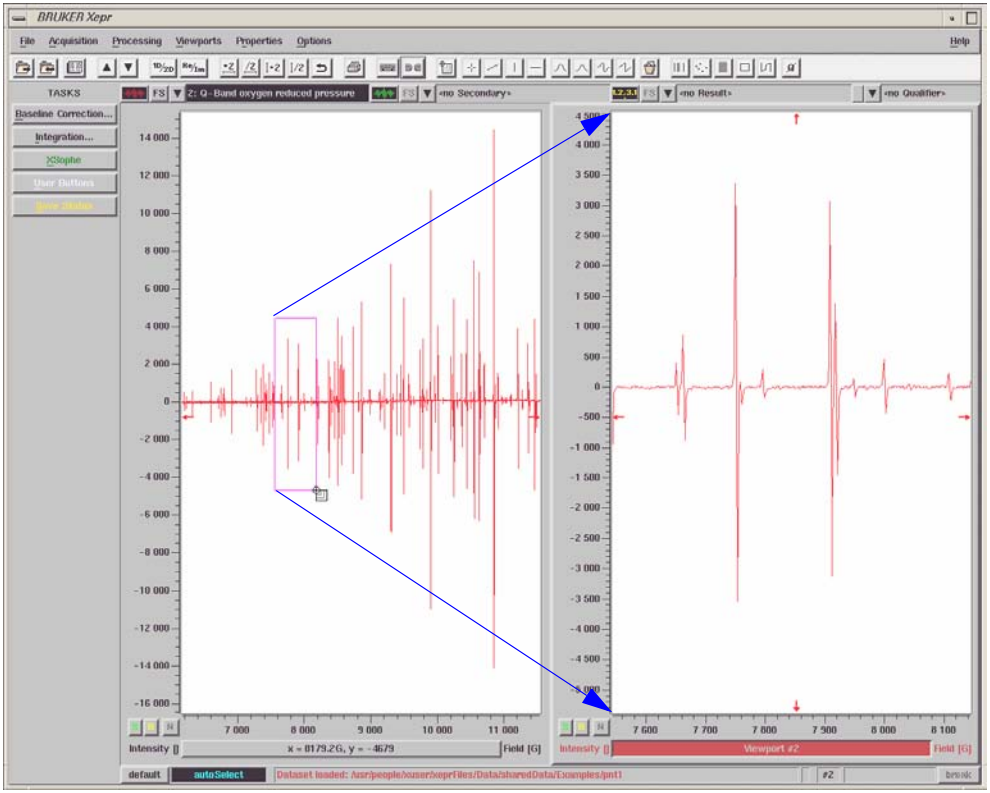


Figure 4-14 Zooming in with the rectangle scaling option.

A second means of zooming not only allows you to zoom in but also to zoom out. Place the mouse pointer in the spectrum area or in the axes area where you want to zoom. Click the right mouse button. The mouse pointer will change into a zoom cursor. Dragging up or right zooms in the spectrum or axis. Dragging down or left zooms out the spectrum or axis. (See Figure 4-15.)

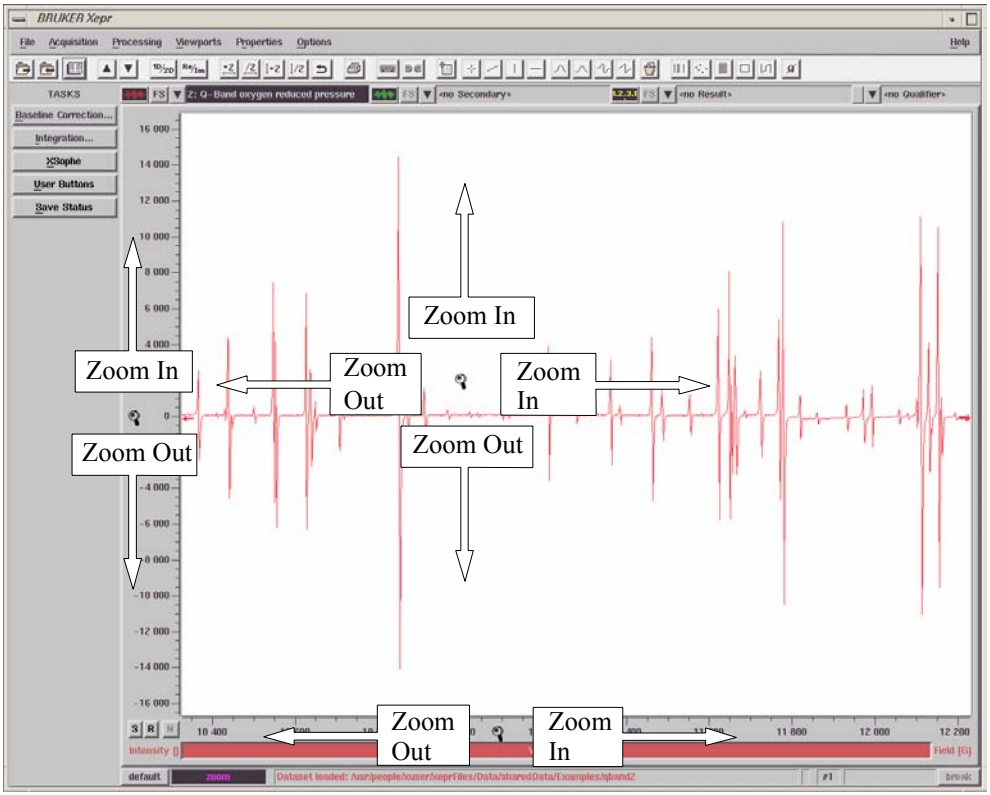


Figure 4-15 Zooming the spectrum.

You can also use the X-Range*2, Y-Range*2, or X-Range/2, Y-Range/2 buttons in the Tool bar to zoom in or out by a factor of 2. The previous range button brings you back to the previous scale. The FS button brings the spectrum back to full scale in case you zoom in too much and get lost.

To display a precisely defined area you can click Properties from the menu bar and then Display Range. (See Figure 4-16.)

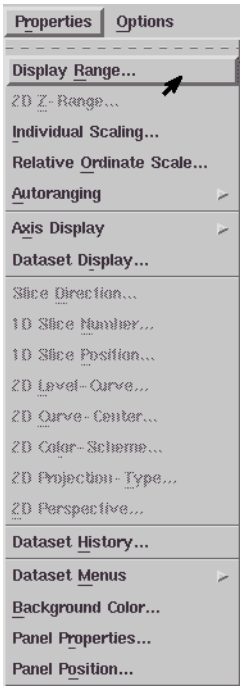


Figure 4-16 Activating the display range function.

A dialog box appears in which you can then select precisely the X- and the Y- range for display. Click the Set button in the dialog box to execute the selected range. (See Figure 4-17.)

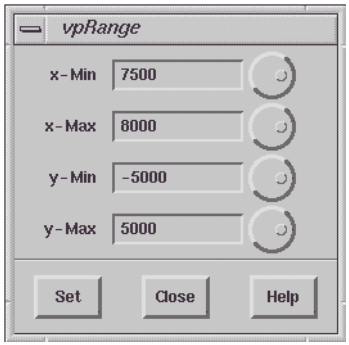


Figure 4-17 The set display range dialog box.

Moving a Spectrum Around 4.5.5

You can move the spectrum around by clicking the middle mouse button while the cursor is in the viewport display area and dragging the spectrum. The cursor changes to a move cursor. You can also place the cursor on either axis area to constrain the movement along one axis. (See Figure 4-18.)

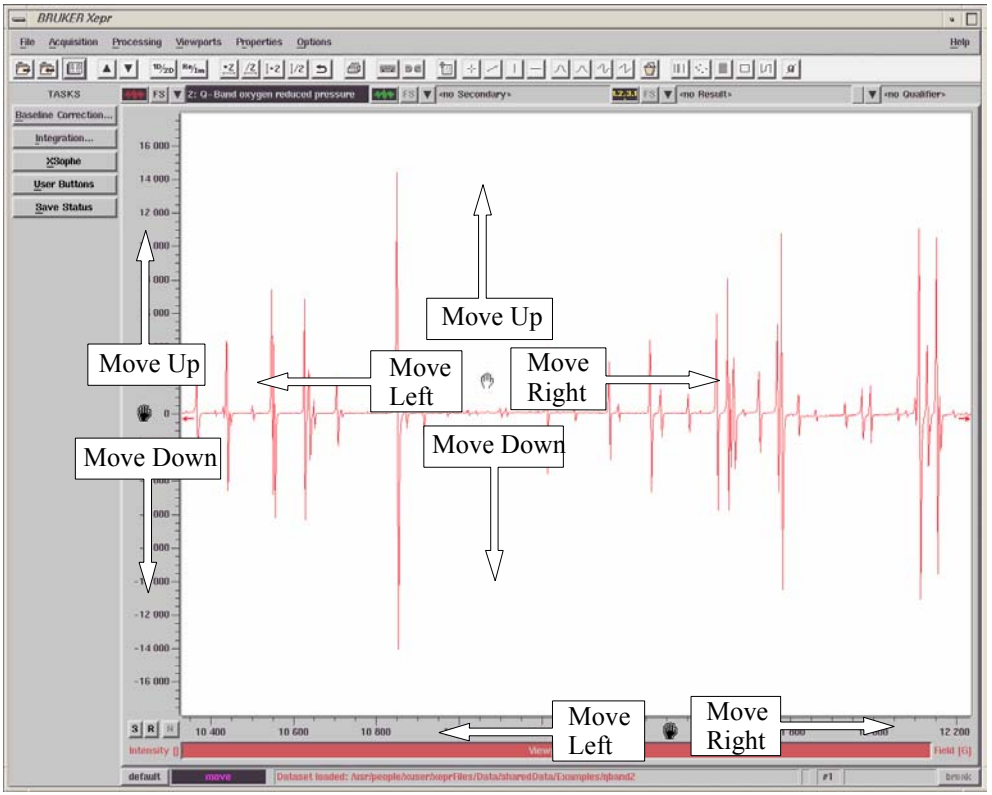


Figure 4-18 Moving the spectrum.

Hot Keys 4.6

Xepr is mouse driven software. However, for those who prefer using the keyboard, there are hot keys for quick access to the commands.

Accessing the Menu with Hot Keys

For all the menu buttons, you can press and hold the Alt key and the key of the underlined letter in that menu button to drop-down the submenu. For example, if you press and hold the Alt key and press "f", the File menu will be pulled down. You can launch the highlighted function by pressing Enter. You can use the arrow keys to move the highlight cursor around and select the function you want to execute. Alternatively you can simply enter the underlined letter of that function in the drop-down menu to launch that function or open a submenu. For example, in the above example you can press "u" to enter the printer setup function.

Accessing the Tasks with Hot Keys

For the Tasks macros you can press and hold the Ctrl key and press the underlined letter in the Tasks bars to launch that Task. You can continue to use this method to go to all the levels of the Tasks.

Changing Parameters Coarsely

You can change parameters in coarse steps by pressing the Ctrl key and clicking the arrow button. Pressing Shift and clicking the arrow button at the same time gives an even bigger stepsize.

Help 4.7

Help Menu

Xepr has a powerful help system to assist you. Clicking on Help in the menu bar will bring up the options you can access. (See Figure 4-19.)

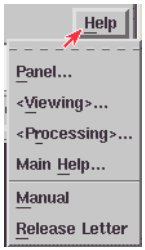


Figure 4-19 The Help menu.

Help Panel

If you click on Panel in the Help menu a window containing information about the VIEWING & PROCESSING PANEL appears. (See Figure 4-20.) Clicking on More in this window will turn to the next page of the topic. You can click Back to turn back to the previous page.

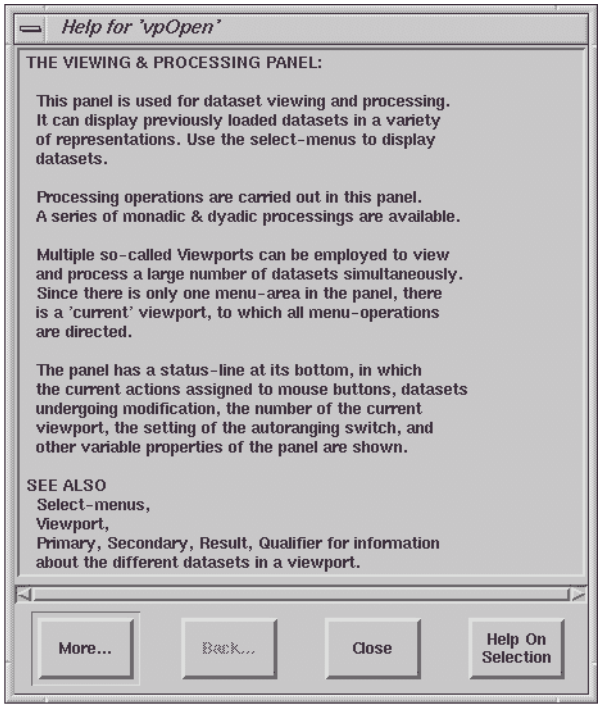


Figure 4-20 A help panel.

If you select a phrase by highlighting it with the mouse and then click on the Help On Selection button, a window displays the help information on that topic. (See Figure 4-21 for details.) Clicking on Close exits Help.

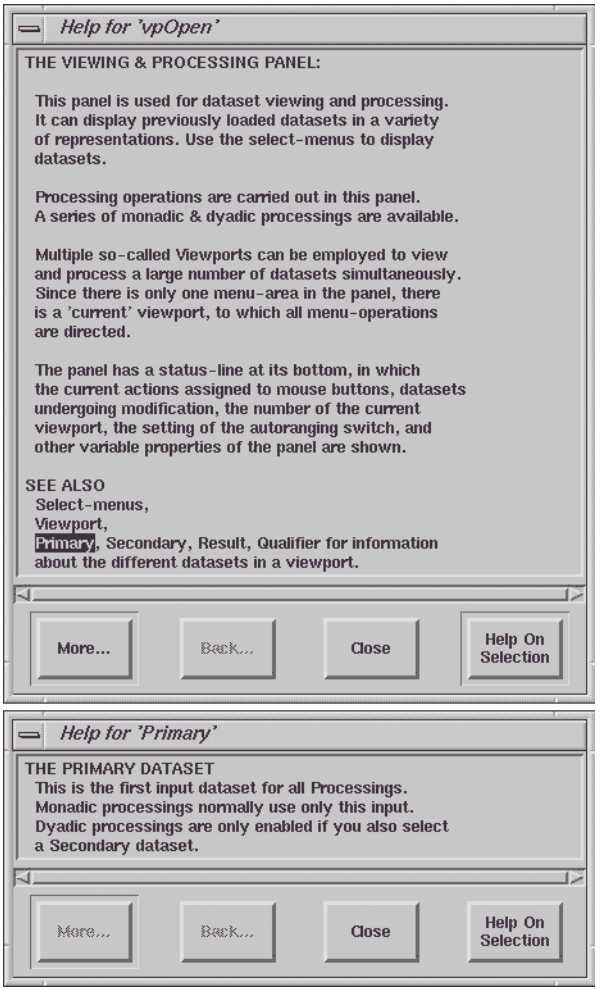


Figure 4-21 Help On Selection.

<Viewing> Clicking on <Viewing> in the Help menu brings up a window containing all the Xepr viewport commands. (See Figure 4-22.) By scrolling up and down, or left and right, you can view the brief descriptions of each processing command. You can highlight the command and use Help On Selection to view the details of that command.

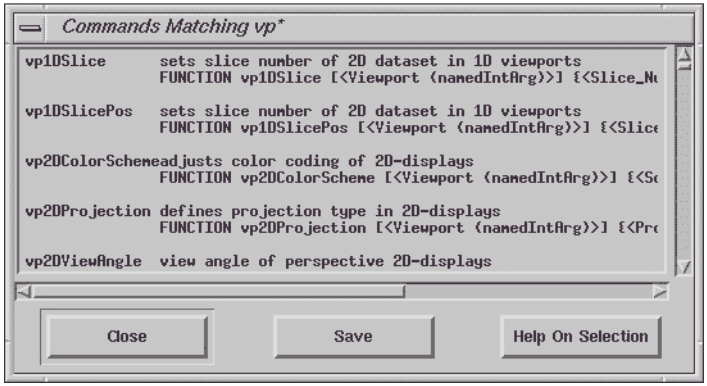


Figure 4-22 The viewport commands.

<Processing> Clicking on <Processing> in the Help menu, allows you to view all the Xepr commands regarding processing. By scrolling up and down, or left and right, you can view the brief descriptions of each processing command. You can highlight the command and use Help On Selection to view the details of that command.

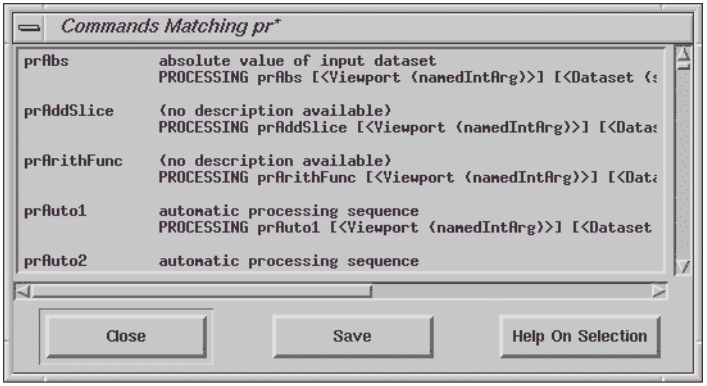


Figure 4-23 The processing commands.

Main Help Main Help in the Help menu is a search tool for the help system. (See Figure 4-24.) Three search methods are available. You can select keyword, apropos, or help_mode.

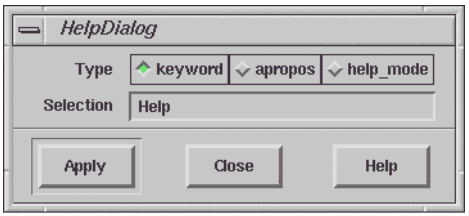


Figure 4-24 The Main Help dialog box.

Enter the string you want to search for in the Selection box. You can use wild cards (*) in the string. Click Apply to search. For practice, you can type Help in Selection and select keyword as Type. Click the Apply button. An explanation of these three types will appear in the window.

Manual Clicking Manual in the Help menu launches Adobe Acrobat Reader and opens the Bruker Xepr software User's Manual. (See Figure 4-25.) You can find detailed information about the software in this document.

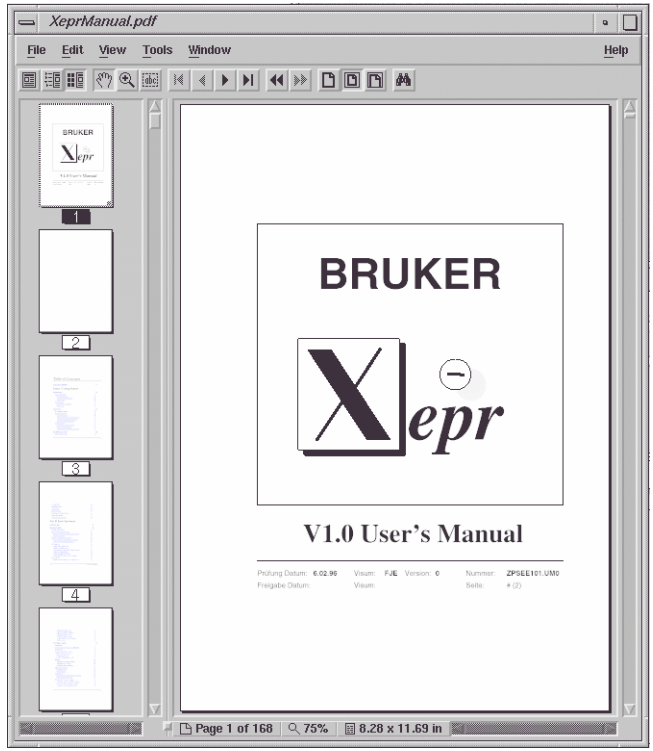


Figure 4-25 The Xepr manual.

Release Note

Clicking on Release Note in the Help menu launches Adobe Acrobat Reader and opens the Release Note for Xepr. (See Figure 4-26.) In the Release Note you can find the version number of the software, instruction for installation, bugs fixed in the current version, *etc*.

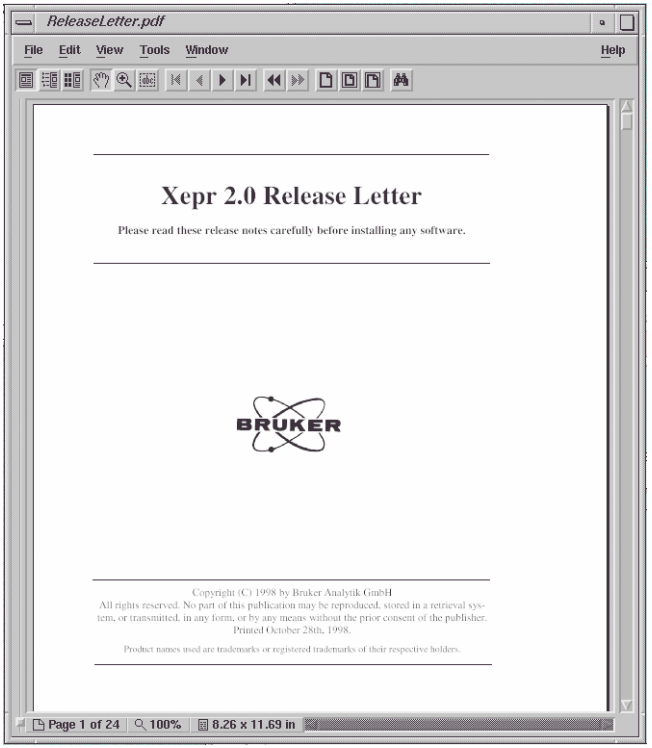


Figure 4-26 The Xepr Release Note.

Data Acquisition Tutorial 5

This chapter contains useful and helpful hints to get the most out of the Xepr Acquisition software. In Chapter 3, we blindly followed many instructions to acquire a spectrum. Here is the opportunity to explore some of the features in a bit more depth. The tutorial is not meant to be an exhaustive treatise on all details of the spectrometer. Instead, it is a starting point from which you can explore the capabilities of the instrument. Many additional topics are covered in the Elexsys E 500 User's Manual: Advanced Operations.

The first topic covers how to control and monitor the spectrometer. The second topic describes how to define an experiment. The third topic discusses the setup scan and interactive adjustment of spectrometer parameters. The fourth topic gives a brief discussion of microwave bridge control. Field sweep experiments and the adjustment of parameters are covered in the fifth topic. The sixth topic deals with time scans. The last topic contains advice on 2D experiments.

Spectrometer Monitoring Panel 5.1

The spectrometer monitoring panel appears in the Xepr window after connecting to the spectrometer. It displays the spectrometer status, hardware information, meters, acquisition tool buttons, and other controlling functions in several sections. The spectrometer monitoring panel can be divided into Experiment Definition, Acquisition Tools, Acquisition Control, Bridge Status, Hardware Information, and Meters sections. (See Figure 5-1.) The following is a brief description of each section.

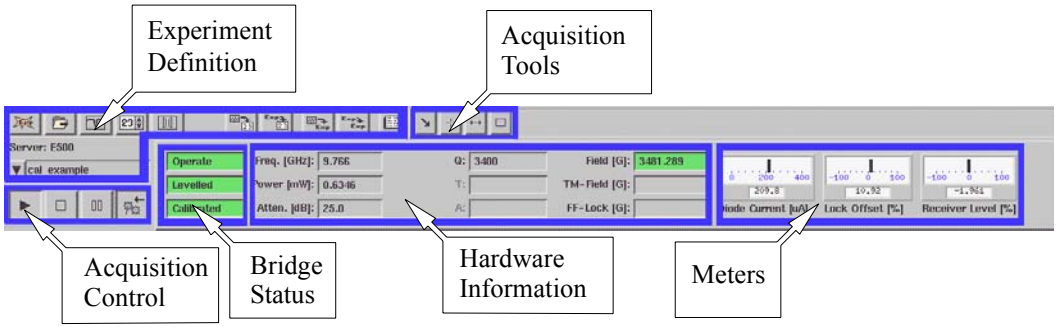


Figure 5-1 The spectrometer monitoring panel.

Experiment Definition 5.1.1

This section consists of various tools to define an experiment. The bridge tuning button is also in this section.

New Experiment Clicking this button opens a dialog box to define a new experiment.

Load Experiment Clicking on this button allows you to load a pre-defined experiment saved on the hard disk.

Bridge Tuning Clicking this button opens the microwave bridge tuning dialog box.

Parameters Clicking this button opens a dialog box for setting acquisition parameters. You need at least one experiment created or loaded to activate this button. Otherwise it is greyed out.

Tesla (gauss) Meter and FFLock Control Clicking this button opens a dialog box where you can control and set parameters for the Tesla (gauss) meter and field frequency lock device if these optional accessories are installed.

Transfer Parameters from a Dataset You can transfer parameters from an existing dataset to the current active experiment by clicking this button.

Transfer Parameters from an Experiment You can transfer parameters from an existing experiment to the current active experiment by clicking this button.

Duplicate an Experiment Clicking this button duplicates the currently active experiment.

Create an Experiment from a Dataset Clicking this button allows you to create a new experiment based on an existing dataset.

Experiment Table Clicking this button brings up a table containing all the currently loaded experiments.

Experiment List Clicking the arrow opens a drop-down menu listing all the existing experiments. Selecting one of the experiment will activate that experiment. The most recently acquired spectrum attached to this experiment will also be displayed in the viewport. The name of the current active experiment appears in the window next to the arrow.

Acquisition Tools 5.1.2

Acquisition tools provide you convenient ways to interactively adjust the center field, sweep width, receiver gain, and other parameters. You need an unstored and unsaved spectrum active in the current viewport to activate the Acquisition Tools. If you have stored or saved the spectrum you just acquired, click the Experiment List button and select the experiment again. A marker can be removed by clicking on the Waste Basket button in the tool bar.

X Marker Clicking this button brings up a dialog box allowing you to select various X-axis markers, such as Center Field, Field Position, RF frequency position, *etc*. You can then move the marker and the associated parameter will be updated with the marker's X-coordinate.

Abscissa Value Indicator Clicking this button brings up a vertical bar. You can use this marker to indicate the abscissa (Y) value.

X-Y Marker Clicking this button brings up a dialog box. You can select X parameter and Y parameter for the X-Y Marker to mark the experimental dataset.

Receiver Level Indicator Clicking this button brings up a dialog box. The X- and Y-parameters have been predefined as FieldPosition and SignalLevel. Click OK to activate the marker.

Center Field and Sweep Width Tool Clicking this button will create a tool in the viewport with which you can change both the center field and the sweep width for a field sweep experiment.

Sweep Width and Receiver Gain Tool This tool is a rectangular shaped box. The width of the box defines the sweep width and the height of the box defines the receiver gain for the next acquisition.

Acquisition Control 5.1.3

There are four handy buttons in this section for controlling the acquisitions such as starting, and stopping acquisitions. If there is no experiment defined, all four buttons are greyed out. Clicking the buttons toggles their functions from an engaged to disengaged state.


Run/Abort Clicking the RUN button starts an acquisition. Clicking this button while an acquisition is in progress aborts the data acquisition. The right button indicates that an acquisition is running whereas the left indicates no acquisitions is running.

Stop You can stop the data acquisition after finishing the current scan by clicking this button.

Pause This button pauses the data acquisition. It interrupts the acquisition at the earliest possibility. In CW EPR experiments it usually stops the acquisition after the current scan finishes. This button is particularly useful for signal averaging and 2D experiments. It temporarily stops the signal averaging or increment of the second variable after the current scan. Data acquisition can be resumed by clicking this button again.

Activate When the Activate button is not engaged, changing the parameters in the Experiment Parameter dialog box does not change the parameters on the instrument until you run a spectrum. When the Activate button is engaged, the parameters are sent to the hardware immediately providing you with interactive optimizations.

If you need to re-tune the bridge, it is advised to disengage the Activate button before you open the Microwave Bridge Tuning dialog box.

Bridge Status 5.1.4

This section indicates the status of the microwave bridge. It has three small windows. The top window indicates which mode the microwave bridge is. It can be Stand By, Tune, or Operate. When you connect to the spectrometer, this window may show a red Stand By display. Wait until it turns green. The middle and the bottom windows indicate whether the microwave power of the bridge is Levelled and Calibrated in Operate mode. (See Figure 5-2.) If the microwave power is not leveled or calibrated, the corresponding window will turn red and indicate Unlevelled or Uncalibrated.

Figure 5-2 The microwave bridge status section.

Hardware Information 5.1.5

Freq. [GHz]: This displays the microwave frequency when you switch the bridge to Operate mode. If you have a frequency counter connected and configured properly, the reading will be read from the frequency counter.

Power [mW]: This shows the current microwave power in milliwatts. If it shows zero, you probably have not engaged the Activate button.

Atten. [dB]: This shows the current microwave attenuation in dB. The leveled microwave power for an X-band bridge is ~200 mW at 0 db.

Q: This displays the approximate Q factor value of the cavity. You need to switch to tune mode and set the Attenuation to 30 dB to read the Q value properly. It is not meant to be an accurate measurement of the Q factor but an estimate.

T: This is the temperature reading from the temperature controller. The temperature controller needs to be connected and configured correctly to display the temperature. You need to engage the Activate button to establish communications between the acquisition server and the temperature controller. Green indicates the temperature has reached the set temperature whereas red indicates the set temperature has not yet been reached.

A: This displays the current sample angle if you are using an automated goniometer.

Field [G]: This shows the current magnetic field regulated by the Hall probe. When it is red, the actual magnetic field has not reached the set value yet. Green indicates that the actual magnetic field value matches the set value. If it is red or switches back and forth from green to red during the field sweep, you probably are sweeping the field too fast. Increase the conversion time to allow the magnetic field to follow the sweep better.

TM-Field [G]: This is the magnetic field value detected by the optional teslameter (gaussmeter) if one is installed on the spectrometer.

FF-Lock [G]: This is the indicator of the optional field frequency lock if one is installed on the spectrometer. When the magnetic field is locked, it turns to green and indicates the offset.

The Meters 5.1.6

There are three meters indicating the status of the spectrometer. Watch these meters closely when you tune the microwave bridge or select the parameters interactively.

Diode Current The Diode Current meter is on the left side of the meter section. It indicates the diode current in a scale from 0 to 400 µA while a digital display underneath gives a numerical value of the diode current. (See Figure 5-3.) When everything is properly tuned, the diode current should be approximately 200 µA (indicator in the center).

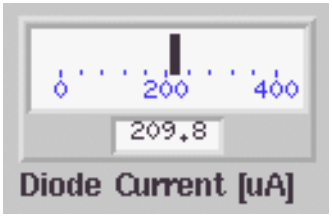


Figure 5-3 The Diode Current meter.

Lock Offset The Lock Offset meter indicates the AFC error signal. (See Figure 5-4.) Keep the indicator in the middle by adjusting the microwave frequency. If it is difficult to keep the indicator in the middle, check the AFC Gain of the microwave bridge.

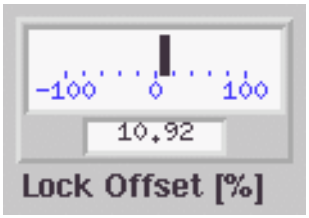


Figure 5-4 The Lock Offset meter.

Receiver Level This meter reflects the level of the receiver. (See Figure 5-5.) Adjust the Receiver Gain to keep the indicator within three quarters of the meter scale during the sweep. You may also need to adjust the Offset so that the indicator is centered when the magnetic field is set on the baseline.

Figure 5-5 The Receiver Level meter.

Working with Experiments 5.2

Defining Experiments 5.2.1

New Experiment

There is a limitation on the number of experiments you can create or load. Keep the total number of experiments under five. You do not need to create multiple copies of an experiment if only the parameters are different. Instead, transfer parameters from existing spectra to the experiment. See Section 5.2.5 for details.

You need to define an experiment to acquire a spectrum. In Chapter 3 we described how to create a new experiment by simply clicking the New Experiment button in the Experiment Definition section. A dialog box appears in which we can define a new experiment. (See Figure 5-6.) Enter a name for the experiment in the Experiment Name box.

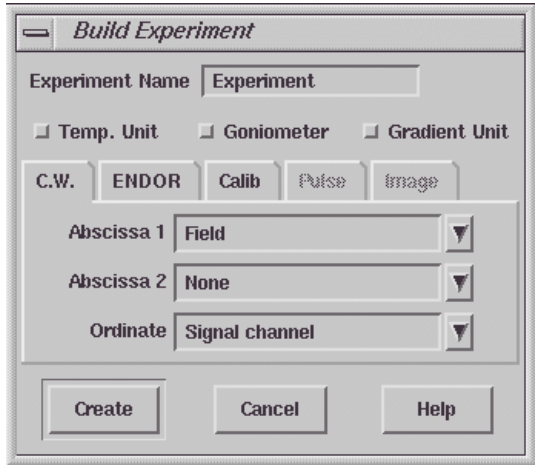


Figure 5-6 The New Experiment dialog box.

There are five folders corresponding to various types of the experiments. For the Elexsys E 500 you can click C.W. for normal acquisitions or Calib if you want to calibrate the signal channel. (See Figure 5-6.)

Next, you need to configure Abscissa 1. Click the arrow button next to the Abscissa 1 box and select the proper variable for Abscissa 1. (See Figure 5-7.) Field for magnetic field sweeps

and Time for time scans are the most commonly used variables. Not all the items are available for Abscissa 1 because some of them need special accessories. If you plan to acquire a 2D spectrum, you need to click the arrow button next to the Abscissa 2 box and select the proper variable for Abscissa 2 such as Sample angle, Sample temperature, Sample concentration, Microwave power, *etc*. Otherwise, select None for a 1D experiment.

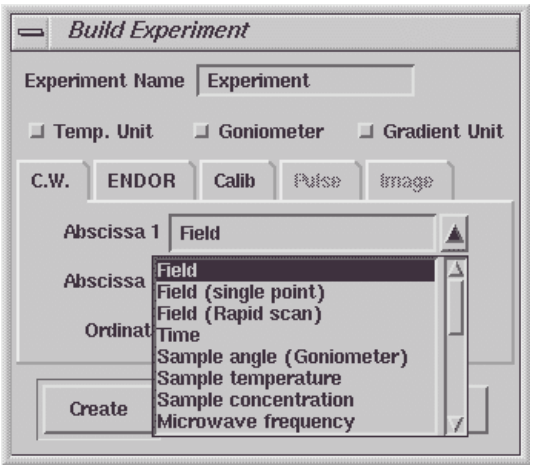


Figure 5-7 Selecting Abscissa 1.

You need to select the Ordinate as well by clicking on its arrow button. From the drop-down list you will normally select Signal channel. (See Figure 5-8.) If you are acquiring rapidly changing spectra, you may need to select Fast digitizer.

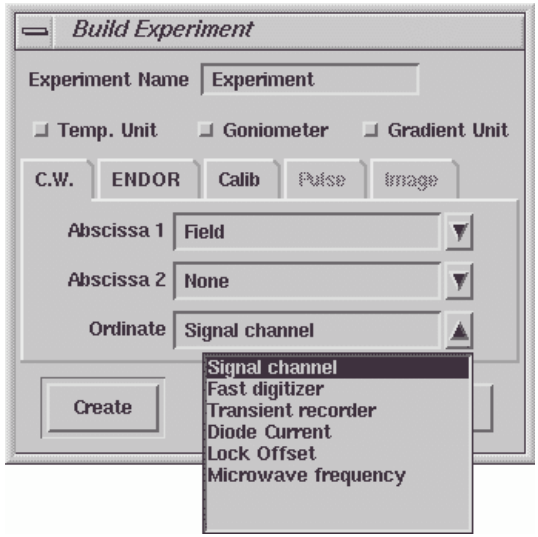


Figure 5-8 Selecting the Ordinate.

If your spectrometer is equipped with gradient coils, a goniometer, or a variable temperature unit and you plan to do an experiment with these accessories, click the corresponding button to activate it. It will turn to green when active. If you are not using the accessory, it is best not to activate it. (See Figure 5-9.)

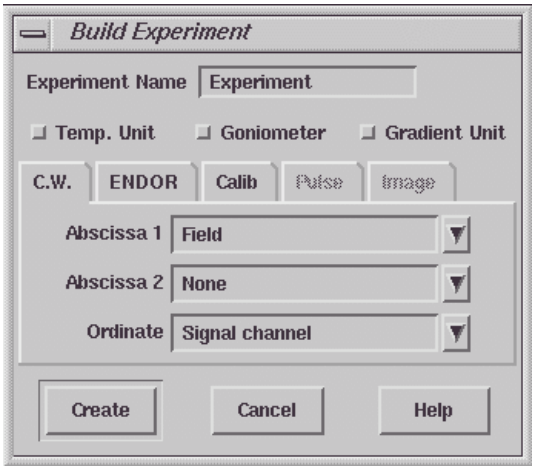


Figure 5-9 Selecting accessories.

Click Create when you finish and the dialog box will close.

Duplicate an Experiment

You can duplicate an existing experiment by clicking on the Duplicate an experiment button. The duplicated experiment will have the same name with a number added to the end of the name.

Create an Experiment from a Dataset

You can create an experiment from a dataset. Load the dataset into Xepr first. Click the Create experiment from a dataset button and a dialog box will appear. (See Figure 5-10.)

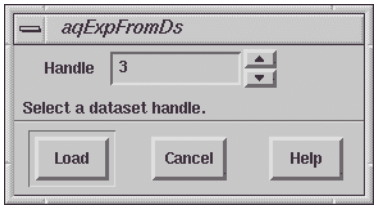


Figure 5-10 Creating an experiment from a dataset.

You need to enter a Handle number in the dialog box. Every dataset in Xepr is assigned with a unique number called the Dataset Handle number. You can find the Handle number by clicking the Dataset Selector. The Dataset Handle is the number to the left of the title. (See Figure 5-11.) Enter the Handle number of the dataset from which you want to create an experiment and click Load to create the new experiment.

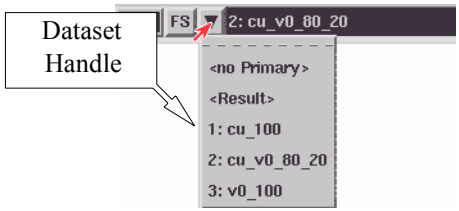


Figure 5-11 Finding a Dataset Handle.

Saving Experiments 5.2.2

You can save the defined experiment for later use. Click on the Experiment Table button to bring up the Experiment Table dialog box. (See Figure 5-12.)

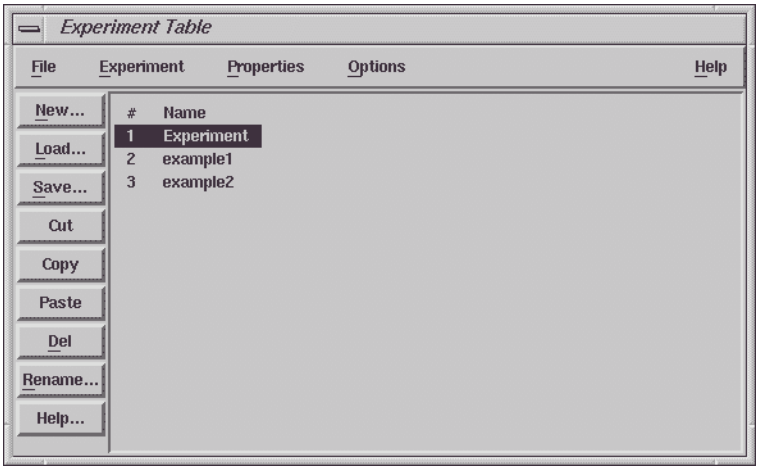


Figure 5-12 Experiment Table.

Click and highlight the experiment you want to save. Click Save to bring up the Save dialog box. (See Figure 5-13.)

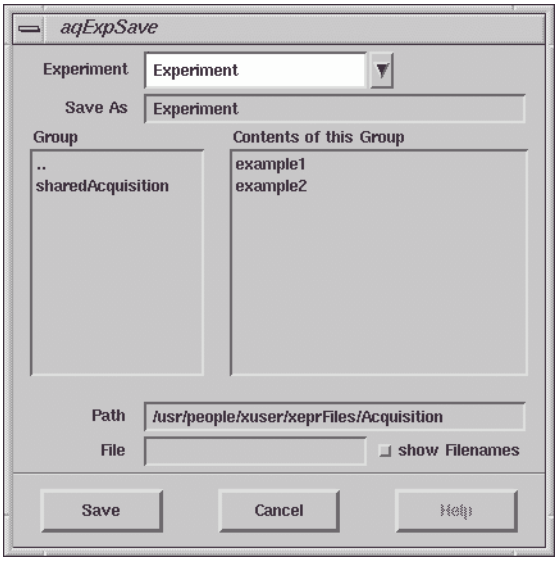


Figure 5-13 Save experiment.

Select the proper path in the Group window. Xepr already created a subdirectory for saving experiment files. The path is *YourHomeDirectory*/xeprFiles/Acquisition. Enter a file name in the File box. Click Save to save the file and exit the dialog box. Xepr will automatically add an extension, .exd, to the file name.

Loading Experiments 5.2.3

You can load any predefined experiment from the hard drive. Click Load in the Experiment Table dialog box and select the path where the saved experiments are. (See Figure 5-14.) Click the experiment file in Contents of this Group and then click Load to load the selected experiment.

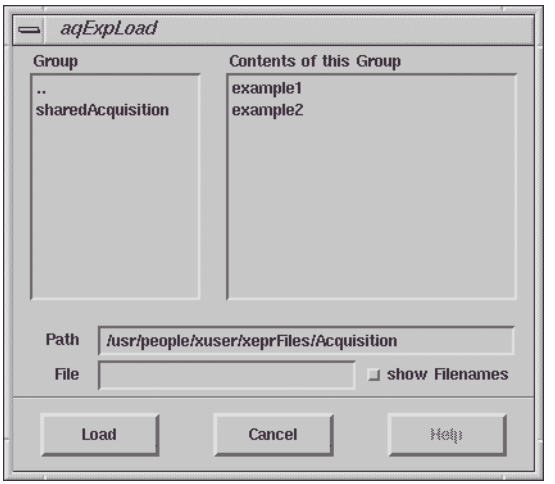


Figure 5-14 Loading experiments.

Selecting Experiments 5.2.4

Xepr allows you to create or load more than one experiment. You can have only one experiment active at a time. To select the experiment you want to execute, click the arrow button of the Experiment list and click on the desired experiment. (See Figure 5-15.)

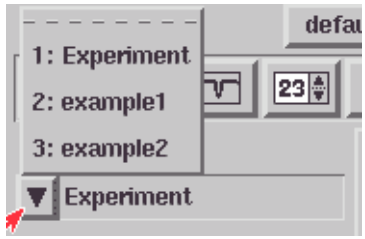


Figure 5-15 Selecting an experiment from the Experiment list.

The name of the active experiment will appear in the window next to the arrow button. It is important to assign a unique name to each experiment. If you do not assign an experiment name, by default it will be Experiment or Experiment:# where # is a consecutive number. The spectrum most recently acquired with that experiment will be attached to that experiment. The Acquisition Tools such as Center Field, Sweep Width can only be applied to the spectrum attached to the experiment. After you store or save the dataset, the spectrum shown in the viewport is no longer attached to the experiment. You need to reselect the experiment to display the attached spectrum in the viewport and then use the Acquisition Tools.

Transferring Parameters 5.2.5

You may often need the same set of parameters to acquire a whole series of spectra. The parameters of a dataset can be easily transferred to an experiment by using the Transfer parameters from a dataset button in the experiment definition section. Clicking this button opens a dialog box asking you from which dataset you want to transfer parameters. (See Figure 5-16.)

Figure 5-16 Transferring parameters from a dataset.

The Handle number is the number Xepr assigns to each dataset. See Figure 5-11 to find out where the Handle number can be found.

Click the arrow buttons to enter the Handle number of the dataset. Click Load to transfer the parameters to the current active experiment.

You can also transfer the parameters from another experiment. Click the Transfer parameters from experiment button in the experiment definition section. (See Figure 5-17.) Click the arrow button to bring a drop-down list of existing experiments. Select the experiment from which you want to transfer parameters. Click Load to transfer the parameters to the currently active experiment.

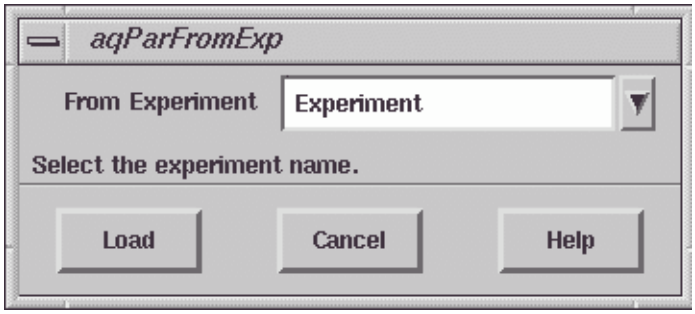


Figure 5-17 Transferring parameters from an experiment.

Interactive Spectrometer Control 5.3

Setup Scan 5.3.1

The Setup Scan offers the immediate visual feedback needed when optimizing spectrometer parameters. To activate the Setup Scan function engage the Activate button and open the Acquisition Parameters dialog box. The dialog box has a Setup Scan option in which the magnetic field is rapidly swept up to 50 Gauss in order to display the EPR spectrum on the screen. This is achieved by setting the main magnetic field with the field controller (thereby setting the center field of the Setup Scan) and sending current through the modulation coils of the cavity to produce the rapid sweep. Click on the Setup Scan button to open the Setup Scan dialog box. Click the Enable button to activate the function. (See Figure 5-18.)

It is best to move the Parameters window above the Setup Scan window to make interactive parameter changes convenient.

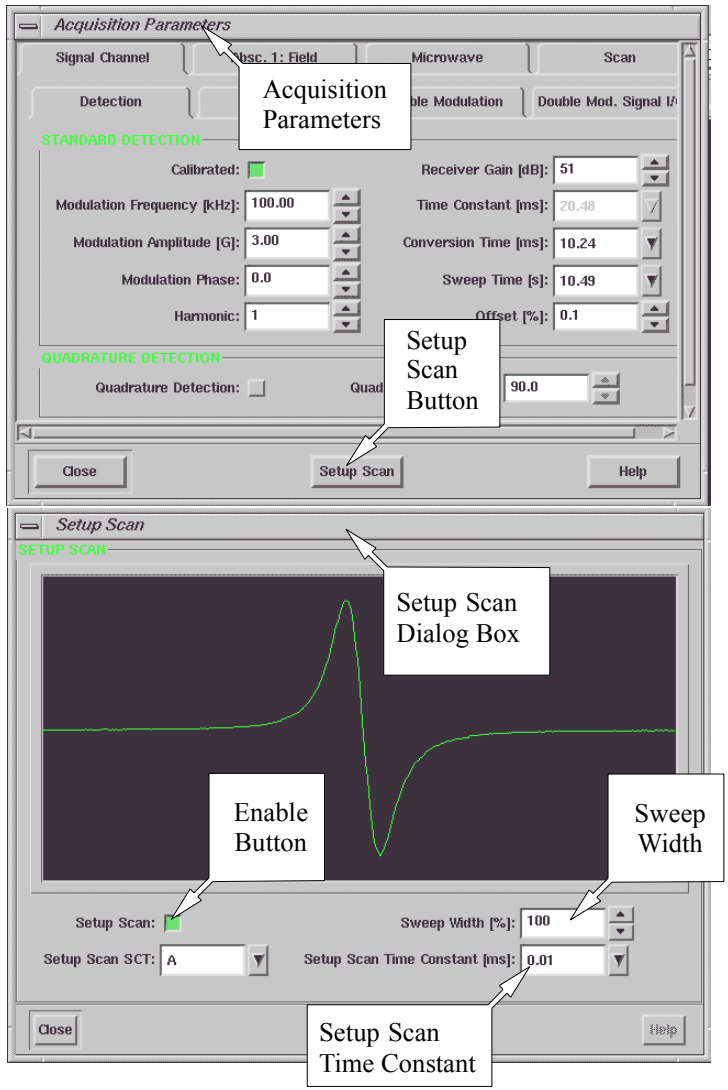


Figure 5-18 The Setup Scan.

The rapid sweep for the Setup Scan may be a little too fast for some signals or parameters. The Setup Scan has its own time constant called Setup Scan Time Constant. It is independent from that in the Signal Detection folder. The Time Constant in the Signal Channel Detection folder will be inactive after the Setup Scan is enabled. It will be re-activated when you disable the Setup Scan. Change the Setup Scan Time Constant so that it does not distort an EPR signal. You can use a longer time constant without distorting the signal by narrowing the width of the Setup Scan so that you are looking at a narrower portion of the signal. The time required to sweep through the EPR signal is then longer. The value in the Sweep Width box indicated in Figure 5-18 can be edited or varied with the arrows next to it. The values are in percentage of the 50 G setup scan sweep.

Click the Abscissa 1 Field tab in the Acquisition Parameters dialog box to bring the Field tab to the front. Using the arrow buttons of the Center Field to center your spectrum in the Setup Scan.

Optimizing a Weak or Broad Signal 5.3.2

If the EPR signal is weak or broad, the Setup Scan may not be the best way to optimize the signal. For such cases, you can use the Receiver Level meter to optimize your EPR signals. First, make sure you have an acquired spectrum and that the experiment is currently active. Make sure the Activate button is engaged. Click the X-marker button and select the proper marker from the drop-down list. Which marker to choose depends on the experiment. For example, if you are acquiring a field sweep spectrum, select the Field Position marker. The position of this marker in the spectrum determines the magnetic field, *i.e.* changing its position changes the actual magnetic field. The indicator in the Receiver Level meter displays the receiver level at the magnetic field at which the marker is placed. The marker is moved by dragging it with the left mouse button to the desired position in your EPR spectrum. Place the marker at the baseline first. (See Figure 5-19.) Watch where the indicator of the Receiver Level meter is.

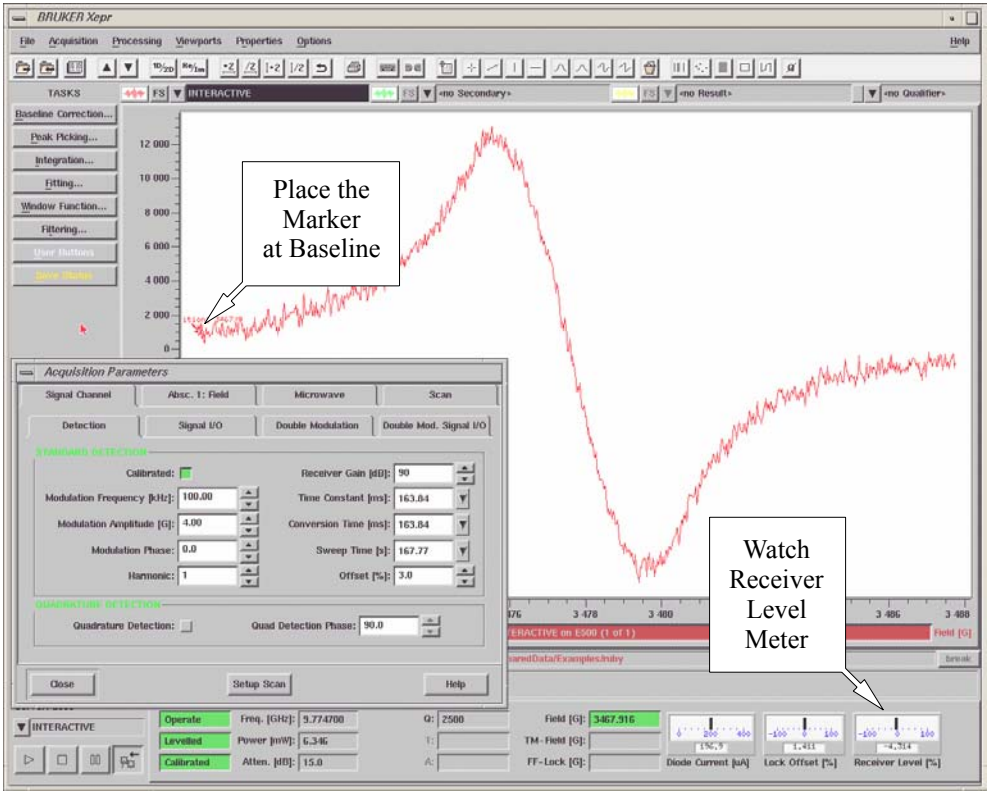


Figure 5-19 Observing the Receiver Level meter when the marker is placed at the baseline.

Move the marker to the upper (or lower) peak of the EPR signal to see if the Receiver Level meter goes up (or down). If the Receiver Level meter does not change much, you may need to increase the Receiver Gain so that there is visible change in the Receiver Level meter when you move the marker from the baseline to the signal peak. (See Figure 5-20.)

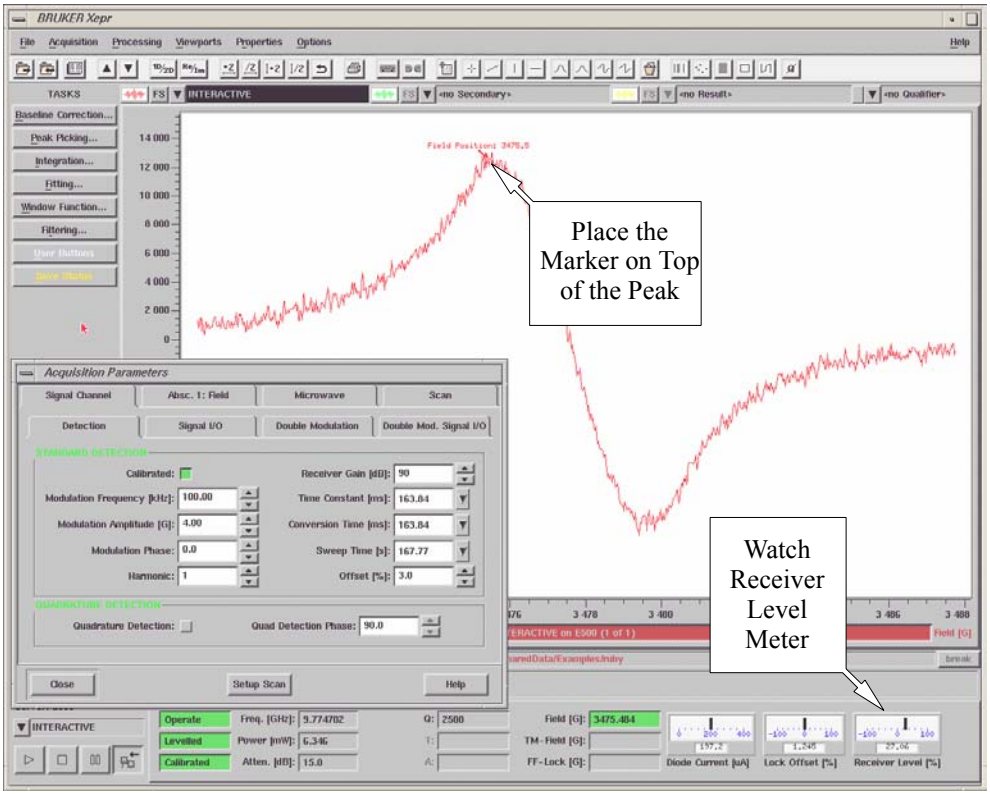


Figure 5-20 Observing the Receiver Level meter when marker is placed on top of the peak and when changing parameters.

Open the Acquisition Parameters dialog box. Now, as you vary parameters such as receiver gain, phase, or microwave power, you can monitor the signal intensity with the Receiver Level meter at that magnetic field value.

The parameter values that you have carefully optimized have no effect on the spectrum that you have already acquired. To use these new parameters for a new acquisition, you need to re-acquire a spectrum in that window by clicking the RUN button. The spectrometer will use the newly optimized parameter set.

Alternatively you can use the Receiver Level Indicator to optimize a signal when you are acquiring a field sweep. Click the Receiver Level Indicator button. A dialog box appears. The X- and Y-Parameters have been preset for a field sweep. Click OK. (See Figure 5-21.) The position of the vertical line is the

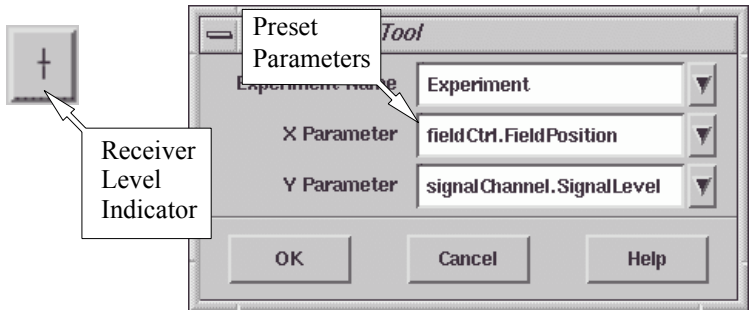


Figure 5-21 Activating the Receiver Level Indicator.

position of the magnetic field. The horizontal bar indicates the receiver level at that field value. Move the indicator to the EPR signal. Open the Acquisition Parameters dialog box. You can monitor the signal intensity with the Receiver Level Indicator at that field value when you vary parameters. (See Figure 5-22.)

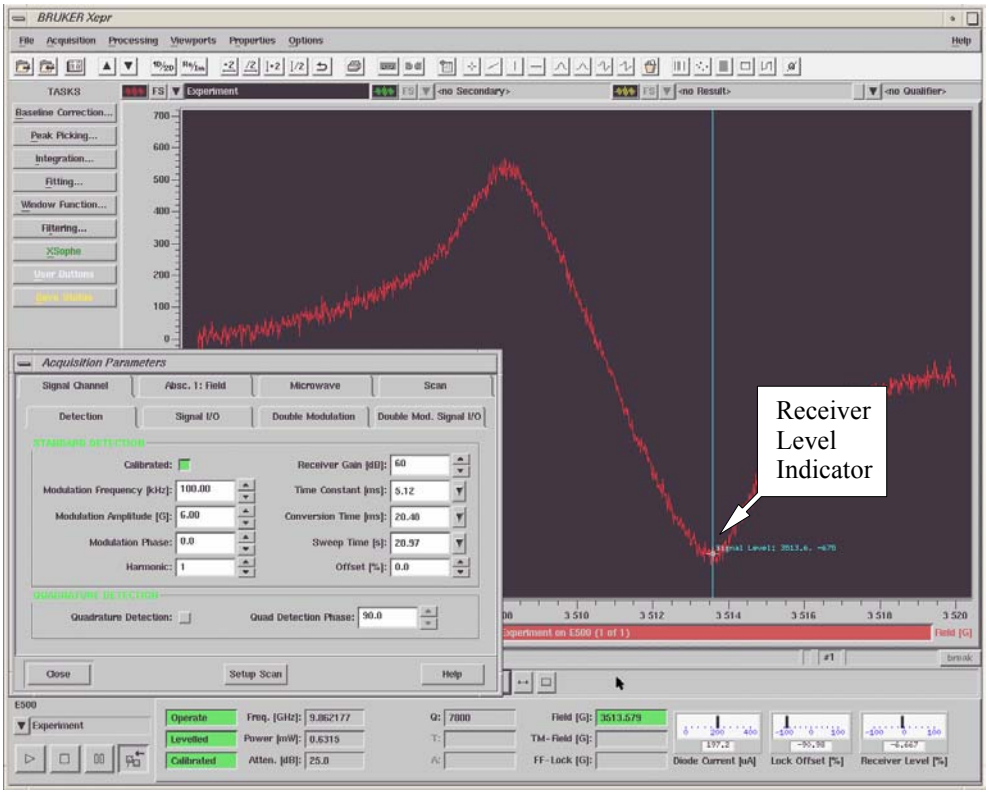


Figure 5-22 Optimizing the signal with the Receiver Level Indicator.

Controlling the Microwave Bridge 5.4

Auto Tune vs. Fine Tune 5.4.1

The time saved by using Fine Tune instead of the full Auto Tune procedure can be particularly important when you are working with unstable and decaying samples.

In Chapter 3, we used the Auto Tune commands to tune the microwave bridge and cavity. This routine tunes everything, including the Bias, Signal Phase, Frequency, and the cavity matching. Quite often, you do not need to adjust all these parameters. For example, unless you have a large change in microwave frequency the Bias and Signal Phase do not need to be adjusted. The parameters that change more frequently are the Frequency and the matching of the cavity. The Fine Tune routine optimizes only the Frequency and the matching (iris position) and therefore is considerably faster than the complete Auto Tune procedure.

A good approach to take is to initially use the Auto Tune routine to make sure that the Bias and Signal Phase are set properly. Then as you change samples (providing they have similar properties) or rotate your sample, *etc.*, you can use the Fine Tune routine to tune the spectrometer. To initiate fine tuning, open the Microwave Bridge Tuning dialog box and press the Fine button under Auto Tuning. (See Figure 5-23.)

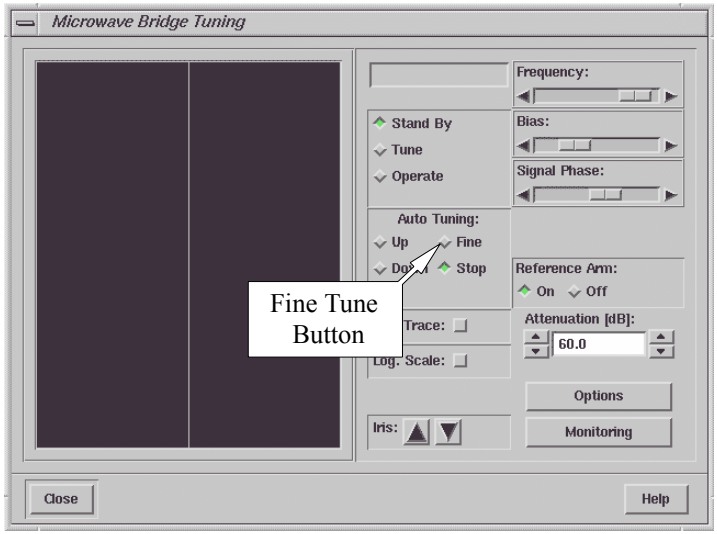


Figure 5-23 The Fine tune button.

You can set up an automatic fine tune before each sweep. Open the Acquisition Parameters dialog box by pressing the button in the experiment definition section. Click the Microwave tab and then click the arrow button next to Acq. Fine Tuning. (See Figure 5-24.) In the drop-down list select Each Slice Scan. Click OK and the fine tune routine will be executed automatically before each scan. If you do not have an auto tune option with your cavity, make sure that Never is selected in the Acq. Fine Tuning drop-down list.

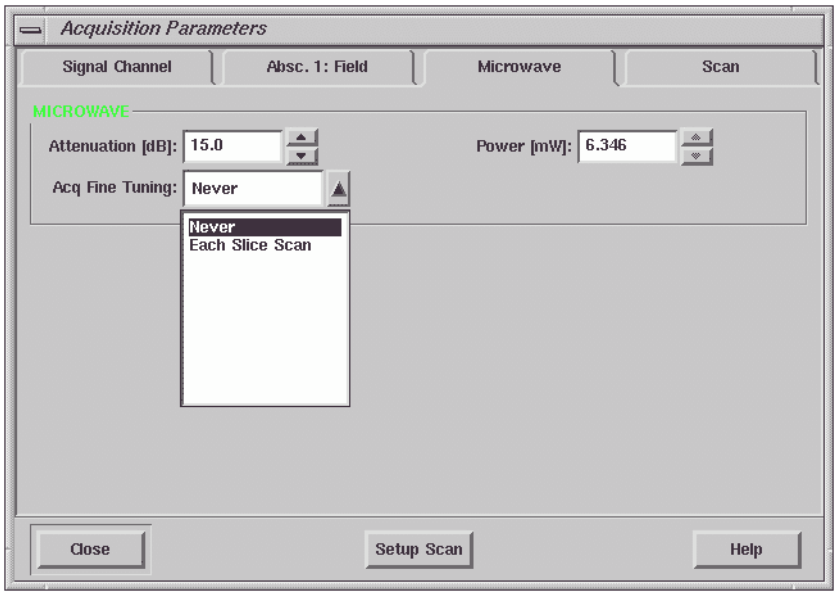


Figure 5-24 Acq. Fine Tuning selections.

Field Sweeps 5.5

Setting Parameters by Acquisition Tools 5.5.1

If you are searching for EPR signals from an unknown species, the most prudent approach to find signals is to make a very broad scan with the center field set to a value where you expect to see a signal. (See Section 8.1, Hints for Finding EPR Signals.) This approach maximizes the probability of finding a signal in your field sweep. If you are lucky, the EPR signals will already be nicely centered in the field sweep, most of the field sweep will contain EPR signals and not empty baseline, and the receiver gain will be set perfectly. Such luck rarely occurs! The Acquisition Tools (See Section 5.1.2, Acquisition Tools) help you to achieve the desired results on your second attempt. The following procedure allows you to use a broad scan to optimize the center field, sweep width, and receiver gain so that you can acquire an aesthetically pleasing as well as meaningful spectrum.

In Figure 5-25, we have used a broad field scan to find our EPR signal. Clicking the Sweep & Gain Tool button in the Acquisition Tool bar creates a zoom rectangle in the spectrum window. You can change the size of the rectangle by dragging the handles. Increasing the vertical dimension of the rectangle decreases the receiver gain while increasing the horizontal dimension of the rectangle increases the sweep width. You can also move the rectangle to change the center field.

Surround the area that you would like to have in your spectrum. You may need to use the zoom tool to see the whole rectangle. Click on the RUN button in the Acquisition Control section.

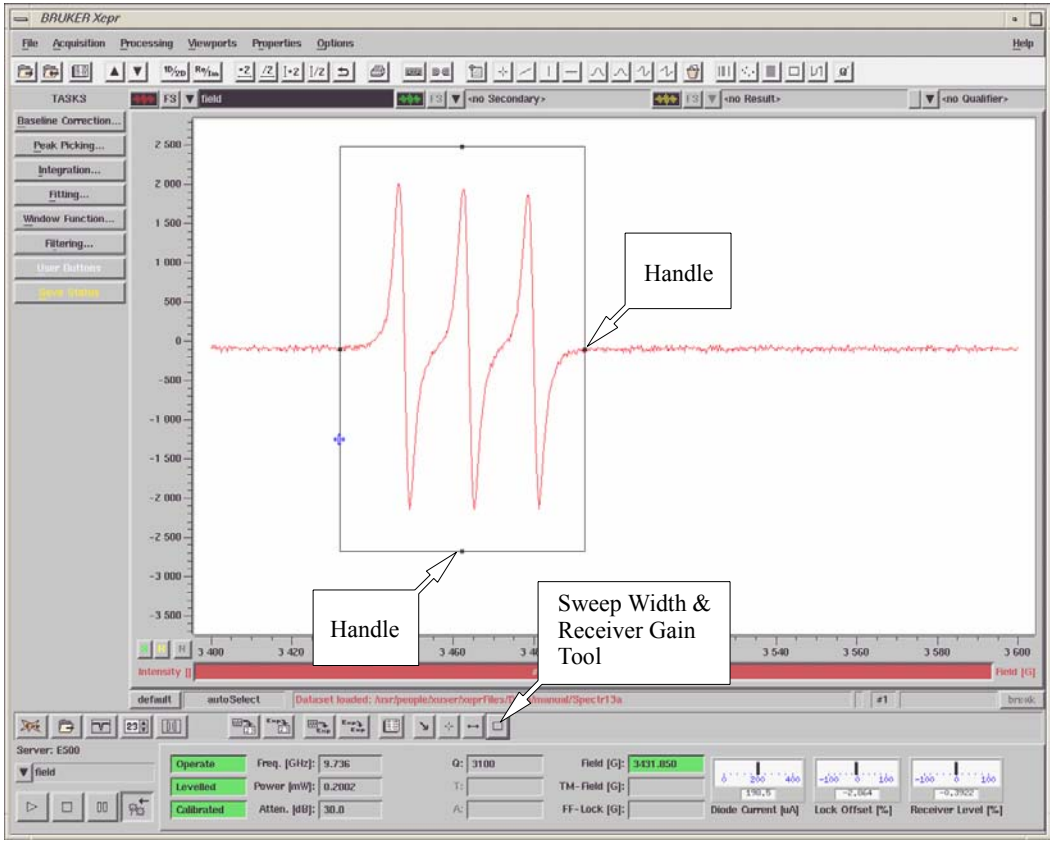


Figure 5-25 The zoom rectangle for interactive adjustment of parameters.

The spectrum will then be nicely acquired with the optimized center field, receiver gain, and sweep width as in Figure 5-26. If you open the Acquisition Parameter dialog box, you will also notice that the receiver gain, offset, center field, and sweep width have been adjusted such that the spectrum will fit in the spectrum window with optimal receiver gain.

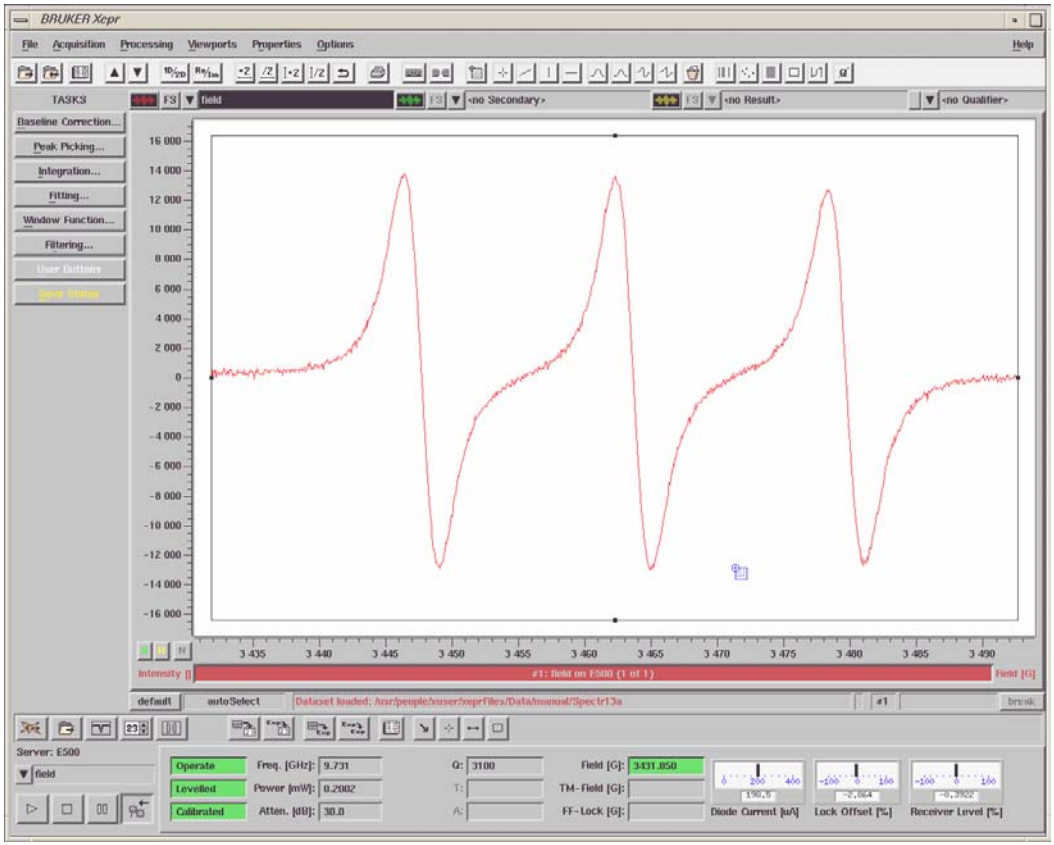


Figure 5-26 The optimized spectrum.

Setting the Center Field and the Sweep Width 5.5.2

If only the center field and the sweep width need to be adjusted, you can use the Center & Sweep Width tool. Click the Center and Sweep Width button in the Acquisition Tools section.

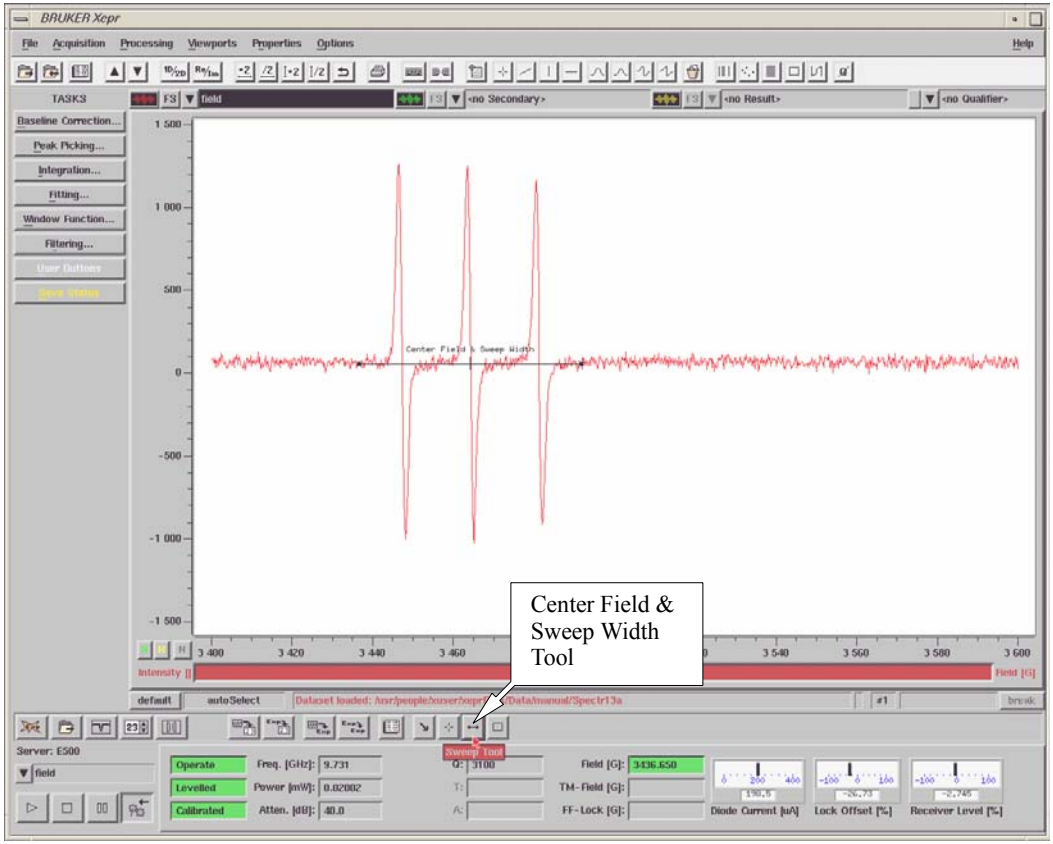


Figure 5-27 Adjusting the center field and the sweep width.

The tool has a center marker and two end markers. Move the center marker to where the center should be. Then change the sweep width by dragging either one of the end markers towards

the center or away from the center to decrease or increase the sweep width. (See Figure 5-27.) Click Run to acquire a well centered spectrum with a proper sweep width. (See Figure 5-28.) If you open the Acquisition Parameters dialog box now, you will find the center field and the sweep width have been changed to the new values.

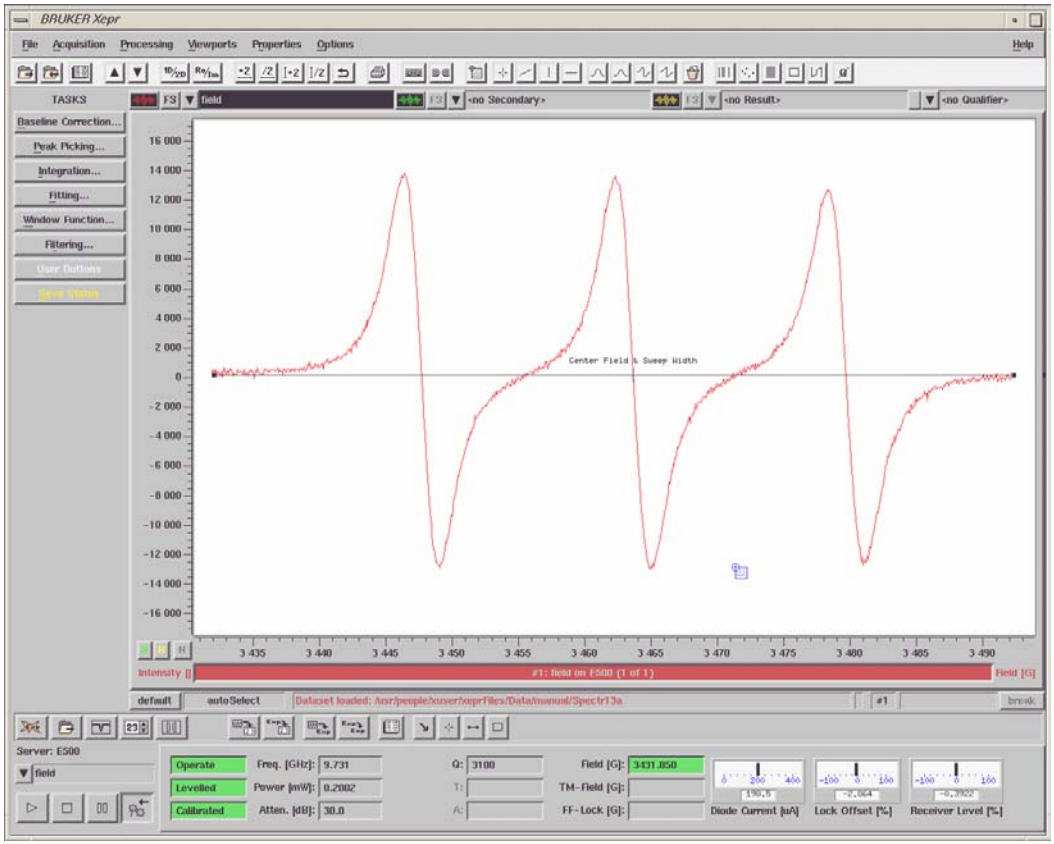


Figure 5-28 A centered spectrum with proper sweep width.

Setting Center Fields 5.5.3

Sometimes you may not have to change all the parameters such as receiver gain and sweep width: setting the center field may be sufficient. To interactively set the center field, click X-Marker in the Acquisition Tool section. Select the correct experiment name and CenterField in the X Parameter drop-down list, and click OK.

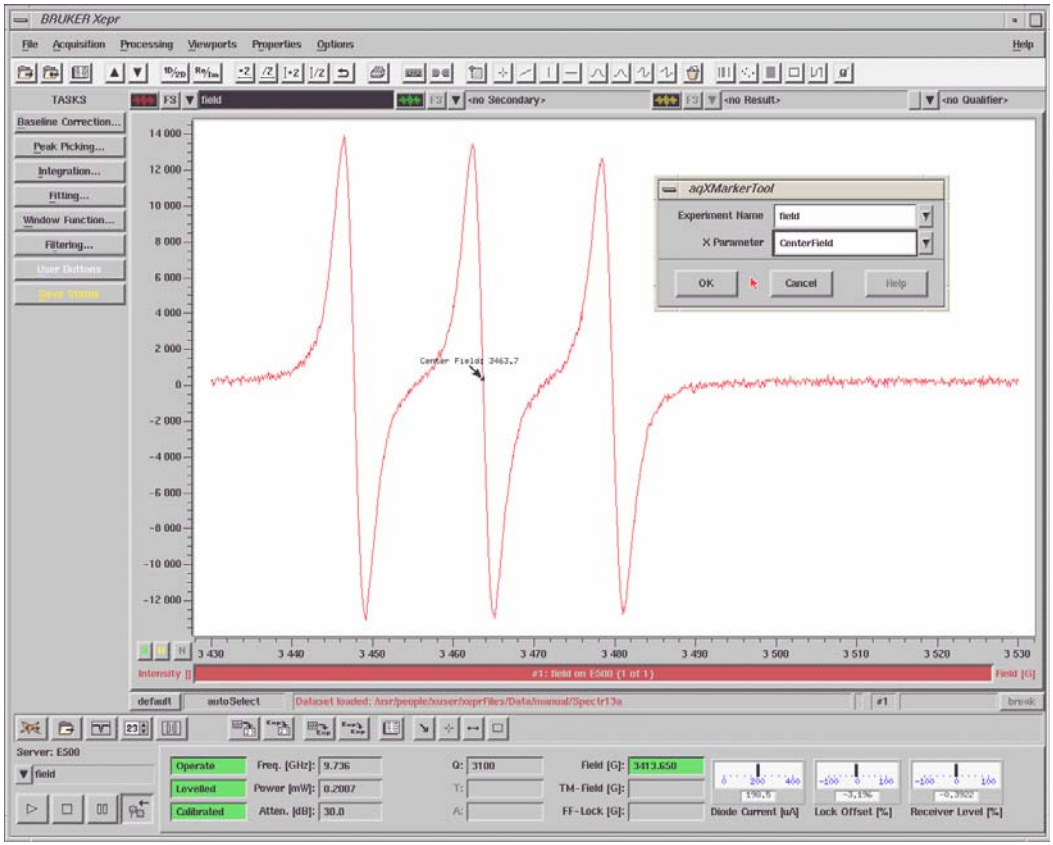


Figure 5-29 The Center Field tool.

A marker labeled as Center Field appears in the viewport window. (See Figure 5-29.) Place the marker where you would like the center field to be and click the Run button. This action replaces the center field value with the magnetic field position of the marker. The newly acquired spectrum will then be nicely centered as in Figure 5-30.

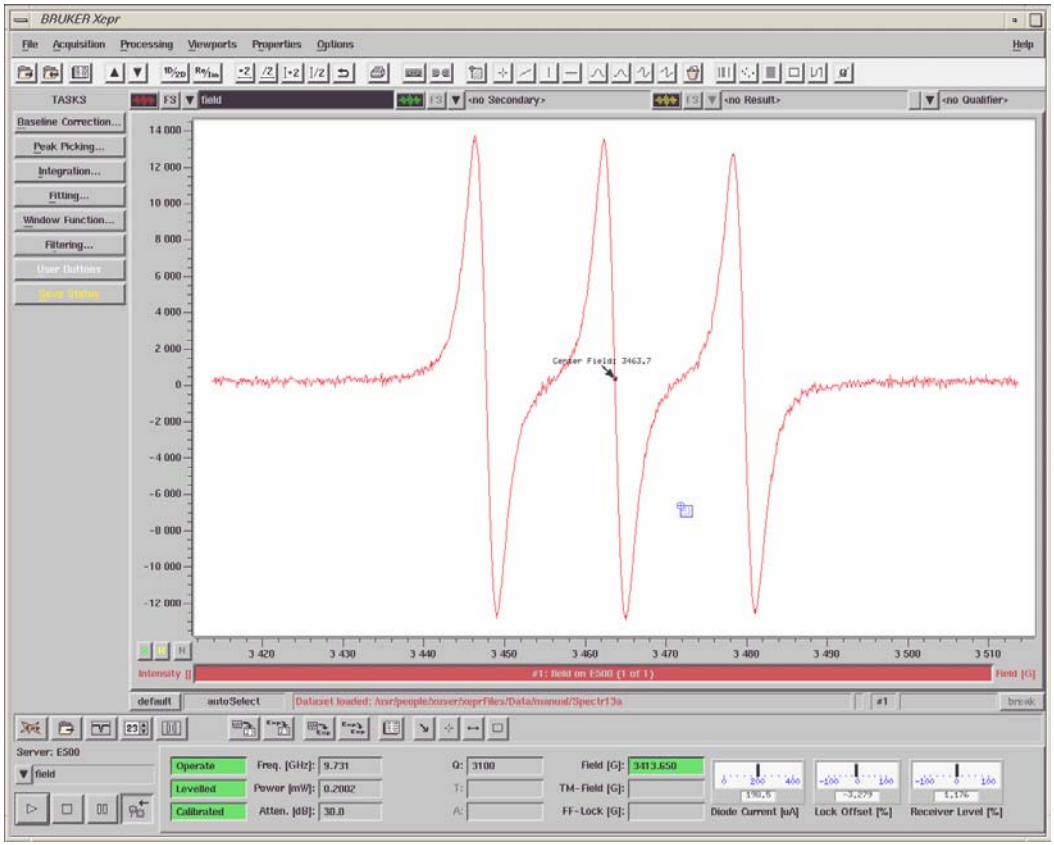


Figure 5-30 A properly centered spectrum.

Signal Averaging 5.5.4

Keep in mind, when measuring peak heights or double integration that you need to normalize the results by the number of scans.

If you are looking for very weak signals, you can increase your signal to noise ratio by signal averaging. This process involves repeatedly acquiring the spectrum and adding each spectrum together. Actually, this is not an average in the strict mathematical sense, (It is not normalized by the number of scans.) but is the sum of the individual spectra. As a result, the signal increases proportionally with N, the number of scans. Owing to the random nature of noise, its increase will only be proportional to $\sqrt{N}$. The resultant enhancement of signal to noise ratio is then proportional to $\sqrt{N}$.

In order to signal average, we must open the Parameters dialog box. Enter the Number Of Scans you wish to average in the Scan folder. You need to turn off the Replace Mode. Otherwise the current scan is going to replace the last scan. (See Figure 5-31.)

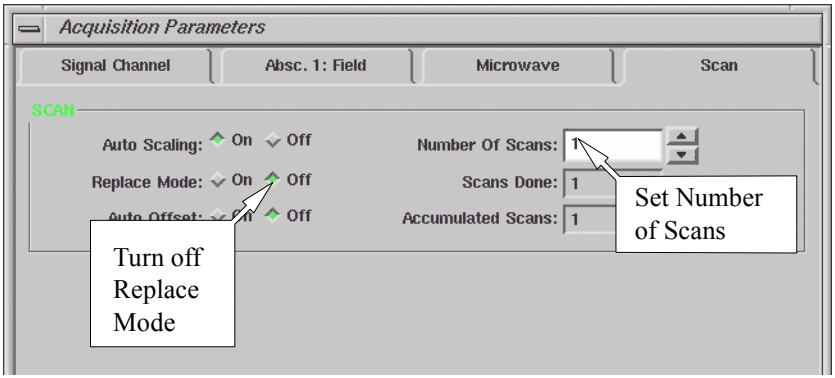


Figure 5-31 The Scan parameters.

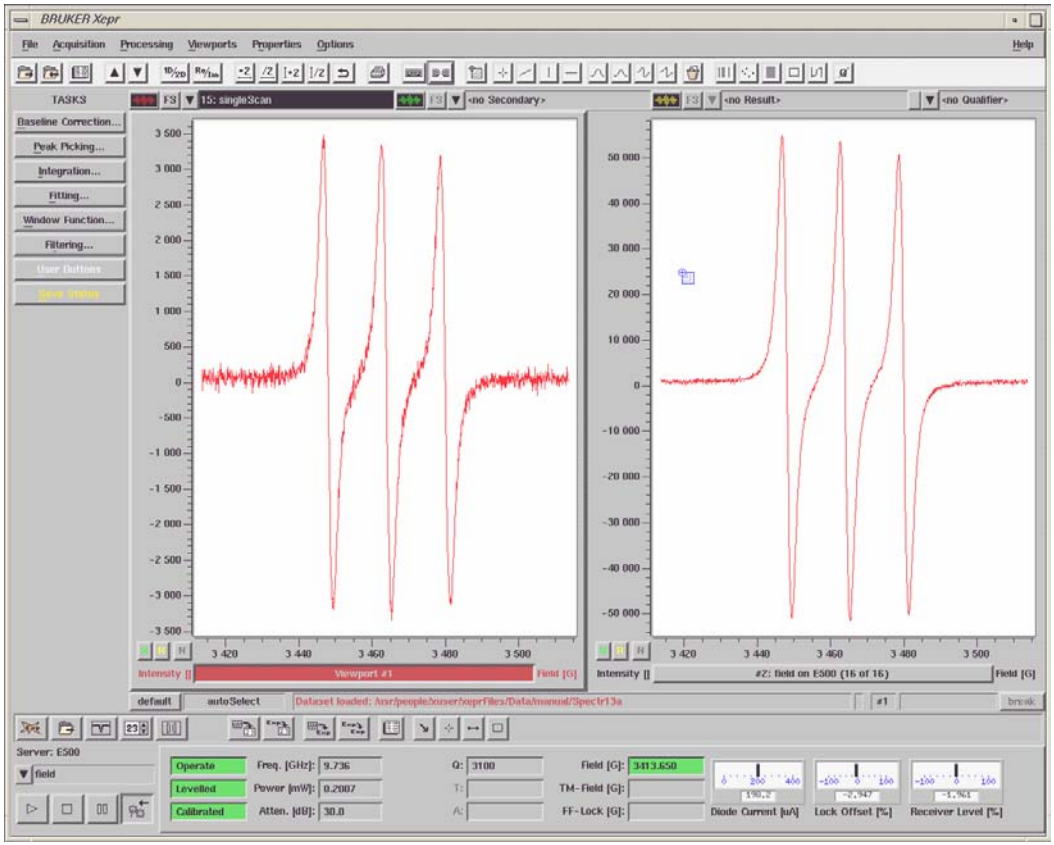


Figure 5-32 A single scan (left) versus 16 scans (right).

Acquire the spectrum by clicking the RUN button in the Acquisition Control section. In the example shown in Figure 5-32, 16 scans results in a four-fold improvement of signal to noise ratio. If you want to stop the averaging, click Pause and the scan will pause at the end of the sweep. Then click Stop.

Number of Data Points 5.5.5

EPR spectra acquired with a computer consist of a list of magnetic field values and corresponding intensities. If you have very narrow lines, care must be taken that there are enough data points to fully characterize the lineshapes. If there is not sufficient resolution, expanded sections of the spectrum will only be crude approximations of the actual signal. The number of points in a spectrum can be chosen in the Parameters dialog box of the Absc. 1: folder. (See Figure 5-33.)

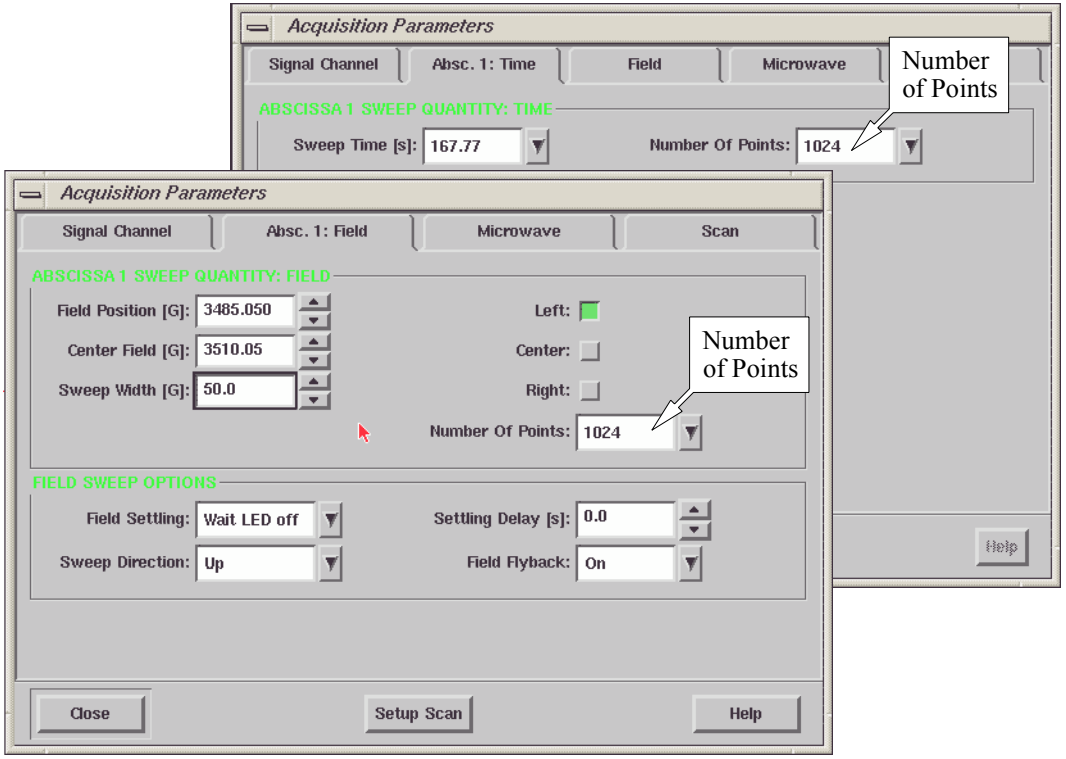


Figure 5-33 Selecting the number of points in the Absc. 1 folder.

The parameter to adjust is the Number of Points. Perhaps the best way of demonstrating this effect is to look at the following two examples. The right spectrum was acquired with only 1024 points. The left spectrum was acquired with 4096 points and reproduces the lineshapes much better than the right example. (See Figure 5-34.)

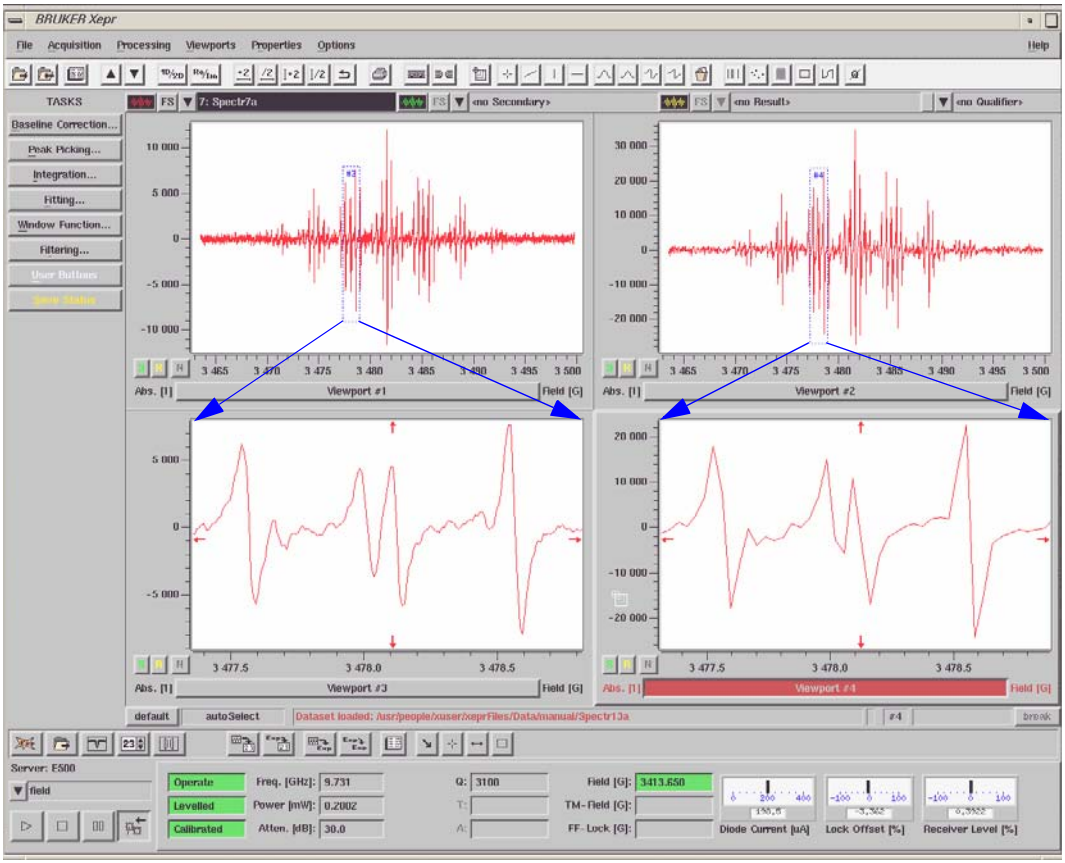


Figure 5-34 A perylene radical cation spectrum acquired with 4096 (left) or 1024 (right) points.

First Harmonic vs. Second Harmonic Spectra 5.5.6

EPR spectra are commonly acquired as the first derivative of the absorption curve. It is the first harmonic component of the field modulated signal. Sometimes, the hyperfine structure of the EPR signal is not resolved in the first harmonic spectrum as shown in Figure 5-35. Only small splittings and shoulders in the first har-

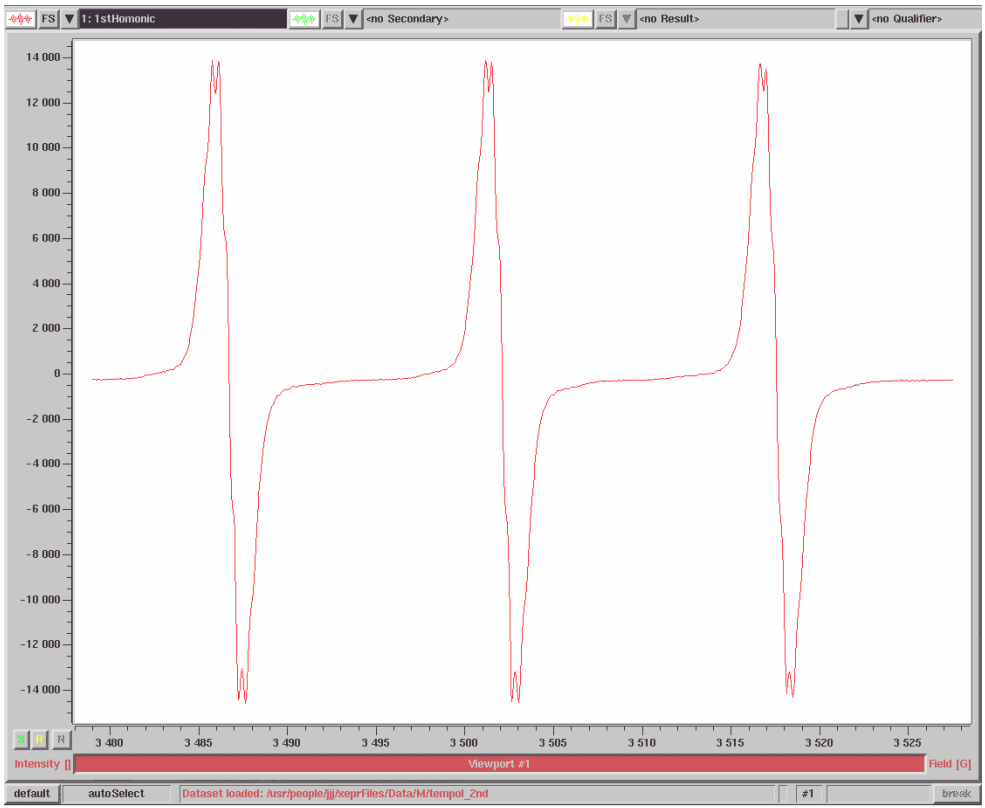


Figure 5-35 A first harmonic spectrum of TEMPOL.

monic spectrum indicate that the hyperfine structure exists. A second harmonic spectrum extracts the EPR signal from the second harmonic component of the field modulated signal. The second harmonic spectrum can help to resolve some of the structure of the EPR signal.

To acquire a second harmonic spectrum you need to have the signal channel calibrated for the second harmonic. (See Chapter 2 of the Elexsys E 500 User's Manual: Advanced Operations for details.) Open the Parameters dialog window. Select 2 in the Harmonic box of the Signal Channel folder. (See Figure 5-36.)

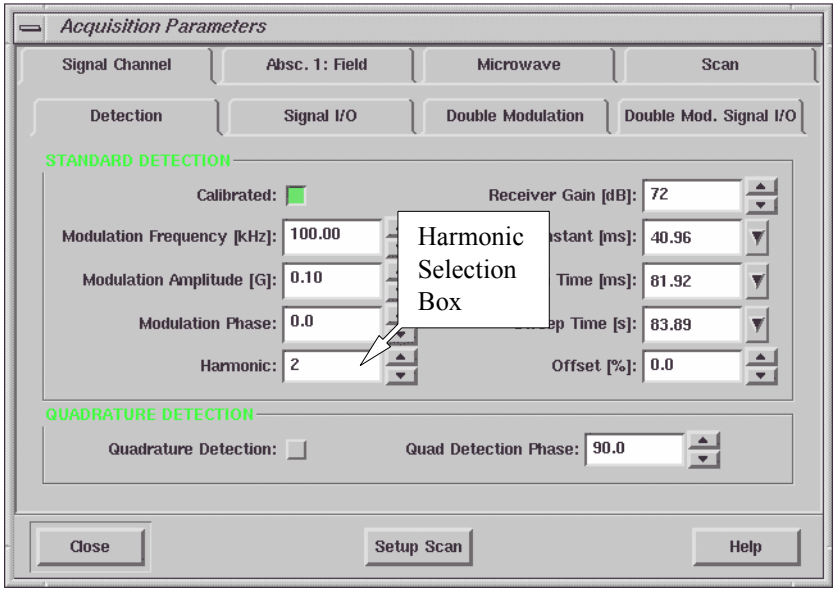


Figure 5-36 Selecting second harmonic detection.

To acquire a dispersion spectrum you need to use a Bruker dispersion bridge.

You can acquire a second harmonic spectrum now. Figure 5-37 shows the second harmonic spectrum of the same sample in Figure 5-35. The hyperfine structure of the EPR signal is much better resolved. The second harmonic spectrum is not a dispersion spectrum although it looks a bit like one. Actually it is the second derivative of the absorption curve.

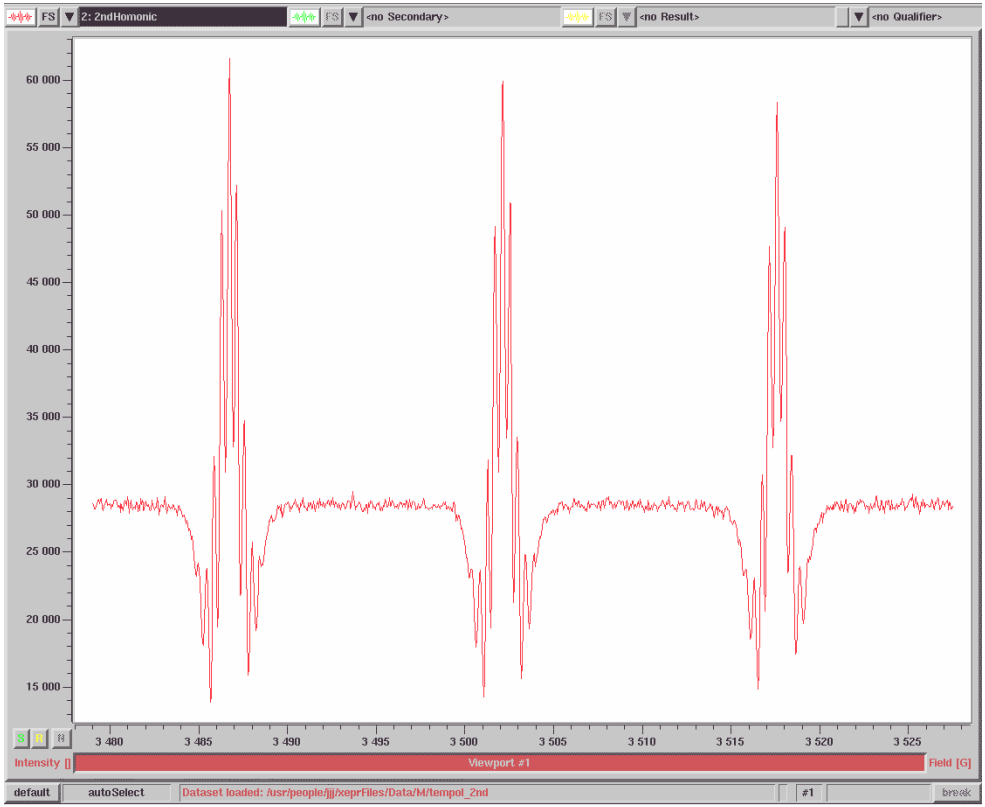


Figure 5-37 A second harmonic spectrum of TEMPOL.

Time Scans 5.6

Not all radicals are very stable: in fact most are very reactive species and will disappear via chemical reactions. Many people are interested in the kinetics of these reactions. The Xepr software has many of predefined experiments to suit your needs. A Time Scan experiment is the one to study the time behavior of such changing systems. The magnetic field is kept fixed at a specified value and the EPR signal intensity is monitored as a function of time.

Acquiring a Field Swept Spectrum 5.6.1

The first task is to acquire a field swept spectrum before acquiring the time scan. This spectrum is usually acquired under steady-state conditions or before the chemical reactions have started. The purpose of acquiring a field sweep spectrum is to find where to fix the magnetic field for the Time Scan experiment. Create a 1D field sweep experiment. Give it a name that you can easily recognize. In this example, we call it "field". Select appropriate parameters and acquire a spectrum.

Creating a Time Scan Experiment 5.6.2

It is convenient to open two viewports when both a field sweep and time scan need to be monitored. Create a new viewport by clicking the Viewport button in the menu bar and then clicking on New Viewport 1D. Click the Unlink button so that you can display the field sweep in one viewport and the time scan in the other. Create a new experiment and assign a name for the time scan experiment such as Time. Select Time for Abscissa 1 and None for Abscissa 2. (See Figure 5-38.)

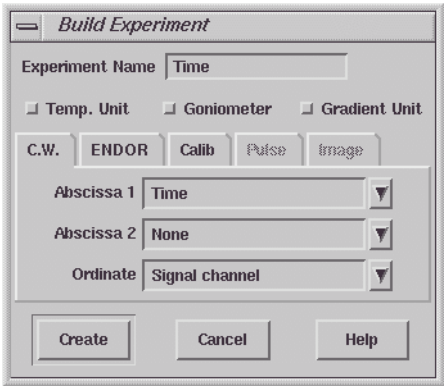


Figure 5-38 Defining a time scan experiment.

Linking Two Experiments 5.6.3

In order to determine where to set our static field we can utilize the Linked Experiments function, a specially designed function in Xepr. You can link two experiments together by sharing a common parameter value. In this example, the common parameter is the field position. You can define how two experiments link together, *e.g.* which parameter two experiments share. After two experiments are linked together, the common parameter in one experiment will be automatically determined by the other experiment. Let us practice this function in the Time scan experiment. Click Acquisition in the menu bar and click Create Experiment Link. (See Figure 5-39.)

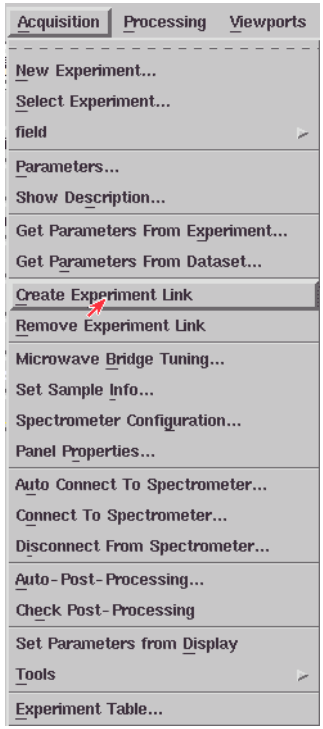


Figure 5-39 Creating an experiment link.

A dialog box will appear asking which parameters and experiments you want to link together. (See Figure 5-40.)

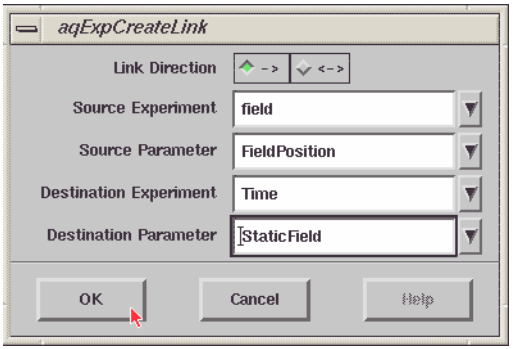


Figure 5-40 The dialog box for linking two experiments.

The Link Direction allows you to choose whether this link is a one-way (-->) or two-way (<-->). Click on one-way link for this experiment. Select the field sweep experiment name as the Source Experiment ("field" in this example). Select Field Position as the Source Parameter. Select the time scan experiment name as Destination Experiment ("Time" in this example.) Select Static Field as the Destination Parameter. Click OK to close the dialog box. The next step is to set the field position in the field sweep experiment so that the static field in the time scan experiment will be automatically set. Click the viewport selection bar of the Viewport containing the field sweep results. Click FS to bring the spectrum to full scale. Click the X-marker tool and select Field Position in the dialog box. (See Figure 5-41.)

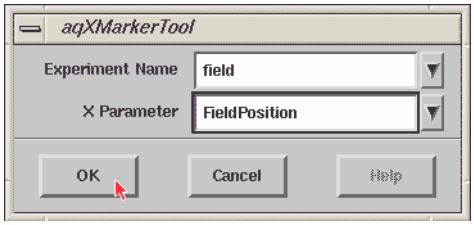


Figure 5-41 Selecting an X-marker.

A marker will appear in the active viewport. Place the cursor where you would like the static field to be. This action replaces the default static field value of the time scan experiment with the magnetic field position of the X-marker in the field sweep experiment.

Once the static field has been selected, we must switch from a Field Sweep to a Time Scan. Click the viewport selection bar of the Viewport containing the Time Scan experiment. Select Time as the current experiment from the Experiment List. Make sure that the Activate button is engaged. Open the Parameters dialog box and set the other parameters such as the Conversion Time and Time Constant so that they are appropriate for the time scales to be encountered with the chemical reaction. (See Figure 5-42.)

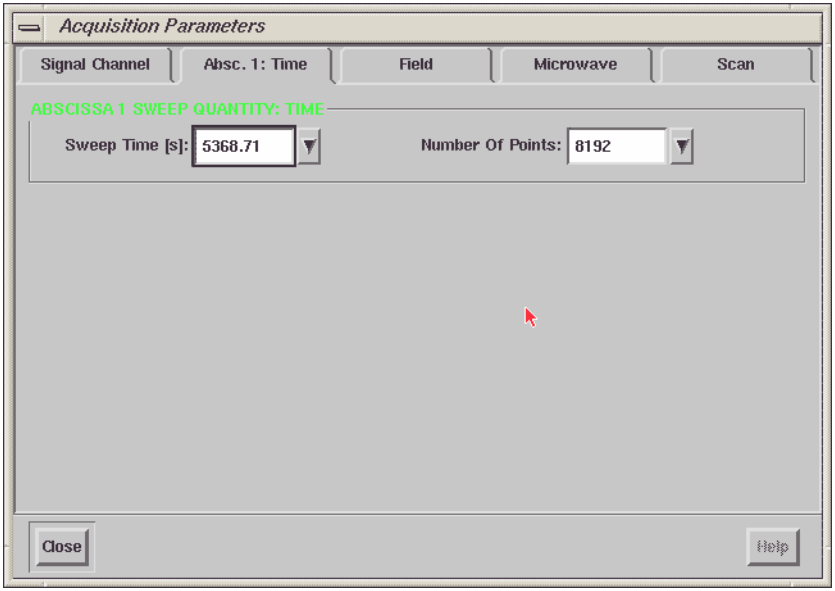


Figure 5-42 Setting parameters for the time scan experiment.

There remains one more task before we can acquire the time scan: we must turn the Automatic Offset off. The Automatic Offset option subtracts the average value of the spectrum at the end of a scan. This feature is convenient for field sweep spectra because the average value should be zero if you sweep through the complete EPR spectrum. Subtraction of the average value therefore makes double integrations easier. A zero average value is not necessarily true for a time scan. You may also want to know the ratio of the initial and final intensity, which would be impossible if the average value were subtracted. To disable the Auto Offset option, click the Scan tab and click the Off button next to Auto Offset. (See Figure 5-43.)

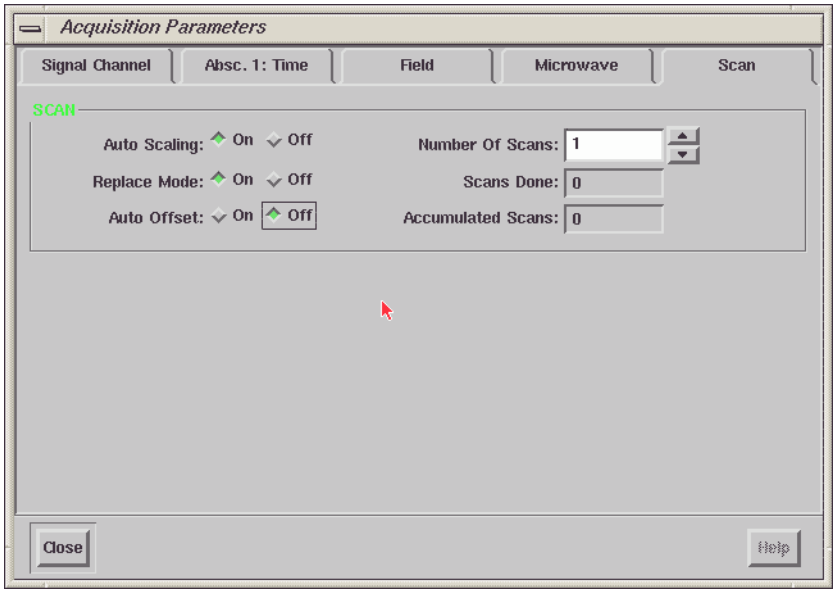


Figure 5-43 Turning Auto Offset off.

Acquire the time scan by clicking the RUN button in the Acquisition Control section. There may be a slight offset, particularly if your signal is very weak. Acquire another spectrum "off resonance". This can be easily done by changing the Static Field with the Field Position marker in the Field Sweep experiment. Store the "on resonance" Time Scan first. Click the selection bar of the field sweep Viewport. Move the Field Position marker off the EPR peak to the base line. Click the selection bar of the time scan Viewport and acquire the "off resonance" spectrum by clicking RUN. Subtract it from the first Time Scan to obtain a baseline corrected result.

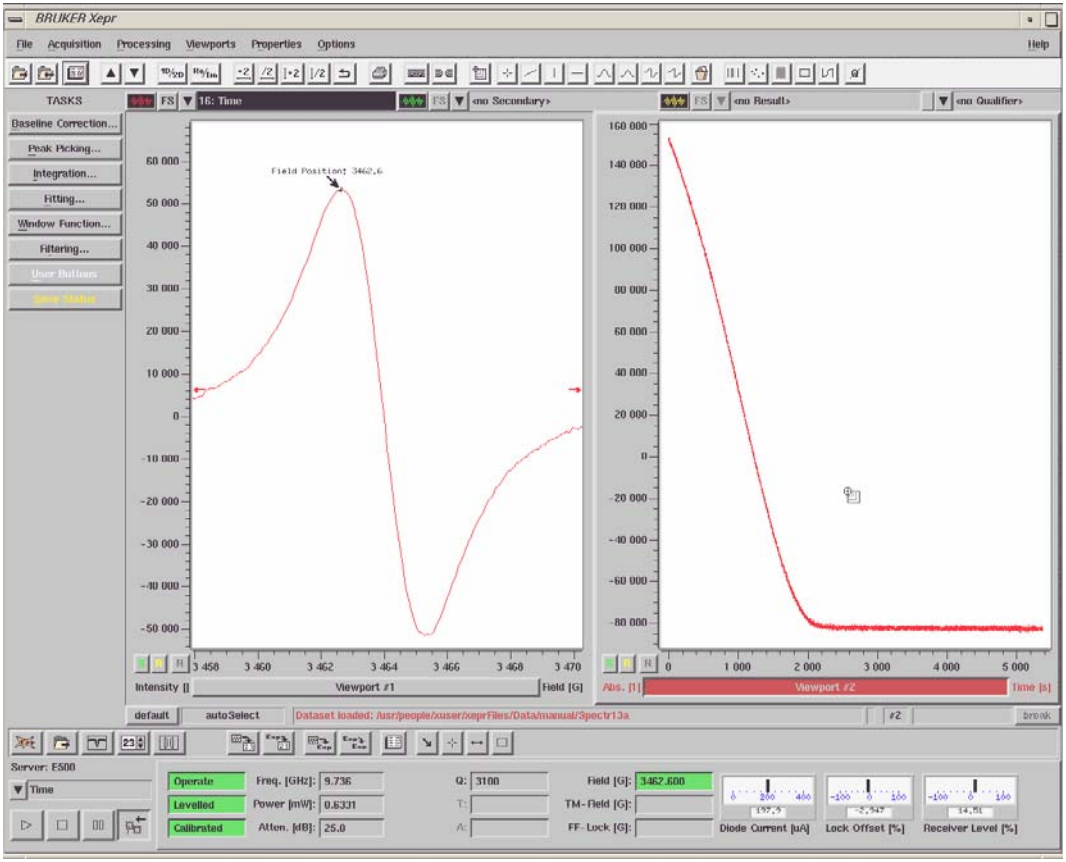


Figure 5-44 A time scan of a rapidly decaying radical.

Performing 2D Experiments 5.7

Using the Xepr software you can perform experiments in which a second parameter (*e.g.*, in addition to the magnetic field) can be varied. For example, you can perform a set of experiments in which the power is increased incrementally over several successive field scans. Alternatively, you might perform several consecutive experiments in which the temperature is ramped either up or down between each field scan. You can then display the 2D dataset in various ways in Xepr. This section describes how to use the Acquisition function to create a 2D experiment and how to display it. The procedure is most easily described by performing an example experiment that investigates the response of the strong pitch spectrum to microwave power.

1. **Insert the strong pitch sample.** Place the strong pitch sample into the cavity and tune the spectrometer as described in Section 3.2, Tuning the Microwave Cavity and Bridge.

2. **Open the New Experiment dialog box**. Click the New Experiment button in the Experiment Definition section. The New Experiment dialog box will then appear.

3. **Define a 2D experiment**. Name the 2D experiment. Select Field as Abscissa 1 and Microwave power as Abscissa 2 in the drop-down list. (See Figure 5-45.) Click OK to close the dialog box.

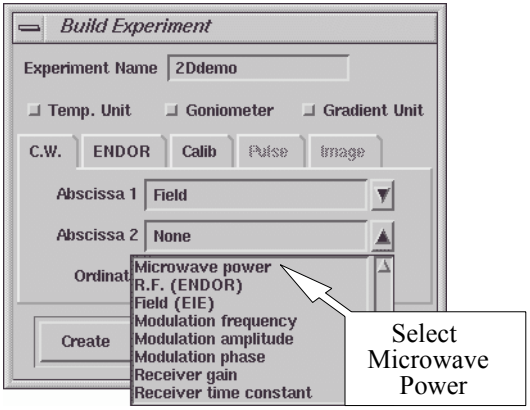


Figure 5-45 Defining a 2D experiment.

4. **Open the Acquisition Parameters dialog box.** Click the Acquisition Parameters button to open the dialog box.

5. **Set parameters.** Follow the instructions in Chapter 3 to select proper parameters. You can use the Setup Scan to help you determine proper parameters. Figure 5-46 shows a sample set of parameters.

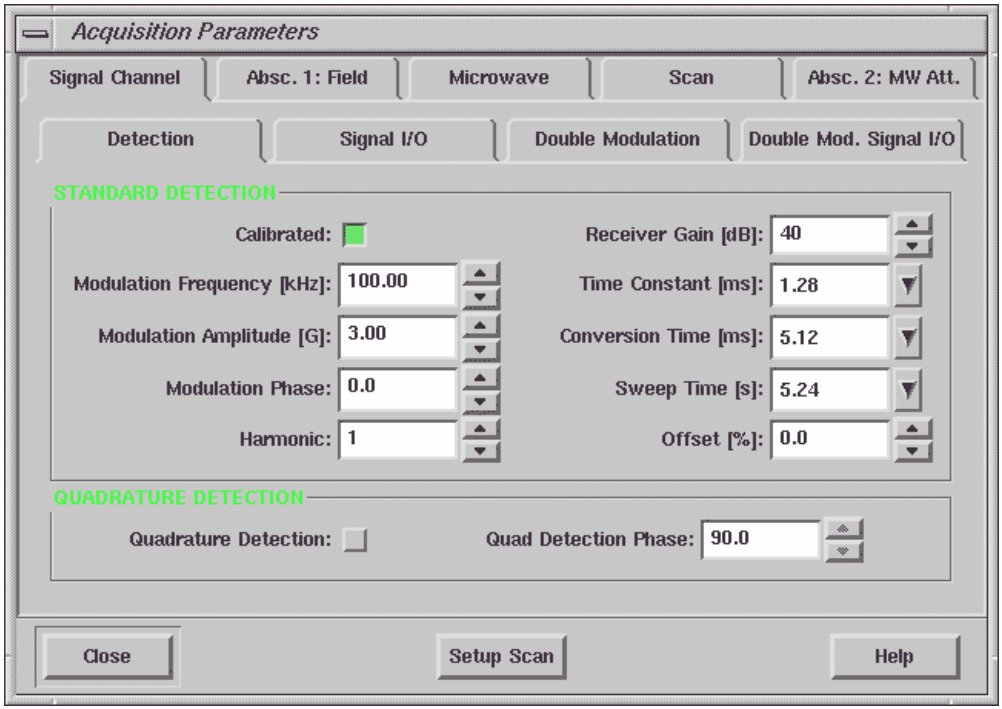


Figure 5-46 A sample set of parameters.

6. **Set the Acq Fine Tuning option.** Select Each Slice Scan. The acquisition software will perform a fine tune before acquiring each slice of the 2D spectrum. (See Section 5.4.1for more details.) This option is particularly important when changing the microwave power or changing the orientation of the sample with a programmable goniometer because the frequency and coupling can change.

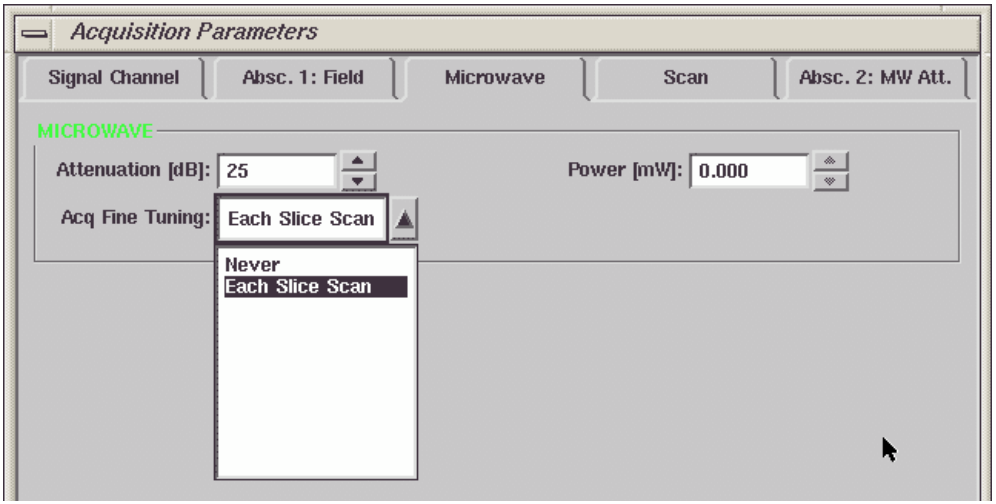


Figure 5-47 Selecting the fine tune option.

7. **Set the Abscissa 2 parameters.** Click Absc. 2: MW ATT. Set the Start Value to 0 db, Increment to 2 db, Number of Points to 31. This setting allows you to acquire a 2D spectrum of total 31 slices with a step size of 2 dB in microwave power. The Settling Time is a delay to wait for the instrument to stabilize. Select a sufficiently long settling time to stabilize the acquisition environment. We use 1000 ms in this example. (See Figure 5-48.)

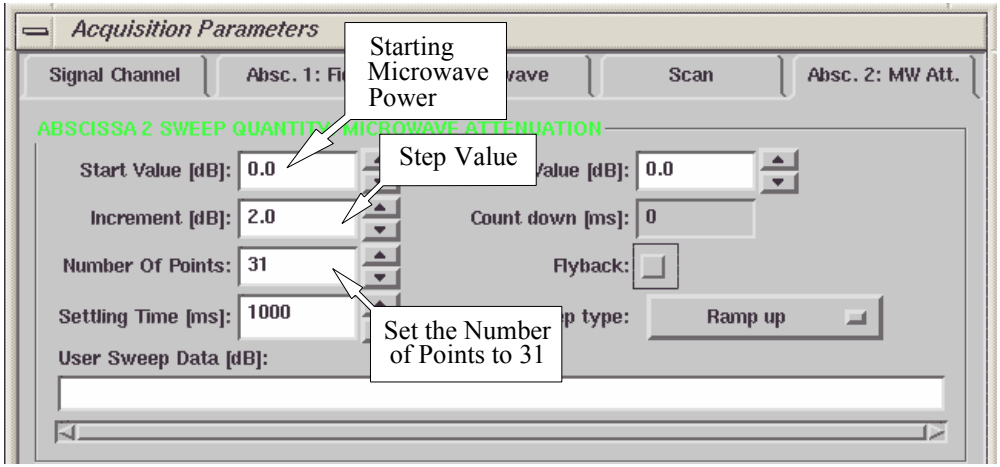


Figure 5-48 Sample parameter settings of Absc. 2: MW Att. for acquiring a 2D dataset.

Set the Current Value of the microwave attenuation to 0 dB. Recheck the matching to make sure it is critically coupled. Leave the Fly Back button unselected. If it is green, it will set the attenuation back to the initial value after the acquisition. Leave Ramp type as Ramp Up. It will increase the attenuation by the increment you have set. If you set it to Ramp Down, it will decrease the value by the increment you set. Click Close to close the Acquisition Parameters dialog box.

8. **Click on Run to acquire your 2D data set.** This will initiate the first of 31 scans with the power decreasing (or the attenuation increasing) in units of 2 dB between each scan. You will notice the scan number updating on the scroll bar of the Viewport (See Figure 5-49.) You can scroll up and down to see one slice at a time after the acquisition finishes.

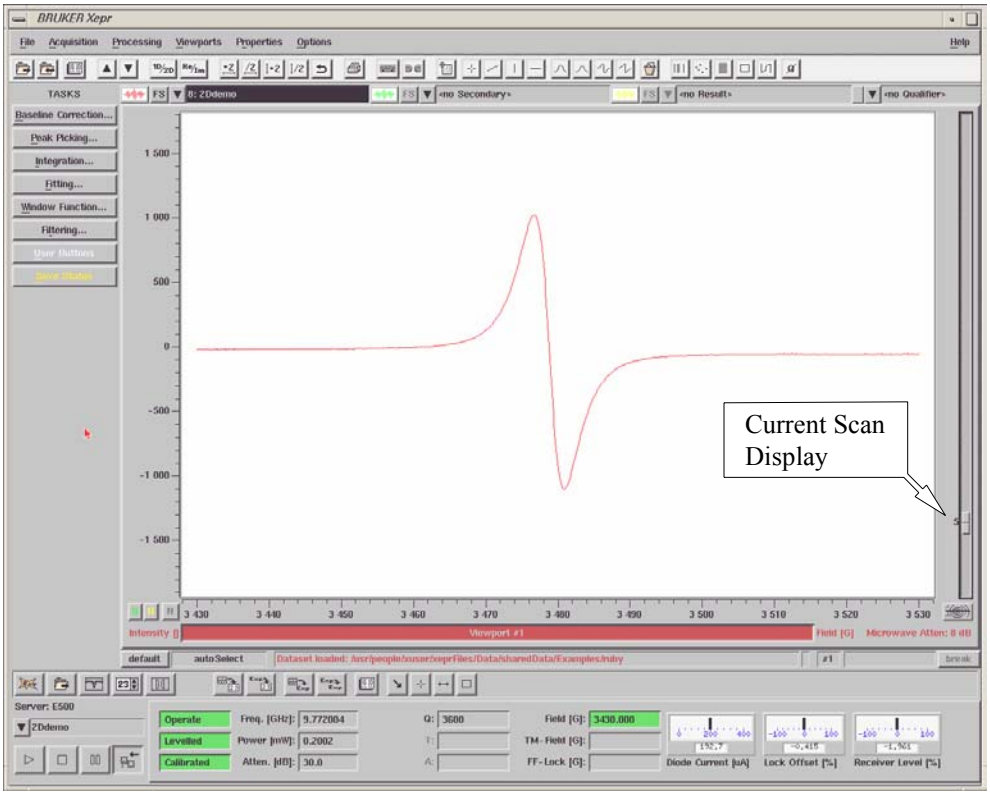


Figure 5-49 Acquiring a 2D spectrum.

9. **Display the data as a 2D Transparent Plot.** Click on the Property menu of the Primary section and then select transparent as the Display Type. The 2D spectrum will be displayed as in Figure 5-50.You can see all the slices as well as the projections on the X and Y axes. You can tilt, rotate, and adjust the lens angle of the 2D transparent display. Click Properties in the menu bar and then click on 2D Perspective. (See Figure 5-51.)

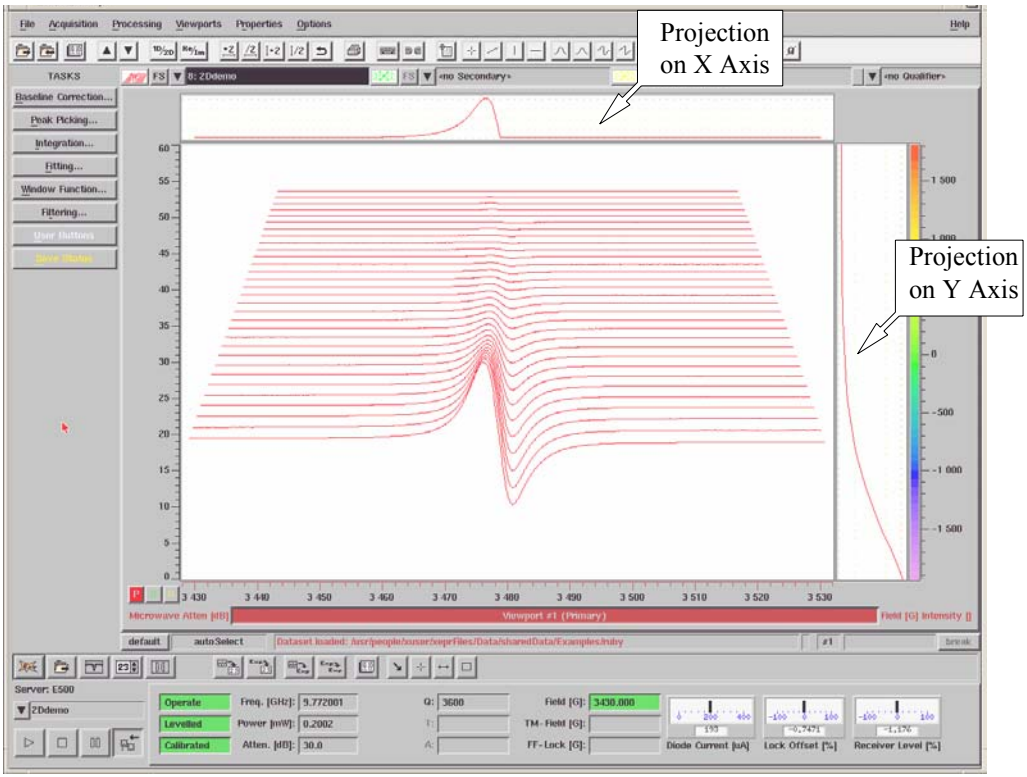


Figure 5-50 A 2D transparent display.

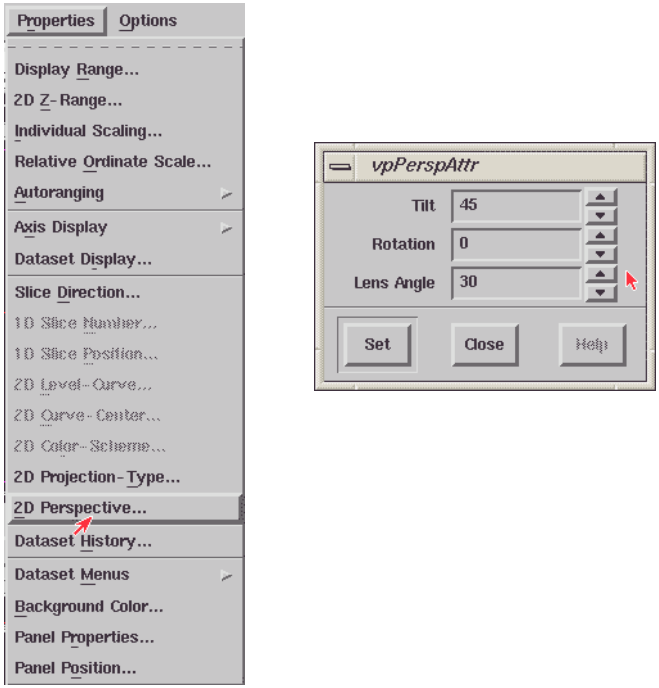


Figure 5-51 Changing the 2D Perspective.

A dialog box appears allowing you to adjust the tilt angle, rotation angle, and lens angle interactively. After you have optimized the display angles click the Set button. (See Figure 5-51.)

10. **Display the 2D dataset as a Density Plot.** Sometimes, displaying a 2D dataset as a Density plot can help you analyze the data. Click the Property menu of the Primary section and select density from the Display type list. You should see a display like that in Figure 5-52.

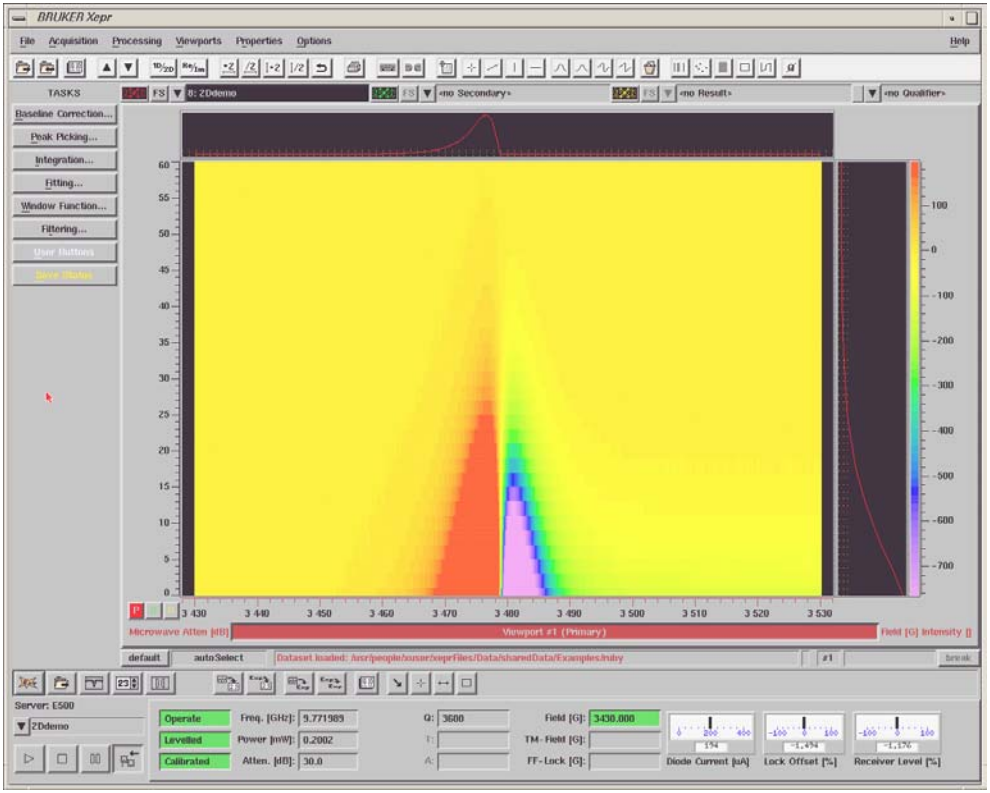


Figure 5-52 A density plot of a 2D dataset.

11. **Display a 2D dataset as a Contour Plot.** You may need to display the 2D dataset as a contour plot. Simply click the Property menu of the Primary section and select contour from the Display type list. The 2D dataset will be displayed as a contour plot. (See Figure 5-53.)

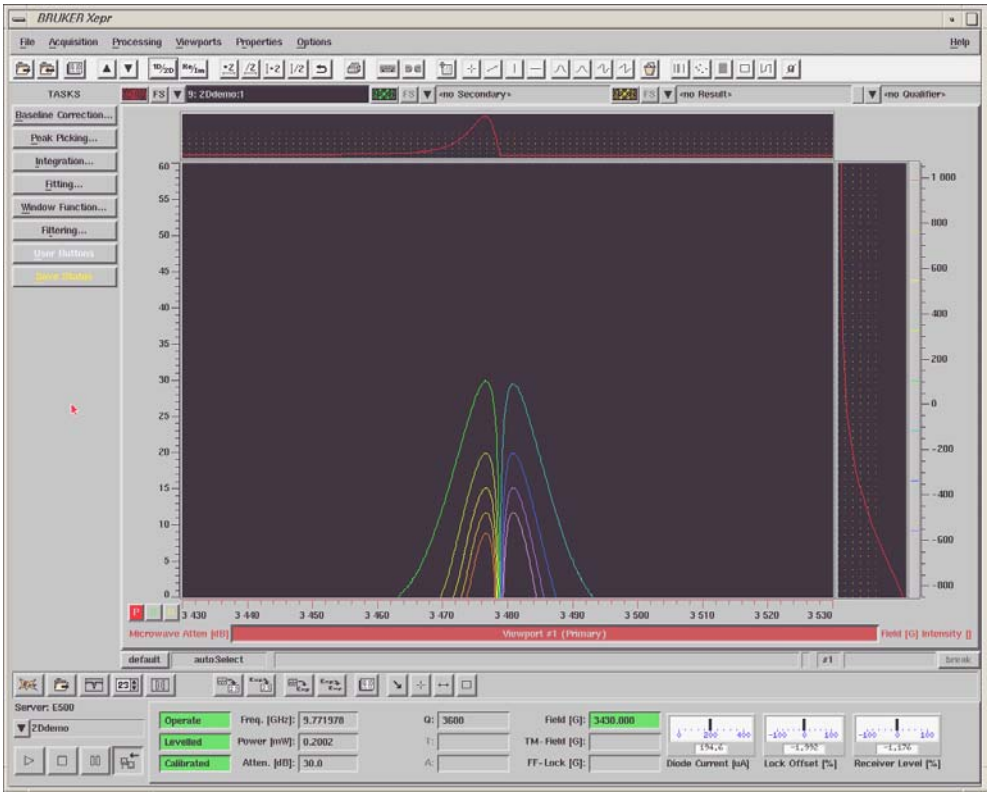


Figure 5-53 A contour plot of a 2D dataset.

12. **Display a 2D dataset in different styles at the same time.** You can display the same dataset in different styles at the same time. Just create as many viewports as you need. Activate each viewport and set the display type you want for that viewport. (See Figure 5-54.)

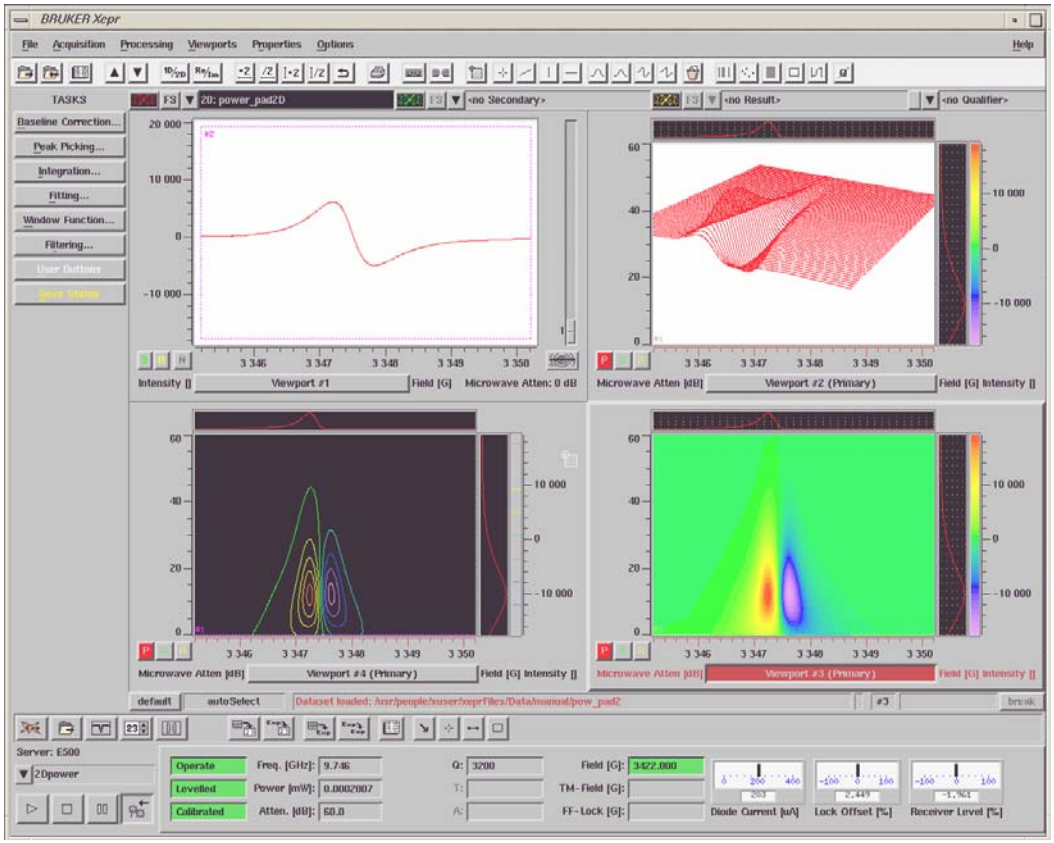


Figure 5-54 Displaying a 2D dataset in various styles.

Data Processing Tutorial 6

This chapter contains useful and helpful hints to get the most out of the data processing capabilities of the Xepr software. In the previous chapter, we focused on acquiring spectra. Here is the opportunity to explore some of the data processing features. The tutorial is not meant to be an exhaustive treatise on all details of data processing. Instead, it is a starting point from which you can explore the capabilities of the software.

The first topic covers data handling including data input, output, and the data table. The following topics describe basic data processing functions such as baseline correction, peak picking, integration, curve fitting, and spectra algebra. The chapter ends with the concept of data history employed in Xepr.

Data Handling 6.1

Data Input 6.1.1

Xepr can read two types of EPR spectra, the BES^{3}T® data files and ESP format data files. The BES^{3}T® data files include two files for each spectrum, the .DSC file and .DTA files. The .DSC file is an ASCII file containing all the parameters for the spectrum. The .DTA is a binary file containing the spectrum data. The ESP data files include two files for each spectrum, the .par file and the .spc file. The .par file is an ASCII file and contains all the parameters of the spectrum. The .spc file is a binary file containing the spectrum data.

Loading in a BES^{3}T® File

Click File in the menu bar and select Load or click the Load button in the tool bar. (See Figure 6-1.)

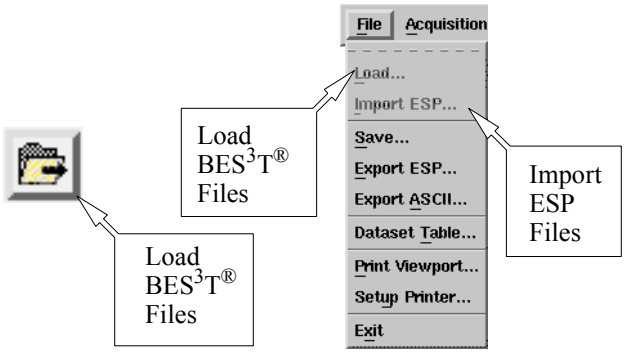
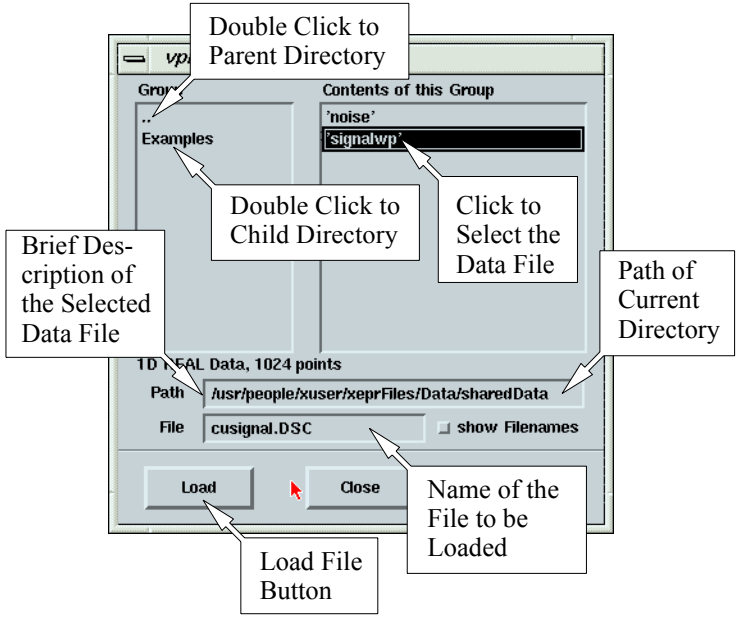


Figure 6-1 The File menu.

A dialog box will appear. (See Figure 6-2.)



The filename is actually used by the file system of the operating system. The title is part of the descriptor file and can be much more descriptive than the filename. It makes finding and identifying spectra easier.

Figure 6-2 The load data set dialog box.

Select the subdirectory where the spectrum is stored. Double click the subdirectory name to enter that subdirectory (the child directory). Double clicking on the two-dots brings you to one level up (the parent directory). You have the option to show either the spectrum title or the file name. By default the title of the data set is displayed. If you click on the FileNames button, all the spectrum files with extension .DSC in the selected subdirectory will appear in the box. (See Figure 6-3.)

Click the spectrum file title or file name and then click Load to read the spectrum into Xepr. Alternatively you can double click the file you want to load. After loading all the spectra click Close to exit the dialog box.

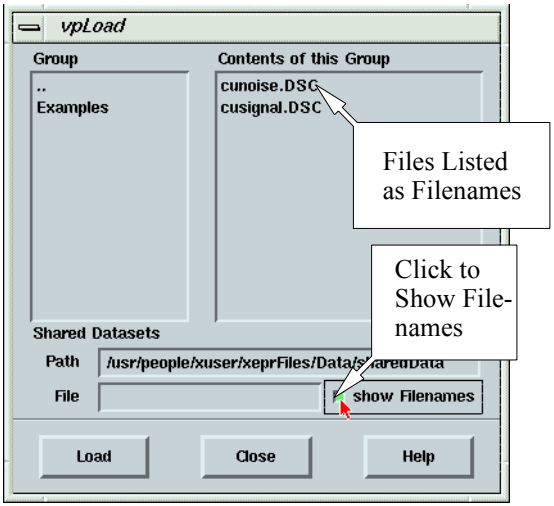


Figure 6-3 Showing file names.

Reading in an ESP File

Click File in the menu bar and then Import ESP. A dialog box appears listing available ESP data files. Select the correct path to find ESP data files. (See Figure 6-4.) Click to select the file and then click Load to import the spectrum into Xepr. For ASCII data files, you need to convert the ASCII file to ESP format and then you can read them into Xepr. WIN-EPR can convert ASCII files to ESP format.

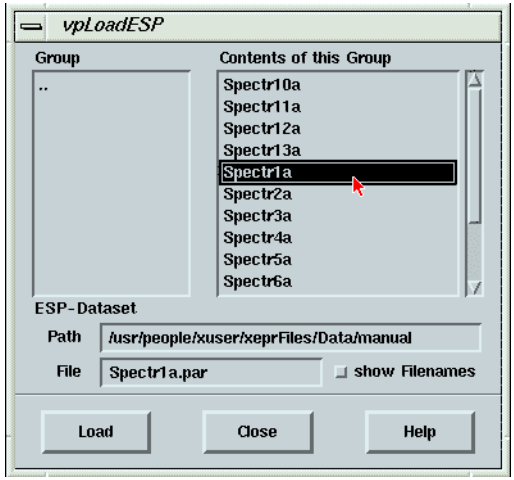


Figure 6-4 Importing an ESP file.

Data Output 6.1.2

To save data in BES^{3}T® format, click File in the menu bar and then Save or the Save button in the tool bar. (See Figure 6-5.)

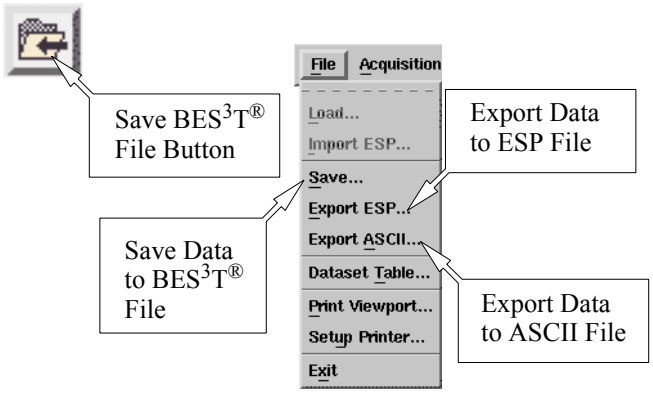


Figure 6-5 Saving a spectrum data file.

A dialog box appears in which you can choose to save the data set from Primary, Secondary, Qualifier, or Result by clicking the corresponding button. Enter a new title in New Title. Select the desired directory or path to save your data. The path you select to save the data files will appear in the Path box. You can make a new directory in this dialog box. Enter the new directory name after the path. Make sure you have permission to write to the path. Click the Create button to create a new directory. Enter a file name without extension in the File box. The software will automatically add the proper extension for you. Click Save to save and exit the Save dialog box. (See Figure 6-6.)

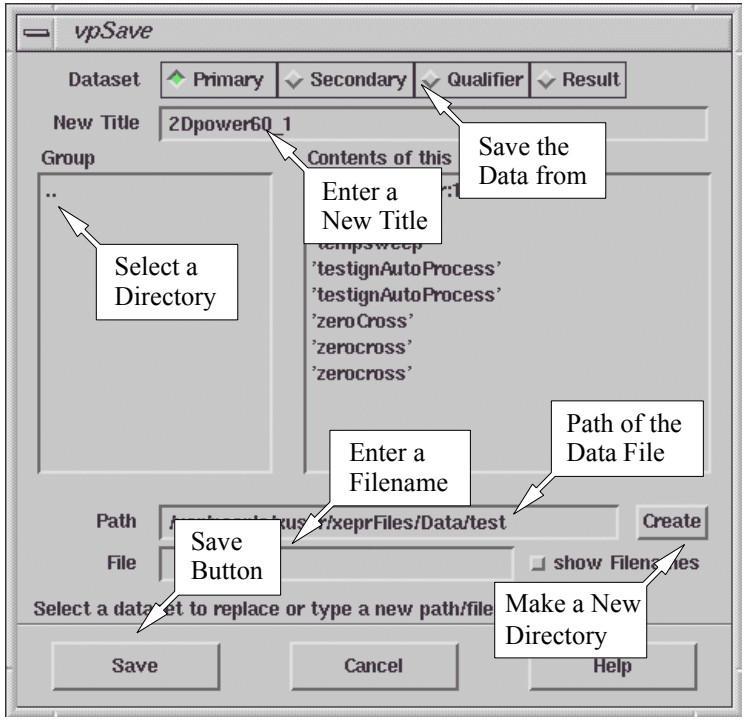


Figure 6-6 Saving an Elexsys data file.

If you want to process the data using Win-EPR or other software you need to export the spectra in either ESP format or ASCII format. Click File in the menu bar and then Export ESP or Export ASCII. The dialog box that appears has the same format as that for saving BES^{3}T® files except the title of the window is either vpSaveEsp or vpSaveAsc. (See Figure 6-7.) Follow the above instructions regarding entering the title, path, and file name, and then click Save to export the file and exit the dialog box.

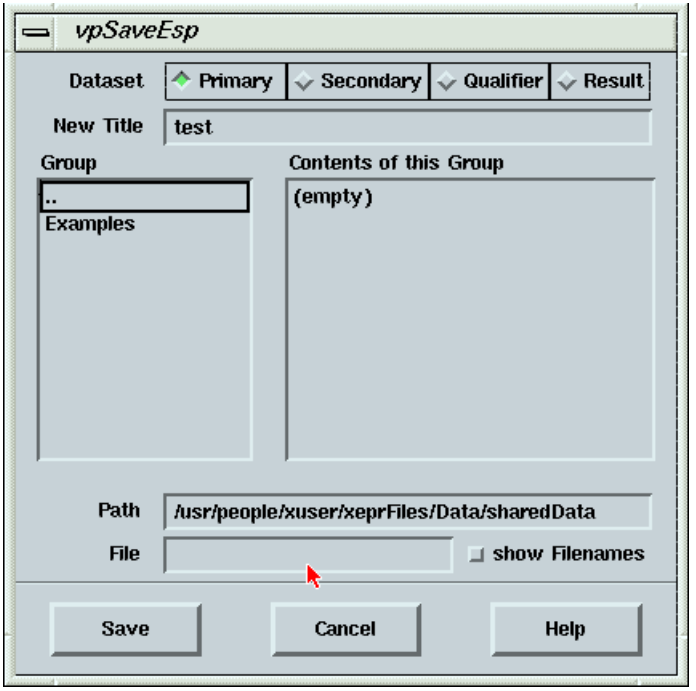


Figure 6-7 Exporting a dataset as an ESP file.

The Data Set Table 6.1.3

All the spectra data sets read into Xepr or acquired and stored/saved in Xepr are listed in the Dataset Table. The Dataset Table is where you can organize datasets and obtain information regarding the datasets. These datasets can also be found in the Data List of the viewport. To display the data in the list, click the Data List of either Primary or Secondary dataset of the viewport and select the spectrum you want to display.

Open Dataset Table

Click the Dataset Table button in the tool bar or click File in the menu bar and click Dataset Table. (See Figure 6-8.)

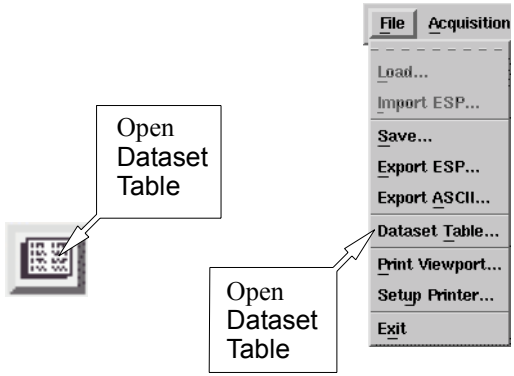


Figure 6-8 Opening the Dataset Table.

The Dataset Table will open. The first column of the Dataset Table is a list of numbers called the Dataset Handles. Each Dataset Handle is assigned to each dataset when it is input into Xepr memory. Some Xepr functions refer to the dataset by its Dataset Handle. By default there are four other columns listed as Class, Filename, Title, and Size. The Class indicates whether the dataset is a 1D spectrum or 2D spectrum. The icon of a regular EPR signal indicates that the dataset is a 1D spectrum as the datasets #1 to #4 shown in the Dataset Table of

Figure 6-9. The contour plot icon in Class indicates that a dataset is a 2D spectrum as in dataset #5. Filenames are also listed. Those which have been stored but not saved yet are listed as <unsaved>. All the titles of the datasets are listed in the next column. The size of the dataset is listed in the last column.

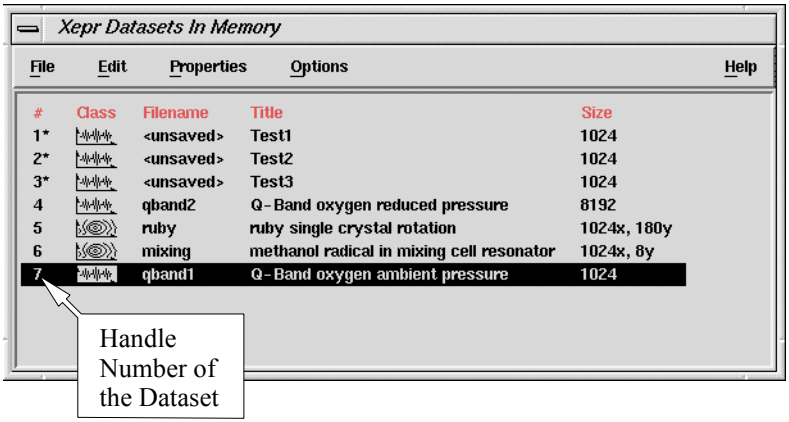


Figure 6-9 The Dataset Table.

File Menu of the Dataset Table

In the Dataset Table you can input and output datasets. Click File in the Dataset Table menu bar and select the command you want to execute. (See Figure 6-10.) To save or export, you need to click the dataset you want to save in order to highlight it. You can also display the description of the highlighted dataset. The description includes all the parameters used during the acquisition. You can take a look at the numerical data by clicking Show Data.

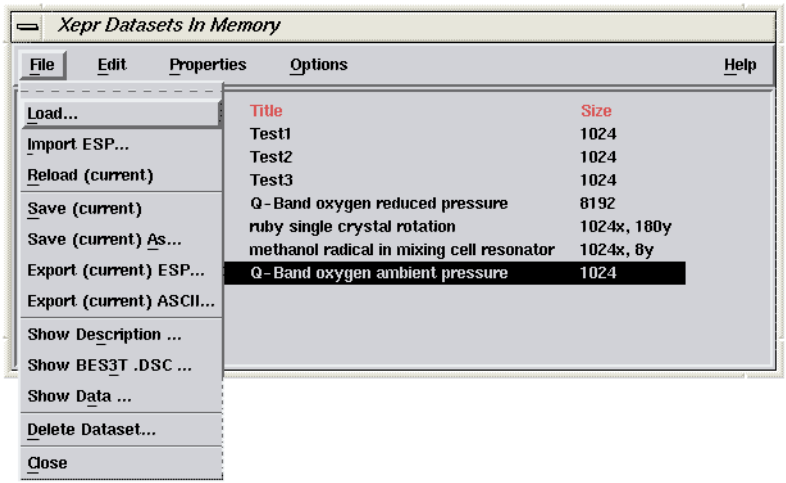


Figure 6-10 The File menu in the Dataset Table.

Edit Dataset Table

You can edit the Dataset Table by clicking Edit in the Dataset Table menu bar. (See Figure 6-11.) You can duplicate the dataset by using Copy and Paste. You can remove selected datasets from the Dataset Table or Remove All the datasets in the Dataset Table. You can check or modify the dataset structure such as Title, Byte Sequence, and other descriptions. However, if you want to modify the dataset or add a description you can only do so with a copy of the original dataset.

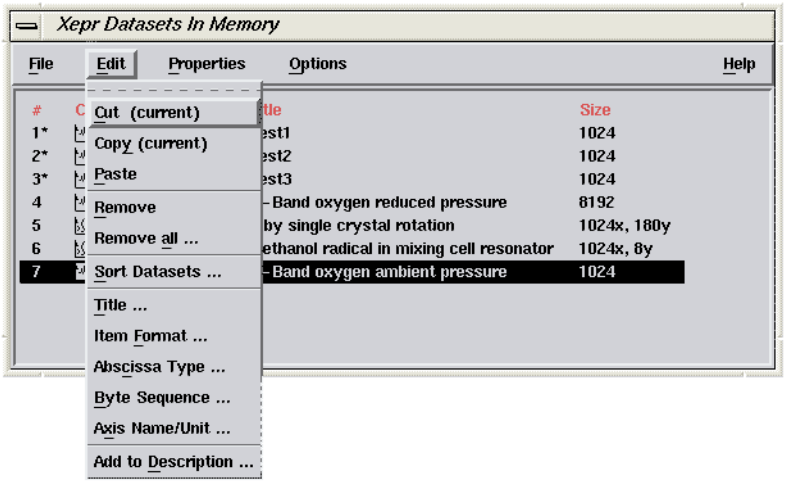


Figure 6-11 The Edit menu in the Dataset Table.

Properties of the Dataset Table

You can customize the Dataset Table by clicking Properties in the Dataset Table menu bar. (See Figure 6-12.) You can choose which dataset properties you want to display in the table by selecting the View items. In addition to the listed features, you can define what to show in the Dataset Table by using UsrDef. For example, click Options in the menu bar and click User Defined Column 1. A dialog box appears in which you can select an item from the list, CMNT, for example, as the feature you wish. Click Properties, View, and UsrDef1 and the comments will be listed in the Dataset Table.

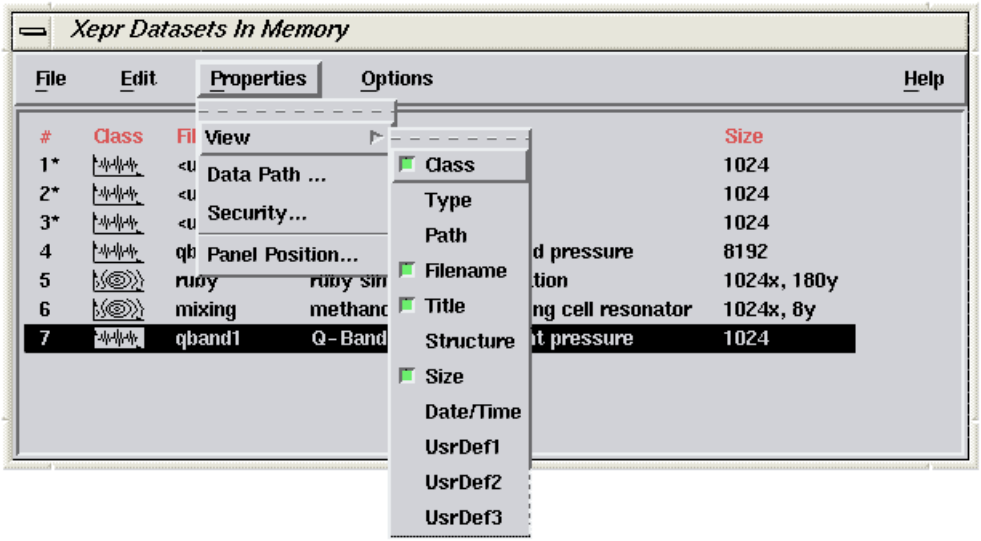


Figure 6-12 The Properties menu in the Dataset Table.

Baseline Correction 6.2

Baseline correction is often used when the baseline fluctuates or there is a broad background signal. Here is an example of how to correct the baseline in Xepr.

1. **Load the spectrum.** Load the spectrum needing baseline correction. Display it in the Primary dataset.

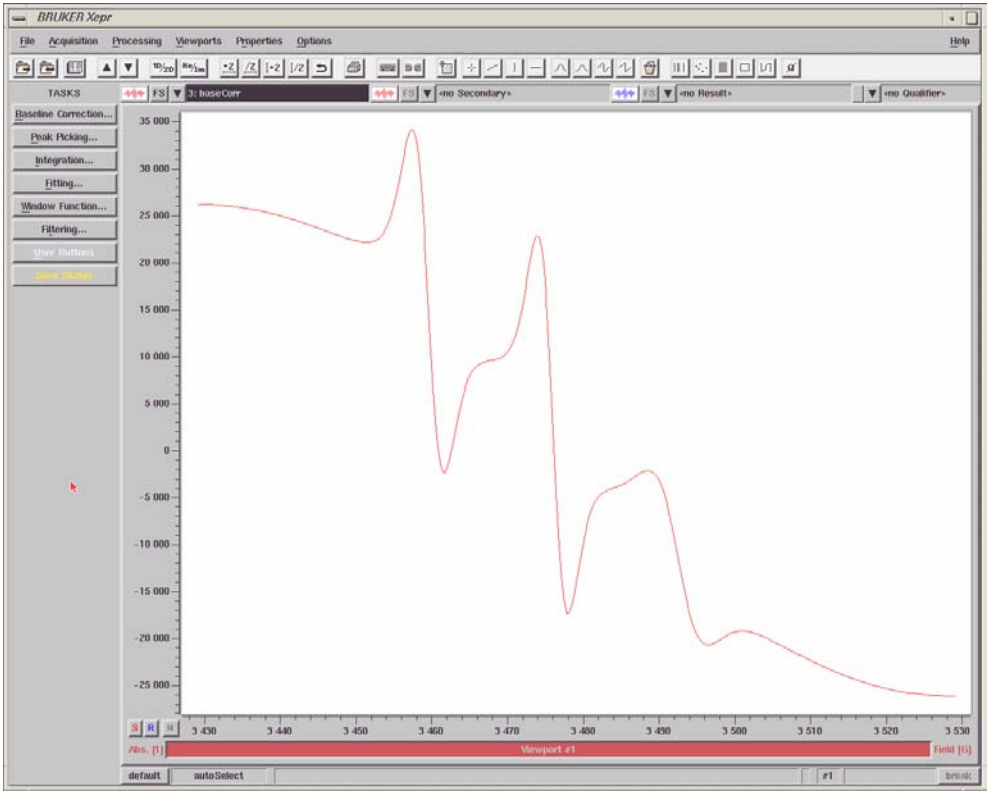


Figure 6-13 A spectrum requiring baseline correction.

In Figure 6-13 we loaded a TEMPO spectrum with a broad background signal.

2. **Start the Baseline Correction Task.** Click the Baseline Correction button in the TASKS menu to launch the Baseline Correction Task. (See Figure 6-14.)

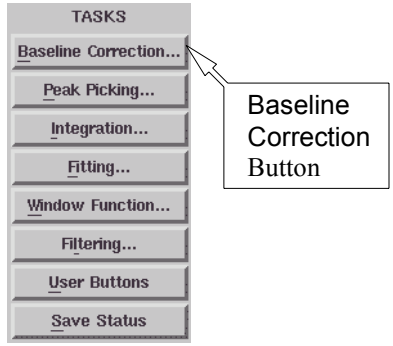


Figure 6-14 Launching the Baseline Correction Task.

3. **Select the desired method.** There are two methods Xepr uses to correct the baseline: Polynomial and Spline. Polynomial uses zeroth to 9th order polynomial functions to simulate the baseline. We shall use the most commonly used method, polynomial functions. (See Figure 6-15.)

Figure 6-15 Selecting the method.

Click Polynomial to enter the submenu for polynomial baseline correction. (See Figure 6-16.)

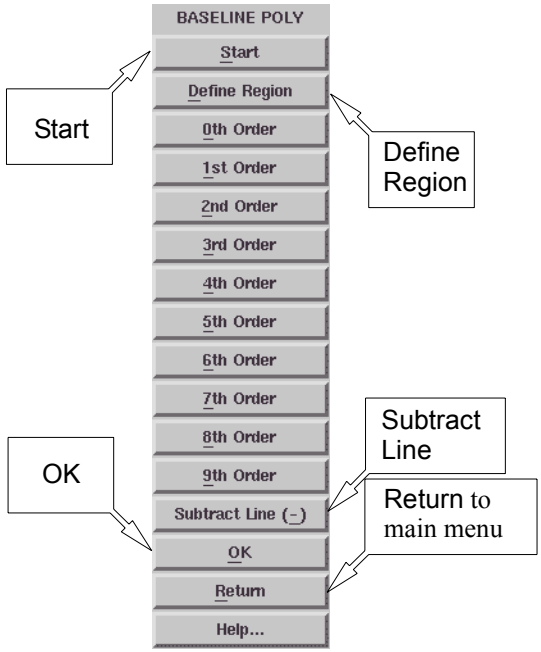


Figure 6-16 The menu for polynomial baseline correction.

4. **Define the Region.** You need to decide which part of the spectrum is considered baseline. Click Define Region and move the mouse pointer to where the baseline starts. (See Figure 6-16.) Click on the left mouse button and drag to where this part of the baseline ends. A qualifier appears and covers the region you selected as baseline. (See Figure 6-17.)

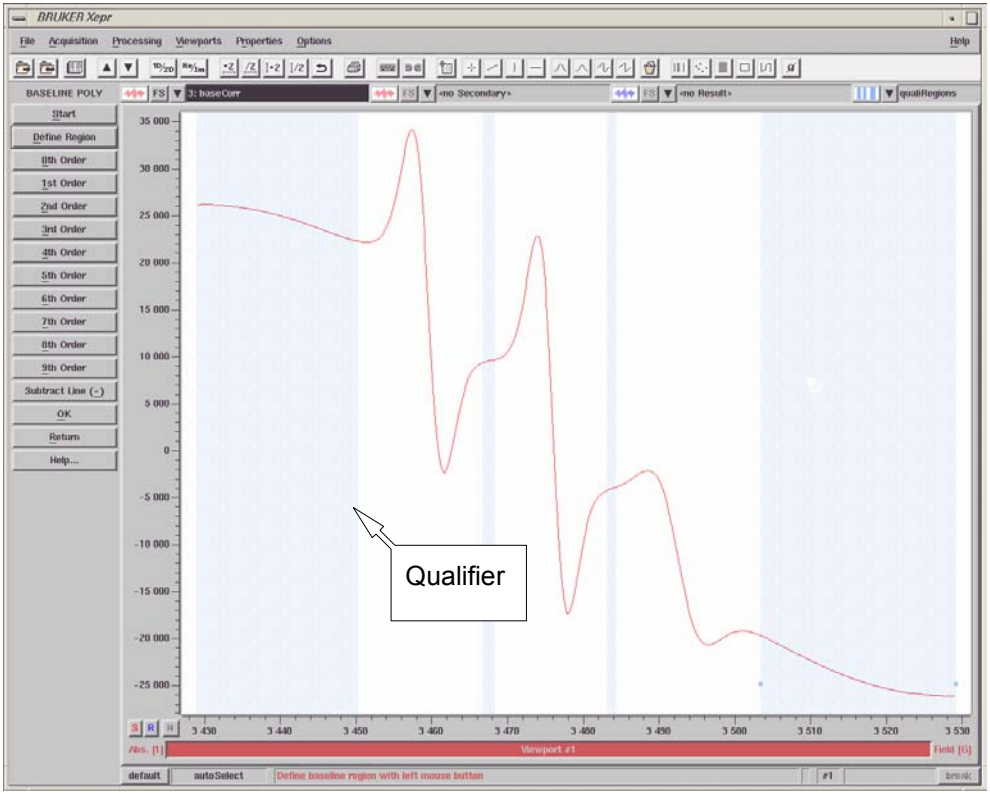


Figure 6-17 Defining the baseline regions.

Click the Define Region button again to select another region of the spectrum you consider as baseline. Repeat this procedure until all the baseline regions are selected by the qualifier. (See Figure 6-17.)

5. **Select the best polynomial function.** Click on one of the ten polynomial functions (Figure 6-16) to see which polynomial function fits the baseline best. The fitted baseline is displayed in the Result dataset. (See Figure 6-18.)

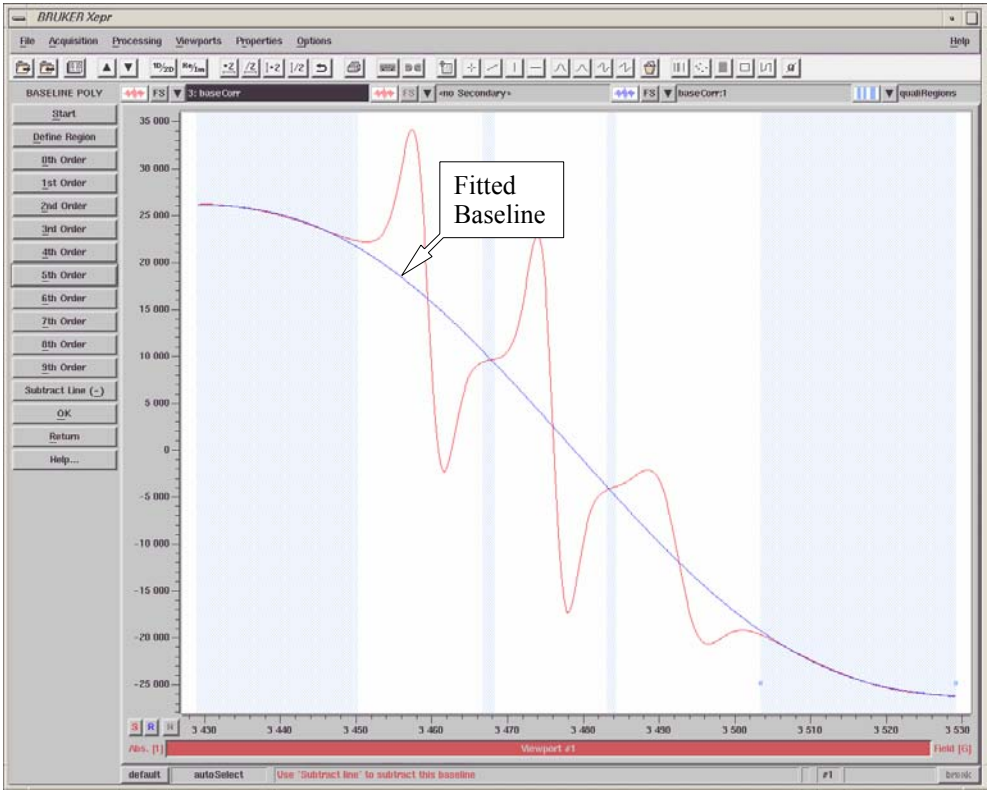


Figure 6-18 Selecting a function to fit the baseline.

6. **Subtract the baseline.** After you find the best fitting polynomial function, click Subtract Line (-). (See Figure 6-16.) It will subtract the fitted baseline from the original spectrum. (See Figure 6-19.)

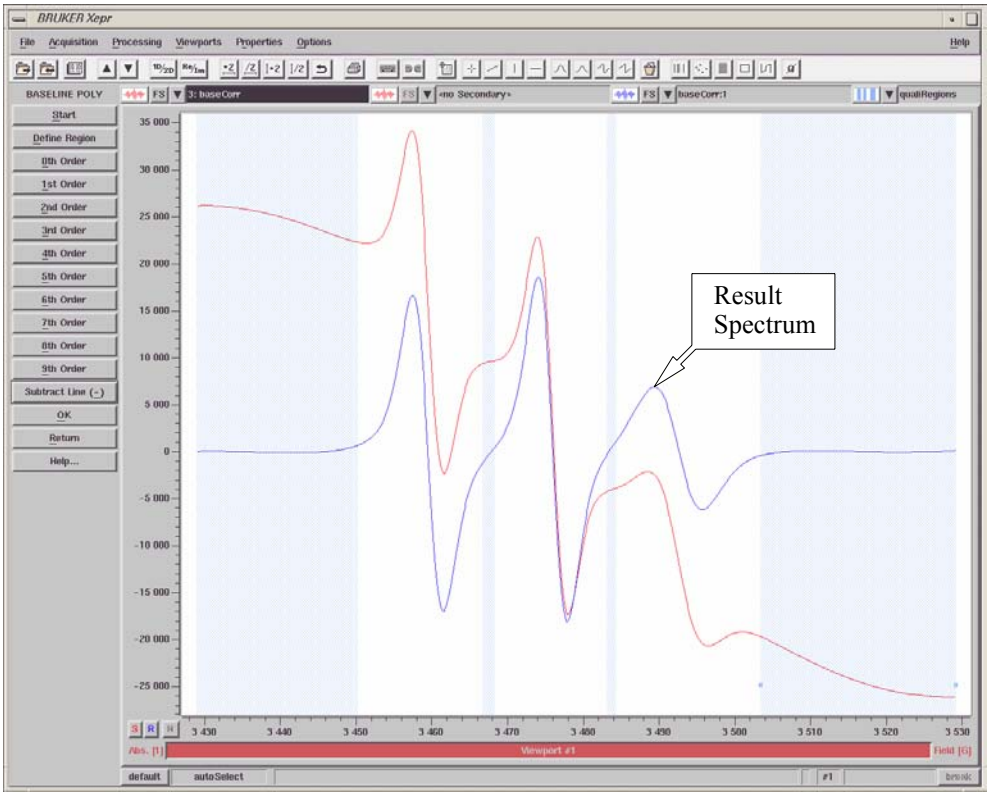


Figure 6-19 The results of the baseline subtraction.

7. **Store the result.** If the result is satisfactory, click OK. (See Figure 6-16.) A dialog window will appear: fill in the title name and click Store to store the baseline-corrected spectrum. (See Figure 6-20.) If the result is not satisfactory, click Start to restart. (See Figure 6-16.) This button clears both the qualifier and the result.

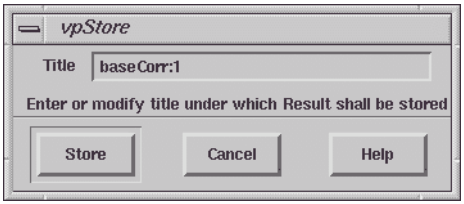


Figure 6-20 Storing the result.

8. **Baseline correction for 2D dataset.** Xepr allows you to fit the baseline for all slices of a 2D dataset. Load a 2D spectrum in the Primary dataset. Select the common baseline area for all slices by using the Define Region. Click one of the polynomial function buttons. A dialog box appears in which you can select either current or all in the Slice box. (See Figure 6-21.)

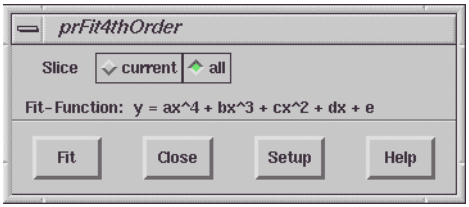


Figure 6-21 A baseline correction for a 2D dataset.

If you select all, Xepr fits and corrects the baselines of each slice of the 2D dataset. If you select current, only the current slice displayed will be fitted and the single fit-

ted baseline will be subtracted from each slice of the 2D dataset. Clicking Fit executes the fitting routine. The Setup button opens a dialog box allowing you to configure the fitting routine. (See Figure 6-22.)

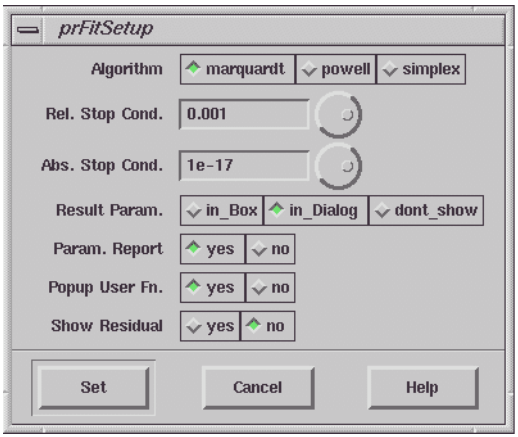


Figure 6-22 Setup of the fitting routine.

9. **Return to the main menu.** Clicking the Return button will bring you back to the TASKS menu. (See Figure 6-16.)

Peak Picking 6.3

Determination of peak positions is critical in EPR spectral analysis. The Peak Picking routine in Xepr offers you a convenient and powerful means of finding your peaks.

1. **Load a spectrum.** Display the spectrum you want to analyze in the Primary dataset of the active viewport.
2. **Enter the Peak Picking task.** Click Peak Picking in the TASKS menu. (See Figure 6-23.) A submenu for Peak Picking replaces the TASKS menu.

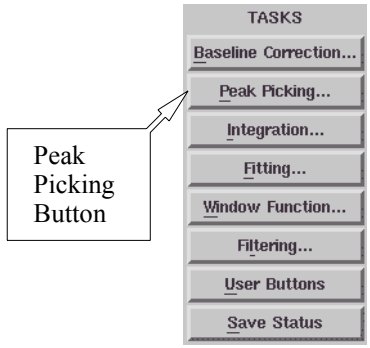


Figure 6-23 The Peak Picking task.

3. **Click the Pick button.** Click Pick in the Peak Picking submenu. (See Figure 6-24.)

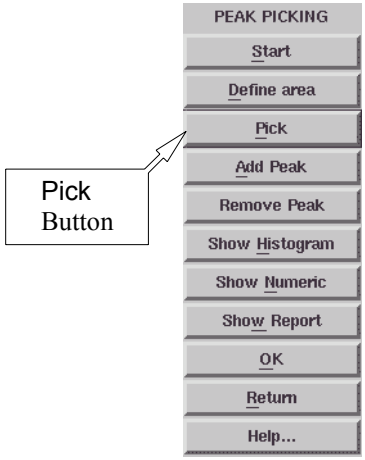


Figure 6-24 The Peak Picking menu.

We have created another linked viewport and zoomed in on a portion of the spectrum to view the results a bit better.

The Peak Picking results will be displayed in the viewport. The left side viewport in Figure 6-25 displays the picked peaks of the spectrum. The right side viewport displays the zoomed-in area of the left viewport spectrum.

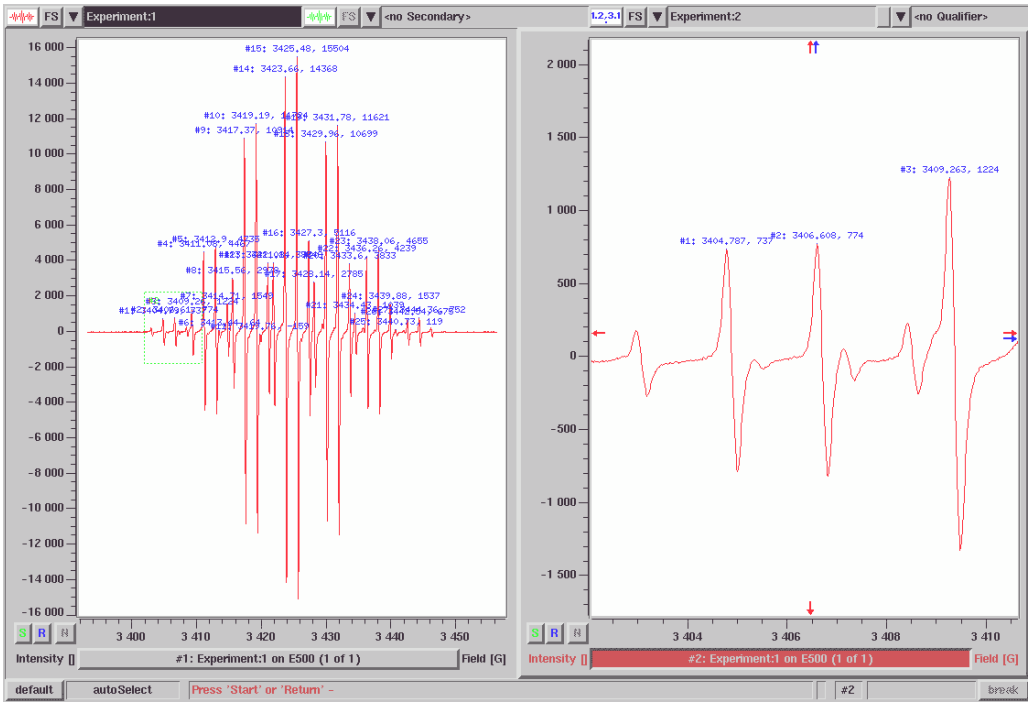


Figure 6-25 Peak Picking results.

4. **Peak Picking dialog box.** In addition to the peak picking results, a dialog box will also appear in which you can select more specific options to find your peaks. If you have a 2D spectrum you have an option to pick peaks on the current slice or apply the operation to all the slices.

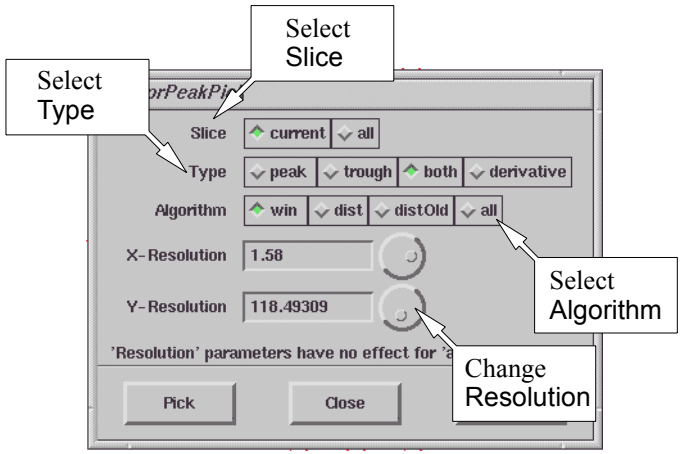


Figure 6-26 The Peak Picking dialog box.

5. **Select the Type.** You can choose to pick the positive peaks only (peak), the negative peaks only (trough), both upper and lower peaks (both), or zero-crossing point of the peak (derivative) by selecting the desired Type. In Figure 6-25, only the upper peaks are picked because peak is selected. If you click the both button in the Type menu, both upper peaks and lower peaks are picked. (See Figure 6-27.)

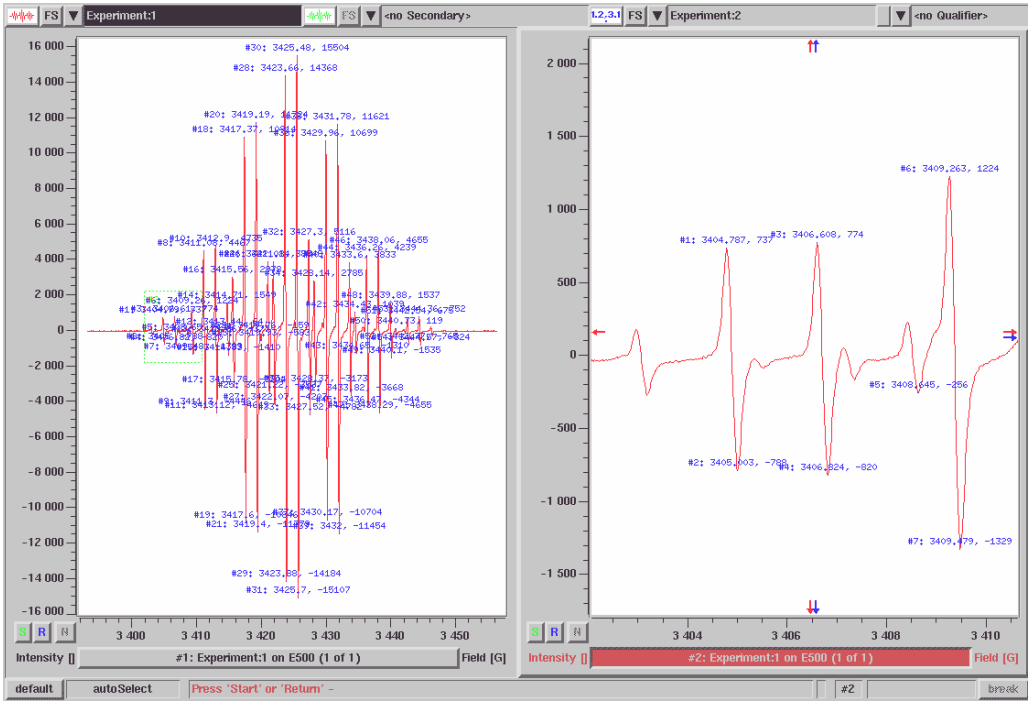


Figure 6-27 Picking both peaks.

6. **Change the resolution.** The X- and Y-resolutions set the threshold for picking the peaks. In Figure 6-27, the small peaks are still not picked. Reduce the Y-Resolution by turning the knob counter-clockwise in the dialog box. (See Figure 6-26.) The small peaks will now be picked by the Peak Picking function. (See Figure 6-28.)

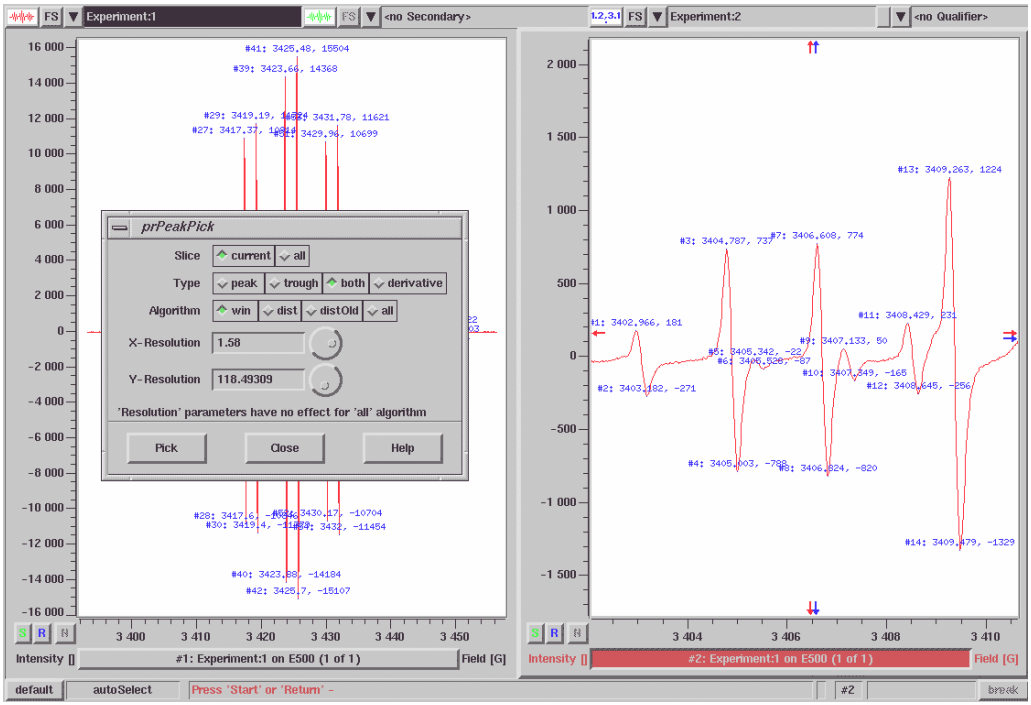


Figure 6-28 Changing the resolution.

7. **Define the Peak Picking area.** If you are only interested in the peaks of only a specific area of the spectrum, you can define the area for the peak picking function. Click Start in the Peak Picking menu to restart the peak picking process. Click the Define Area button. A rectangular qualifier appears. (See Figure 6-29.) Resize the qualifier to fit the area where you want to pick peaks and then click the Pick button. The peaks within the area you defined are now picked.

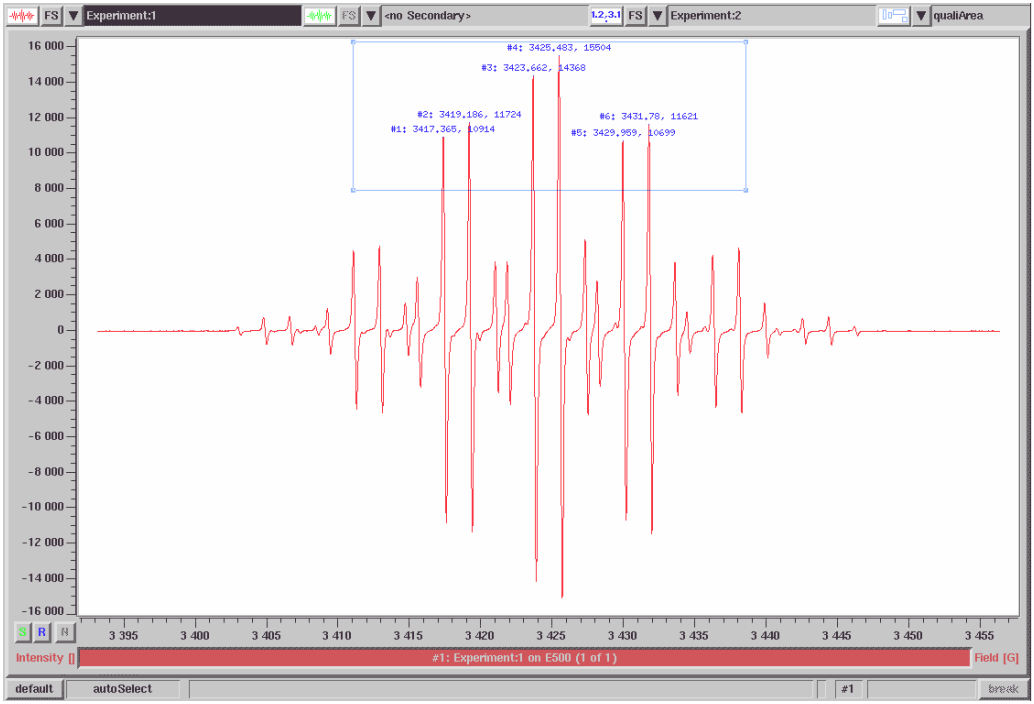


Figure 6-29 Defining the Peak Picking area.

8. **Add and Remove Peaks.** When dealing with multiple species or noisy spectra, it is difficult to pick only the peaks you want by adjusting the resolutions or qualifier area. Add and Remove Peak allow you to add the peaks that the program missed or remove the unwanted peaks. Click Add Peak (or Remove Peak) in the Peak Picking menu. Move the mouse pointer to where the peak is and click the left mouse button. The peak will be added (or removed). (See Figure 6-30.)

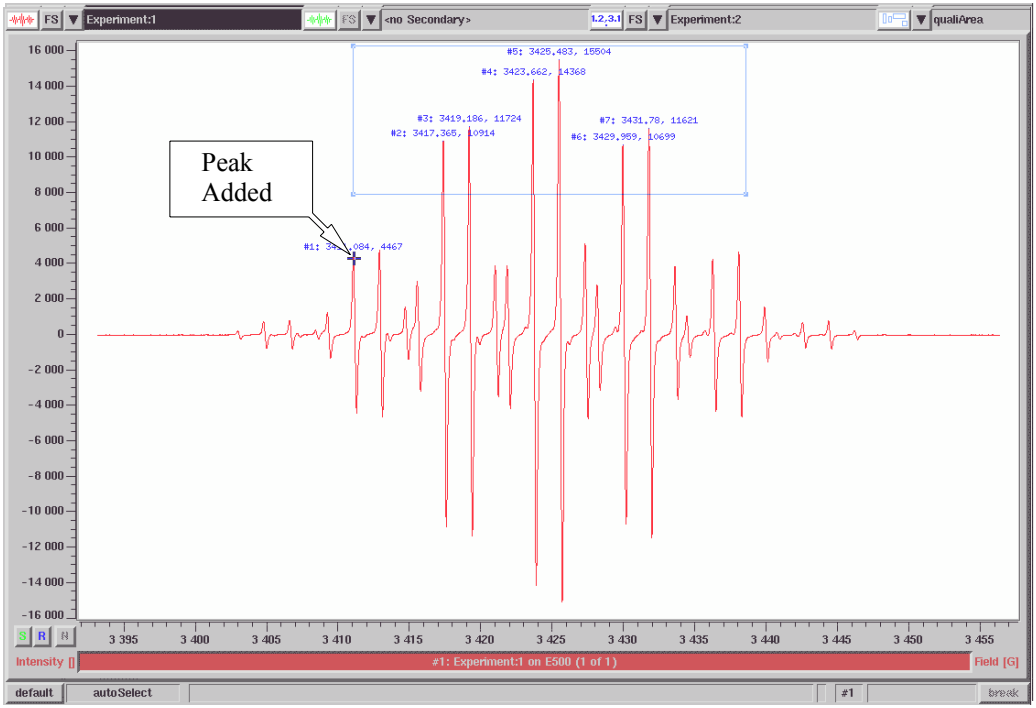


Figure 6-30 Adding a peak.

9. **Show a Histogram.** You can select to display the peaks picked in numerical (default) or histogram format. Click Show Histogram in the Peak Picking menu. The numbers will change to vertical bars. (See Figure 6-31.)

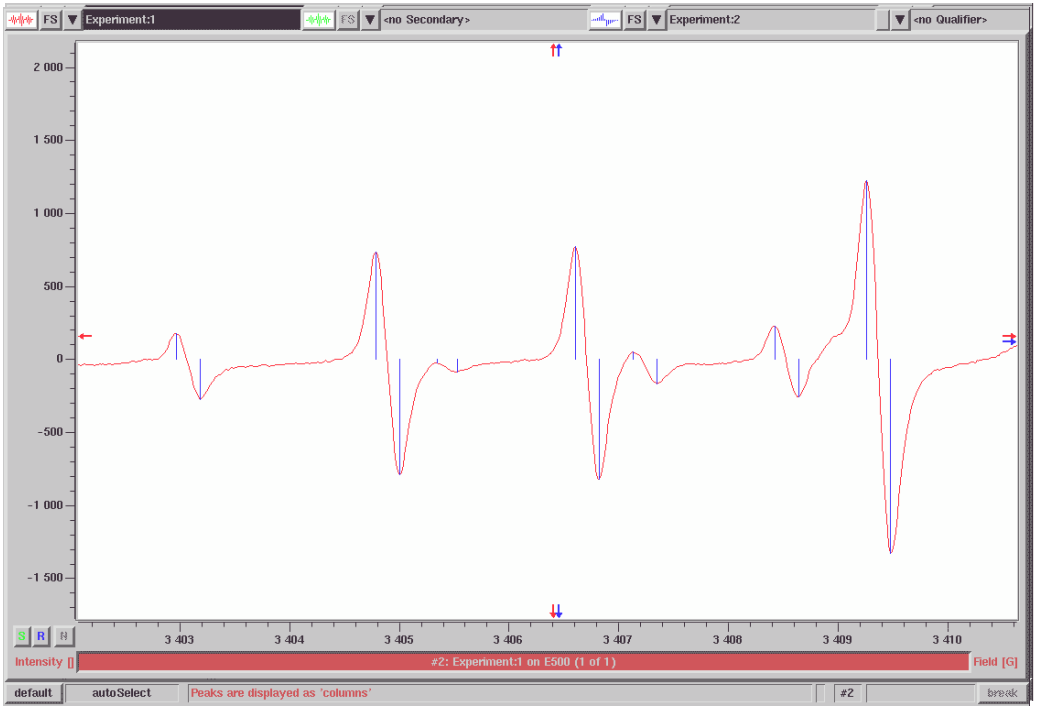


Figure 6-31 A Histogram display of the Peak Picking results.

10. **View the report.** Click View Report in the Peak Picking menu and a window with a list of all the picked peaks appears. (See Figure 6-32.) You can save the results in an ASCII file by simply clicking the Save button.

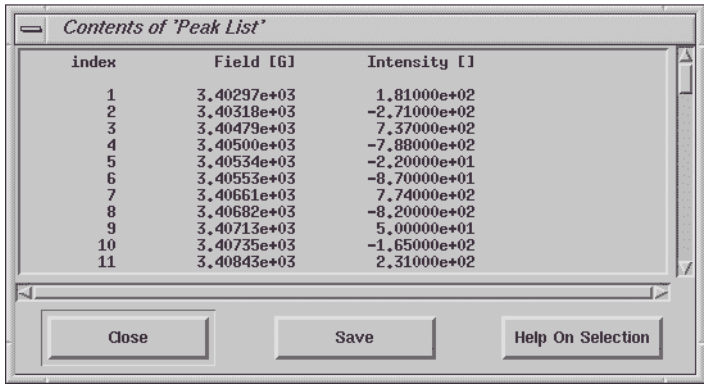


Figure 6-32 Report of the peak picking result.

A note will appear to remind you about the name of the file where results have been saved. Click OK to continue. (See Figure 6-33.)

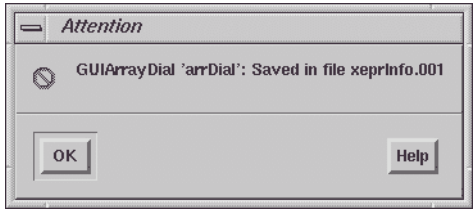


Figure 6-33 The filename of the result.

11. **Store the result.** Click OK in the Peak Picking menu and a dialog box appears asking you under which title you want to store the results as a dataset. You can store the result for further processing. Clicking OK will automatically bring you back to the main TASKS menu.

12. **Return to the main TASKS menu.** To exit the Peak Picking menu you can click Return in the Peak Picking menu.

Integration 6.4

Integration is often applied to view the first derivative EPR spectrum as an absorption spectrum. More importantly, double integration is often used for quantitation.

Integration from the Menu 6.4.1

For a strong, clean EPR spectrum, integration or double integration can be directly carried out from the Processing menu. Click Processing in the menu bar and then Diff & Integ. You can select from Derivative, Integral, Integral (auto-baseline), Double Integral, and Double Integral (auto-baseline). (See Figure 6-34.)

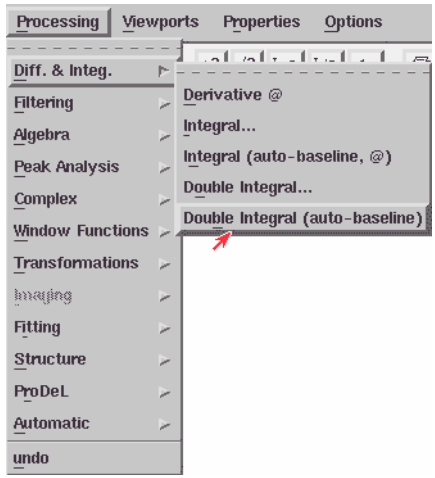


Figure 6-34 Selecting Double Integration.

Auto-baseline means the process automatically applies a linear baseline correction. It corrects the offset and slope of the base-

line. Figure 6-35 shows an EPR signal and the result of a Double Integral with automatic baseline correction.

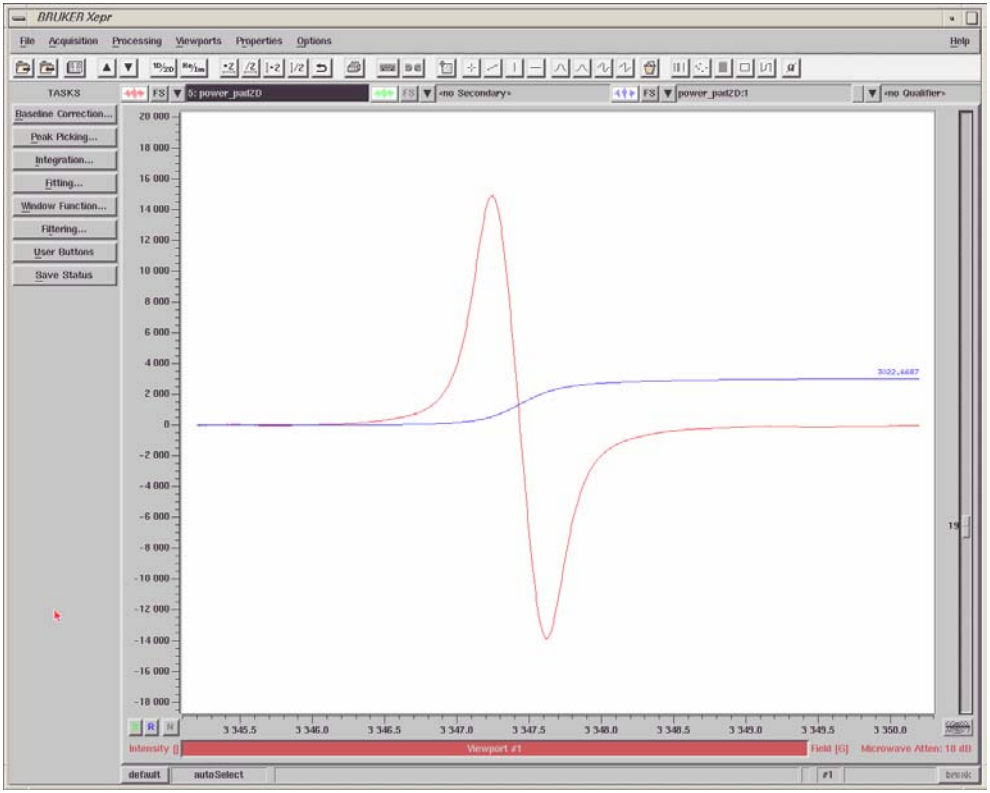


Figure 6-35 Double Integral with automatic baseline correction.

The result is displayed as both a curve and a number. If the dataset is a 2D dataset, the integration or differentiation can be applied to all slices of the 2D dataset. You can also correct the baseline manually by clicking Integral or Double Integral. A dialog box will appear allowing you to change the Offset and Slope. Clicking on the Integrate button will update the result

with the most recent changes in the baseline adjustment. (See Figure 6-36.)

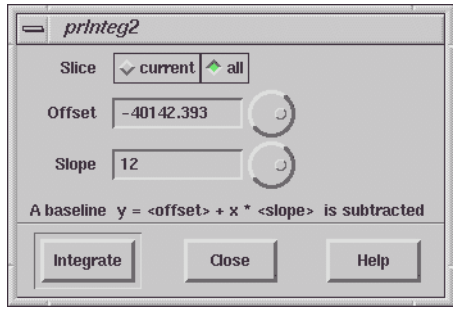


Figure 6-36 Manually adjusting the Offset and Slope of the baseline.

Integration from the TASKS Bar 6.4.2

You can also use the integral function in the TASKS bar.

1. **Load the dataset.** Load the spectrum into the Primary dataset.

2. **Start the Integration task.** Click the Integration button in the TASKS menu. The Integration menu will replace the TASKS menu. (See Figure 6-37.)

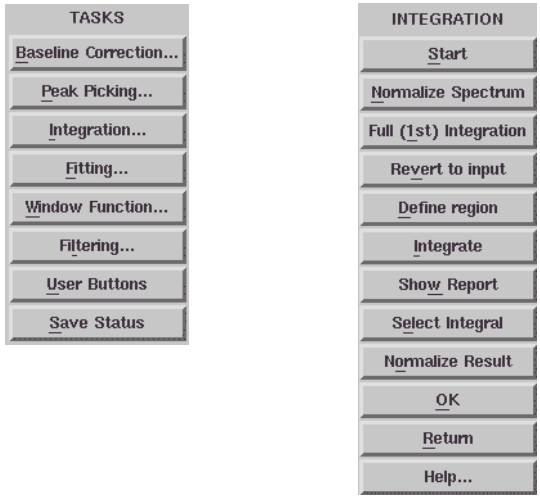


Figure 6-37 The Integration button and menu in the TASKS bar.

3. **Normalize the spectrum.** The experimental parameters such as number of data points, receiver gain, conversion time, and sweep width directly affect the value of the integral. Clicking Normalize Spectrum will normalize the integral with respect to the parameters: number of data points, receiver gain, conversion time, and sweep width of the spectrum. Normalized integrals are easy to compare

with each other even though they are acquired under different instrumental conditions.

4. **Define the integration region.** Clicking on the Define Region button activates the integral qualifier. A left mouse click sets the starting point of the integration. Dragging the mouse pointer and then clicking with the left mouse button sets the end point of the integration region.

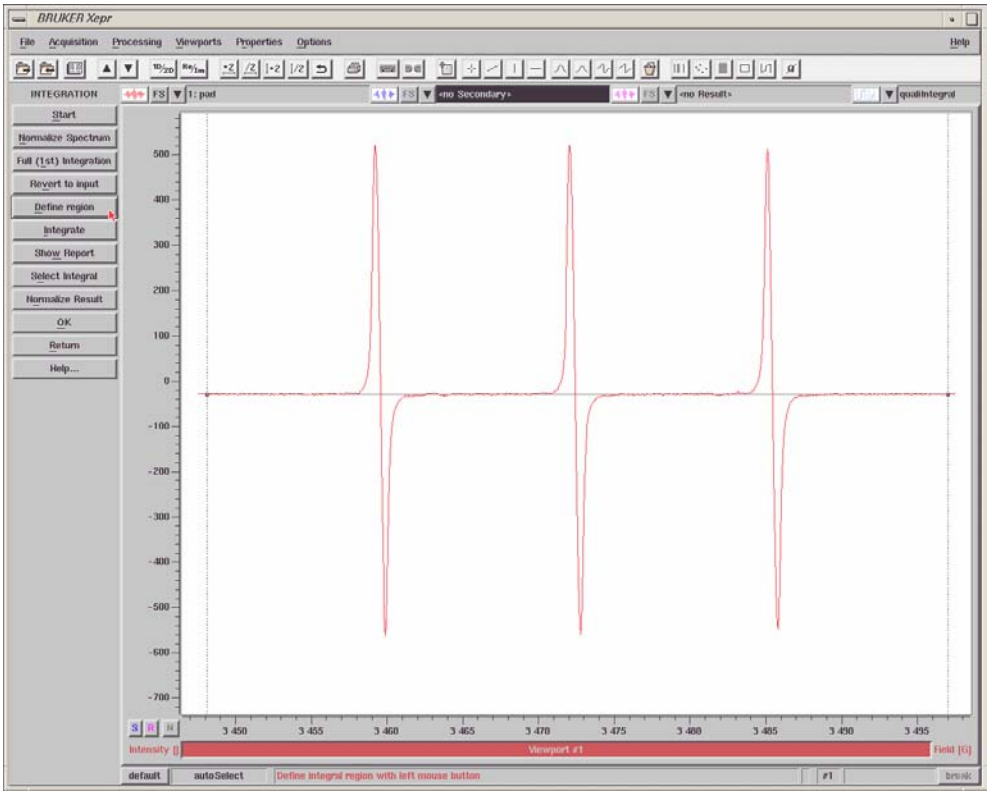


Figure 6-38 Defining the integration region.

The area between the two vertical lines is the integration region. The horizontal line indicates the linear correction for the base line. (See Figure 6-38.) You can change the integration region and the baseline correction by dragging the handles at the end of the line.

5. **Integrate the spectrum.** Click Integral. The region of the spectrum you selected will be integrated once and displayed in the Result dataset. (See Figure 6-39.)

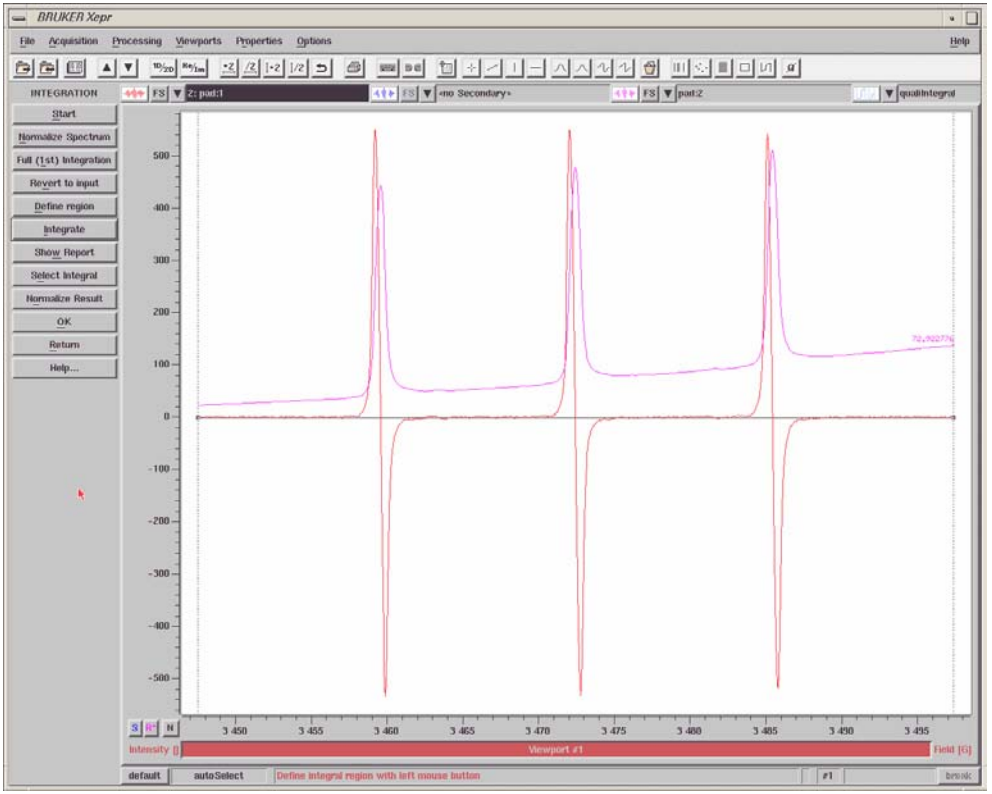


Figure 6-39 The first integral of the selected region.

6. **Double integrate the spectrum.** You can double integrate the spectrum by applying the same process to the integral you get from the above steps. To display the original spectrum, the first integral, and the double integral in the same viewport, first we need to transfer the first integral to the Secondary dataset. Click the Secondary Dataset List and select <Result>. Click on the dataset title label of the Secondary dataset to activate the Secondary dataset. All the operations will apply to the Secondary dataset now. (See Figure 6-40.)

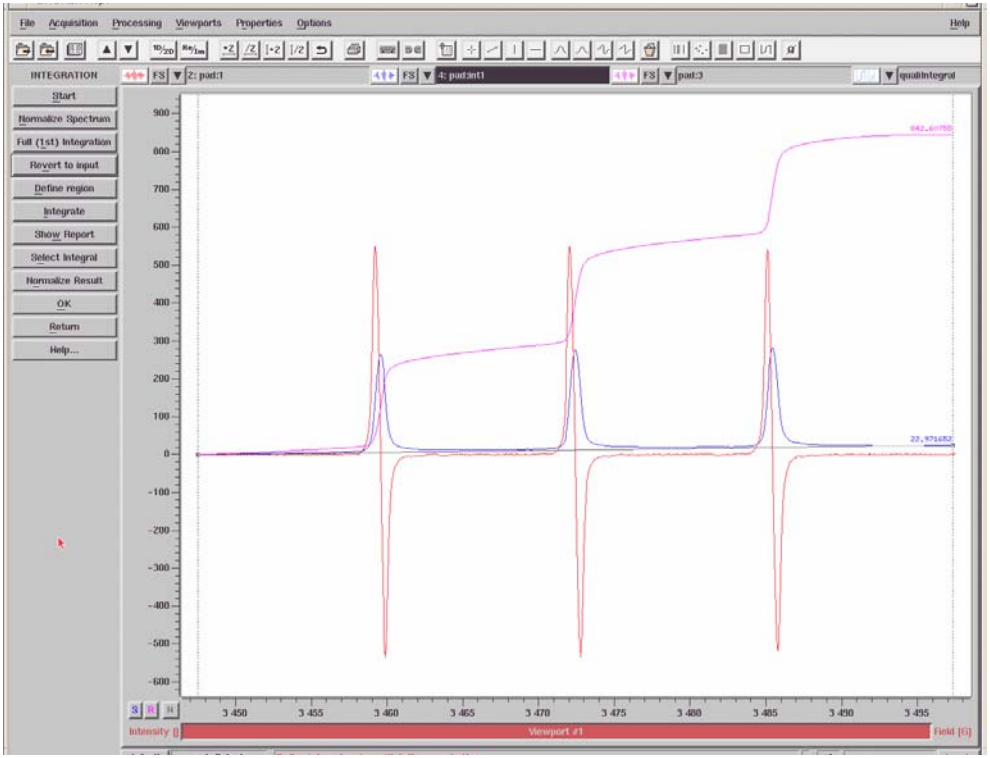


Figure 6-40 The double integral of the selected region.

Adjust the slope and the offset of the qualifier to fit the baseline of the single integral. Click the Integral button in the menu again. A double integral will be displayed in the Viewport. Click Report to view the numerical result. Click OK to store the result.

7. **Select individual peaks for integration.** You can integrate each EPR peak separately with Xepr. Click Define Region and move the qualifier to cover the EPR peak you want to integrate. Click Define Region again to get another qualifier to cover another peak. Repeat this procedure until all the peaks you want to integrate have been covered by individual qualifiers. Adjust each qualifier to fit the slope and offset of the baseline. (See Figure 6-41.)

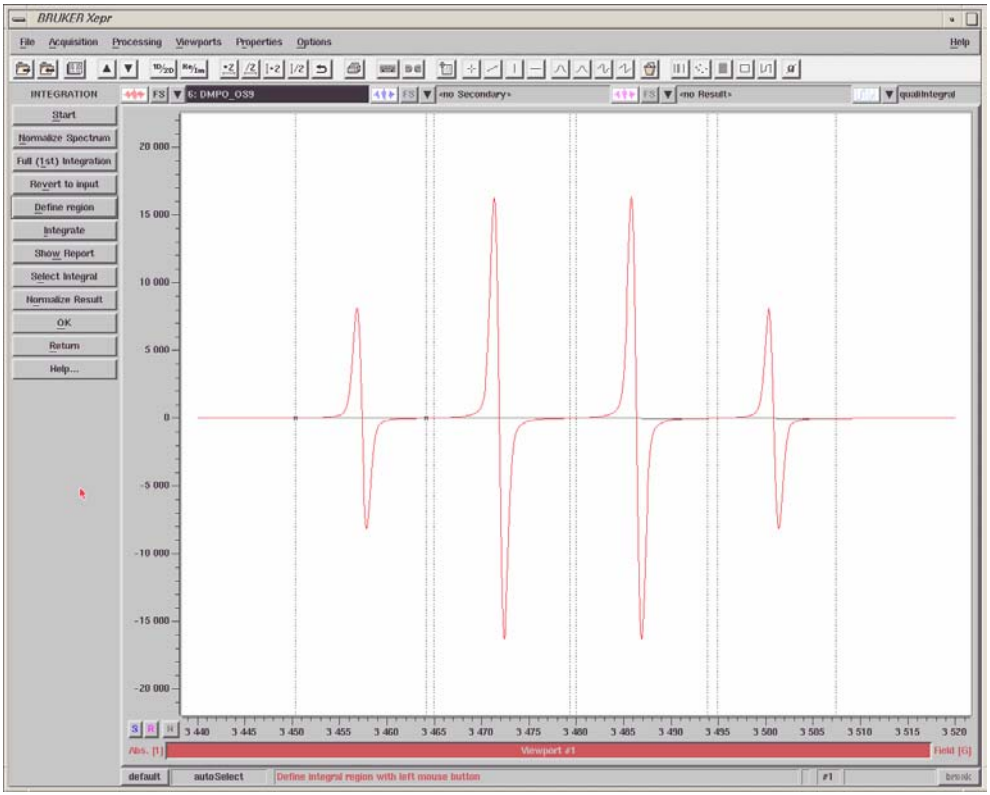


Figure 6-41 Selecting regions with individual qualifiers.

8. **Integrate the individual peaks.** Click the Integral button. Each area will be integrated separately. (See Figure 6-42.)

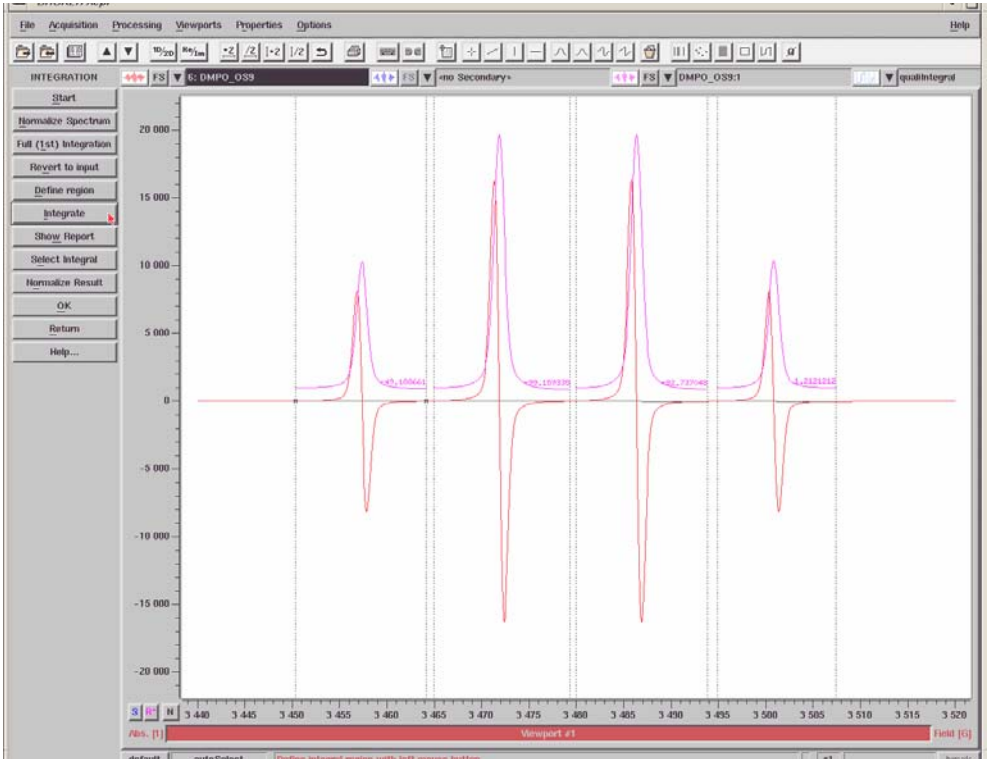


Figure 6-42 Integrals of individual region.

9. **Double integrate the individual peaks.** You can double integrate individual peaks as well. Click <Result> in the Secondary Dataset List and activate the Secondary dataset. Adjust each qualifier to fit the slope and offset of the baseline in each area. Click Integral. The double integrals of all the regions you selected will be displayed in the viewport. (See Figure 6-43.)

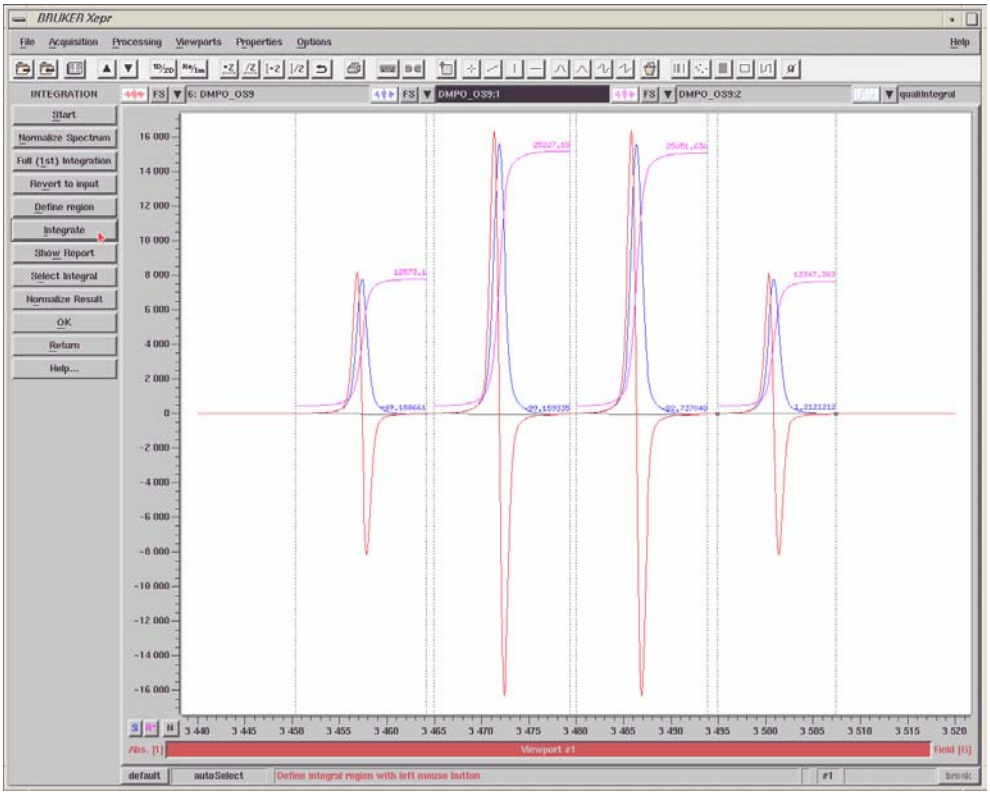


Figure 6-43 Double integration of individual peaks.

10. **Normalization to one of the integrals.** Quite often, the relative ratios of the integrals is important in the data analysis. (*E.g.* hyperfine patterns and quality of a spectrum.) You can normalize the integrals with respect to one of the integrals to obtain these relative ratios. Click Select Integral and then Normalize Result A dialog box appears allowing you to select the integral for normalization. (See Figure 6-44.) Click the up or down arrow to select the integral. Click the Normalize button in the dialog box. All the integrals will be normalized with respect to the integral you select.

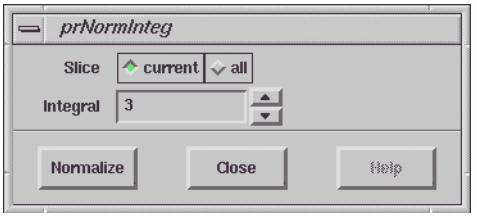


Figure 6-44 Selecting an integral to apply normalization.

Figure 6-45 shows the results for a DMPO/$OH^{\cdot}$ spectrum and the normalization gives a 1:2:2:1 pattern.

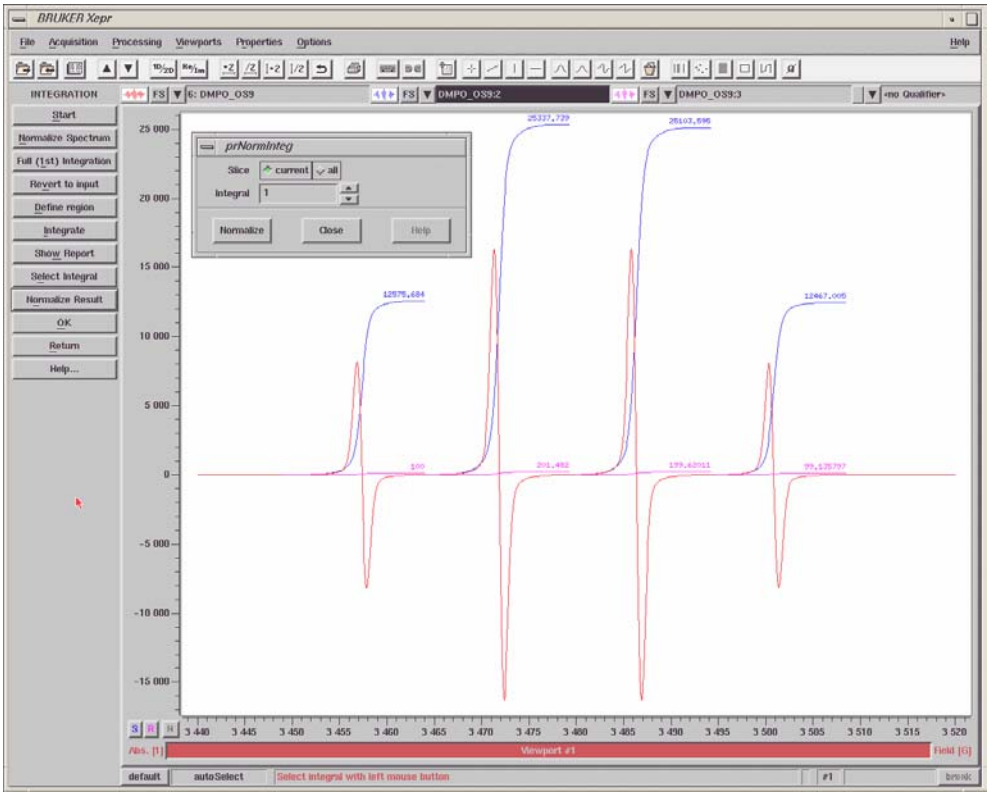


Figure 6-45 Normalizing with respect to the first integral.

You can select any integral as the normalization integral. Figure 6-46 shows the result of normalization with respect to the third integral.

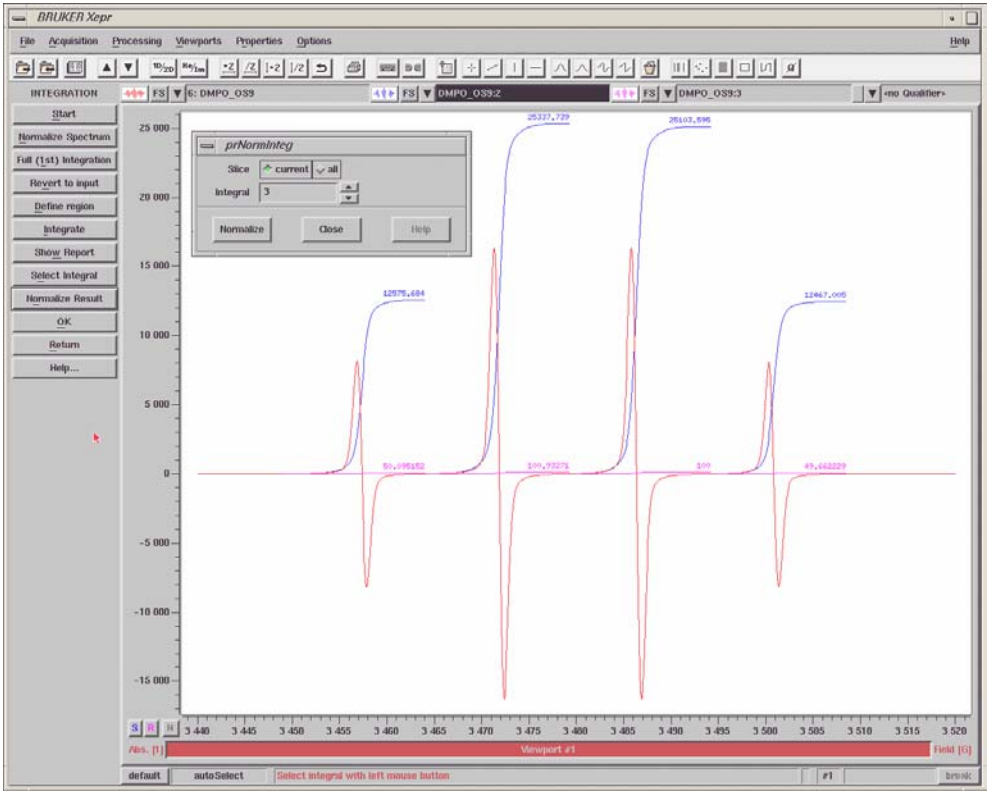


Figure 6-46 Normalizing with respect to the third integral.

Curve Fitting 6.5

You can fit the experimental curve with polynomials, lineshapes, and exponential functions. Here we present an example of fitting a first derivative EPR line using a Voigt function.

1. **Load the spectrum.** Load the first derivative EPR spectrum into the Primary dataset.
2. **Start the Fitting routine.** Click Fitting in the TASKS menu. (See Figure 6-47.) The TASKS menu will change to a menu with a list of the fitting functions.

Figure 6-47 The Tasks menu.

3. **Select a BASELINE fitting function.** In the BASELINE menu, there are three types of fitting functions: Polynomials, Lineshapes, and Exponentials. (See Figure 6-48.) Click Lineshapes for this example and the Lineshape Fit menu will replace the current menu.

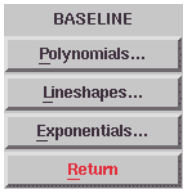


Figure 6-48 The BASELINE menu.

4. **Define the fitting region.** The first thing you need to do is to define the spectrum region to fit. Click the Define Region button in the LINESHAPE FIT menu. (See Figure 6-49.)

Figure 6-49 The LINESHAPE FIT menu.

It activates the qualifier so you can click on the spectrum where you want to start and then drag to the place where you want to stop.

5. **Select the fitting function.** There are six lineshape functions you can choose. In this example we use Mixture Derivative. Click the Mixture Derivative button and a dialog box will appear for the fitting parameters.

6. **Set up for fitting.** You can set up the fitting options by clicking the Setup button. A dialog box appears in which you can select from three optimization Algorithms: marquardt, powell, and simplex. You can define the Relative and Absolute Stop Conditions. You can select where to display the resulting parameters, whether or not to have a parameter report, and whether to show the residuals. Click Set after you chosen your options.

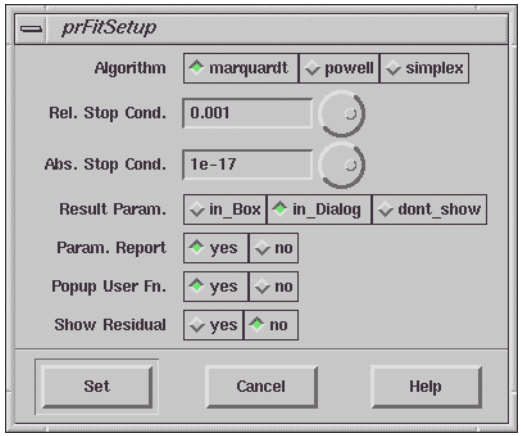


Figure 6-50 Setup of the fitting options.

7. **Select the fitting parameters.** (See Figure 6-51.) You can choose whether or not to fit the amplitude, x offset (resonant magnetic field value), line width, and the percentage of the gaussian lineshape (gauss-character) by clicking the yes or no button. Xepr provides a set of initial values for the fitted parameters.

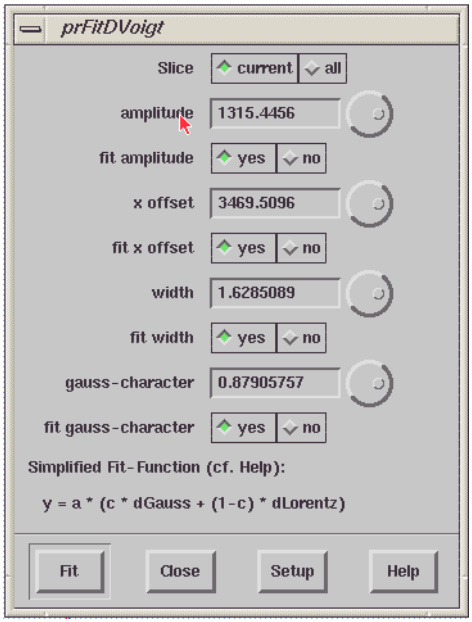


Figure 6-51 The fitting parameters.

8. **Fit the curve.** Click Fit in the fitting parameters dialog box. The result will be displayed in the Result dataset. (See Figure 6-52.) If you are not satisfied with the results, you can manually change these parameters by either turning the turning knobs or typing in numbers and re-running the fit. If you are satisfied with the result you can click Close to exit the fitting parameters dialog box.

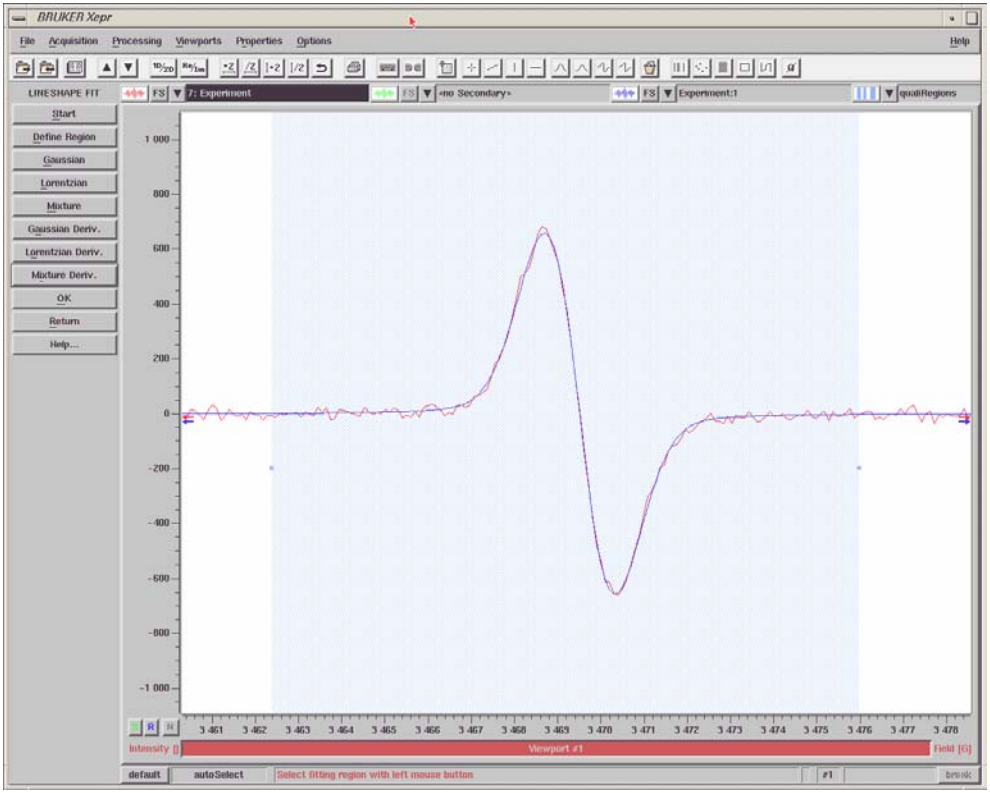


Figure 6-52 The fitted curve.

9. **Return to the TASKS menu.** Click OK in the LINE-SHAPE FIT menu. A dialog box appears asking if you want to store the fitting result. Click Return to return to the TASKS menu.

Spectrum Algebra 6.6

A commonly required operation for data processing is adding, subtracting, multiplying or dividing two spectra. Here we shall subtract two spectra (A and B) from one another in order to separate one species from a multicomponent spectrum.

1. **Load the spectra.** Load spectrum B into the Primary dataset and spectrum A into the Secondary dataset.

2. **Start the process.** Click Processing in the menu bar and then Algebra. Select Primary - Secondary. (See Figure 6-53.)

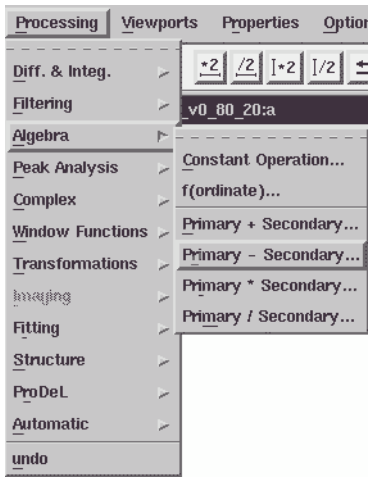


Figure 6-53 Launching the Algebra function.

3. **Adjust the parameters.** A dialog box will appear and allow you to change the parameters of this operation. You can change the Gain of the Secondary dataset (*i.e.* how much of the Secondary is subtracted from the Primary). You can shift the X-axis (X-Shift) of the Secondary dataset to align both spectra. You can also stretch

(X-Stretch) the Secondary dataset so that the scale of the X-axis matches that of the Primary dataset. Click Subtract in the dialog box and the resulting spectrum of the subtraction will appear in the Result dataset. (See Figure 6-54.) You can store or save the result by using the Store or Save As commands from the File menu.

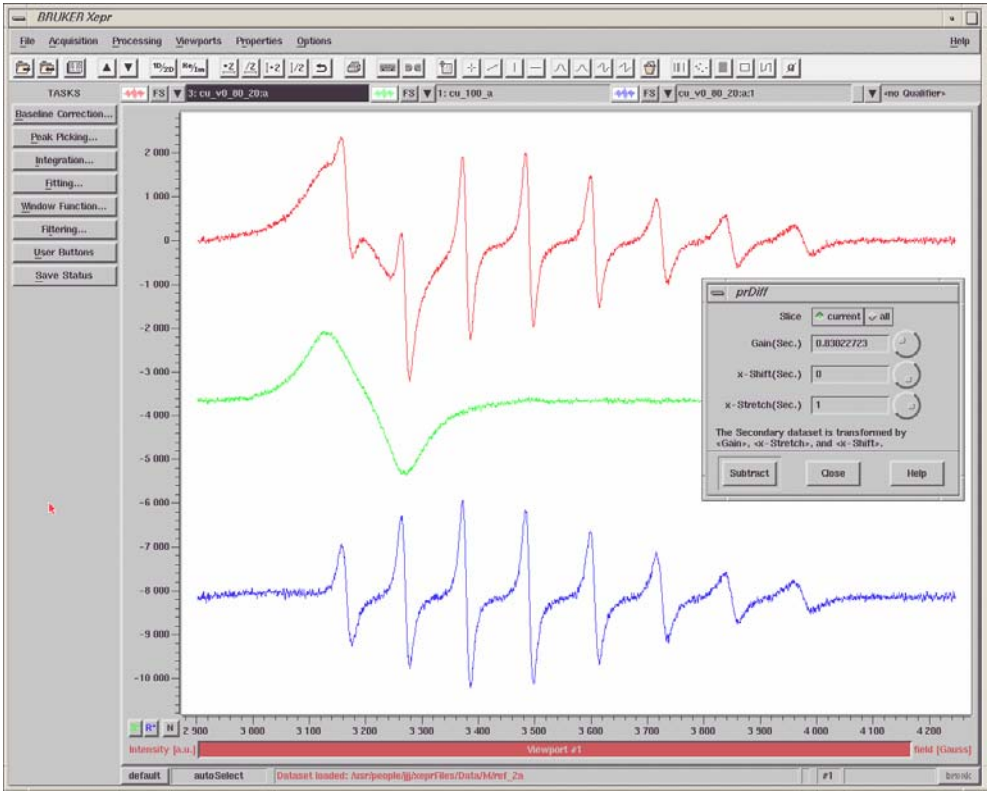


Figure 6-54 Subtracting the Secondary dataset from the Primary dataset.

Data Processing History 6.7

Xepr records the data processing history and appends it to the descriptor file. You can view the history of the dataset by double clicking the dataset title label or selecting Show Description or Show BES3T.DSC in the File menu of the Dataset Table. (See Figure 6-55.)

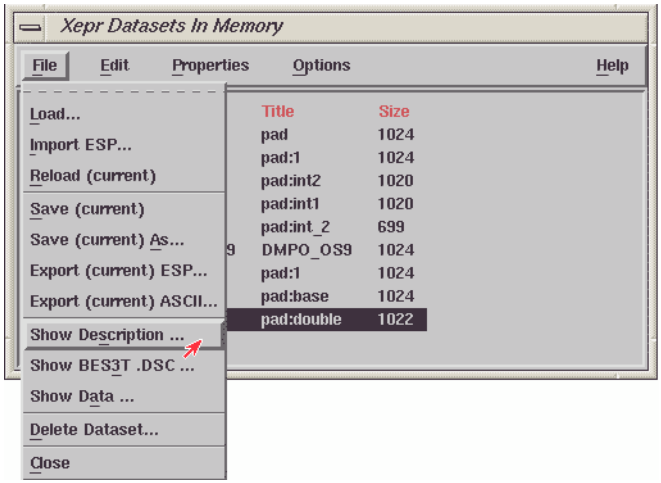


Figure 6-55 Selecting Show Description from the File menu of the Dataset Table.

A window displays the contents of the dataset description. It includes the records of the original dataset and the MANIPULATION HISTORY. The MANIPULATION HISTORY indicates the Xepr commands used as well as the associated parameters. It

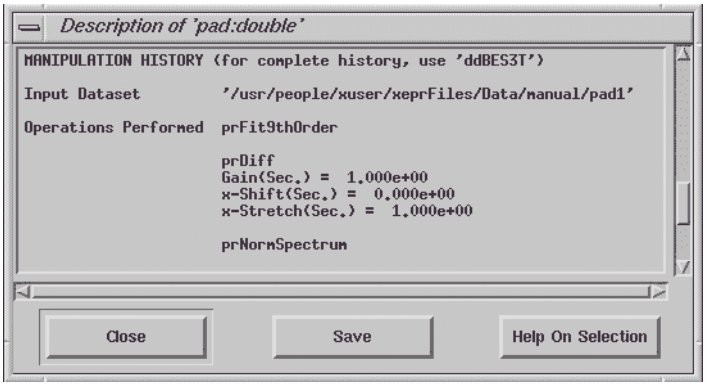


Figure 6-56 Manipulation History in the dataset description.

not only provides the information of how the dataset was generated and processed but also is a reference resource for writing macros and ProDeL programs. (See Figure 6-56.)

Additional Techniques 7

This chapter provides instructions for procedures that are routine for some users, but may be infrequently encountered by others. Specifically, the chapter will describe manually tuning the Elexsys E 500 spectrometer, changing cavities, and optimizing the AFC settings. We assume that you are already familiar with the material in Chapters 3-6 before performing these additional techniques.

Manually Tuning a Microwave Bridge 7.1

The Auto Tune routine of the Elexsys E 500 software is effective at tuning the cavity and bridge under most circumstances. However, there are some circumstances where automatic tuning may have difficulties. Lossy samples such as water can be problematic, particularly when you work at high microwave power levels. Some cavities and resonators are not able to auto tune. These instructions will help you to tune the spectrometer when using these difficult samples or cavities without the auto tuning feature.

Newer microwave bridges have solid-state (Gunn diode) microwave sources while older bridges often have klystron microwave sources. If you have an E 500 installed as an upgrade, you may have a klystron. This section describes the manual tuning procedure for both solid-state and klystron sources.

Visual Aids for Manually Tuning a Bridge 7.1.1

Xepr has a few visual aids that can help you to tune the bridge.

1. **Logarithm Scale display of the cavity dip.** When the cavity Q is relatively low or there are severe microwave reflections it is difficult to view the cavity dip. This function can differentiate the cavity dip from other reflec-

tions. It employs a logarithmic display to make the cavity dip easier to identify. Press the Log. Scale button in the Microwave Bridge Tuning dialog box. The tuning mode picture will be displayed in logarithmic scale. (See Figure 7-1.)

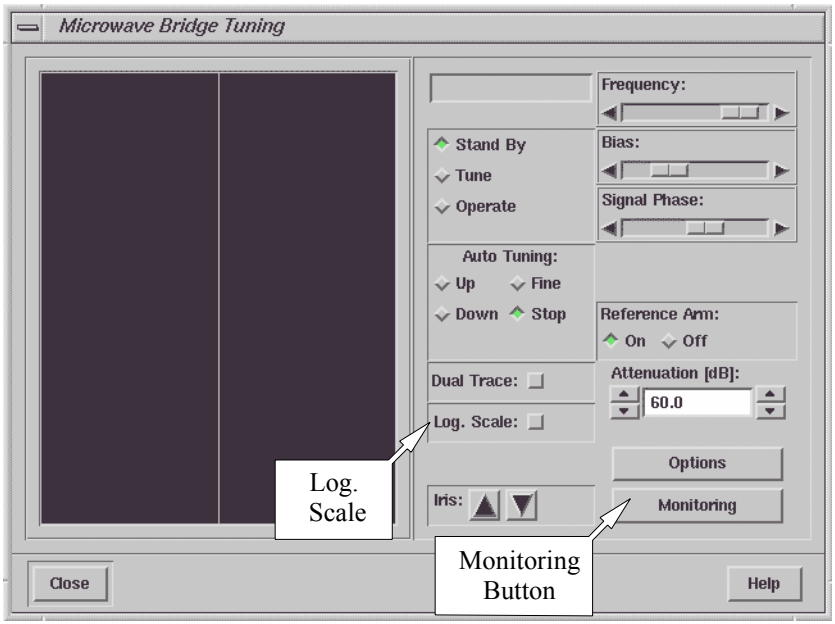


Figure 7-1 Helpful visual tools.

2. **Monitoring tool.** Sometimes the operator needs to stand far away from the computer screen to change the coupling and the normally sized meters for AFC, diode current, and receiver level are too small to be seen. Click the Monitoring button. (See Figure 7-1.) A floating frame containing three meters will appear. You can enlarge the size of the meters till you can see them clearly from a distance.

Manual Tuning Method 7.1.2

1. **Open the Microwave Bridge Tuning dialog box.** If this window is not already open, click its button in the monitoring panel. The microwave bridge tuning dialog box will then appear. (See Figure 7-2.)

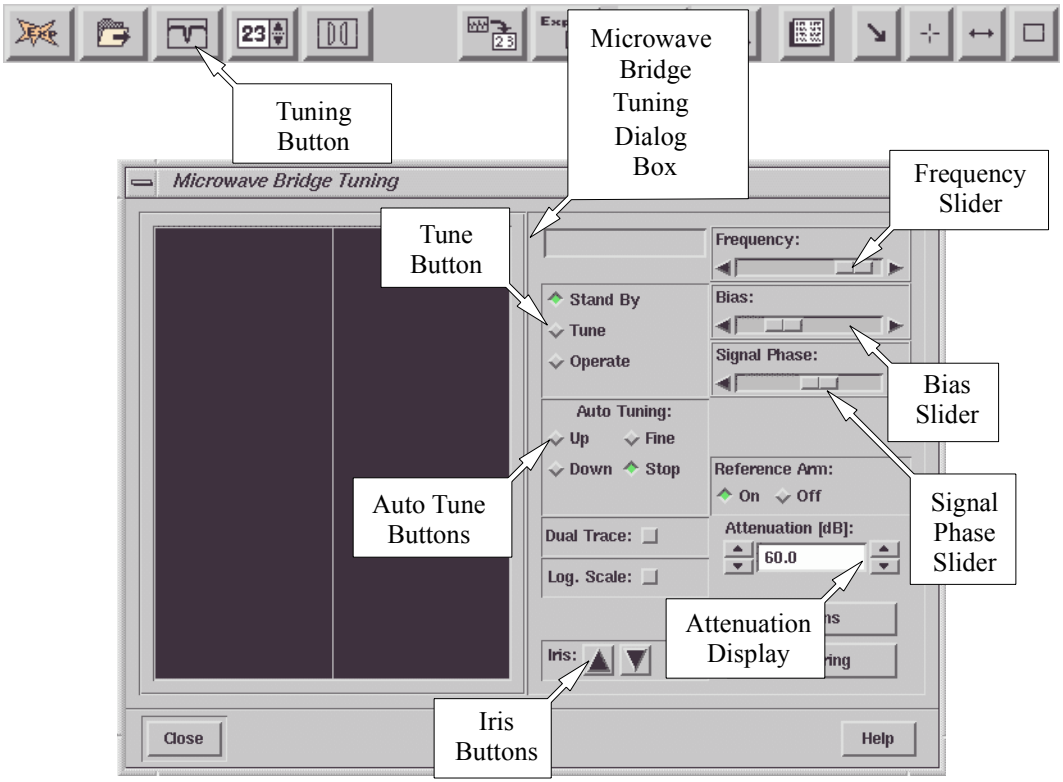


Figure 7-2 The Microwave Bridge Tuning dialog box.

Most new bridges have solid-state sources. If you have an old klystron bridge and the Stand By indicator is red, wait a minute. There is a time delay of approximately three minutes between the time the console is turned on and the time the klystron can be turned on. This allows the klystron to warm up sufficiently.

2. **Switch the microwave bridge to Tune mode.** The bridge status indicator shows the three states or modes for the microwave bridge, Stand By, Tune, and Operate (See Figure 7-3.). In Stand By the power to the microwave source is shut off. When you switch to Tune, the source turns on and you produce a frequency sweep that allows you to see the tuning dip for your cavity. Switching to Operate causes power only at the resonant frequency to be transmitted to the cavity. When you turn on your spectrometer and connect to the spectrometer, it should be in Stand By mode, which is indicated by Stand By appearing in the Bridge Status Indicator and the Microwave Bridge Tuning dialog box. (See Figure 7-2 and Figure 7-3.) If you have been acquiring spectra already, your bridge will probably be in Operate mode. Click the Tune button in the dialog box to change to the Tune mode.

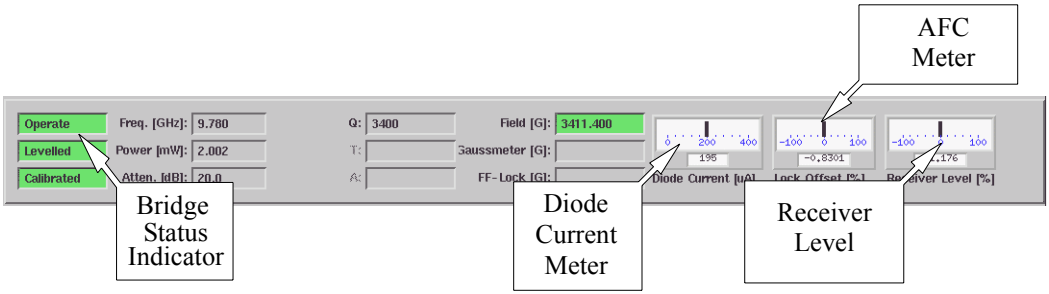


Figure 7-3 The indicators for the microwave bridge.

3. **Set the microwave attenuator to 30 dB.** The microwave attenuation is set by clicking the arrows on either side of the attenuation display. (See Figure 7-2.)

4. **Turn the Reference Arm off.** Click the Reference Arm Off button. Having the reference arm turned off makes finding the cavity "dip" easier.

5. **Observe the tuning display on the monitor.** This tuning display shows the microwave power reflected from the microwave cavity and the reference arm power as a function of the microwave frequency. If the tuning display resembles one of the displays in Figure 7-4, you have a solid-state source bridge. If the tuning display resembles one of the displays in Figure 7-5, you have a klystron source bridge. It is important to know what source you have in some of the tuning procedure steps.

6. **Adjust the microwave power.** If the mode pattern amplitude is too small, increase the microwave power in 1 dB steps by decreasing the attenuation. If the mode pattern amplitude is too large, decrease the microwave power in 1 dB steps by increasing the attenuation.

The LEVELLED light underneath the bridge status indicator will turn on when you switch from STANDBY to the TUNE or OPERATE modes. The UNCALIBRATED indicator activates when you are in TUNE and refers to the detection diode. However, this is not a problem as the diode does not need to maintain its 200 microamp setting in the TUNE mode.

Figure 7-4

Tuning display for a solid-state microwave source.

a) Off resonance.

b) Slightly off resonance.

c) On resonance, phase 180° off.

d) On resonance, phase 90° off.

e) On resonance, correct phase, undercoupled.

f) On resonance, correct phase, overcoupled.

g) On resonance, correct phase, critically coupled.

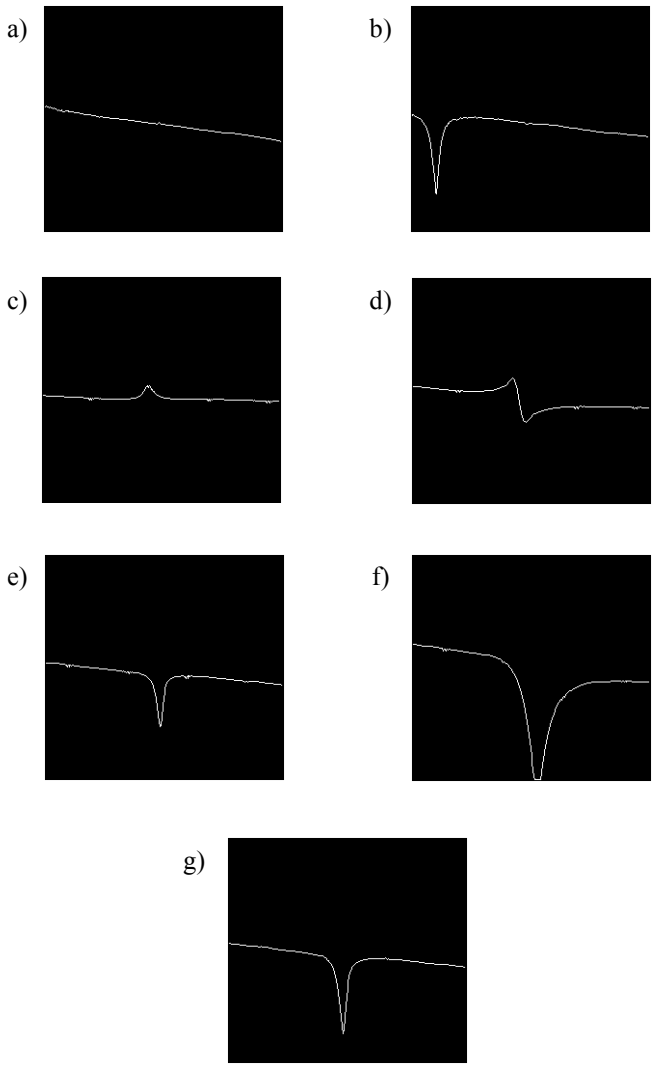


Figure 7-5

Tuning display for a klystron microwave source.

a) Off resonance.

b) Slightly off resonance.

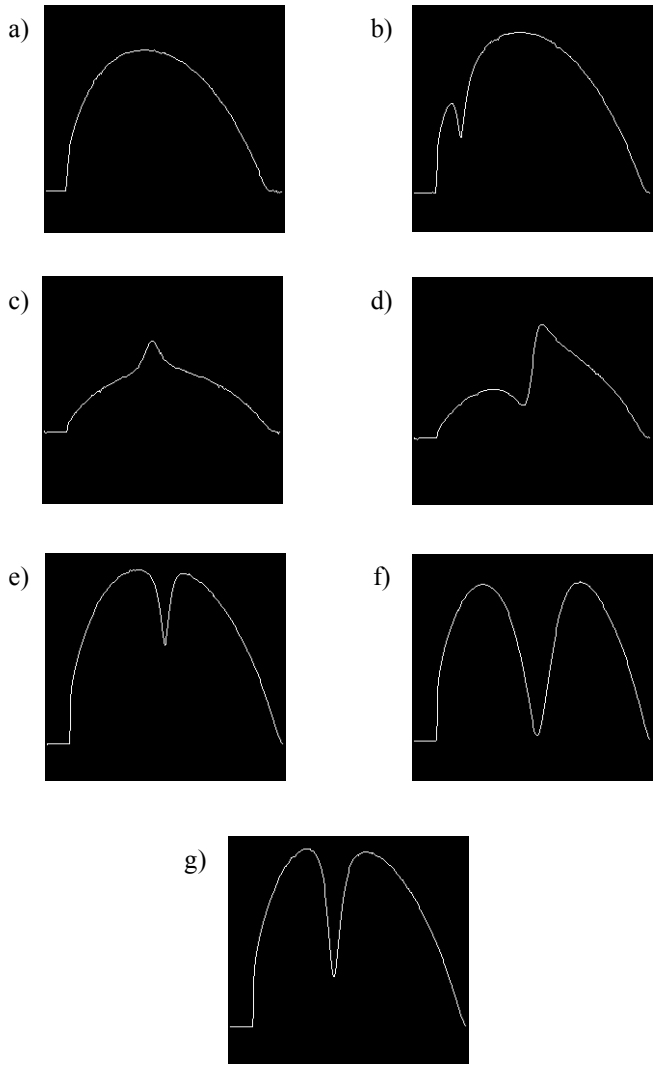
c) On resonance, phase 180° off.

d) On resonance, phase 90° off.

e) On resonance, correct phase, undercoupled.

f) On resonance, correct phase, overcoupled.

g) On resonance, correct phase, critically coupled.



The resonant frequency of most cavities is usually approximately 9.8 GHz.

A cryostat will drop the frequency to approximately 9.4 GHz.

7. **Tune the microwave source.** Adjust the Frequency slider bar to locate and center the tuning pattern “dip” in the display monitor. The “dip” corresponds to the microwave power absorbed by the cavity, and thus, is not reflected back to the detector diode. By centering the “dip” on the display monitor, the microwave source is set to oscillate at the same frequency as the cavity resonant frequency.

8. **Clean the sample tube to be inserted into the cavity.** Wiping the outside of the sample tube with tissue paper is usually adequate. It is vital to avoid contaminating the microwave cavity as paramagnetic contaminants may result in spurious EPR signals or distorted base lines in your EPR spectra.

9. **Insert the sample tube carefully into the cavity.** (See Figure 7-6.) Make sure you have the appropriate collet size for your sample tube size. The tube should be slightly loose before you tighten the collet nut. The bottom of your sample should rest in the indentation on the pedestal. This ensures that your sample is centered horizontally. If you have a small sample (less than 2 cm in length), you should visually judge how far the tube should go into the cavity in order to vertically center the sample in the cavity. You can adjust the sample position by loosening the bottom collet nut and moving the pedestal up and down. Tighten the top collet nut to firmly hold the sample tube in place and the bottom collet to firmly hold the pedestal.

Make sure that the pedestal is not in the cavity, as it can give an EPR signal or prevent proper tuning.

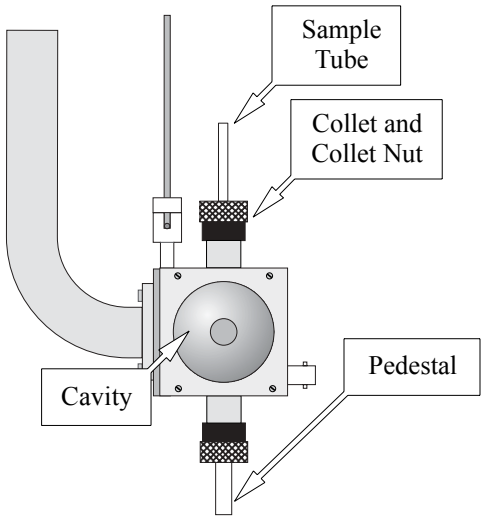


Figure 7-6 A Bruker ER 4122SHQ cavity.

10. **Retune the microwave source.** Repeat the procedure of Step 7. You may notice a shift in frequency or change in width and depth of the cavity "dip" when the sample is inserted. This is an indication that the microwave field patterns in the cavity are perturbed by the sample and tube. Lossy or conductive samples will greatly perturb the field patterns, resulting in large shifts in the resonant frequency. Highly conductive samples tend to increase the resonant frequency by decreasing the effective cavity volume. Lossy samples and other high dielectric constant material will decrease the resonant frequency because of their large dielectric constants.

11. **Turn the Reference Arm on.** Click the Reference Arm On button. The Bias slider should be about in the center to ensure that you have some microwave power in the reference arm. (See Figure 7-2.)

12. **Tune the signal (reference) phase. (Solid-state Microwave Sources)** While the "dip" is in the center of the display, adjust the Signal Phase slider (See Figure 7-2.), until the depth of the dip is maximized and the "dip" looks somewhat symmetric. (See Figure 7-4.) We shall fine-tune this phase later, but this procedure gets us close to the correct phase. Proceed to Step 14.

13. **Tune the signal (reference) phase. (Klystron Microwave Sources)** While the "dip" is in the center of the display, adjust the Signal Phase slider (See Figure 7-2.), until the shoulders on each side of the "dip" appear to be approximately the same height and the "dip" looks somewhat symmetric. (See Figure 7-5.) We shall fine-tune this phase later, but this procedure gets us close to the correct phase.

Sometimes the AFC meter may rush off either to the right or left and lose lock at 50 dB. In most cases, the AFC will lock again at higher microwave power levels. If the AFC does not re-lock, switching between Operate and Tune modes and back to Operate again at 30 dB attenuation will lock the AFC once more.

Critical coupling results in a maximum power transfer between the waveguide and the cavity.It also means that no incident microwaves are reflected back from the cavity. If the cavity and waveguide are truly matched, the reflected microwave power seen by the detector should remain constant (i.e. 0) when we vary the attenuation. This is the criterion we use for critical coupling.

14. **Fine-tune the microwave source frequency.** Click the Operate button in the dialog box to change to the Operate mode. Adjust the Frequency slider until the needle of the AFC meter is centered. You can locate the AFC meter by referring to Figure 7-3. Sometimes the needle may rush off to the right or left edges of the meter. This happens when the AFC (Automatic Frequency Control) is no longer locked. If this happens, click the Tune button to return to the Tune mode. Repeat Step 10. and then try again.

15. **Adjust the bias level.** Change the microwave attenuation to 50 dB. Adjust the Bias slider (See Figure 7-2.), until the Diode Current meter needle is centered. You can locate the Diode Current meter by referring to Figure 7-3. The center corresponds to 200 microamperes of diode current.

16. **Match the cavity.** For maximum sensitivity, we need to critically couple (or match) the cavity to the waveguide. The coupling or matching is varied by adjusting the iris screw or coupling screw. Increase the microwave power by 10 dB. (*i.e.* attenuator setting 40 dB). Click the Up or Down iris buttons for the iris screw motor or adjust the coupling screw on the cavity until the diode current again returns to 200 microamperes. (*i.e.* The needle is centered.) Repeat the procedure (-10 dB steps in the attenuator setting and adjust the current to 200 microamperes with the iris screw) until you have reached an attenuator setting of 10 dB. You will notice that as the microwave power is increased, the diode current becomes more sensitive to the position of the iris screw. Another thing you may notice is that the AFC meter also changes with the iris screw position. Simply adjust the frequency slider until the needle is centered again.

There are usually two Signal Phase settings that work. If the slider bar is very near the left or right edge of the display, choose the setting closest to the center of the Signal Phase slider bar.

17. **Fine tune the Signal Phase.** When you have reached 10 dB microwave attenuation, adjust the Signal Phase slider until you achieve a local maximum in the diode current. You should not have to adjust it very much. Verify that you have achieved critical coupling by changing the microwave attenuation from 10 dB to 50 dB with virtually no change in the diode current. Repeat the matching and Signal Phase adjustment procedures if necessary. If you need to operate at power levels greater than 20 mW (10 dB), set the attenuation to 0 dB and once again adjust the diode current to 200 microamperes with the iris screw. The current can sometimes drift because the high microwave power starts to heat the sample. If this happens, wait a minute or two and readjust the coupling.

18. **An alternative way of matching the cavity.** Follow the instructions through Step 14. Set the attenuation to 50 dB. Turn off the reference arm by clicking the Reference Arm Off button. The indicator of the Diode Current meter should stay at the very left and the current should be 0 or very close to 0 (under 10 microamperes is acceptable). Reduce the attenuation to 40 dB. If the diode current increases, adjust the iris screw or coupling screw to keep the diode current minimum. Continue to reduce the attenuation and adjust the iris crew to keep the diode current minimum until the attenuation reaches 10 dB. Set the attenuation to 20 dB. Click the On button under the Reference Arm. Adjust the Signal Phase slider until you achieve a local maximum in the diode current. Adjust the bias so that the diode current is about 200 microamperes or the indicator is centered. Change the attenuation to see if the diode current changes. Adjust the iris screw to keep the needle centered if the diode current changes. Verify that you have achieved critical coupling by changing the microwave attenuation from 10 dB to 50 dB with virtually no change in the diode current.

Changing EPR Cavities 7.2

We assume that the spectrometer is turned on, connected, and an experiment loaded before performing the following operations.

1. **Click the Activate button.** If this button is not already activated, click its button in the Acquisition Control Tool section. (See Figure 7-7.) This button allows you to interactively control the spectrometer when it is activated.

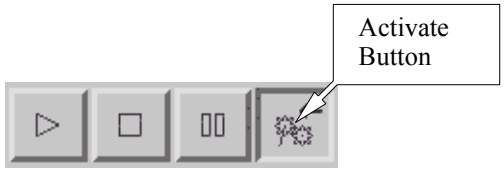


Figure 7-7 The Parameter to Hardware button.

If the Open Parameter Panel button is grey, you can not open the Parameter dialog box. Create or load an experiment so you can open the Parameter dialog box.

2. **Click the Parameter button.** Click this button to open the Acquisition Parameter dialog box. (See Figure 7-8.)

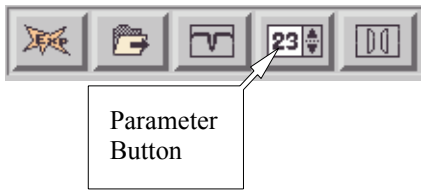


Figure 7-8 The Parameter button.

3. **Set the modulation amplitude to zero.** Click the Signal Channel tab. Enter a value of 0.00 in the Modulation Amplitude box. (See Figure 7-9.)

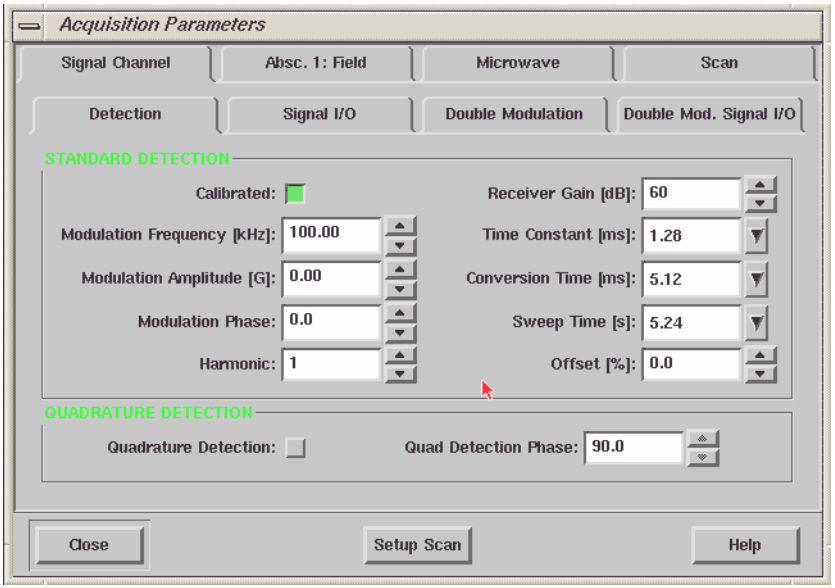


Figure 7-9 Set the Modulation Amplitude to zero.

4. **Set the magnetic field to the minimal value.** Click the Absc. 1:Field tab. Enter in a value of 0.00 in the Sweep Width box and then a value of 0.00 in the Center Field box.

5. **Close the Acquisition Parameter dialog box.** Click the Close button of the Acquisition Parameter dialog box. Click the Activate button again to exit the interactive control mode.

Setting the magnetic field to the minimum value avoids the risk of magnetizing your watch when changing cavities.

6. **Open the Microwave Bridge Tuning dialog box.** If this window is not already open, click its button in the monitoring panel. The button toggles the dialog box open and closed. The Microwave Bridge Tuning dialog box will then appear. (See Figure 7-10.)

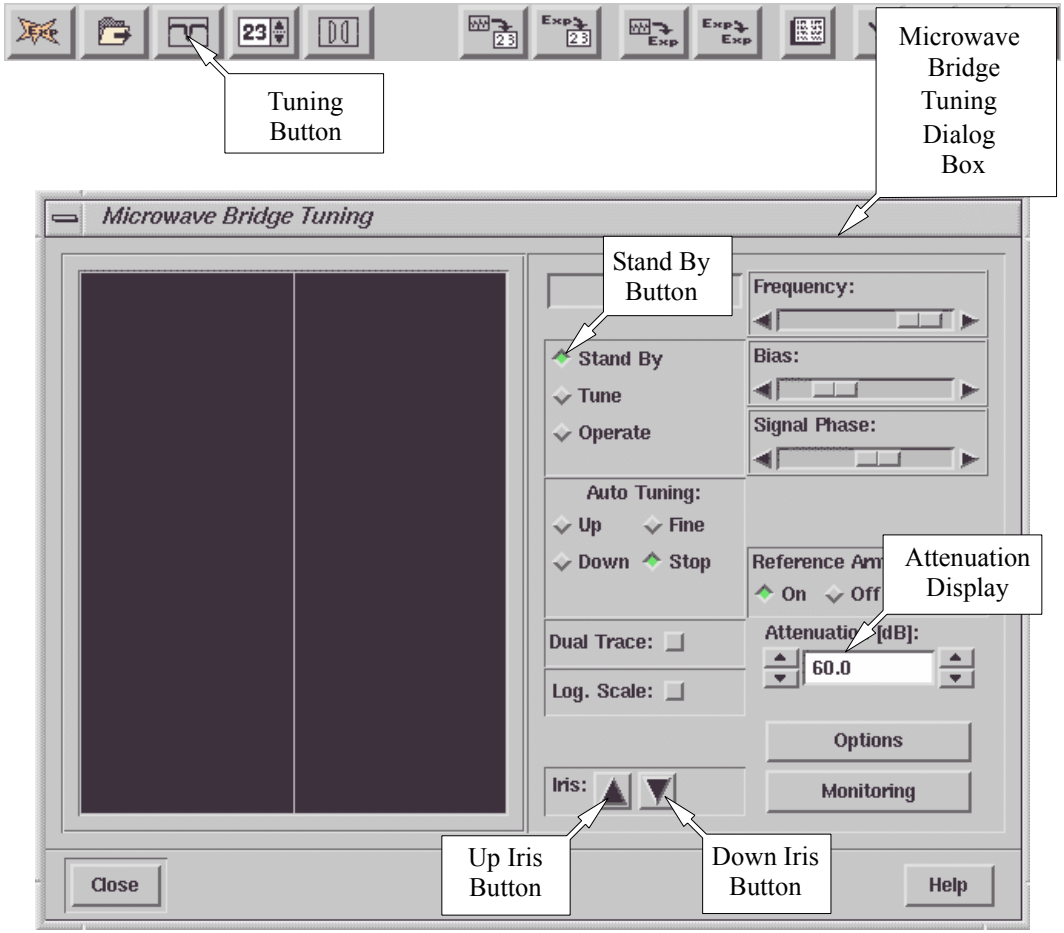


Figure 7-10 The Microwave Bridge Tuning dialog box.

7. **Switch the microwave bridge to Stand By mode.** (See Figure 7-10.) Click the Stand By button in the dialog box to change to the Stand By mode.

8. **Disconnect any accessories.** If a variable temperature dewar assembly is installed, disconnect the coolant transfer line and the thermocouple connections from the cavity.

9. **Disconnect the modulation cable from the cavity.** This is the twin-ax cable labeled with a white connector and attached to the front of the standard cavity. To remove it, push the connector in, turn counter-clockwise and gently pull the cable away. (See Figure 7-11.)

Not all cavities have a rapid scan cable.

10. **Disconnect the rapid scan cable from the cavity.** Disconnect the 50 Gauss rapid scan cable if it is connected to the cavity. This is the twin-ax cable labeled with a yellow connector and attached to the front left of the standard cavity.

11. **Disconnect the nitrogen purge line from the port on the waveguide.** The port is half way down the waveguide attached to the cavity. (See Figure 7-11.)

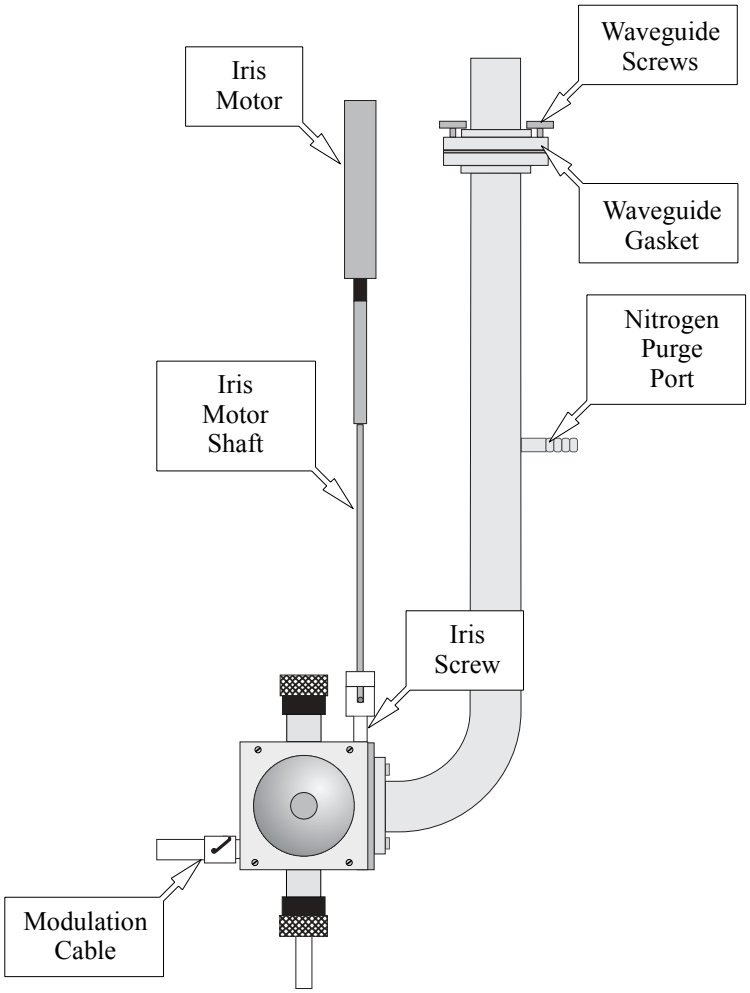


Figure 7-11 Connections on the ER 4122SHQ cavity.

Store the lock nut in a place where it will not be lost.

12. **Disconnect the iris motor shaft from the iris screw.** First unscrew the lock nut from the iris screw. Lift the shaft upwards to disconnect. Move the iris motor to the side where it is out of the way. (See Figure 7-12.)

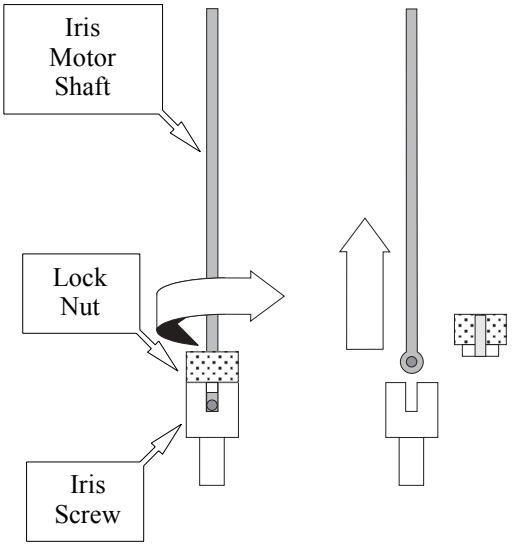


Figure 7-12 Disconnecting the iris motor shaft from the iris screw.

13. **Disconnect the cavity.** While grasping the waveguide attached to the cavity with one hand, unscrew the four waveguide screws joining the two sections of waveguide. (See Figure 7-11.) Loosen the waveguide stabilizers by rotating the screws and carefully remove the cavity from the air gap of the magnet. (See Figure 7-13.) Take care not to lose the gasket which was between the two wave guide flanges. Remove the waveguide stabilizers. (See Figure 7-14.) Seal the cavity with the solid collets and put the cavity in a safe clean place.

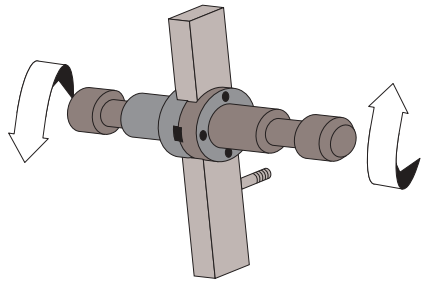


Figure 7-13 Loosening the waveguide stabilizers.

14. **Install the waveguide stabilizers on the new cavity.** (See Figure 7-14.) Visually position them just above the magnet pole caps.

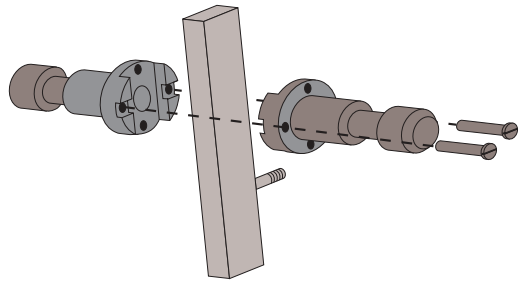


Figure 7-14 Removing/Installing the waveguide stabilizers.

Steps 16. and 21. are used to set the limit switches in the iris motor. The limit switches prevent you from screwing the iris in too far and thereby breaking the iris screw.

15. **Attach the appropriate size collet and pedestal on the cavity**.

16. **Screw in the iris.** Manually (By hand!) turn the iris screw almost all the way in. The iris screw will stop rotating. Back the screw out at least one turn after it hits the bottom. This will further decrease your chances of accidentally breaking the iris screw during the tune procedure.

17. **Connect the modulation cable to the cavity.** (See Figure 7-11.)

18. **Connect the 50 Gauss Rapid Scan cable to the cavity.** If you plan to do rapid scan experiments and there are rapid scan coils on your cavity, connect the 50 G rapid scan cable (the yellow twinax cable) to the front left connector of the cavity.

Make sure you connect the modulation cable to the MOD (modulation) connector and not the R.S. (Rapid Scan) connector. Not all cavities have rapid scan coils.

19. **Reconnect the waveguide sections and tighten the stabilizers.** Do not forget to install the waveguide flange gasket between the two flanges; make sure it is oriented correctly. (See Figure 7-15.) Position the cavity in the center of the magnet air gap by moving the bridge on the table. Carefully tighten the stabilizers. Be careful not to stress the waveguide when expanding the stabilizers. Reconnect the nitrogen purge line and adjust the flow rate for a light flow.

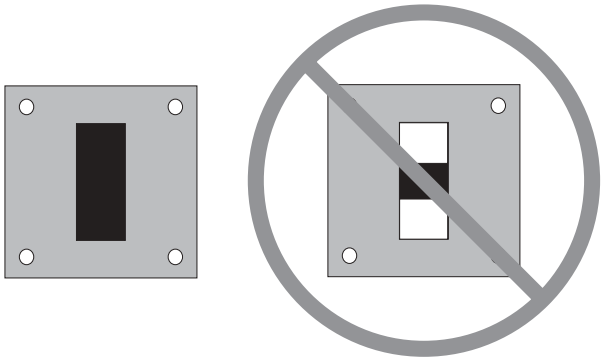


Figure 7-15 Installing the waveguide gasket properly.

20. **Reposition the iris motor.** Move the iris motor into a position such that the iris motor shaft hangs freely in the magnet. It should not be in contact with other objects.

21. **Lower the iris motor.** Open the Microwave Bridge Tuning dialog box. Click the Options button.

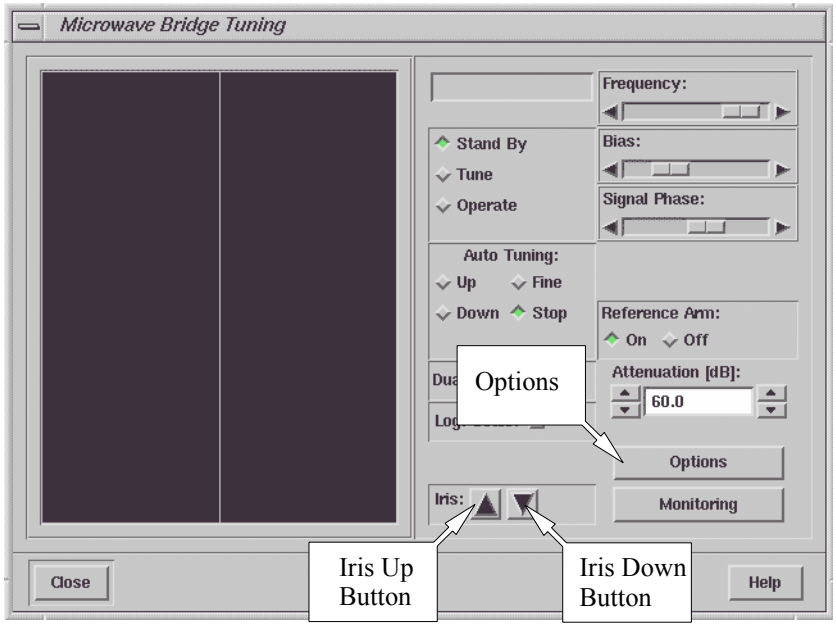


Figure 7-16 Iris controls in the Microwave Bridge Tuning dialog box.

A dialog box for lowering the iris screw appears. (See Figure 7-17.) Click the button next to Iris Run Down. A

Figure 7-17 The Iris Control dialog box.

message reminding you to disconnect the iris motor pops up. Heed the message and then click the Yes button to close the dialog box. (See Figure 7-18.) The iris motor will turn until it reaches the lower limit. Click Close on the Iris Control dialog box when the iris motor stops. You can also manually lower the iris motor. Click and hold the Iris Down button. In the Microwave Bridge Tuning dialog box (See Figure 7-16.), activate the Iris Down button until the iris motor stops; this is the lower limit of the motor.

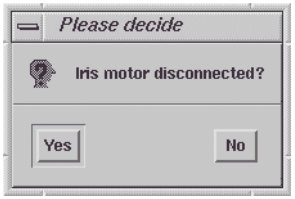


Figure 7-18 Make sure disconnecting the iris motor.

The end of the iris motor shaft should fit easily in the top of the iris screw. If it does not, rotate the iris screw until it fits easily.

22. **Reconnect the iris motor shaft to the iris screw.** The procedure here is like Step 12. performed in reverse. Reposition the iris screw motor. Screw the lock nut on the iris screw. Click and hold the up iris button in the Microwave Bridge Tuning dialog box (See Figure 7-10.) until the iris screw is approximately 0.5 to 1 cm. above the top surface of the cavity body.

23. **Read in the calibration file for the cavity.** Click Acquisition in the menu bar and then click Spectrometer Configuration. (See Figure 7-19.) The Spectrometer Configuration dialog box will then appear. (See Figure 7-20.)

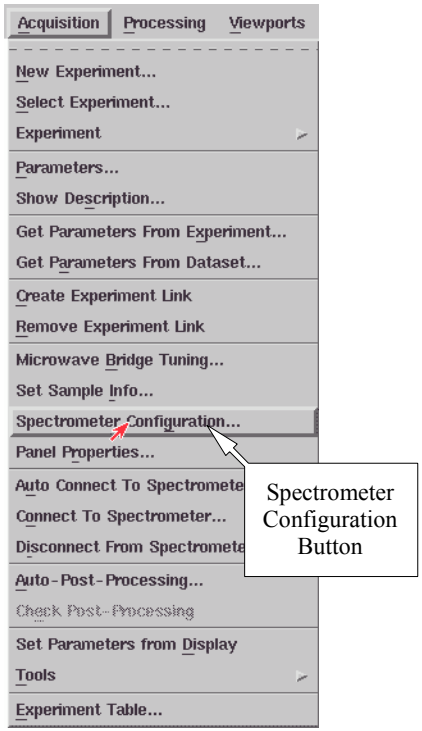


Figure 7-19 The Spectrometer Configuration button.

Click the Signal Channel tab. In the Standard Calibration folder there is a box called Calibration Data Set. Click the arrow to view the drop-down list. Select the appropriate calibration file for your cavity and click the

Apply button at the bottom of the folder. This will automatically load the calibration data you have selected.

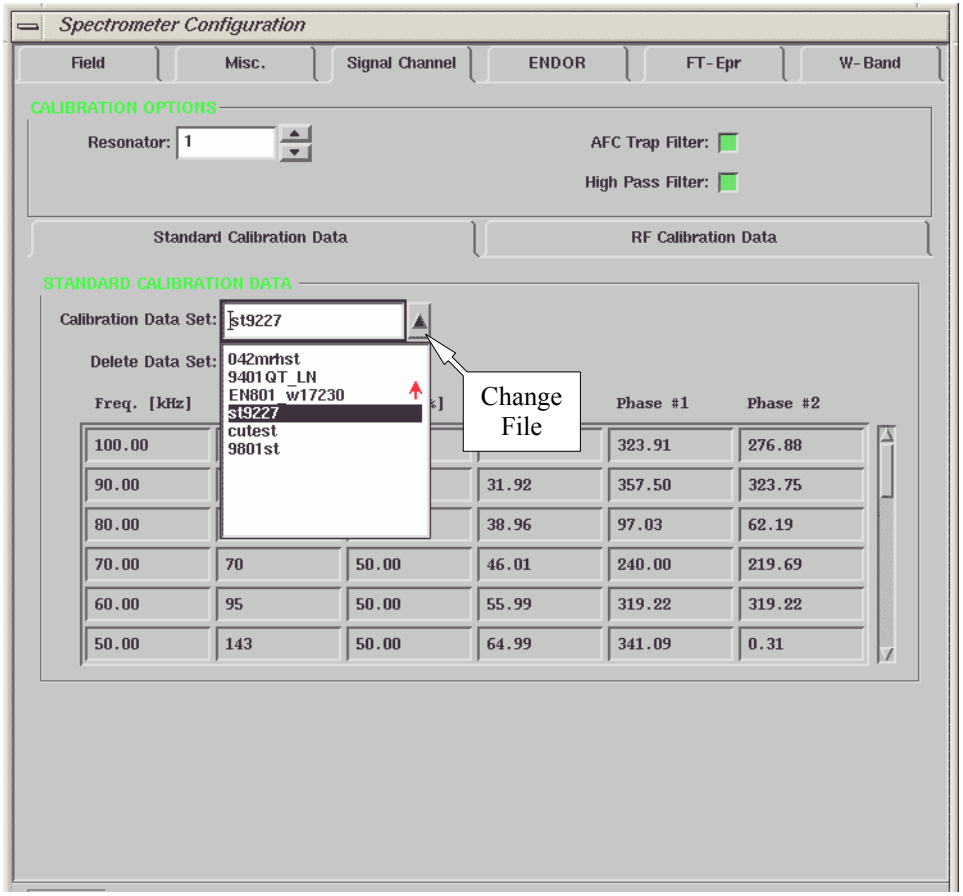


Figure 7-20 Selecting a calibration file.

Confirm that the calibration file is the correct one for the cavity. The calibration file name usually consists of two or three letters that identify the type of cavity (ST for ER 4102ST or TM for ER 4103TM) followed by the serial number of the cavity. This number is found on the back or front of the cavity. Click Close to exit. If you can not find the calibration file for the cavity you need to do the calibration first. Follow the instruction in Chapter 2 of the Elexsys E 500 User's Manual: Advanced Operations to create a calibration file.

AFC Adjustments 7.3

AFC Adjustments for Low Power Operation 7.3.1

The AFC (Automatic Frequency Control) is the circuitry used to "lock" the microwave source frequency to the resonant frequency of the cavity. In most cases, particularly if the microwave attenuation is less than 40 dB, the AFC works very well without any need for fine-tuning. Experiments at low microwave power require that you follow the instructions in this section to optimize the AFC performance.

Please note that this procedure is not required for klystron bridges. You can determine the type of bridge you have by looking at the model designation on the front plate of the bridge. A model designation containing a G, for example ER 041 XG, indicates a microwave bridge with a Gunn diode microwave source. In contrast, a bridge with a model designation with a K, such as ER 041 XK, has a klystron microwave source.

1. **Set the FINE AFC potentiometer to zero.** The potentiometer for the AFC can appear in two different locations on the bridge depending on when your bridge was manufactured. (See Figure 7-21.)

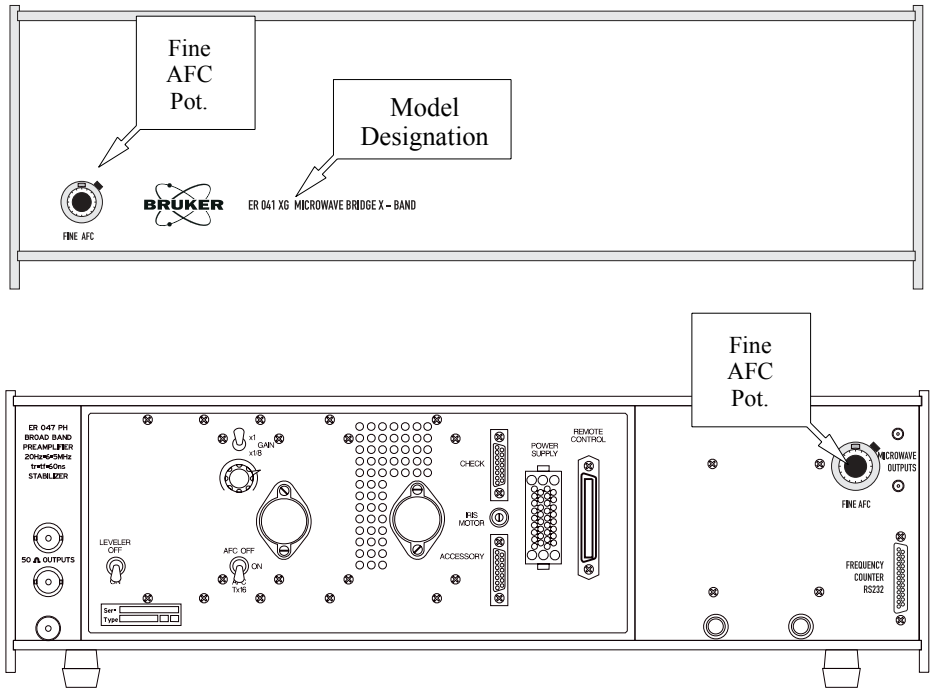


Figure 7-21 Two possible locations for the Fine AFC potentiometer.

2. **Tune the microwave bridge.** Follow the procedures in Section 3.2 for automatic tuning or Section 7.1 for manual tuning. The frequency, bias, phase, and iris screw should be adjusted so that the needles of the AFC and Diode meters remain centered as the microwave attenuation is changed from 10 to 40 dB. (See Figure 7-22.)

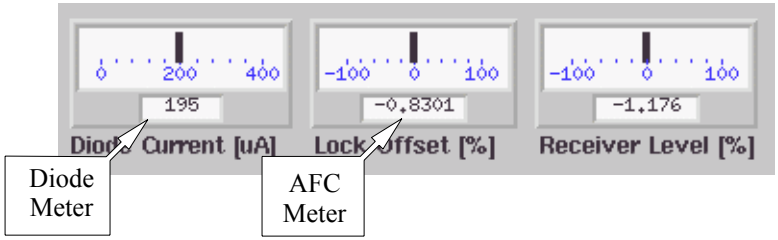


Figure 7-22 The location of the AFC and diode current meters.

3. **Switch the microwave attenuation from 40 dB to 50 dB.** The AFC meter may drift to the right or left. (See Figure 7-23.)

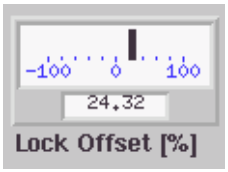


Figure 7-23 The AFC needle drifting towards the right.

4. **Increase the microwave attenuation slowly.** Increase the attenuation in 1 dB increments between 50 and 60 dB until you observe a significant deflection of the needle. (See Figure 7-24.)

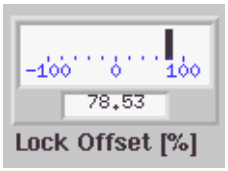


Figure 7-24 A significant AFC needle deflection.

5. **Adjust the FINE AFC Potentiometer.** Turn the knob until the AFC needle is once again centered in the AFC meter. (See Figure 7-25.)

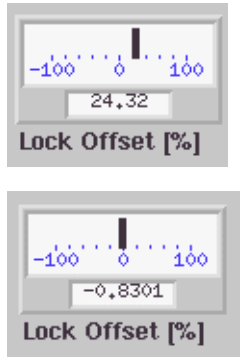


Figure 7-25 Centering the AFC meter.

6. **Verify that the AFC needle remains centered.** Vary the microwave attenuation between 10 and 60 dB (or 80 dB for high dynamic range bridges). Also, the needle may rush off to the left or right at low powers because the AFC loses lock. In most cases, the AFC will lock again at higher microwave power levels. If not, switch to Tune and back again to Operate at 30 dB attenuation to lock the AFC once more. Now increase the attenuation using 1 dB steps. Repeat Step 2. through Step 6. until the needle remains centered.

7. **Record the microwave frequency and FINE AFC potentiometer setting.** This setting is microwave frequency dependent and reproducible. Because only the insertion of a cryostat substantially shifts the microwave frequency, you will typically only need a setting for a cavity with and without a cryostat.

If you record the FINE AFC potentiometer setting at that microwave frequency, you need not perform this whole procedure every time you use low microwave power levels.

AFC Adjustments for Optimal Sensitivity 7.3.2

You need proper AFC gain and modulation level settings in order to achieve optimal sensitivity. Improper AFC settings may make it difficult to lock the frequency or it may introduce extra noise. The proper AFC settings depends on your cavity, your sample, and any accessories you may be using. Usually one AFC setting covers a relatively large locking range of the microwave source without introducing extra noise. However, in certain cases such as experiments using a liquid nitrogen finger dewar or changing from a low Q cavity to a very high Q cavity, you may need to optimize the AFC gain or modulation depth.

1. **Turn on the spectrometer and tune the bridge.** Turn on the spectrometer if it is not turned on yet. Set up any accessories (*i.e.* finger dewars or variable temperature systems) you will be using and insert your sample. Tune the bridge and cavity.

2. **Adjust the initial AFC settings.** There are two parameters to set, the AFC gain and modulation level. (See Figure 7-26.) You can set the AFC gain via a flip switch allowing you to select between X1 or X1/8. To start with, set the AFC gain level to 1/8 for high Q cavities such as ER 4122SHQ cavities and ER 4119HS cavities and set it to 1 for lower Q cavities such as the ER 4102ST cavity. The AFC modulation level is adjusted via a knob scaled from 1 to 10. Turn the AFC modulation level knob to 1.

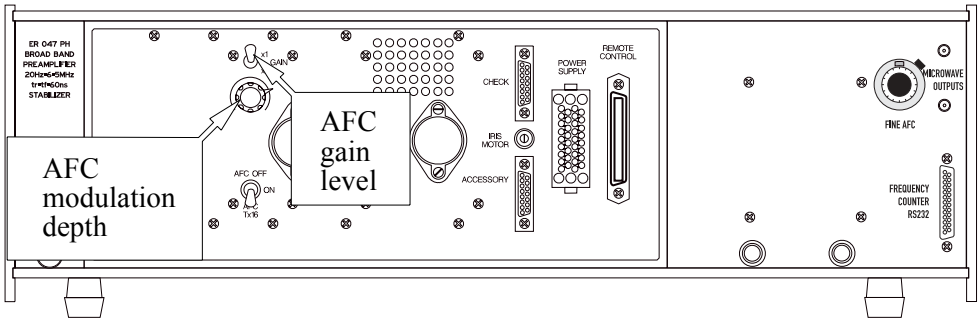


Figure 7-26 AFC adjustments for optimal sensitivity.

3. **Create a new experiment.** Create a 1D CW field scan experiment.

4. **Open the Acquisition Parameter window.** Click the Activate button and then click the Parameter button to open the Acquisition Parameter window.

5. **Open the Setup Scan window.** Click the Setup Scan button to open the Setup Scan window.

6. **Activate the Setup Scan function.** Click the Setup Scan button in the Setup Scan window. Set the Sweep Width to 0. (See Figure 7-27.)

7. **Adjust the parameters in the Acquisition Parameters dialog box.** Set the time constant to 0.08 ms or less. Set the magnetic field far from any EPR signal. Increase the microwave power. For non-lossy samples, you can increase the power to 0 db. For lossy samples, increase the power until you see the Diode Current starting to drift. You may also have to adjust the receiver gain and offset so that the noise trace is vertically centered in

the window and the noise is easily visible. (See Figure 7-27.)

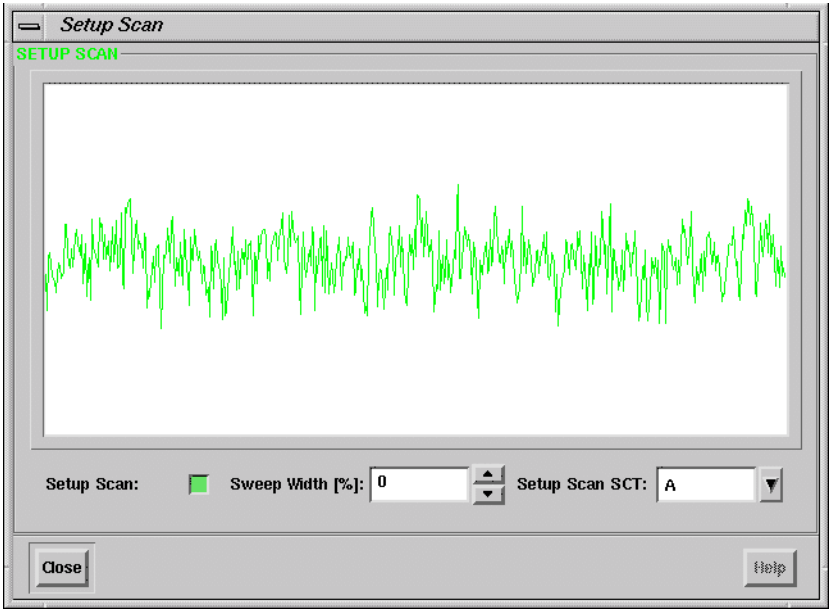


Figure 7-27 A Setup Scan of a noise trace used to adjust the AFC gain.

8. **Increase the AFC modulation level.** Gradually increase the AFC modulation level by turning the knob. (See Figure 7-26.) Watch the noise trace closely in the setup scan window when you increase the AFC gain. (See Figure 7-28.) If the knob is turned to maximum and the noise level is not increasing, turn it back to minimum and flip the AFC gain switch to 1. Then increase the modulation level again by turning the knob. If you observe an increase in the noise level as you increase the AFC modulation depth, turn the knob back until the noise level no longer decreases. This is the optimal AFC modulation level you can set for that cavity with that sample. You

may need to turn the potentiometer knob back a unit or two to make sure no extra noise is introduced by the AFC.

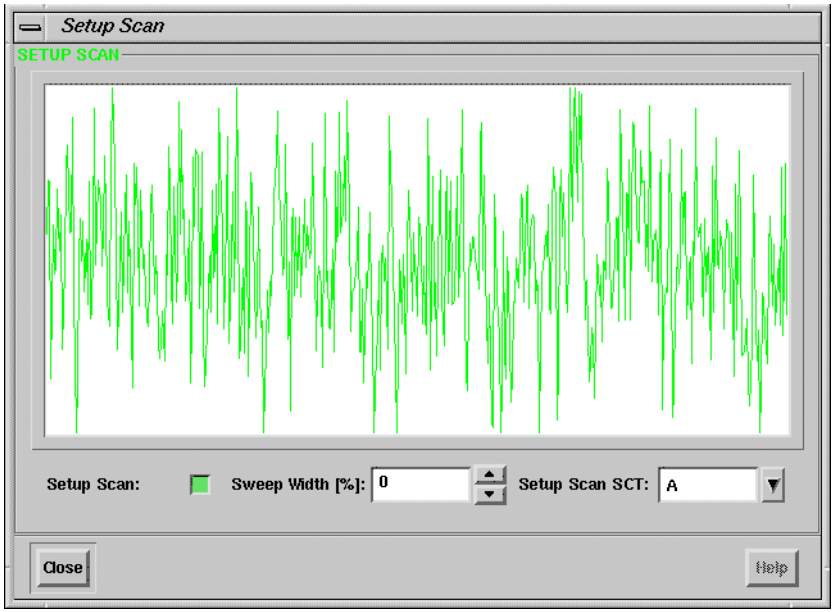


Figure 7-28 Too high of AFC gain causes extra noise.

Helpful Hints 8

This chapter contains useful hints for getting the most out of your Elexsys E 500 spectrometer and its hardware. The first half of this chapter advises you on what to do if you do not observe an EPR signal from your sample. The second half of the chapter covers optimizing the performance of the EPR spectrometer for your particular sample and operating conditions. It is assumed that you are familiar with the material presented in Chapter 2 and Chapter 3.

Hints for Finding EPR Signals 8.1

- **Make sure that the spectrometer is functioning properly.** If you followed the directions of Chapter 3, this should not be a problem. There are many common mistakes. Is the modulation cable connected properly to the cavity and console? Is the waveguide gasket installed properly? Is everything turned on? Advice on troubleshooting is presented in the next chapter.

Cryostats shift the resonant frequency of the cavity and hence the frequency of the spectrometer to a lower value. The field for resonance of the signals will therefore occur at lower field values than you would expect for a cavity without a cryostat.

- **Scan over the correct magnetic field range.** If you do not sweep over the correct magnetic field range, you will miss your signals. This mistake occurs quite often when using a cryostat in the EPR cavity. Consult literature references to determine approximate g-values for the species in your sample. You can then estimate and choose the appropriate magnetic field for your sample by using the following formula:

$$B_0 = \frac{714.48}{g} \cdot \nu \qquad [8\text{-}1]$$

where ν is the microwave frequency in GHz, g is the g factor, B_0 is the magnetic field in Gauss. Most organic radicals will have a g-value of approximately 2. This corresponds to a field for resonance of approximately 3480 Gauss at a microwave frequency of 9.78 GHz. Metal ions can have large departures from g = 2 as well as large zero-field splittings, making it difficult to guess where the resonance(s) might occur. Performing a wide scan in your initial experiment will maximize your probability of finding the EPR signal.

- **Finding an EPR signal**. Sometimes you may have difficulty finding the EPR signal from an unknown sample or a sample you are not familiar with. Here we provide two examples of parameter sets that are useful for finding EPR signals from unknown samples that you suspect will consist of either an organic radical or a transition metal ion, respectively. (See Table 8-1.) These parameters are by no means optimized, but they will serve to help you find the signal. After you find the EPR signal you need to reset the field center and scan range. (See Section 3.3 or Section 5.5.) You also need to optimize your EPR signal using the method described later in this chapter. If you still cannot find the signal you may have to adjust parameters such as the microwave power, modulation amplitude, scan time, *etc*.

Parameter	Organic Radicals	Metal Ions
Microwave Power (mW)	10	10
Center Field (G)	3480	3100
Sweep Width (G)	300	6000
Receiver Gain (dB)	70	70
Modulation Frequency (kHz)	100	100
Modulation Amplitude (G)	4	4
Time Constant (ms)	327.68	327.68
Conversion Time (ms)	327.68	81.92
Resolution in X (points)	1024	4096

Table 8-1 Recommended parameter sets for unknown samples.

- **Make sure your sample is positioned correctly in the cavity.** Only the central region of the cavity contributes significantly to the EPR signal. If you place the sample sufficiently out of this region you may not detect a signal.
- **Use an appropriate microwave power level.** Using more microwave power does not necessarily result in a more intense EPR signal. Saturation can occur. (See Section 2.1.4 and Section 8.2.) Organic radicals in non-viscous solvents or many samples at cryogenic temperatures are susceptible to saturation effects. Try running the EPR experiment at several different power levels.

If you do not know what type of signals to expect, try a variety of parameter value combinations.

- **Use appropriate signal channel parameters.** The parameters should be optimized for the type of signal to be expected. (See Section 8.2.) If you get a straight noiseless line for a spectrum, the signal channel may be overloaded. The needle of the Receiver Level meter will be pegged on either side of the meter. If this occurs, change the offset to bring the needle of the Receiver Level meter back to the center. If changing of the offset does not help, turn down the receiver gain, microwave power or the modulation amplitude.
- **Optimize the sensitivity.** You may have a very weak signal in which case you will need to optimize your parameter settings for sensitivity. The chart on the next page summarizes common factors that are important for getting the optimum sensitivity from your EPR measurements. The pages that follow the chart provide a more in-depth discussion of these factors.

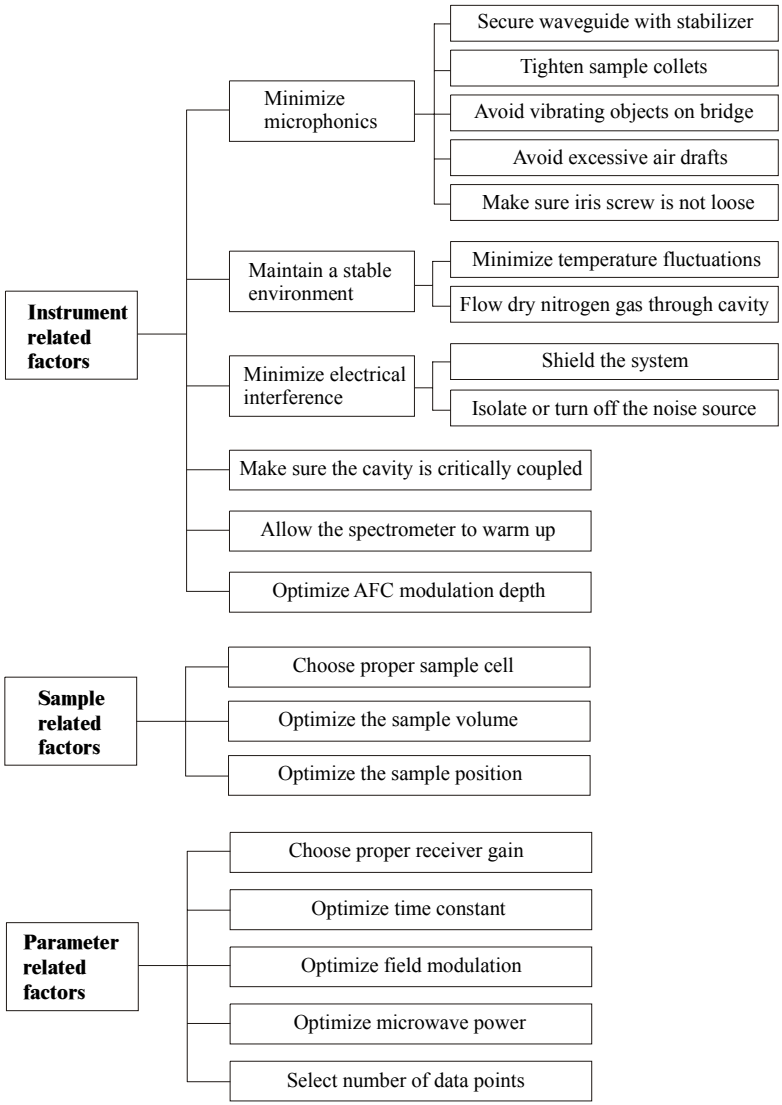


Figure 8-1 Flowchart for optimizing sensitivity.

Optimizing Sensitivity 8.2

Instrumental Factors 8.2.1

- **Minimize microphonics.** Microphonics are unwanted mechanical vibrations in the spectrometer. Depending on the nature and frequency of the microphonics, these vibrations may generate noise in your EPR spectrum. The most common microphonic sources include the cavity, the sample and the bridge. Prevent microphonic noise by securing the waveguide with the waveguide stabilizers. Rigidly secure the sample in the cavity by tightening the collets on the cavity sample stack. Do not place objects on the microwave bridge that may vibrate or are free to move. Avoid placing a frequency counter with a fan on top of the bridge.

For better spectrometer stability, keep the spectrometer away from windows and ventilation ducts.

- **Maintain a controlled environment for the best spectrometer performance.** Air drafts past the spectrometer, especially the cavity, may induce temperature fluctuations or microphonics from sample vibration. Large fluctuations in the ambient temperature may degrade performance by reducing the frequency stability of the cavity. Very humid environments may cause water condensation. You can reduce condensation inside the cavity by maintaining a constant purging stream of dry nitrogen gas. Note that excessive gas flow rates can generate microphonic noise through sample vibration.
- **Minimize electrical interference.** Noise pick-up from electromagnetic interference (EMI noise) may be encountered in some environments. You may be able to minimize EMI noise by shielding or perhaps by turning the noise source off if generated by equipment near the spectrometer. There is often less EMI at night.

- **Allow the spectrometer to warm up.** One hour is usually adequate to achieve a stable operating temperature. For maximum stability under extreme operating conditions such as any combination of high microwave power, high magnetic field modulation amplitudes, and variable temperature work, allow the system to equilibrate under the same conditions as the experiment will be performed.
- **Periodically check the iris coupling screw for tightness of fit.** A worn iris screw thread will make the iris susceptible to microphonics which can modulate the cavity coupling.
- **Critically couple the cavity.** Best cavity performance is obtained with a critically coupled cavity. Maximum transfer of power between the cavity and the waveguide occurs under this condition.
- **Optimize the AFC.** See Section 7.3.2.
- **Insert a cryostat in the cavity.** Quartz has a dielectric constant of 3.8 but a low dielectric loss. Insertion of high purity quartz sleeves, such as the variable temperature dewar, actually concentrates the microwave magnetic field intensity at the sample. The increased field intensity produces an EPR spectrum with a larger signal to noise ratio than is achieved in the absence of the dewar insert. If your experiments approach the sensitivity limit and your samples are nonlossy you may benefit from the use of the variable temperature quartz dewar insert, even if the experiment is run at room temperature.

Cryostats can protect your cavity from contamination due to sample tube breakage.

Optimize the Sample 8.2.2

- **Select the proper sample cell**. For nonlossy and nonconductive samples you can use large diameter quartz tubing (e.g. 3 mm or larger i.d. for X-band) to increase the filling factor by increasing the sample volume and therefore increasing the signal intensity. For conductive or lossy samples, you need to reduce the sample diameter (e.g. less than 1 mm for aqueous sample in X-band) to critically couple the system. Specially designed sample cells, such as flat cells or tissue cells, allow you to use more sample and still be able to critically couple the system.
- **Optimize the sample volume.** In general, large sample volume corresponds to high filling factor and therefore high signal intensity. For lossy material, large sample volume usually results in low Q and consequently low signal intensity. Balance the Q factor and the sample volume to maximize the signal intensity.
- **Optimize the sample position.** Properly positioning the sample requires two adjustments. First, make sure the sample is vertically centered in the cavity. This is particularly important for point samples. Second, rotate and center the sample to maximize the Q factor. This is particularly important for samples exhibiting a large dielectric loss and using flat cells. Improper sample positioning may perturb the microwave field mode patterns in the cavity, resulting in reduced sensitivity.

Parameter Selection 8.2.3

- **Optimize the receiver gain.** You need to have sufficient receiver gain in order to see all the details in your spectrum. Figure 8-2 shows the results of insufficient as well as excessive receiver gain. If the receiver gain is too low you will see the effect of digitization in the spectrum (spectrum b), whereas at high gain the signals will clip due to an overload in the signal channel (spectrum c). A good way to optimize your receiver gain is either to use the interactive spectrometer control method described in Section 5.3 or use the acquisition tools described in Section 5.5.1.

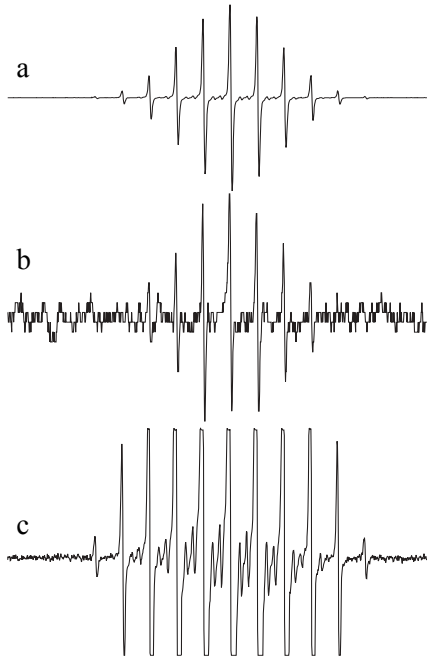


Figure 8-2 The effect of using gain settings that are either (a) optimal, (b) too low, or (c) too high on an EPR spectrum.

- **Optimize the conversion time.** The conversion time you select will affect the dynamic range of your experiments. The conversion time is actually the amount of time the analog-to-digital converter spends integrating at one field position before moving to the next field value in the sweep. If you need to detect lines that are very intense as well as lines that are very weak (i.e, carbon 13 satellites) within the same spectrum you will need to use a sufficiently long conversion time. If the conversion time is too short the smaller signals will be lost in the steps of the digitizer. The conversion time you select will also determine the sweep time. That is, the sweep time will be equal to the conversion time multiplied by the number of data points in the spectrum. (See selecting the number of data points below.)

- **Optimize the time constant for the selected conversion time.** The time constant filters out noise; however, if you choose a time constant that is excessively high relative to your sweep time, you may actually filter out your signal! You should adjust your time constant to "fit" the conversion time you have selected. These two parameters are actually very related because the conversion time will determine the total sweep time. You need to use a time constant that will be sufficiently long to filter out undesirable noise yet short enough that you do not distort your signal. Therefore, if you want to use a longer time constant you will need to increase the scan time as well. Figure 8-3 shows the effect of progressively increasing the time constant while maintaining the same sweep time. All the spectra are at the same scale. A safe rule of thumb is to make sure that the time needed to scan through an EPR signal (*i.e.* one EPR line) is ten times greater than the length of the time constant. A time constant that is 1/4 that of the conversion time will guarantee that your spectrum is not distorted. However, for samples limited by a low signal to noise ratio, you may want to make the time constant equal to the conversion time or greater.

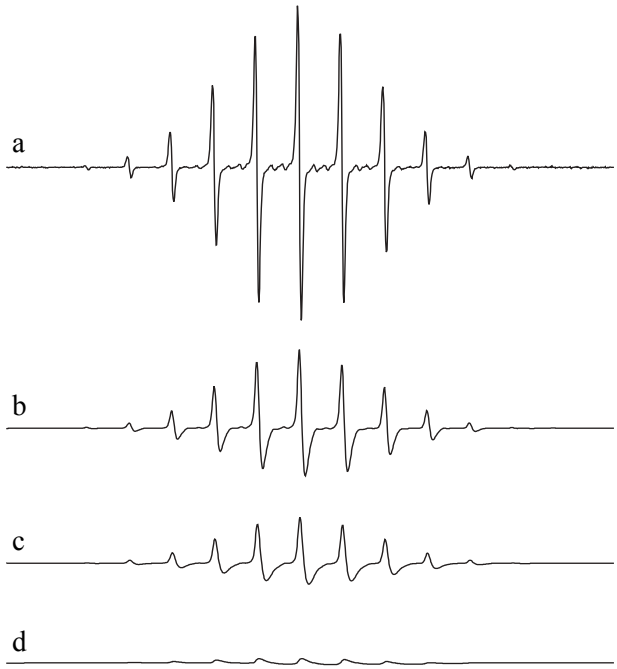


Figure 8-3 The effect of using a progressively longer time constant (a-d) on an EPR spectrum.

- **Selecting the number of data points.** The number of data points is the other parameter that will determine the appropriate sweep time. A general rule is to make sure that you have at least 10 data points within the narrowest line that you are trying to resolve. This means that for EPR signals with very narrow lines you will need to increase the number of data points that are collected for a given field sweep. However, if the lines of your EPR signal are sufficiently wide, increasing the number of data points will not yield any additional information, but will only result in longer sweep times. With the Elexsys you can select 512, 1024, 2048, 4096 or 8192 data points. Figure 8-4 shows the enhancement in resolution achieved by increasing the number of data points.

Remember, you may increase the time constant by a factor of two as you double the number of data points while keeping the conversion time constant.

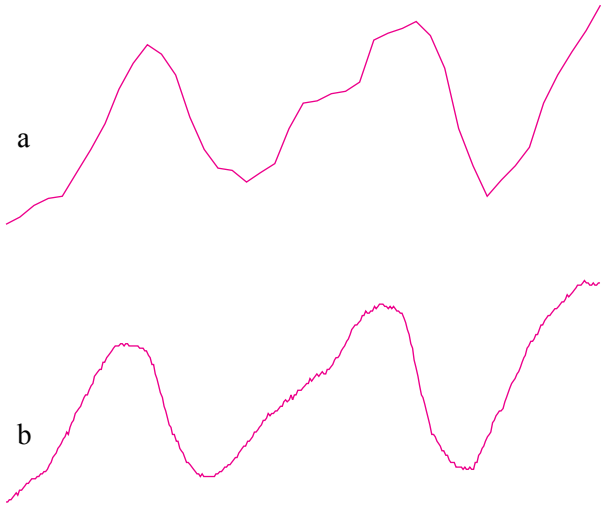


Figure 8-4 An expanded view of narrow lines in an EPR spectrum using 1024 points (a) or 8192 points (b).

- **Optimize the field modulation amplitude.** Excessive field modulation broadens the EPR lines and does not contribute to a more intense signal. Figure 8-5 shows the results of excessive field modulation. You can see how some of the smaller lines in spectrum a were lost in spectrum b even after increasing the modulation only slightly. A good "rule of thumb" is to use a field modulation amplitude that is approximately one quarter the width of the narrowest EPR line you are trying to resolve. Keep in mind that there is always a compromise that must be made between resolving narrow lines and increasing your signal to noise ratio. If you have a very weak signal, you may need to sacrifice resolution (*i.e.*, by using a higher field modulation) in order to even detect the signal. However, if you have a high signal to noise ratio, you may choose to use a much lower field modulation amplitude in order to maximize resolution.

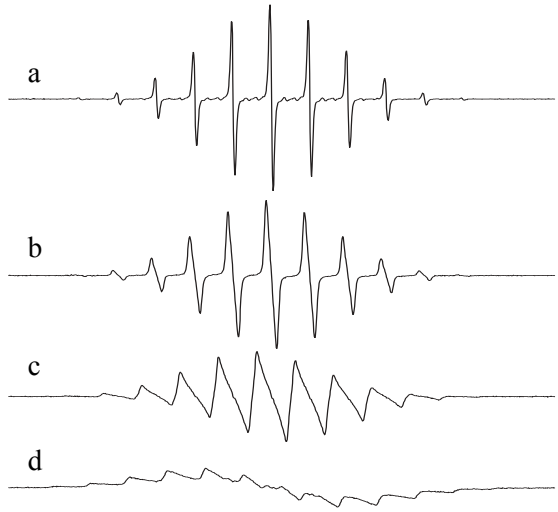


Figure 8-5 Effect of using progressively higher field modulation amplitudes (a-d) on an EPR spectrum.

- **Optimize the microwave power level.** The intensity of an EPR signal increases with the square root of the microwave power in the absence of saturation effects. When saturation sets in, the signals broaden and become weaker. EPR signals with very narrow lines are particularly susceptible to distortion by excessive power. Figure 8-6 shows the result of excessive microwave power. You should try several microwave power levels to find the optimal microwave power for your sample. A convenient way to find the optimum power is to use the 2D experiment routine described in Section 5.7.

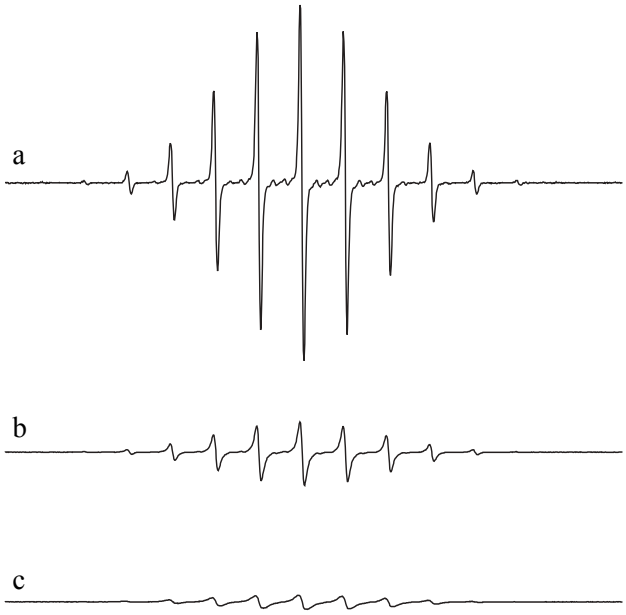


Figure 8-6 Effect of using progressively higher power (a-c) on an EPR spectrum.

- **Signal averaging.** With a perfectly stable laboratory environment and spectrometer, signal averaging and acquiring a spectrum with a long scan time and a long time constant are equivalent. Unfortunately, perfect stability is usually impossible to attain and slow variations can result in considerable baseline drifts. A common cause of such variations are room temperature changes or air drafts around the cavity. For a slow scan, the variations cause broad features to appear in the spectrum as is shown in spectrum b of Figure 8-7. You can achieve the same sensitivity without baseline distortion by using the signal averaging routine with a small time constant and shorter scan time. For example, if you were to signal average the EPR spectrum using a scan time that was significantly shorter than the variation time, these baseline features could be averaged out. In this case, the baseline drift will cause only a DC offset in each of the scanned spectra. Spectrum a shows the improvement in baseline stability through the use of short time scans with signal averaging when the laboratory environment is not stable.

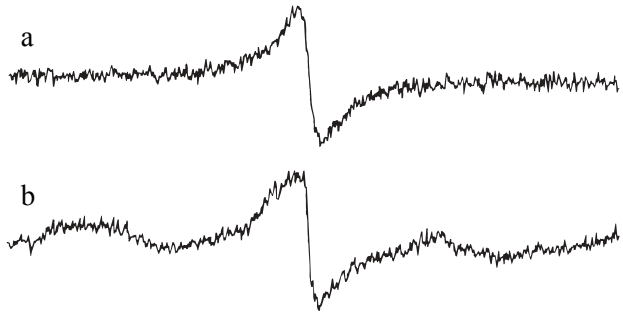


Figure 8-7 a) Signal acquired with short time sweeps and signal averaging.

b) Signal acquired with long time sweep and long time constant.

Troubleshooting 9

This chapter lists some common problems you may encounter with your Bruker Elexsys E 500 EPR spectrometer. Major hardware malfunctions are not covered. We concentrate on problems due to operator errors, set up errors, or protective circuitry. The material presented in Chapter 2, 3, 4, 5, and 6 is useful in understanding much of what is discussed in this chapter. Many problems are easily solved by the user. The flow diagram on the next page will help you diagnose the majority of problems that occur when you can not find a signal. If you fail to find a solution to your problem after reading this chapter, call your Bruker EPR service representative.

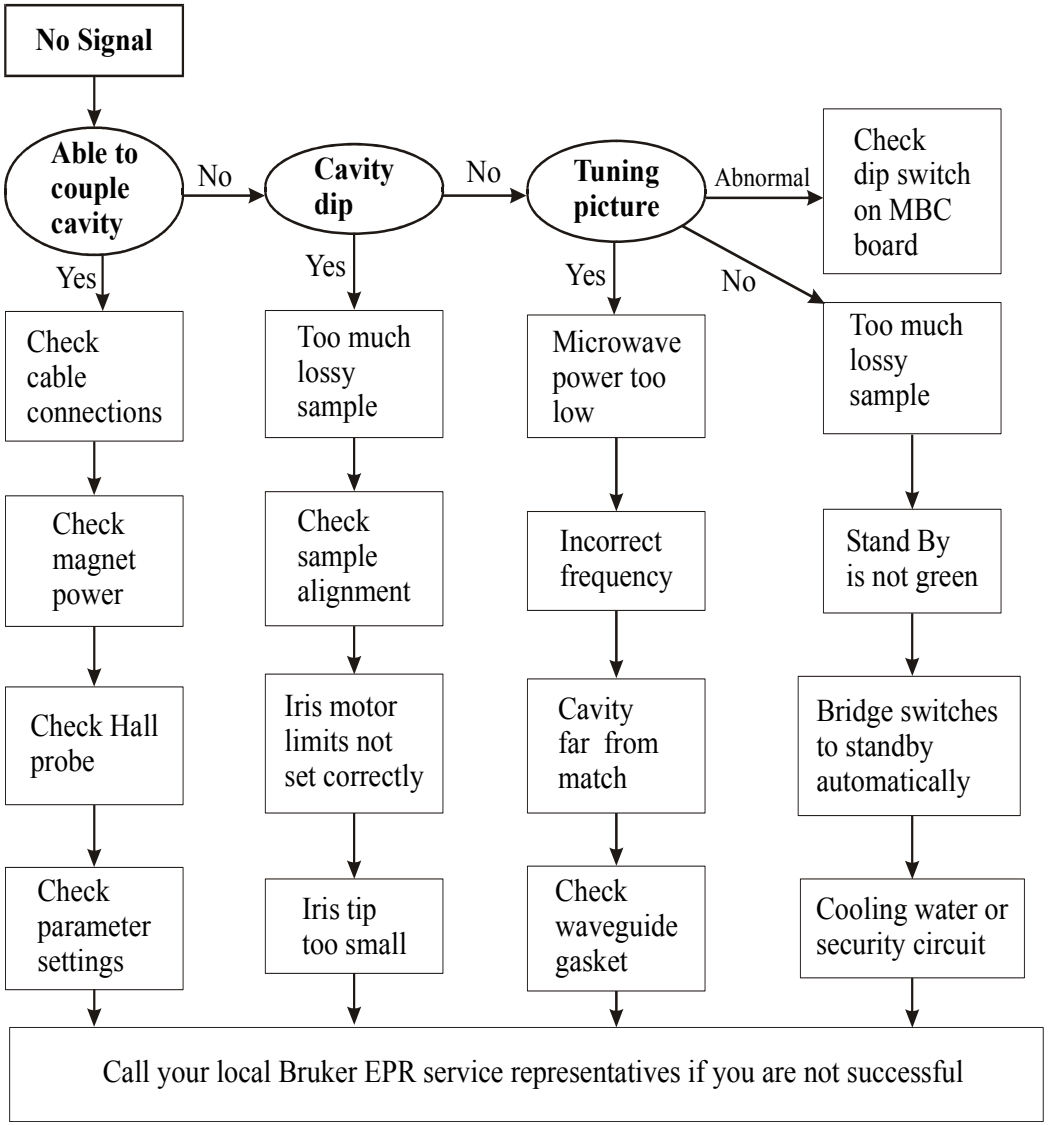


Figure 9-1 Flow Chart for diagnosing problems.

No Cavity Dip. 9.1

- **Waveguide gasket installed improperly.** See Figure 7-15 for the proper orientation of the gasket.
- **Cavity undercoupled or overcoupled.** First, look at the microwave frequency where you normally expect the cavity to resonate and then adjust the iris screw for better coupling. This can occur when working with lossy samples such as aqueous solutions in flat cells or capillaries.
- **You need more microwave power.** If you are using insufficient microwave power, it can be difficult to see the cavity dip. We recommend setting the microwave attenuator at 30 dB for the best visibility.
- **You are not at the correct frequency.** By putting the sample in, you may cause the cavity to resonate at a lower frequency. Thus, you will usually need to lower the frequency after you have placed the sample in the cavity in order to see the dip. A cryostat will also cause a drop in the cavity resonant frequency. (*I.e.* from 9.8 to 9.5 GHz.)

Tuning Error 9.2

Both the auto-tune and fine-tune procedures of the microwave bridge controller will terminate with an appropriate error message if a particular parameter cannot be set or optimized. Here are the possible error messages.

- **Tuning Frequency.** Both the upper and lower limits of the frequency range (i.e., 9.2-9.9 GHz) have been reached and no defined dip has been detected. Check manually if a dip can be found. A very slight dip (e.g. very lossy sample) may not be detected by the auto-tune routine. A very sharp dip may be missed by the auto-tune routine.
- **Adjusting Ref. Arm Phase.** The full 360° range of the signal phase has not resulted in an optimal phase setting.
- **Adjusting Ref. Arm Bias.** The system is unable to set the diode current to 200 microamperes at 50 dB attenuation.
- **Adjusting AFC Lock Offset.** The system is unable to set the AFC lock offset to zero. Check the back of the bridge to make sure the AFC is on. If this error occurs during fine-tune, try auto-tune or manual-tune.
- **Critically coupling cavity.** The iris motor has reached both of its limit switches and has been unable to obtain a diode current of 200 microamperes. Check if the iris motor is still connected to the screw and that the limit switches have been set properly. (See Section 7.2.) If you are using a flat cell when this happens, it is likely that you need to adjust the position of the flat cell. It is easier to optimize the cavity dip if you adjust the flat cell while you are looking at the tuning picture. If this error occurs during fine-tune, try auto-tune or manual-tune.

No Tuning Picture 9.3

- **Microwave bridge controller automatically switches from Tune to Stand By.** There is insufficient cooling for the microwave source. The protection circuitry will shut the microwave source off if the temperature rises too high. Make sure that the valves for the coolant lines leading to the bridge are open. Make sure that the heat exchanger is on and has sufficient water flow.
- **Microwave bridge controller automatically switches from Tune to Stand By (klystron bridge only).** There is protection circuitry which protects the microwave source from voltage spikes. To reset the protection circuitry, turn the console power off for approximately three seconds and turn it on again. The voltages used in the Gunn diode bridge are not sufficiently high to require this type of protection circuitry.
- **Tune mode delay period not expired (klystron bridge only).** After you turn on the spectrometer, a delay of approximately three minutes is required before a klystron will activate as you switch from Stand By to Tune. This does not apply to solid-state source bridges.
- **Reference microwave power too low.** Carefully adjust the Bias slider bar of the Microwave Bridge Tuning dialog box until you observe a tuning mode pattern on the display.

Unable to Critically Couple Cavity 9.4

A Q value of less than 1800 will usually prevent you from critically coupling the cavity.

Not all cavities can use a larger iris tip.

- **Lossy samples.** If too much of a lossy sample is in the microwave electric field in the cavity, you will not be able to critically couple the cavity. Reduce the diameter of the sample tube until you are able to critically couple. If the lossy sample is not positioned properly, you may also experience difficulties coupling the cavity. The sample position is particularly critical for flat cells and capillaries. Move the sample until the coupling improves.
- **Iris tip size.** When working with lossy samples, it is advisable to use a larger iris tip to increase the coupling range of the cavity. This is particularly important when working with flat cells or capillaries. Contact your Bruker EPR service representative for advice.
- **Microwave reference phase.** If the microwave reference phase is not set properly, you will not be able to critically couple the cavity. Carefully follow the instructions in Section 3.2 and Section 7.1 when tuning the spectrometer.
- **Iris motor limits improperly set.** If the iris motor limits were improperly set, the iris can not be screwed in sufficiently. Follow the procedure in Section 7.2 to properly adjust the iris motor limits.

Magnet Power Supply Shuts Down 9.5

- **Insufficient cooling capacity.** Make sure that the heat exchanger is on and that there is sufficient cold water flowing through it. Either the Ext. or Temp. warning LED's on the magnet power supply will light up with this fault.
- **Hall probe inserted with the wrong polarity.** The magnetic field will go to the maximum field.
- **Hall probe fallen out of the magnetic air gap.** If the Hall probe has fallen from the pole piece of the magnet, the power supply may go to the maximum current value, which will cause it to shut down.

Baseline Distortion 9.6

- **Linear baseline drifts.** The use of very large modulation fields can produce large eddy currents in the cavity side walls. These currents can interact with the magnetic field to produce a torque on the cavity and create a resonant frequency shift. A linear field dependent or modulation amplitude dependent baseline is indicative of such an effect. This phenomenon should not be observed if the cavity end plates are properly fitted and torqued. Do not attempt to adjust the torque on the plates. Contact your Bruker EPR service representative.
- **Slowly and randomly varying baseline.** The use of high microwave power or large modulation fields can heat the cavity and the sample. The ensuing thermal drifts in the coupling of the cavity, as well as the frequency of the cavity, can result in a fluctuating offset in the signal. Allow the tuned cavity and sample to come to thermal equilibrium before performing the final tuning of the cavity. Once the cavity is equilibrated and properly tuned under the equilibrated condition, you can start acquiring a spectrum. Avoid air drafts around the cavity, as they can randomly change the temperature of the cavity and sample and hence, the baseline of the spectrum.
- **Variable temperature operation.** Cavity frequency and coupling instability may be induced during variable temperature operation, especially at very low or very high temperatures. Increase the flow rate of the cavity and waveguide purging gas as the operating temperature departs further from room temperature. Wait for the cavity to stabilize at each new operating temperature before recording the spectrum. Retune the cavity to compensate for any frequency shift and re-establish critical coupling at each temperature.

- **Background signal.** Your cavity, cryostat, sample tube, or sample may be contaminated. First, determine if the signal is from your sample tube or cryostat and not a contaminated cavity. Call your Bruker EPR Service representative for advice. Never take the cavity apart to clean it.

Excessive Noise Output 9.7

- **Electromagnetic interference.** Verify that laboratory equipment is not a source of electromagnetic interference (EMI). If possible, turn off all other equipment in the laboratory and observe spectrometer noise output. Determine if radio, microwave, or TV broadcasting stations are operating in proximity to the spectrometer. Record the noise level while operating at various times of the day and night. EMI related noise will often be reduced at night.
- **Power line noise.** Check the noise content of the AC power lines feeding the spectrometer. Line transients or momentary blackouts will drastically degrade the performance of high gain detection systems such as EPR spectrometers.
- **Ground loops.** Ground loops are very common and often difficult to avoid. Disconnect accessory equipment, especially if it is plugged into remote AC outlets and observe the noise level. Turn off the magnet power supply and observe the noise level. If the noise level changes during either of these tests, consult your Bruker EPR service representative for alternate installation planning.
- **Microphonic generated noise.** Secure the waveguide and cavity assembly by using the plastic waveguide stabilizers. Secure the sample firmly in the collet. If you use a cryostat, make sure that the cryostat sits firmly in the cavity. Make sure that an excessive nitrogen gas flow rate through the cryostat does not vibrate the sample.
- **Worn iris screw.** Check for a worn iris coupling screw. An iris screw that does not fit snugly in the waveguide may generate noise by modulating the cavity coupling. Replace the worn iris screw with a new one.

- **Boiling liquids.** If you are using a dewar with a boiling refrigerant such as liquid nitrogen, you will need to increase the AFC modulation level.

Poor Sensitivity 9.8

- **Excessive microwave power.** The microwave power may be set too high, which will cause your sample to saturate. Optimize the power for your sample by recording spectra at a variety of power levels.
- **Wrong cavity type for sample.** The type of cavity you use for a particular sample can make a large difference in sensitivity. Consult the Bruker literature on the full line of EPR cavities to determine which one is best for your samples.
- **Low cavity Q.** The cavity Q can be degraded because of improper sample positioning. Having your sample positioned in the microwave electric field will reduce the sensitivity by degrading the cavity Q, especially for samples with high dielectric loss. This can happen if you are using flat cells or capillaries. Observe the dip or Q value read-out in the hardware information section of the monitoring panel when you are adjusting the sample position.
- **Cavity not critically coupled.** Maximum power is transferred between the cavity and waveguide when the cavity properly matches the impedance of the waveguide. (*I.e.*, is critically coupled.) A drastically undercoupled iris will not transmit power to the cavity and so will not excite EPR transitions. A drastically overcoupled cavity will have a lower Q, resulting in lower sensitivity. These effects can occur when using lossy samples such as aqueous solutions or conducting samples.

- **Water condensation.** During low temperature operation, water can condense inside the cavity. Water, being a high dielectric loss material, will absorb the microwave power in the cavity and destroy the cavity Q. Avoid condensation by using a purging nitrogen gas flow through the cavity.
- **Signal channel not calibrated.** The modulation amplitude and phase of the signal channel may not be properly calibrated. Make sure that you load the proper calibration file into Xepr. Also, make sure that the Calibrated check box in the Acquisition Parameters dialog box is activated.
- **Receiver gain or modulation not optimized.** See Section 8.2.3.
- **Sample not positioned properly.** Center your sample in the cavity.

Poor Resolution 9.9

- **Microwave power set too high.** Saturating microwave power levels will broaden your resonance line. Verify that the linewidth is independent of the microwave power level by recording the spectrum at various power levels.
- **Modulation amplitude set too high.** Large field modulation amplitudes will broaden your resonance line, particularly as the modulation amplitude approaches the linewidth. Reduce the modulation amplitude to ensure that the spectrum is independent of the modulation amplitude. (See Figure 8-5.)
- **Modulation frequency set too high.** The spectral resolution is limited by the field equivalence of the modulation frequency used. Reduce the modulation frequency to verify that the linewidth is independent of the frequency. (See Figure 2-17.)
- **Time constant too long for sweep time.** A larger time constant will begin to filter out the high frequency components of your signal. Consequently, if the sweep rate is too fast relative to the time constant, the spectrum will appear distorted and broadened. To avoid this problem make sure that the time required to sweep through one of your EPR lines is at least ten times the length of the time constant. (See Figure 8-3.)

- **Magnetic field inhomogeneities or gradients.** Extremely narrow lines, less than 20 milliGauss, may be limited by magnetic field irregularities. Vary the position of the cavity in the magnet air gap. If the linewidth changes, check for magnetic objects in or around the magnet. If possible, suspend these objects by a string and watch for a deflection in the same field strength as used in the experiment. Do not attempt this with the cavity in the magnet. The force of a ferromagnetic object being pulled into the magnet air gap can cause serious damage to accessories in the air gap.
- **Spectrometer not thermally stabilized.** Be sure that the spectrometer has been turned on for several hours. Verify that the laboratory conditions are within specified limitations, *i.e.*, temperature fluctuations, *etc.*

Lineshape Distortion 9.10

- **Microwave power too high.** The effect of saturating microwave fields is to broaden the resonance. This is easily apparent for single structureless lines; however, small splittings may become unresolvable if strongly saturating levels of microwave power are used. Lower the microwave power until you obtain a power independent lineshape.
- **Modulation amplitude too high.** Large field modulation will broaden the resonance line. Lower the modulation amplitude to a region where the lineshape is independent of the modulation amplitude. (See Figure 8-5.)
- **Time constant too long for sweep time used.** A safe rule of thumb is that the time required to sweep through an EPR line should be ten times the length of the time constant. (See Figure 8-3.)
- **Modulation frequency too high.** The modulation frequency can determine the resolution of the experiment. The spectral profile may also change, due to the effect of molecular dynamics, if saturating microwave fields are applied. These effects are especially pronounced if the motional frequency for the spin dynamics is similar to the applied modulation frequency. The technique of saturation transfer is based on this mechanism. The spectral profile may change markedly if the modulation frequency is varied while applying strong microwave fields. (See Figure 2-17.)
- **Magnetic field gradients.** These may produce highly asymmetric lineshapes. Reposition the cavity within the magnet air gap to check the magnet for homogeneity. Check for magnetic objects in or around the air gap. Magnetic field inhomogeneity could also obscure small splittings due to overlapping spectral components.

- **Anisotropic g matrix.** It is natural for a sample with a highly anisotropic g-matrix to produce asymmetric lines.
- **Background signal.** A strong background signal from contamination of the EPR cavity or the sample can distort your EPR spectrum.
- **High conductivity.** High conductivity exhibited by samples with mobile electrons will result in asymmetric lines known as Dysonian lineshapes. This results from a mixing of absorption and dispersion components induced in the sample itself.
- **Lossy samples.** If you put large lossy samples in a cavity, you can also obtain Dysonian lineshapes. Use progressively smaller capillaries until you obtain a symmetric lineshape.
- **Microwave reference phase.** The dispersion signal from easily saturated samples can be very large compared to the absorption signal. To minimize the contribution of the dispersion signal, carefully adjust the microwave reference phase. In addition, make sure that the AFC offset is close to zero.
- **Magnetic field drifts.** Magnetic field drift may produce an asymmetric or distorted line for samples exhibiting very narrow resonance linewidths. This problem may arise for linewidths less than 20 mG. Use a field-frequency lock system to eliminate field drift problems.

No Signal When Everything Works 9.11

- **Check cables.** Make sure that all the cables are connected. Check the modulation cable and the preamplifier cable.
- **Sample position.** If you have a small sample, make sure that the sample is centered in the cavity.
- **Magnetic field values.** Are you using the correct field values to see your EPR signal? If you are using a cryostat, remember that the microwave frequency drops and hence the field for resonance will also be lower. Is the Hall probe positioned properly in the magnet?

Warning Noises 9.12

- **High pitched noise from the heat exchanger.** The heat exchanger will emit a high pitched noise when it requires more distilled and deionized water.
- **Warning sound from the console.** The ventilator units emit a warning noise when they are not functioning properly. There are two ventilators (three for a double console). Check the Temp LEDs. Frequently it is because the filters are dirty. Turn off the spectrometer and take out the filters. Reinstall them after cleaning. The filters should be cleaned every month.
- **Funny noises from the iris motor.** Stop turning the iris motor immediately. You may be breaking the iris screw.

Bibliography 10

Abragam, A. *The Principles of Nuclear Magnetism:* Clarendon Press, Oxford, International Monographs of Physics, 1961.

Abragam, A., B. Bleaney. *Electron Paramagnetic Resonance of Transition Ions:* Clarendon Press, Oxford, 1970.

Abragam, A., M. Goldman. *Nuclear Magnetism: Order and Disorder:* Clarendon Press, Oxford, 1982.

Aleksandrov, I.G. *The Theory of Nuclear Magnetic Resonance:* Academic Press, New York, 1966.

Alekseev, B.F., Yu. V. Bogachev, V.Z. Drapkin, A.S. Serdjuk, N.B. Strakhov, S.G. Fedin. *Radiospectroscopy of Natural Substances (by EPR and NMR):* Norell, Mays Landing, New Jersey, 1991.

Alger, R.S. *Electron Paramagnetic Resonance Techniques and Applications:* Interscience (Wiley), New York, 1968.

Allen, P.S., E.R. Andrew, C.A. Bates, Editors. *Magnetic Resonance and Related Phenomena, Proceedings of 18th Ampere Congress:* North-Holland and American Elsevier Publishing Co., New York, 1975.

Allendoerfer, R.D. *Magnetic Resonance:* M.T.P. Inter. Rev. Sci. Phys. Chem. Sec 2, Vol 4, McDowell, C. A., Editor Butterworth Publications, London 1972, pp 29-53.

Al'tshuler, S.A., B.M. Kozyrev. *Electron Paramagnetic Resonance:* New York, 1964, C. P. Poole, Editor.

Al'tshuler, S.A., B.M. Kozyrev. *Electron Paramagnetic Resonance in Compounds of Transition Elements:* 2nd Ed., Halsted, New York, 1974.

Andrew, E.R. *Nuclear Magnetic Resonance:* Cambridge University Press, 1954.

Assenheim, H.M. *Introduction to Electron Spin Resonance:* Hilger and Watts, London, Hilger Monographs on ESR, 1960.

Atherton, N.M. *Electron Spin Resonance, Theory and Application:* Halsted, New York, 1973.

Atherton, N.M. *Principles of Electron Spin Resonance:* Ellis Horwood Ltd., Chichester, England, 1993.

Atkins, P.W., M.C.R. Symons. *The Structure of Inorganic Radicals (An Application of Electron Spin Resonance to the Study of Molecular Structure):* Elsevier, Amsterdam, New York, 1967.

Averbuch, P., Editor. *Magnetic Resonance and Radio-frequency Spectroscopy, Proceedings of the 15th Colloque Ampere:* North Holland, Amsterdam, 1969.

Axel, F.S. *Biophys. Struct. Mechanism:* 2, 181-218, 1976.

Ayscough, P.B. *Electron Spin Resonance in Chemistry:* Methuen, London, Barnes and Nobel, New York, 1967.

Ayscough, P.B. *Electron Spin Resonance, Volumes 1-5.* American Chemical Society.

Bagguley, D.M.S., Editor. *Pulsed Magnetic Resonance: NMR, ESR, and Optics:* Clarendon Press, Oxford, 1992.

Bass, A.M., H.P. Broida, Editors. *Formation and Trapping of Free Radicals:* Academic Press, New York, 1960.

Bencini, A., D. Gatteschi. *Electron Paramagnetic Resonance of Exchange-coupled Systems:* Springer Verlag, Berlin, 1990.

Benedek, G.B. *Magnetic Resonance at High Pressure:* Interscience, New York, 1963.

Berliner, L.J., Editor. *Spin Labeling: Theory and Applications:* Academic Press, New York, 1976.

Berliner, L.J., Editor. *Spin Labeling II: Theory and Applications:* Academic Press, New York, 1979.

Berliner, L.J., J. Reuben. *Biological Magnetic Resonance, Volumes 1-:* Plenum New York, 1978-.

Bernheim, R. *An Introduction to Optical Pumping:* W.A. Benjamin, New York, 1965.

Bersohn, M., J.C. Baird. *An Introduction to Electron Paramagnetic Resonance:* W. A. Benjamin, New York, Frontiers in Chemistry, 1966.

Bertini, I., R. Drago. *ESR & NMR of Paramagnetic Species in Biological and Relates Systems:* NATO Advanced Studies Institute, Kluwer, Boston 1980.

Bielski, B.H., J.M. Gebicki. *Atlas of Electron Resonance Spectra:* Academic Press, New York, 1967.

Bleaney, B., K.W.H. Stevens. *Reports Prog. Phys:* 16, 108, 1953.

Blinc, R. *Magnetic Resonance and Relaxation:* North Holland Publishing Co., Amsterdam, 1967.

Bloch, F., Editor. *Spectroscopic and Group Theoretical Methods in Physics:* North Holland Publishing Co., Amsterdam and Interscience (Wiley), New York, 1968.

Bloembergen, N. *Nuclear Magnetic Relaxation:* Drukkery fa. Schotanus and Jens, Utrecht, 1948.

Blois, M.S. *et. al.*, *Free Radicals in Biological Systems:* Academic Press, New York, 1961.

Blumenfel'd, L.A, V.V. Voevodskii, A.G. Semenov. *Applications of ESR in Chemistry:* Academic Nauk. SSSR, Sibirsk, Old. 1962.

Blumenfel'd, L.A, W.W. Wojewolski, A.G. Semenov. *Die Anwendug der Paramagnetischen Elektronen Resonanz in der Chemie:* Akademische Verlagsgesellschaft, Leipzig, 1966.

Bowers, K.D, J. Owen. *Reports Progr. Physics:* 18, 304, 1950.

Boyer, R.F., S.E. Keinath, Editors. *Molecular Motion in Polymers by ESR:* Harwood Academic Publishers, New York, 1980.

Box, H.C. *Radiation Effects: ESR and ENDOR Analysis:* Academic Press, New York, 1977.

Buchachenko, A.L. *ESR of Stable Radicals:* Consultants Bureau, New York, 1965.

Carrington, A., H.C. Longuet-Higgins. *Quarterly Reviews:* London, 14, 427, 1960.

Carrington, A., A.D. McLachlan. *Introduction to Magnetic Resonance with Applications to Chemistry and Chemical Physics:* Harper and Row, Chemistry Series, 1967.

Caspers, W.J. *Theory of Spin Relaxation:* Interscience, New York, 1964.

Catoire, B., Editor, *Electron Spin Resonance (ESR) Applications in Organic and Bioorganic Materials:* (1990 Conference Proceedings), Springer Verlag, Berlin, 1992.

Clarke, R.H., Editor, *Triplet State ODMR Spectroscopy:* Wiley, New York, 1982.

Cohen, G., B. Giovannini. *EPR of Magnetic Ions in Metals:* (Conf. Proc., Haute-Nendez, Switz., 3-5 Sept. 1973), Universite de Geneve, Geneve, 1974.

Coogan, C.K., Editor. *International Symposium on Electron and Nuclear Magnetic Resonance:* Melbourne, 1963.

Coogan, C.K., N.S. Ham, S.N. Stuart, J.R. Pilbrow, G.V.H. Wilson. Editors. *International Symposium on Electron and Nuclear Magnetic Resonance:* Melbourne, 1969, Plenum Press, New York, 1970.

Cross, R.C., Editor. *Molecular Relaxation Processes:* Academic Press, New York, 1966.

Czoch, R., A. Francik, *Instrumental Effects in Homodyne EPR Spectrometers:* Horwood, Chichester, UK, 1989.

Dalal, D.P., S.S. Eaton, G.R. Eaton. *The Effects of Lossy Solvents on Quantitative EPR Studies:* J. Magn. Res., 44, 415, 1981.

Dalton, L.R., Editor, *EPR and Advanced EPR Studies of Biological Systems:* CRC Press, Boca Raton, 1985.

DeWitt, C., B. Dreyfus, P.G. de Gennes, Editors. *Low Temperature Physics:* Les Houches Lecturers, University Grenoble, 1961, Gordon and Breach, New York, 1962.

Dikanov S.A., Y.D. Tsvetkov. *Electron Spin Echo Envelope Modulation (ESSEM) Spectroscopy:* CRC Press, Boca Raton, 1992.

Dixon, W.T. *Theory and Interpretation of Magnetic Resonance Spectra:* Plenum Press, New York

Dorio, M.M., J.H. Freed, Editors. *Multiple Electron Resonance Spectroscopy:* Plenum, New York, 1979.

Drago, R.S. *Physical Methods in Chemistry:* W.B. Saunders Co., Philadelphia, 1977.

Eaton G.R., S.S. Eaton. *Electron Paramagnetic Resonance:* in Ewing G.W., Editor. *Analytical Instrumentation Handbook:* Marcel Dekker, New York, 1990.

Eaton G.R., S.S. Eaton, K. Ohno. *EPR Imaging and In Vivo EPR:* CRC Press, Boca Raton, 1991.

Ehrenberg, A., B.G. Malmstroem, T. Vaenngard, Editors. *International Conference on Magnetic Resonance in Biological Systems:* Stockholm, 1966, Pergamon Press, London and New York, 1967.

Erbeia, A., Editor. *Resonance Magnetique:* Centre d'actualisation scientifique et technique Monographies, no. 4, Recueil de travaux des sessions de perfectionement, Institut National des sciences appliquees, Lyon, September 1967; Masson Paris, 1969.

Faraday Society. *Microwave and Radio Frequency Spectroscopy - General Discussions of the Faraday Society:* Aberdeen University Press, Aberdeen, 1955.

Fischer, H., H. Heimgartner, Editors., *Organic Free Radicals, Proceedings of the Fifth International Symposium:* Springer Verlag, Berlin, 1988.

Feher, G. *Electron Paramagnetic Resonance with Applications to Selected Problems in Biology:* Les Houches Lectures, 1969, Gordon and Breach, New York, 1970.

Forester, A.R., J.M. Hay, R.H. Thomson. *Organic Chemistry of Stable Free Radicals:* Academic Press, New York, 1968.

Foster, M.A., *Magnetic Resonance in Medicine and Biolodgy:* Pergamon Press, Oxford, 1984.

Fraenkel, G.K. *Ann. New York Acad:* Science 67, 546, 1957.

Fraissard, J.P., H.A. Resing, Editors, *Magnetic Resonance in Colloid and Interface Science:* Reidel, Hingham, MA, 1980.

Franconi, C. *Magnetic Resonance of Biological Systems:* Gordon and Breach, New York, 1971.

Freed, J.H. *Electron Spin Resonance* in *Annual Review of Physical Chemistry:* H. Erying, C.J. Christensen, H.S. Johnston, Editors, Annual Reviews Inc., Palo Alto, CA, 1972, Vol. 23, pp 265-310.

Freeman, A.J., R.B. Frankel. *Hyperfine Interactions:* Academic Press, New York, 1967.

Fujiwara, S., Editor. *Recent Developments of Magnetic Resonance in Biological Systems:* Hirokawa, Tokyo, 1968.

Gaffney, B.J., C.M. McNamee. *Spin Label Measurements in Membranes: Methods Enzymol.* 32, 161-198, 1974.

Gerson, F. *High Resolution E.S.R. Spectroscopy:* J. Wiley and Sons, London, Chemical Topics for Students, 1, 1970.

Geschwind, S., Editor. *Electron Paramagnetic Resonance:* Plenum Press, New York, 1972.

Goldberg, I.B., A.J. Bard. *Electron Spin Resonance Spectroscopy;* in *Treatise on Analytical Chemistry:* 10, 225: P.J. Elving - Editor (2nd Ed.); John Wiley & Sons, New York, 1983.

Gordy, W. *Techniques of Chemistry, Vol. 15, Theory and Applications of Electron Spin Resonance:* John Wiley and Sons, New York, 1979.

Gorter, C.J. *Paramagnetic Relaxation:* Elsevier Publishing Co., New York, Amsterdam, London, and Brussels, 1947.

Gorter, C.J., Editor. *Progress in Low Temperature Physics:* Annual Series, Interscience, New York, began in 1957.

Griffith, O.H., A.S. Waggoner. *Nitroxide Free Radicals: Spin Labels for Probing Biomolecular Structure:* Accounts Chem. Res. 2, 17-24, 1969.

Haar ter, D. *Fluctuation, Relaxation and Resonance in Magnetic Systems:* Oliver and Boyd, London, Edinburgh, 1961.

Harriman, J.E. *Theoretical Foundations of Electron Spin Resonance:* Academic Press, New York, 1978.

Hecht, H.G. *Magnetic Resonance Spectroscopy:* Wiley, New York, 1967.

Hellwege, K., A. Hellwege, Editors. *Magnetic Properties of Free Radicals:* Springer, Berlin, 1967.

Herak, J.N., K.J. Adamic, Editors. *Magnetic Resonance in Chemistry and Biology:* (Lectures at the Ampere Int. Summer School, Basko Polje, Yugoslavia, June 1971), Marcel Dekker, New York, 1975.

Hershenson, H.M. *Nuclear Magnetic Resonance and Electron Spin Resonance Spectra Index:* 1958-63, Academic Press, New York, 1965.

Hill, H.A.O., P. Day, Editors. *Physical Methods in Advanced Inorganic Chemistry (ESR, NMR, Moessbauer):* Wiley, New York, 1968.

Hoff, A.J. *Advanced EPR, Applications in Biology and Biochemistry:* Elsevier Science Publishers B.V., 1989.

Holtzman, J.L., *Spin Labeling in Pharmacology:* New York, 1984.

Hovi, V., Editor. *Magnetic Resonance and Related Phenomena*, *Proceedings of the XVII the Congress Ampere:* North-Holland Publishing Company Amsterdam, 1973.

Hudson, R.P. *Principles and Applications of Magnetic Cooling:* North-Holland Publishing Company, Amsterdam, and American Elsevier Publishing Company, New York, 1972.

Hutchison Jr., C.A. *Determination of Organic Structures by Physical Methods:* Chapter 7, E.A. Braude and F.C.Nachod, Editors, Academic Press, New York, 1955.

Hyde, J.S. *Paramagnetic Relaxation,* in *Annual Review of Physical Chemistry:* Eyring, H., C.J. Christensen, H.S. Johnston, Editors, Annual Reviews, Inc., Palo Alto, CA, 1974.

Hyde, J.S. *Saturation Transfer Spectroscopy* in *Methods in Enzymology:* Enzyme Structure. Part F. : C.H.W. Hiss, S.N. Timasheff, Editors, Academic Press, New York, 1978, Vol. 49G, No. 19, pp. 480-511.

Ikeya, M. *New Applications of Electron Spin Resonance, Dating, Dosimetry, and Microscopy:* World Scientific, Singapore, 1993.

Ingram, D.J.E. *Free Radicals as Studied by Electron Spin Resonance:* Butterworths, London, 1958.

Ingram, D.J.E. *Biological and Biochemical Application of Electron Spin Resonance:* Butterworths, London, 1958.

Ingram, D.J.E. *Spectroscopy at Radio and Microwave Frequencies:* Butterworths, London, 1967.

Ingram, D.J.E. *Radio and Microwave Spectroscopy:* Butterworths, 1975.

Jeffries, C.D. *Dynamic Nuclear Orientation:* No. 23, Interscience Publishers, John Wiley and Sons, New York, 1963.

Jones, R.A.Y., *et. al. Techniques of NMR and ESR:* United Travel Press Ltd., London. 1965.

Jost, P.C., O.H. Griffith. in *Methods in Pharmacology:* Vol. II, Physical Methods, F. Chignell, Editor, Appleton-Century-Crafts, New York, 1972, pp 223-276.

Jost, P.C., A.S. Waggoner, O.H. Griffith. *Spin Labeling and Membrane Structure,* in *Structure and Function of Biological Membranes:* Rothfeld, Editor, Academic Press, New York, 1971.

Kaiser, E.T., L. Kevan, Editors. *Radical Ions:* Interscience, New York, 1968.

Kalmanson, A.E., G.L. Grigoryan. *Spin Labels in EPR Investigation of Biological Systems,* in *Experimental Methods in Biophysical Chemistry:* Nicolau, E., Editor Wiley, New York, 1973, pp 589-612.

Keijzers, C.P., E.J. Reijerse, J. Schmidt. *Pulsed EPR: A New Field of Applications:* Koninklijke Nederlandse Akademie van Wetenschappen, 1989.

Kevan, L., R.N. Schwartz, Editors. *Time Domain Electron Spin Resonance:* Wiley-Interscience, New York, 1979.

Kevan, L., M.K. Bowman. *Modern Pulsed and Continuous-wave Electron Spin Resonance:* John Wiley and Sons, New York, 1990.

Kevan, L., L.D. Kispert. *Electron Spin Double Resonance Spectroscopy:* John Wiley and Sons, New York, 1979.

Kliava, J. *EPR Spectroscopy of Disordered Solids:* Zinatne Publ., Moscow, 1988 (in Russia).

Knowles, P.F., D. Marsh, H.W.E. Rattle. *Magnetic Resonance of Biomolecules:* Wiley-Interscience, New York, 1976.

Kundla, E., E. Lipmaa, T. Saluvere, Editors, *Magnetic Resonance and Related Phenomena:* Springer Verlag, Berlin, 1979.

Kwiram, A.L. *Electron Nuclear Double Resonance* in *Annual Review of Physical Chemistry:* Annual Review Inc., Palo Alto, CA 1971, Vol. 22, pp 133-170.

Kwiram, A.L. in *Magnetic Resonance, M.T.P. Int. Rev. Sci. Phys. Chem. Ser. 2:* C.A. McDowell, Editor, Butterworths Publication, London, 1972, Vol. 4, pp 271-316.

Kurreck, Harry., Burkhard Kirste, Wolfgang Lubitz. *Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution:* VCH Publishers, Inc., 1988.

Lancaster, G. *Electron Spin Resonance in Semiconductors:* Hilger and Watts, London, 1966.

Lebedev, Ya. S. *Atlas of Electron Spin Resonance Spectra:* Consultant Bureau, New York, 1963-1964.

Lichtenstein, G.I. *Spin Labeling Methods in Molecular Biology:* Wiley Interscience, New York, 1976.

Low, W. *Solid State Physics, Vol 2:* Supplement, Academic Press, New York, London, 1960.

Low, W. *Paramagnetic Resonance in Solids:* Academic Press, New York, 1960.

Low, W. *Paramagnetic Resonance, Vol. 2:* (Proceedings of the First International Conference held in Jerusalem), Academic Press, New York, London, 1963.

Mabbs, F.E., D. Collison, *Electron Paramagnetic Resonance of d-transition Metal Compounds,* in *Studies in Inorganic Chemistry:* Vol 16, Elsevier Science, Amsterdam, 1992.

McConnell, H.M., B.G. McFarland. *Quart. Rev. Biophys., Vol. 3:* 91-136, 1970.

McDowell, C.A., Editor. *Magnetic Resonance:* MTP International Review of Science, Vol. 4, Butterworths, London, University Park Press, Baltimore, Physical Chemistry Series, 1972.

McGlynn, S.P., Ti, Azumi, M. Kinoshita. *Molecular Spectroscopy of the Triplet State:* Prentice-Hall, New York, 1969.

McLachlan, A.D. *Electron Spin Resonance:* Harper and Row, New York, 1969.

McLauchlan, K.A. *Magnetic Resonance:* Oxford University Press, Don Mills, Ontario, Oxford Chemistry Series, 1974.

McMillan, J. *Electron Paramagnetism:* Reinhold, New York, 1960.

McWeeny, R. *Spins in Chemistry:* Academic Press, New York, 1970.

Manenkov, A.A., R. Orbach. *Spin Lattice Relaxation in Ions Solids:* Harper and Row, New York, Evanstown, London, 1966.

Memory, J.D. *Quantum Theory of Magnetic Resonance Parameters:* McGraw-Hill, New York 1968.

Microwave and Radio-Frequency Spectroscopy - General Discussion of the Faraday Society: Aberdeen University Press, Aberdeen, 1950.

Mims, W.B. *The Linear Electric Field Effect in Paramagnetic Resonance:* Oxford Press, Oxford, 1976.

Minkoff, G.J. *Frozen Free Radicals:* Electron Spin Relaxation in Liquids, Plenum Press, New York, 1972.

Molin, Yu N., K.M. Salikhov and K.I. Zamaraev. *Spin Exchange - Principles and Applications in Chemistry and Biology:* Springer Verlag, Berlin, New York, 1980.

Muus, L.T., P.W. Atkins. *Electron Spin Relaxation in Liquids:* Plenum Press, New York, London, 1972.

Myers, R.J. *Molecular Magnetism and Magnetic Resonance Spectroscopy:* Prentice-Hall, Englewood Cliffs, New Jersey, 1973.

NMR and EPR, Selected Reprints: American Institute of Physics, New York.

Nelson, S.F. in *Free Radicals:* J.K. Kochi, Editor, Wiley, New York, 1973, Vol. II, Chapter 21, pp 527-594.

Norman, R.O.C., Editor. *Specialist Periodical Reports. Electron Spin Resonance:* The Chemical Society, Burlington House, London WIV OBN 1973 and following years.

Ohnishi, S. *The Spin Label Technique:* Seibutsu Butsuri, Vol. 8, 118-129, 1968.

Orton, J.W. *Electron Paramagnetic Resonance, An Introduction to Transition Group Ions in Crystals:* Iliffe, London, 1968.

Orton, J.W. *Reports Progr. Phys.* , 22, 204, 1959.

O'Reilly, D.E., J.H. Anderson. *Magnetic Properties:* Reprinted from *Physics and Chemistry of the Organic Solid State,* Vol. II: Edited by D. Fox, M. Labes, and A. Weisberger.

Owens, F.J., C.P. Poole, Jr., and H.A. Farach, Editors. *Magnetic Resonance of Phase Transitions:* Academic Press, New York, 1979.

Pake, G.E. *Paramagnetic Resonance:* W.A. Benjamin, Inc., New York, 1962.

Pake, G.E., T.L. Estle. *The Physical Principles of Electron Paramagnetic Resonance:* Addison Wesley, Reading, Mass., 1974.

Peisach, J., W.E. Blumberg. *Electron Spin Resonance of Metal Complexes:* Plenum Press, New York, 1969.

Petrakis, L., J.P. Fraissaird, Editors, *Magnetic Resonance: Introduction, Advanced Topics and Applications to Fossil Energy:* NATO ASI Sries C124, Reidel, Dordrecht, 1984.

Pilbrow J.R., *Transition Ion Electron Paramagnetic Resonance:* Clarendon Press, Oxford, 1990.

Poole, C.P. *Electron Spin Resonance, A Comprehensive Treatise on Experimental Techniques:* First Ed., Interscience Publishers, New York, 1967.

Poole, C.P. *Electron Spin Resonance, A Comprehensive Treatise on Experimental Techniques:* Second Ed., J. Wiley, New York, 1983.

Poole, C.P., H.A. Farach, Editors. *Handbook of Electron Spin Resonance, Data Sources, Computer Technology, Relaxation, and ENDOR:* AIP Press, New York, 1994.

Poole, C.P., Editor. *Magnetic Resonance Reviews, Vol. I:* Gordon and Breach, New York, 1971.

Poole, C.P., and H.A. Farach. *Relaxation in Magnetic Resonance: Dielectric and Mossabauer Applications:* Academic Press, New York, 1971.

Poole, C.P., and H.A. Farach. *The Theory of Magnetic Resonance:* Wiley Interscience, New York, 1972.

Rado, G.T., H. Suhl. *Magnetism, Vol. II, Part A:* Academic Press, New York, London, 1965.

Ramsey, N.F. *Nuclear Moments:* John Wiley and Sons, New York, Chapman and Hall, Ltd., London, 1953.

Ranby, B., J.F. Rabek. *ESR Spectroscopy in Polymer Research:* Springer, New York, 1977.

Royal Society of Chemistry. *Electron Spin Resonance - Specialist Periodical Reports, Vol. 1:* Roy. Soc. Chem., London, 1971.

Rozantsev, E.G. *Free Nitroxyl Radicals:* Plenum Press, New York, 1970.

Rozantsev, E.G., V.D. Scholle. *Synthesis and Reactions of Stable Nitroxyl Radicals:* Synthesis, 1971, pp 190-202.

Salikhov, K.M., A.G. Semenov, D. Yu. Tsvetkov. *Electron Spin Echo and its Applications:* Novosibirsk, Nauka, 1976.

Salikhov, K.A., Yu. N. Molin, R.Z. Sagdeev and A.L. Buchachenko. *Spin Polarization and Magnetic Effects in Radical Reactions,* Elsevier, Amsterdam, 1984.

Schoffa, G. *Electronensprinresonanz in der Biologie:* G. Braun, Karlsruhe, 1964.

Schumacher, R.T. *Introduction to Magnetic Resonance:* Benjamin, New York, 1970.

Schweiger, A., *Pulsed Electron Spin Resonance Spectroscopy: Basic Priciples, Techniques, and Examples of Applications:* Angew. Chem. Int. Ed. Engl., 30, 265, 1991.

Seitz, F., D. Turnbull, Editors. *Solid State Physics, Advances in Research and Applications, Vol. 5:* Academic Press, New York, 1957.

Servant, R., A. Charru, Editors. *Electronic Magnetic Resonance and Solid Dielectrics, Proceeding of the 12th Colloque Ampere:* North Holland Publishing Co., Amsterdam, 1964.

Sixl, H., *Festkoerperspektroskopie II - Resonanzspektroskopie:* Hochschulverlag, Stuttgart, 1979.

Sigel, H., A. Sigel. *Metal Ions In Biological Systems: ENDOR, EPR, and Electron Spin Echo for Probing Coordination Spheres, Vol. 22*: Marcel Dekker, Inc, New York and Basel, 1987.

Skobel'tsyn, D.V., Editor. *Quantum Electronics and Paramagnetic Resonance:* Plenum Press, New York.

Slichter, C.P. *Principles of Magnetic Resonance:* Harper and Row, New York, Evanstown, London, 1963. 2nd Edition, Springer Verlag, Berlin and New York, 1978. 3rd Edition 1989.

Smidt, J., Editor. *Magnetic and Electric Resonance and Relaxation, Proceedings of the 11th Colloque Ampere:* Amsterdam, North Holland Publishing Co., 1963.

Snipes, W., Editor. *Conference on Electron Spin Resonance and the Effects of Radiation on Biological Systems:* Gatlinburg, Tennessee, 1965, National Academy of Science, National Research council, 1965.

Sorin, L., M.V. Vlasova. *Electron Spin Resonance of Paramagnetic Crystals:* Plenum Press, New York.

Spaeth, J.-M., J.R. Niklas and R.H. Bartram. *Structural Analysis of Point Defects in Solids, An Introduction to Multiple Magnetic Resonance Spectroscopy:* Springer Verlag, Berlin, 1982.

Specialist Periodical Reports: Electron Spin Resonance: R.O.C. Norman (Ed. Vol. 1-3), The Chemical Society, London, P.B. Ayscough (Ed. Vol. 4).

Speight J.G. *The Application of Spectroscopic Techniques to the Structural Analysis of Coal and Petroleum:* Applied Spectroscopy Reviews, 5, 211, 1971.

Squires, T.L. *An Introduction to Electron Spin Resonance:* Academic Press, New York, 1964.

Squires, T.L. *Introduction to Microwave Spectroscopy:* G. Newnev, London, 1963.

Standley, K.J., R.A. Vaughan. *Electron Spin Relaxation Phenomena in Solids:* Adam Hilger Ltd., London, 1969.

Stepin, L.D. *Quantum Radio-Frequency Physics:* Translated by Scripta Technica, Inc., Edited by H.H. Stroke, MIT Press, Cambridge, 1965.

Stoneham, A.M., *Theory of Defects in Solids:* Calrendon Press, Oxford 1975, Chapter 13.

Strandberg, M.W.P. *Microwave Spectroscopy:* Wiley, New York, 1954.

Sugano, S., Y. Tanabe, H. Kamimura, *Multiplets of Transition-metal Ions in Crystals:* Academic Press, New York, 1970.

Swartz, H.M., J.R. Bolton and D.C. Borg, Editors. *Biological Applications of Electron Spin Resonance:* Wiley-Interscience, New York, 1972.

Symons, M.C.R. *Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy:* J. Wiley, New York, 1978.

Symons, M.C.R. *Electron Spin Resonance. Specialist Periodical Reports, Volumes 10 A,B:* Royal Society of Chemistry, London, 1987.

Talpe, J. *Theory of Experiments in Paramagnetic Resonance:* Pergamon Press, Oxford and New York, International Series of Monographs in Natural Philosophy, Vol. 33, 1971.

Teh, F.Y., Editor. *Symposium on Electron Spin Resonance of Metal Chelates:* Cleveland, 1968, *Electron Spin Resonance of Metal Complexes:* Plenum Press, New York 1958.

Townes, C.H., and A.L. Schawlow. *Microwave Spectroscopy:* McGraw-Hill, New York, 1955.

Ursu, I. *La Resonance Electronique:* Dunod, Paris, 1968.

Ursu, I. *Resonata Electronic de Spin:* (Bucuresti) Editura Academiee, Republicii Socialiste Romania ,1965.

Ursu, I., Editor. *Magnetic Resonance and Related Phenomena, Proceedings of the 16th Colloque Ampere:* Acad. Socialist Repub. Romania, Bucharest, 1971.

Van Gerven, L., Editor. *Koninlijke Vlaamse Academie voor Wetenschappen, Proceedings of the 13th Colloque Ampere:* North Holland, Amsterdam, 1965.

Van Reijen, L.L. *Electron Spin Resonance Studies of Pentavalent and Trivalent Chromium:* Amsterdam, 1964.

Varian Associates. *Workshop on Nuclear Magnetic Resonance and Electron Paramagnetic Resonance:* Pergamon Press, New York, 1959.

Vonsovskii, S.V., Editor. *Ferromagnetic Resonance:* U.S. Dept. of Commerce, Washington, 1965.

Waugh, J.S., Editor. *Advances in Magnetic Resonance, Vol. 1:* Academic Press, New York, 1965.

Weil, John A., Editor, *Electronic Magnetic Resonance of the Solid State*: The Canadian Society for Chemistry, Ottawa, Ontario, Canada, 1987.

Weil, John A., J.R. Bolton, and Wertz, J.E.. *Electron Paramagnetic Resonance, Elementary Theory and Practical Applications:* Wiley-Interscience, New York, 1994.

Weissbluth, M. *The Triplet State in Molecular Biophysics:* B. Pullman and M. Weissbluth, Editors, Academic Press, New York, 1965, p 205.

Weissbluth, M., *Phonon-Atom Interactions:* Academic Press, New York, 1989, Chapter 3.

Weltner, W.W. Jr. *Magnetic Atoms and Molecules:* Scientific and Academic Editions - Van Nostrand Reinhold, New York, 1983.

Wertheim, G.K., A. Hausmann, W. Sander. *The Electronic Structure of Point Defect as Determined by Moessbauer Spectroscopy and by Spin-Spin Resonance:* American Elsevier, New York, 1971.

Wertz, J.E. *Nuclear and Electronic Spin Magnetic Resonance:* Chemical Reviews, Vol. 55, No. 5, October 1955.

Wertz, J.E., J.R. Bolton. *Electron Spin Resonance, Elementary Theory and Practical Applications:* McGraw-Hill, New York, McGraw-Hill Series in Advanced Chemistry, 1972.

Whiffen, D.H. *Quarterly Reviews:* London, Vol. 12, 250, 1958.

Wilmhurst, T.H. *Electron Spin Resonance Spectrometers:* Adam Hilger Ltd., London, momograph, 1967.

Winter, J. *Magnetic Resonance in Metals:* Oxford University Press, 1971.

Wyard, S.J. *Solid State Biophysics:* McGraw-Hill, New York, 1969.

Yariv, A., *Quantum Electronics:* Wiley, New York, 1967, Chapter 8.

Yen, T.F., Editor. *Electron Spin Resonance of Metal Complexes:* Plenum Press, New York, 1969.

Yordanov, N.D., *Electron Magnetic Resonance of Disordered Systems:* World Scientific, Singapore, 1989.

Yordanov, N.D., *Electron Magnetic Resonance of Disordered Systems:* World Scientific, Singapore, 1991.

Zahlan, A.B., Editor. *Excitons, Magnons and Phonons in Molecular Crystals:* Beirut Symposium, 1968.

Zahlan, A.B and others, Editors: *The Triplet State, International Symposium on the Triplet State:* Cambridge University Press, Cambridge, 1967.

Brief Tips on SGI IRIX A

If the workstation coming with your Elexsys spectrometer current UNIX operating system coming with your Elexsys spectrometer is a PC the UNIX operating system is Linux. Go to Appendix B for brief tips on Linux.

Not everyone may be familiar with the UNIX operating system. If the workstation coming with your Elexsys spectrometer is an SGI O2 the UNIX operating system is IRIX. This chapter explains some basic aspects of UNIX based on IRIX. It is not meant to be an in-depth treatise: the UNIX documentation should be consulted for more details. If you are already familiar with UNIX, you can easily skip this section. If you have not used UNIX before, we highly recommend SGI's on-line book, especially the end user's manual. The manual can be found under Help in the Toolchest.

Login A.1

One of the advantages of the UNIX system is security. Security is accomplished by assigning each user an account with a user name and a password. There are two types of accounts: root or super user, and user. You will typically use the user accounts for all operations. The root or super user account is solely for administration and maintenance only. It is common to create a guest account that everyone can log into without a password. (Note: the data and files in a guest account are not protected.) Before you start you need to login into your own account. If you don't have an account yet ask the system administrator to create one for you or login as guest.

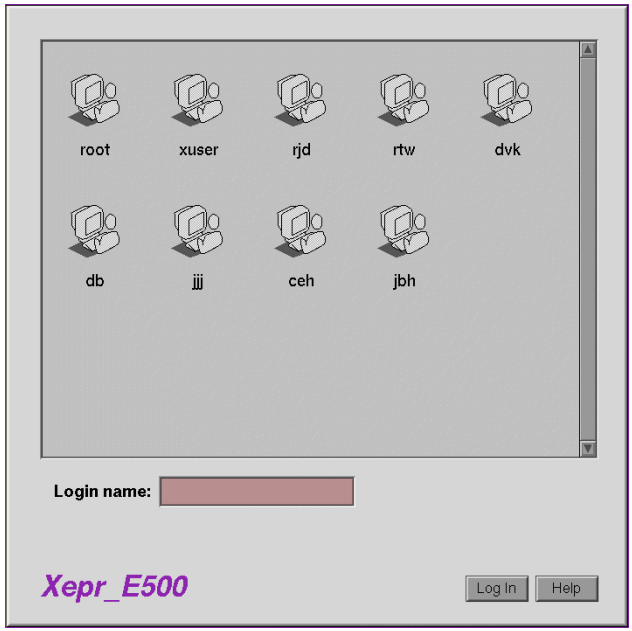


Figure A-1 The login screen.

UNIX is case sensitive. Make sure you use the correct case for every character of your user name, password, as well as any commands.

The login screen looks like that in Figure A-1. Double click the icon with your user name or type your user name in the Login name box and press ENTER: the system will prompt you for your password. Typing the password and pressing ENTER brings you to the desktop of your account.

The Desktop A.2

On the right side of the desktop, there are a few icons for quick access to commonly used programs or utilities. Double-clicking an icon launches that application or opens that folder. (See Figure A-2.)

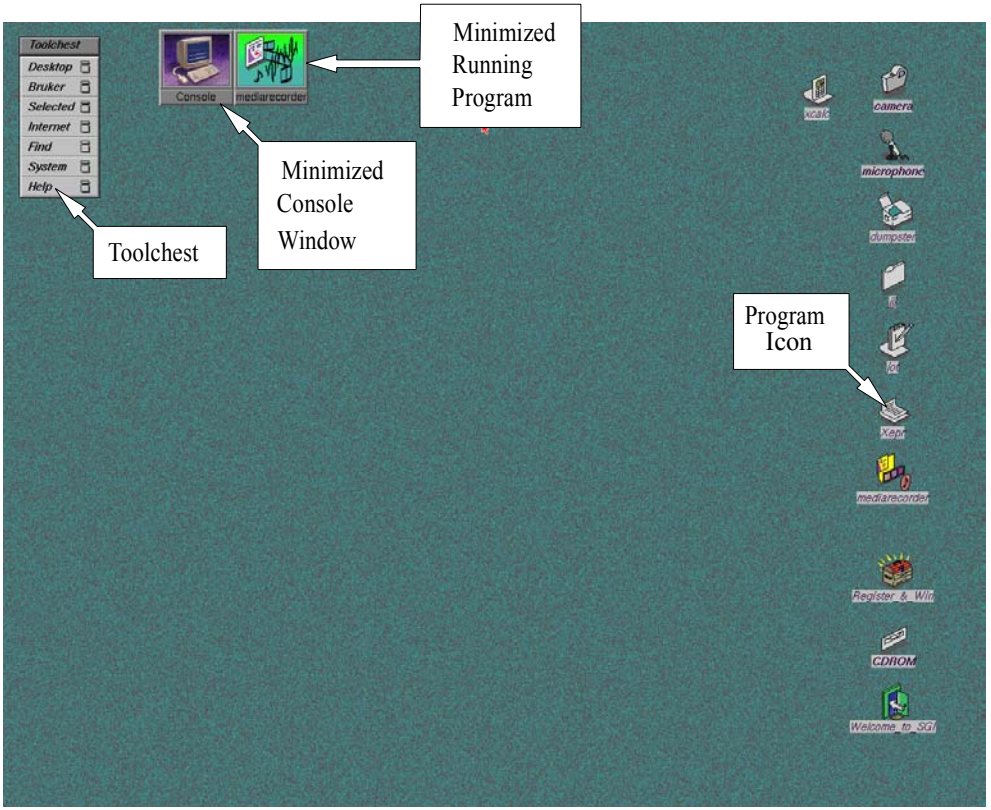


Figure A-2 An IRIX desktop.

By default there is an iconized window called the console. The console window displays system error messages. You can open it by left-clicking with your mouse. Leave the console window on. On the top left corner you will find the Toolchest. From the Toolchest you can access the UNIX shell, application programs, help manuals, utilities, system information, and your desktop configurations.

The Toolchest A.2.1

The Desktop tool contains many useful features. (See Figure A-3).

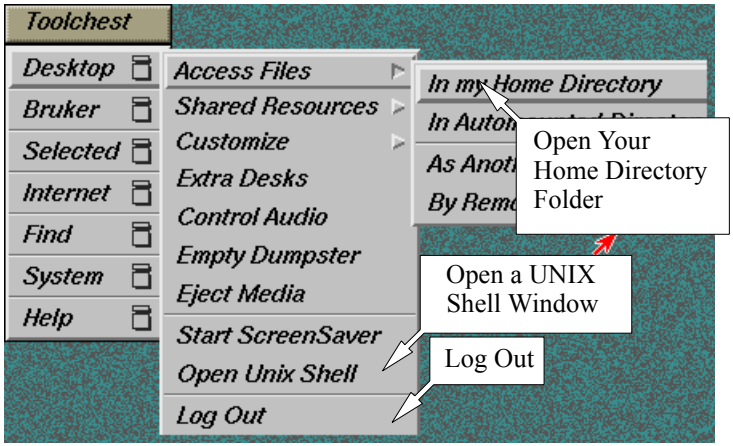


Figure A-3 The Desktop tool.

Opening your Home Directory A.2.2

You can open your home directory folder by clicking Desktop and Access Files, and then In my Home Directory. A window will open showing the contents of your home directory. (See Figure A-4.)

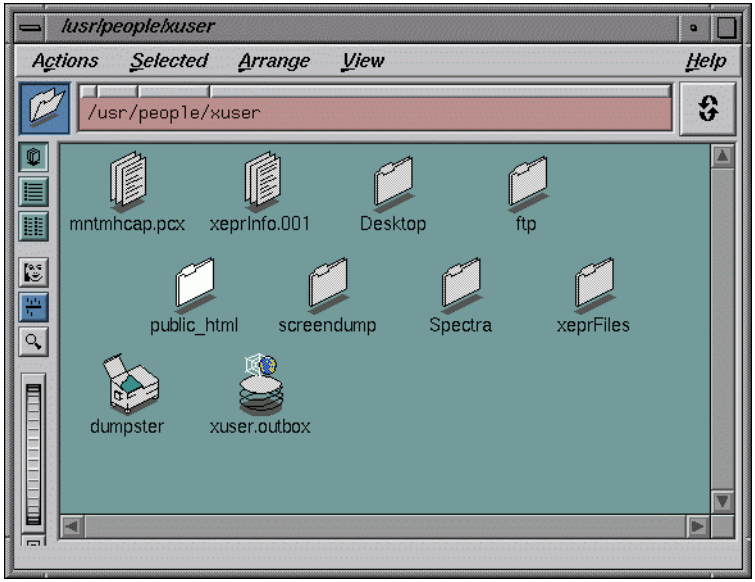


Figure A-4 A window of your home directory.

You can access other paths and view the contents of other directories or subdirectories. Drag the folder you want to open to the small box on the top left corner. (See Figure A-5.) The contents of the window will change to the folder you just selected. You can also double click on that folder to open another window and show the contents of that folder.

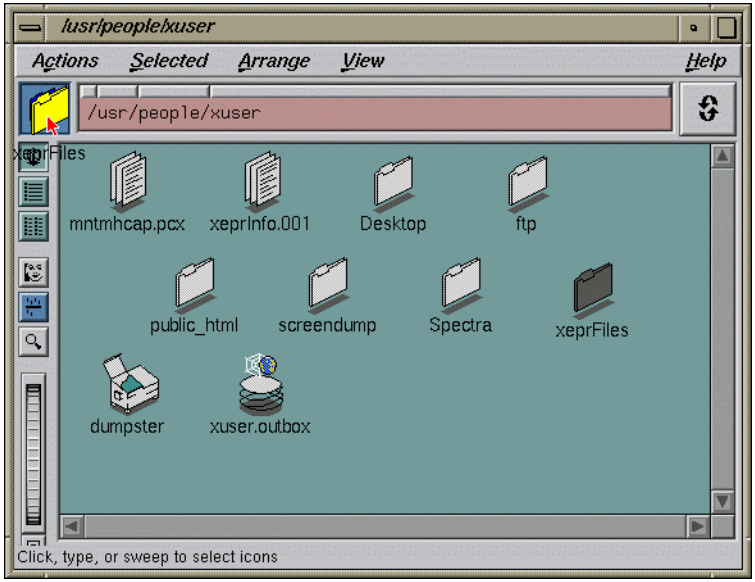


Figure A-5 Changing to a subdirectory.

Creating a New Directory A.2.3

You can create a new directory or a new folder. Click Actions on the menu bar and then New Directory. (See Figure A-6.) A new folder named empty.dir will appear in the window.

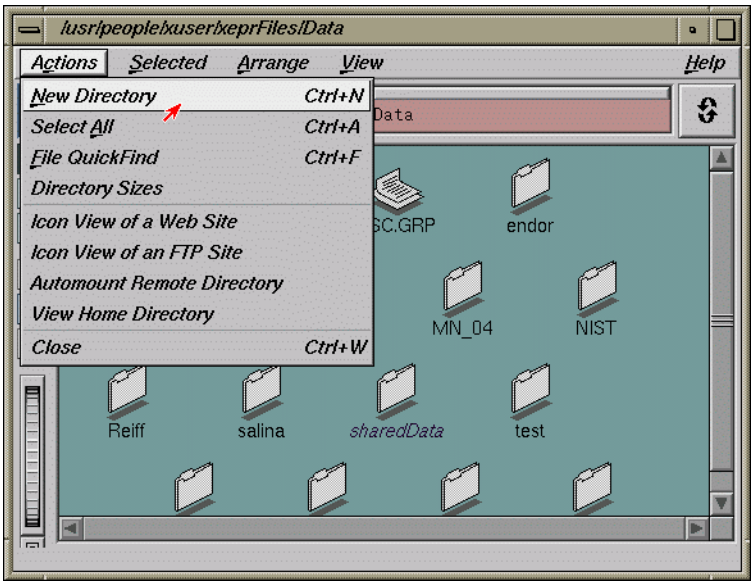


Figure A-6 Creating a new directory.

Clicking on the name of the folder allows you to change the name of the folder. After you enter the name of the new folder press the Enter key. (See Figure A-7.)

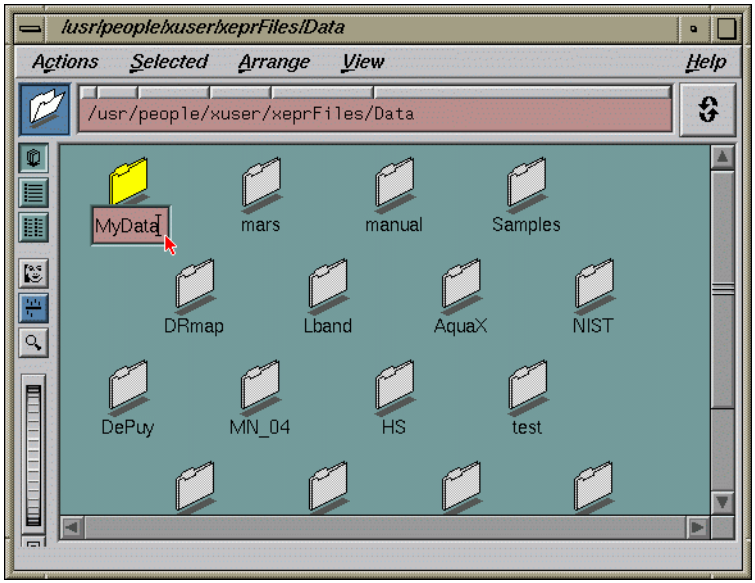


Figure A-7 Naming a new folder.

The UNIX Shell A.2.4

A UNIX shell is a command line interpreter. You can execute UNIX commands in this shell. Commonly used UNIX shell commands are listed below:

ls <directory>	list the contents of a directory
passwd	change the password
pwd	display the working directory
cd <directory>	change the directory
mkdir <directory>	make a new directory
cp <file1> <file2>	copy *file1* to *file2*
rm <file or directory>	remove or delete a file or directory
mv <file1> <file2>	move or rename a file
cat <file>	display the contents of a file
less <file>	display file contents using paging
man <command>	launch the on-line technical reference
whatis <command>	display a short description of a command

You need to move the mouse pointer inside the window so that you can start to type.

To find a list of UNIX shell commands you can type xman in a UNIX shell.

Use the man command to find out how to use the above commands.

Logging Out A.2.5

You can log out from your account by clicking the Log Out button under Desktop in the Toolchest. (See Figure A-3.)

The Find Tool A.2.6

The Find tool is very useful when you need to find a file or a program. (See Figure A-8.) Clicking the Applications button under Icon catalog will bring you to a folder that contains various application programs. (See Figure A-9.)

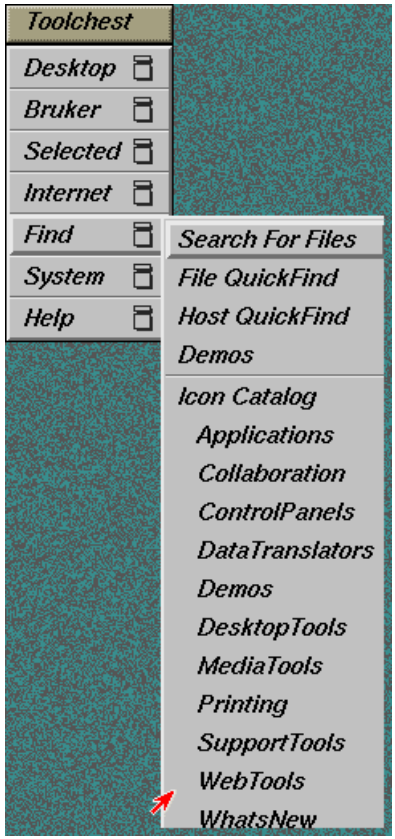


Figure A-8 The Find tool.

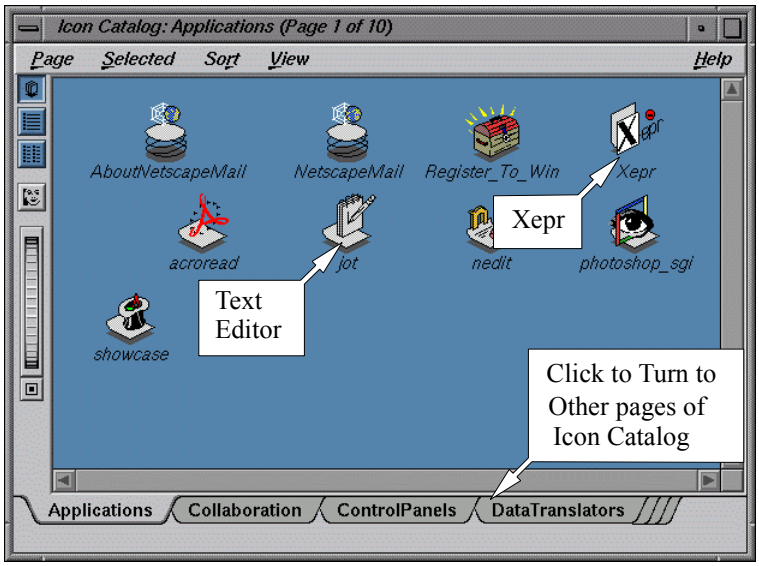


Figure A-9 Application icons.

Among them is the Xepr program. You can also find a text editor called jot. Double clicking any of these icons launches the program. You can drag the icon by clicking and holding the left mouse button and drop it on the desktop for your convenience.

The System Tool A.2.7

Using the system tools you can get information on your system configurations. (See Figure A-10.) You can also configure the printers. If you do not have a console window you can start a new one by clicking Utilities and then Start New Console.

You can also shut down the system with this tool. However, you need to consult the system administrator unless it is an emergency because root or super user privileges are needed to shut the system down or change the configuration.

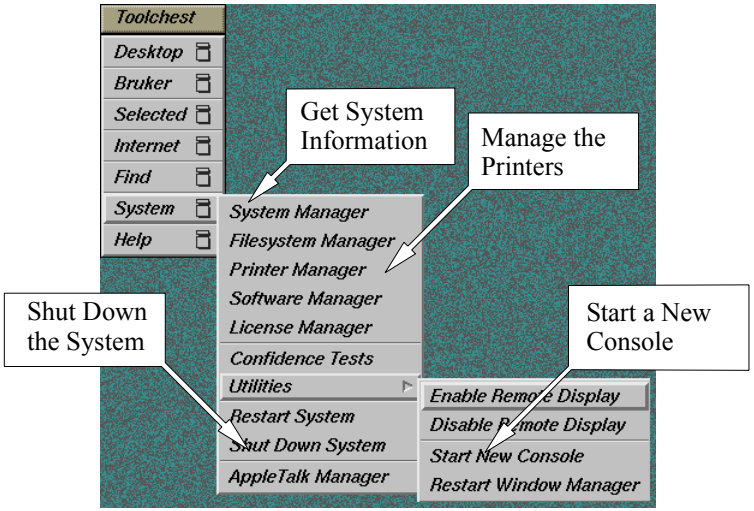


Figure A-10 The System tools.

The Help Tool A.2.8

You can find many different kinds of help using the Help tool. (See Figure A-11.) Use the Info Search tool to quickly find any information you need. We recommend that you at least read the End User's Book in On-line Books.

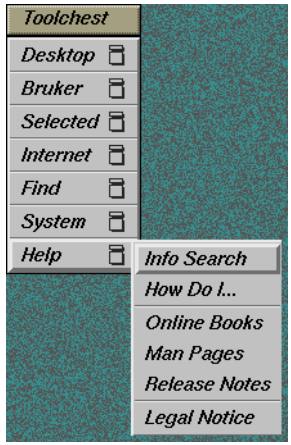


Figure A-11 The Help tool.

Changing the Password A.3

To change your password you can open a UNIX shell window and type passwd. (See Figure A-12.)

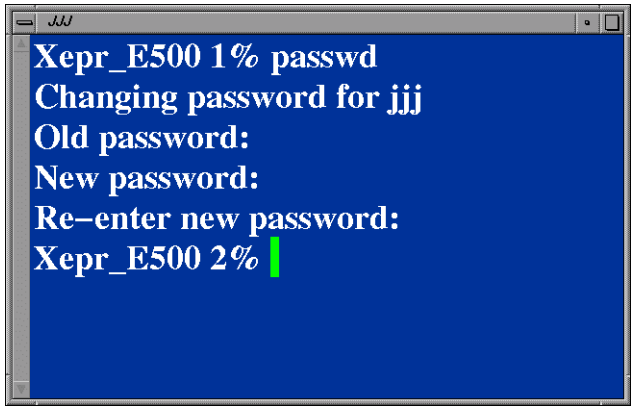


Figure A-12 Changing your password.

You will be prompted for your old password and a new password. You need to re-enter the new password to confirm it. For security reasons, passwords are not displayed as you type them. We recommend changing your password every two months. The system expects your password to be at least six characters long with at least two alphabetic characters and at least one numeric or special character. Only the first eight characters are used. The new password must differ from the old one by at least three positions. Avoid using Ctrl characters, your name, or other easy-to-guess words in your password.

Basic Mouse Functions A.4

The SGI basic mouse functions by default are:

Left mouse button:	operation
Middle mouse button:	paste
Right mouse button:	menu

An Application Window A.5

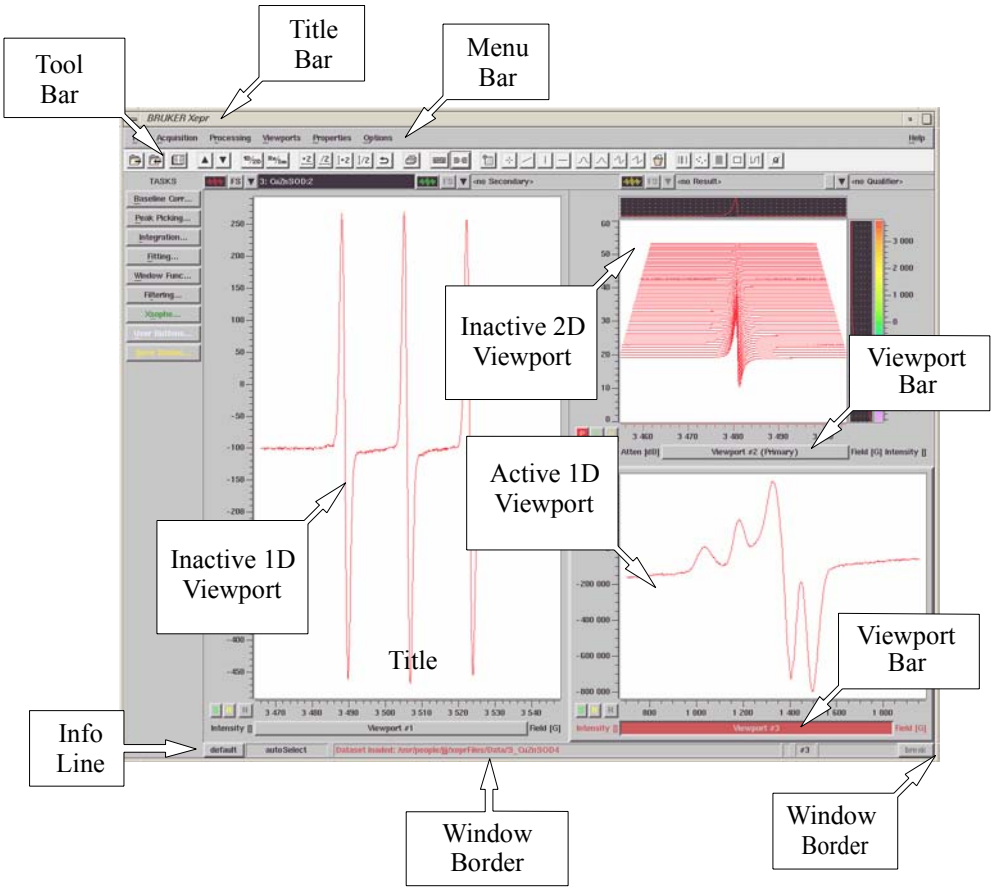


Figure A-13 The parts of an applications window.

Application Window

Most SGI programs operate in an application window. (See Figure A-13.) Xepr displays all its commands and spectra in the application window.

Viewport Each application window has a working area. The working area for Xepr is called a viewport. Acquired spectra are displayed in a viewport. You may have multiple viewports open at the same time, however, only one is active at a time. The active viewport is the one upon which operations will be performed.

Viewport Bar The viewport bar displays the number of the viewport. The active viewport has a red viewport bar at the bottom and the inactive viewports have grey bars. You activate a viewport by clicking the viewport bar.

Title Bar The bar on the top of a window is the title bar. It shows the name of the application. The color of the title bar indicates whether a window is active or not. Moving the mouse pointer inside the window activates that window. You can type in the window only when it is active. By clicking and dragging the title bar, the window may be moved.

Other elements in the title bar are:

Maximize Button The maximize button of the application window expands it to fill the entire screen. You may restore the window to its original size by clicking this button again.

Minimize Button The minimize button of the application window shrinks the window and places it on the desktop. A click on the minimized window opens it up to its original size.

Control Menu Button Double-clicking this button closes the window and exits the program. A single mouse click opens a drop-down menu. Consult your SGI documentation for further information regarding the commands in the menu.

Menu Bar

The horizontal bar under the title bar of the application window is the menu bar. It displays the names of the available drop-down menus. Choose the desired menu by clicking on it with the left mouse button. The menu consists of a collection of commands. You choose a command by clicking on it with the left mouse button.

Tool Bar

The horizontal bar below the menu bar is the tool bar. It displays buttons to activate the most commonly used commands. Clicking on a button activates the commands.

Info Line

This area of the application window displays program status information including mouse button status, guiding messages or the confirmation line, macro record indicator, and elapsed time.

Window Border

The perimeter of the window is the window border. When the cursor is placed anywhere on the straight edge of a window border, a red arrow with a short line replaces the regular cursor. If you click and drag, the window can be resized to the desired size. When the cursor is placed on a corner of a window, a red right angle with an arrow replaces the regular cursor. If you click and drag a corner, the two sides that form the corner are resized simultaneously.

Dialog Boxes A.5.1

Many commands open a dialog box. (See Figure A-14.) The dialog box allows you to enter required input for acquisition or processing. What follows is a description of the basic elements of a dialog box and how to use them.

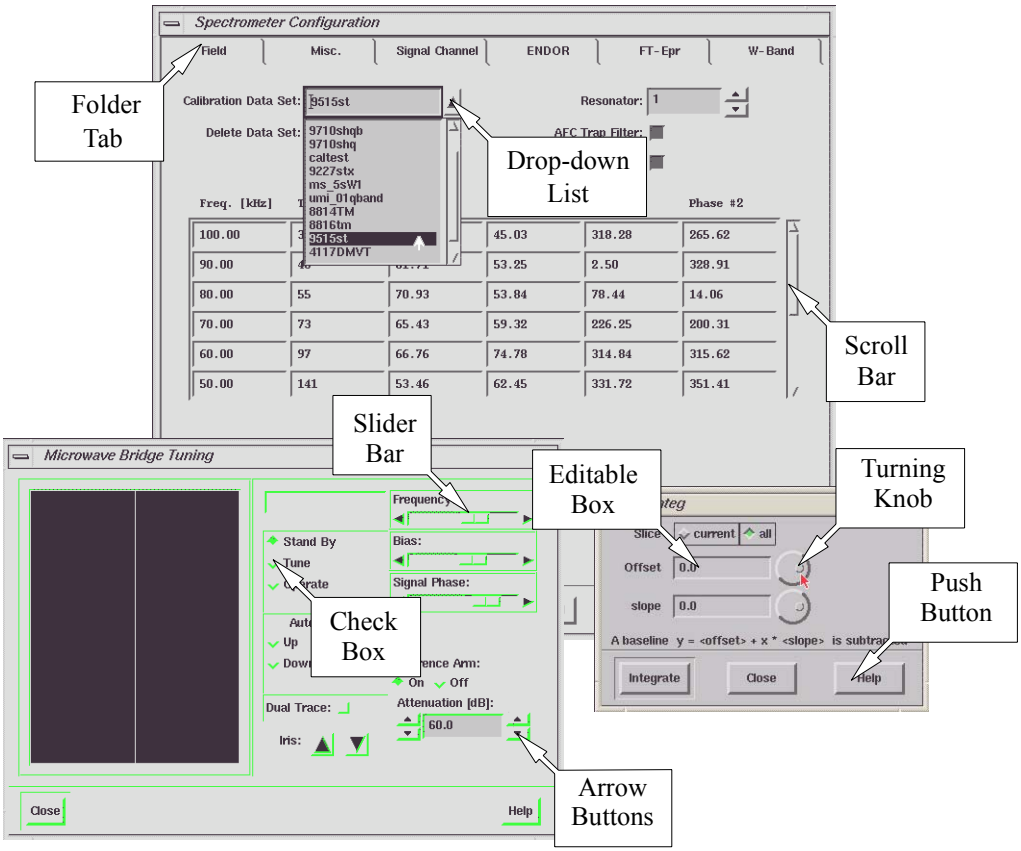


Figure A-14 The parts of a dialog box.

Editable Box

The editable box is a plain box with a white background. As the name suggests, you may edit the value in the box. It is used for the input and display of quantities that are not restricted to specific values but may have a continuum of values such as the center field. After a click with the left mouse button in the text of the box, an insertion marker appears (a vertical line). Any text (or numbers) you type are inserted after the insertion marker. Several characters may be selected or highlighted simultaneously by clicking and dragging over the desired text. Any typed text replaces the highlighted text. The selected text may also be deleted by pressing the Del key. The left and right arrow keys of the keyboard move the insertion marker left and right. Keeping the keys pressed repeats the action automatically.

Drop-down List

This input method is used for parameters that have a limited number of options or choices. After clicking on the downward pointing arrow next to the box, the allowed values appear in a drop-down list and the arrow points upward. The presently active option is highlighted. The highlighted choice is changed by pressing the up and down arrow keys of the keyboard. You may also select the desired choice by clicking the value with the left mouse button. Click the upward pointing arrow. The drop-down list then disappears with the newly selected value or option displayed in the box.

Check Box

The check box acts like a toggle. When clicked, the action turns the option on or off. The color of the box turns into green indicating an on (or active) state.

Push Button

A push button will execute a command when you click it with the left mouse button. The command, such as OK, Cancel, Close, or Help is displayed in the center of the button.

Arrow Buttons The arrow buttons are used to change a variable in a discrete step-wise fashion. If the box has a white background, the values may be edited as in an editable box. Clicking the up or down arrow button increases or decreases the parameter with a fixed step size. For example, the step size for modulation amplitude is 0.1 Gauss. Sometimes there are two sets of arrow boxes. The left arrow buttons allow you change the value in coarse steps while the right arrow buttons change the value in fine steps. The up and down arrows next to the box move you through the allowed values for the variable sequentially. If the background of the box were gray, you are then not able to edit the values, but must change them with the arrows.

Slider Bar The slider bar is used to vary a parameter continuously between its allowed limits. For example, it is used to vary the microwave source frequency from 9.2 to 9.9 GHz. Clicking to the left or right of the rectangular bar acts as a coarse adjustment while clicking the left or right arrows allows fine adjustments. Keeping the mouse button pressed repeats the action automatically. The value of the parameter is indicated graphically by the rectangle to supply you with visual feedback. The parameter may be varied as well by clicking and dragging the rectangular bar.

Scroll Bar The scroll bar looks like a slider bar but functions differently. It is used to view entries in a list. For example, it is used in the Save As dialog box to choose subdirectories. Clicking the up or down arrows scrolls the list up and down. Keeping the mouse button pressed repeats the action automatically. The position of the viewed entry in the list is indicated graphically by the square. The list may be scrolled as well by clicking and dragging the square.

Folder Some dialog boxes have several folders in a dialog box. Clicking on the tab of the folder brings that folder to front.

Turning Knob

A turning knob is used to change the parameter continuously. Click and hold the left mouse button on the knob and turn it clockwise (increasing the value) or counter-clockwise (decreasing the value).

Brief Tips on Linux B

If your Elexsys EPR spectrometer is equipped with an SGI O2 workstation, the UNIX operating system you have is IRIX. Please go to Appendix A.

Not everyone may be familiar with the UNIX operating system. If your Elexsys EPR spectrometer is equipped with a PC the UNIX operating system is Linux. This chapter explains some basic aspects of UNIX based on Linux. It is not meant to be an in-depth treatise: the Linux documentation should be consulted for more details. If you are already familiar with UNIX, you can easily skip this section. If you have not used UNIX before, we highly recommend Linux's on-line help. The icon of the integrated help system can be found in the bottom panel of the screen if you are using the GNOME graphic interface. The Linux Documentation Project http://www.linuxdoc.org/ is an organized collection of documents which offer step-by-step instruction on various Linux tasks. These documents are called HOWTOs. You may find and install them from the CDs that come with your system.

Login B.1

One of the advantages of the UNIX system is security. Security is accomplished by assigning each user an account with a user name and a password. There are two types of accounts: root or super user, and user. You will typically use the user accounts for all operations. The root or super user account is solely for administration and maintenance only. Before you start you need to login into your own account. If you don't have an account yet ask the system administrator to create one for you or login as xuser.

Figure B-1 The login screen.

UNIX is case sensitive. Make sure you use the correct case for every character of your user name, password, as well as any commands.

The login window looks like that in Figure B-1. Type your user name in the Login box and press ENTER: the system will prompt you for your password. Typing the password and pressing ENTER brings you to the desktop of your account.

The Desktop B.2

On the left side of the desktop, there are a few icons for quick access to commonly used programs or utilities. Double-clicking an icon launches that application or opens that folder. (See Figure B-2.)

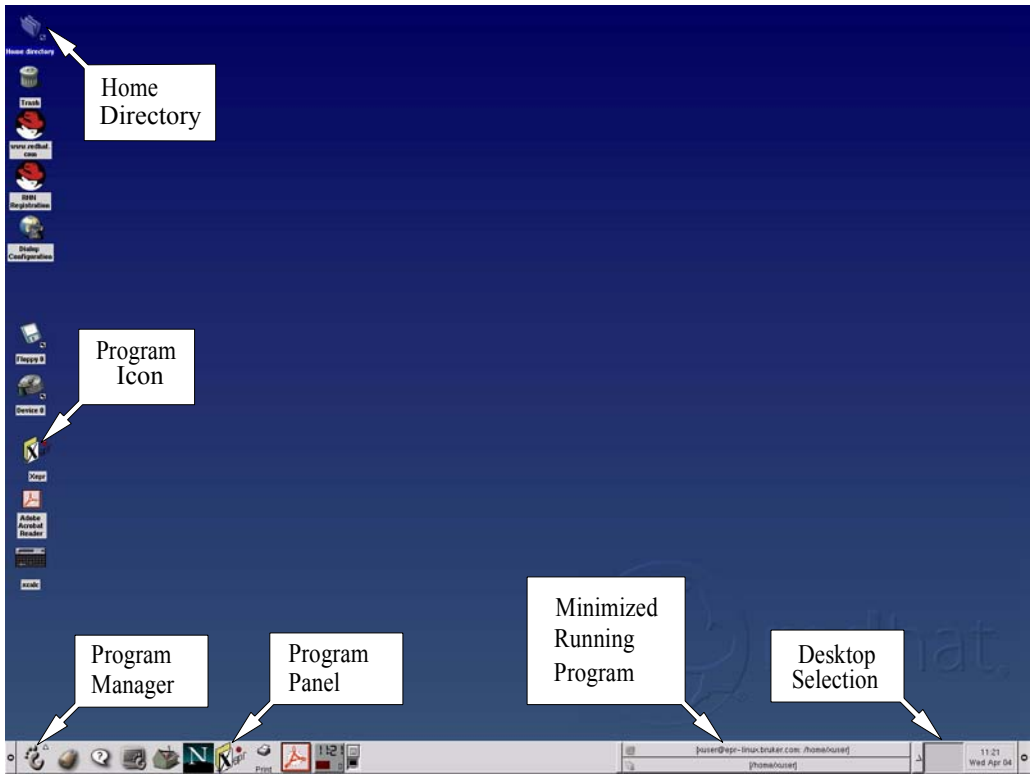


Figure B-2 A GNOME desktop.

On the bottom of the screen you will find a panel. From the panel you can access the Main Menu, commonly used application programs, iconized running windows, the help system, and the desktop selector.

Opening your Home Directory B.2.1

You can open your home directory folder by clicking the Home Directory icon on the desktop. A window will open showing the contents of your home directory. (See Figure B-3.) You can access the subdirectories by clicking the folders in the right window. You can also change to other directories by clicking the folders in the tree on the left window.

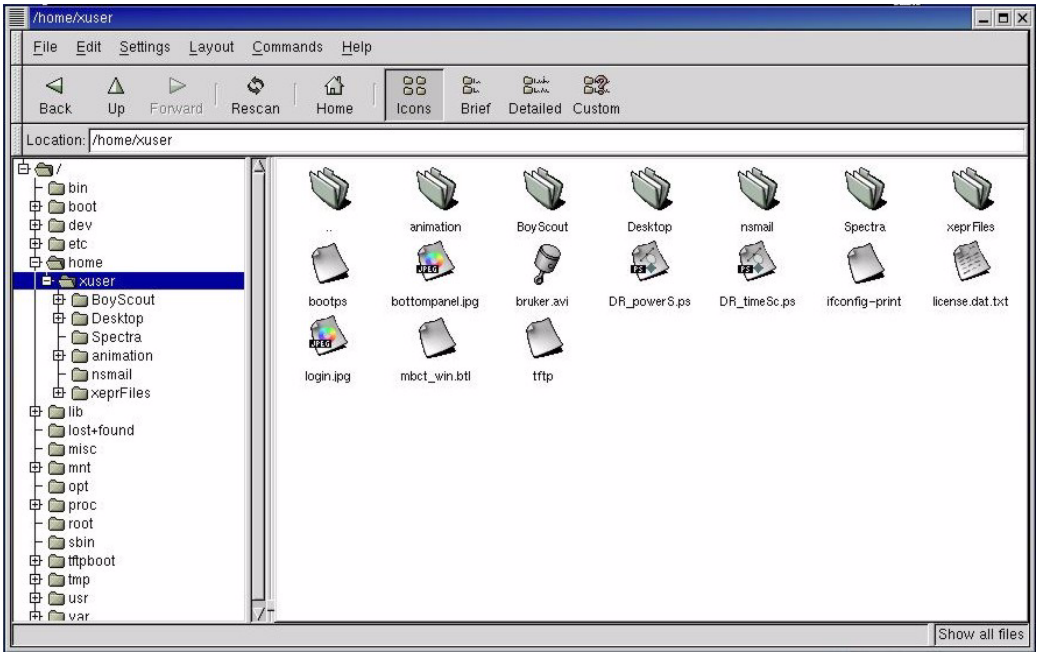


Figure B-3 The home directory window.

Creating a New Directory B.2.2

You can create a new directory or a new folder from the directory window you just opened. Click File on the menu bar and New > Directory. (See Figure B-4.)

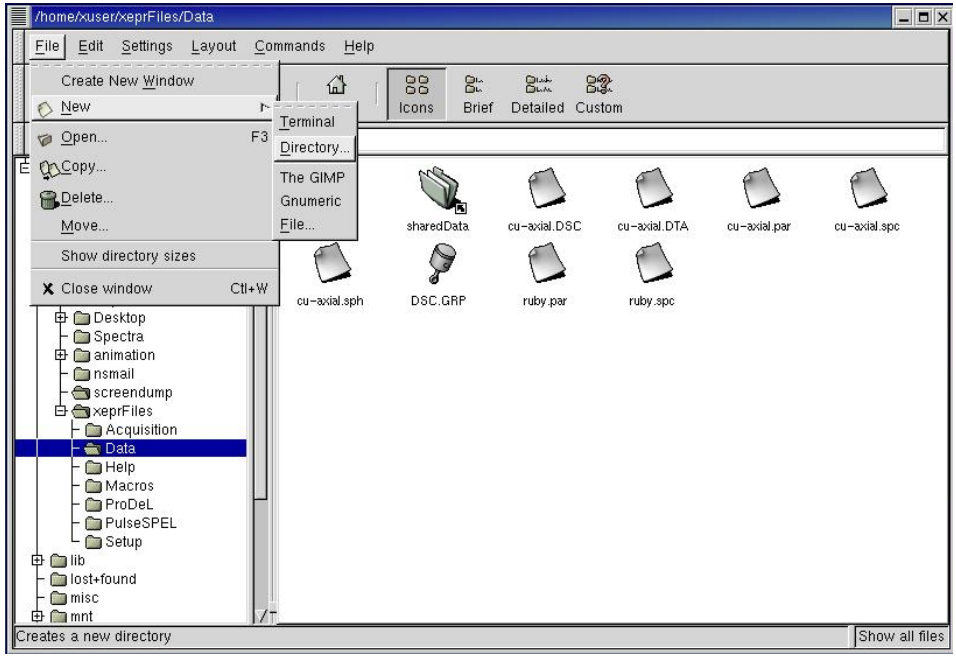


Figure B-4 Creating a new directory.

A dialog window appears requesting the name for the new directory. (See Figure B-5.) Type in the name for the new directory and click OK to close the dialog box. A new directory with that name will be created in the current directory.

Figure B-5 The dialog box for creating a new directory.

The Find File Tool B.2.3

The Find File tool is very useful when you need to find a file or a program. In the directory window, click Commands > Find File. (See Figure B-6.)

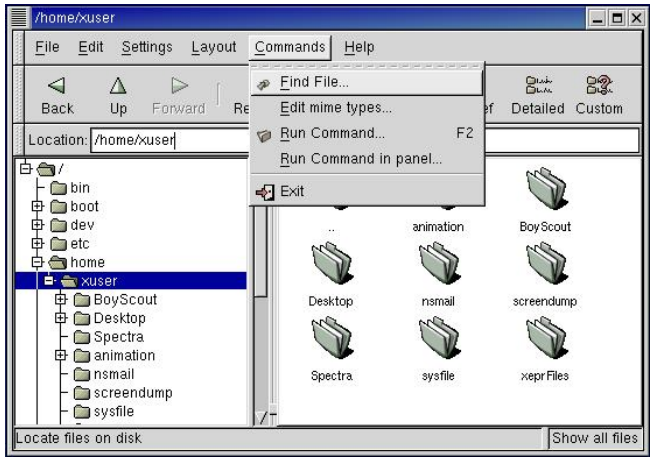


Figure B-6 Launching the Find File tool.

In the dialog box that appears, enter the directory that you want to search. If you enter "." the search will start from the current directory; Entering "~" starts the search from your home directory. Entering "/" starts the search from the root directory. You need to enter a file name. If you do not know the entire file name, you can use a wild card, *e.g.* "*" or "?".

You can also find files that have certain content by entering a string in the Content box. Click OK to start the search. (See Figure B-7.)

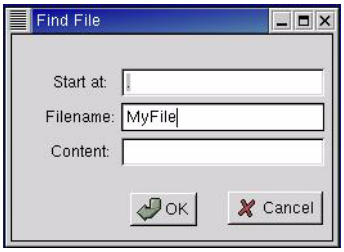


Figure B-7 The Find File dialog box.

The UNIX Shell B.2.4

All the Linux functions we introduced above can be executed by shell commands. A UNIX shell is a command line interpreter in which you can enter UNIX commands. (See Figure B-8.)

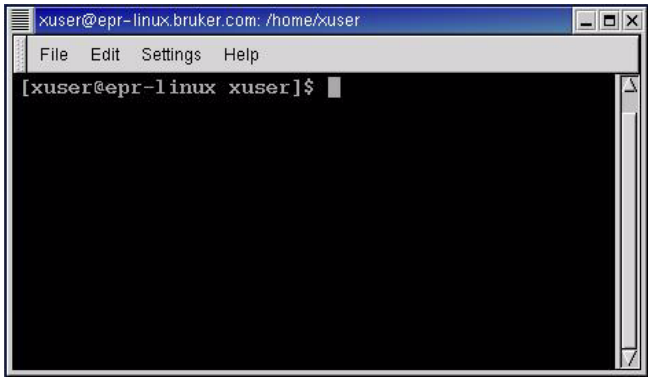


Figure B-8 A shell window.

To open a shell window, you can simply click the terminal emulation program icon in the bottom panel to open a shell window. (See Figure B-9.)

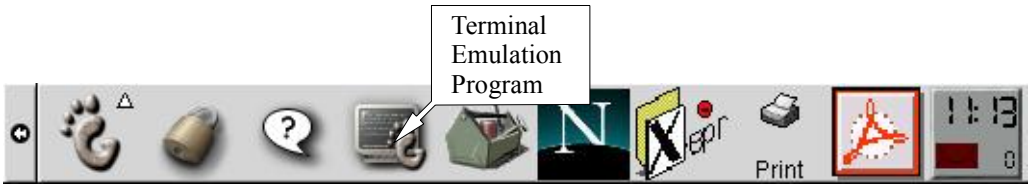


Figure B-9 The terminal emulation program in the bottom panel.

You can also click the right mouse button on the desktop to bring up a menu and then click New > Terminal. (See Figure B-10.)

Figure B-10 Starting a shell window by right- clicking the desktop.

Commonly used Linux shell commands are listed below:

ls <directory>	list the contents of a directory
passwd	change the password
pwd	display the working directory
cd <directory>	change the directory
mkdir <directory>	make a new directory
cp <file1> <file2>	copy *file1* to *file2*
rm <file or directory>	remove or delete a file or directory
mv <file1> <file2>	move or rename a file
cat <file>	display the contents of a file
less <file>	display file contents using paging
man <command>	launch the on-line technical reference
whatis <command>	display a short description of a command

Depending on your window manager setting you may need to move the mouse pointer inside the window in order to start typing.

To find a list of UNIX shell commands you can type xman in a UNIX shell. It brings up a manual browser, the xman window. (See Figure B-11.)

Figure B-11 The xman manual browser.

You can also use the man command to find out how to use the above commands.

Changing the Password B.2.5

To change your password, open a UNIX shell window and type passwd. (See Figure B-12.)

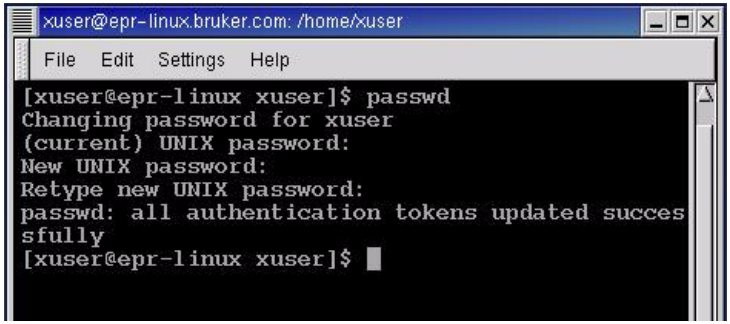


Figure B-12 Changing your password.

You will be prompted for your old password and a new password. You need to re-enter the new password to confirm it. For security reasons, passwords are not displayed as you type them.

We recommend changing your password every two months. The system will warn you if the password is too short or it is too easy to guess. Avoid using Ctrl characters, your name, or other easy-to-guess words in your password.

The Main Menu B.2.6

The main menu in the bottom panel contains various application programs, tools, as well as system configuration. (See Figure B-13.)

Figure B-13 The main menu icon.

The Help Tool B.2.7

You can find many different kinds of help by clicking the Integrated Help System icon in the bottom panel. (See Figure B-14.)

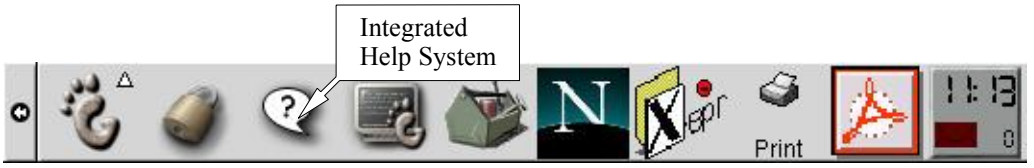


Figure B-14 The Integrated Help System (info, man, HTML).

Logout B.2.8

It is always a good practice to log out after you finish your work. Click the main menu icon and then click Log out. (See Figure B-15.)

Figure B-15 Logging out from the Main Menu.

A dialog box appears with three radio buttons: Logout, Halt, and Reboot. (See Figure B-16.) Select Log out and then click Yes. Clicking No brings you back to the desktop of your account. If you want to halt or reboot the system, please consult your system administrator first.

Figure B-16 The log out dialog box.

Basic Mouse Functions B.3

The basic mouse functions by default are:

Left mouse button:	operation
Middle mouse button:	paste
Right mouse button:	menu

An Application Window B.4

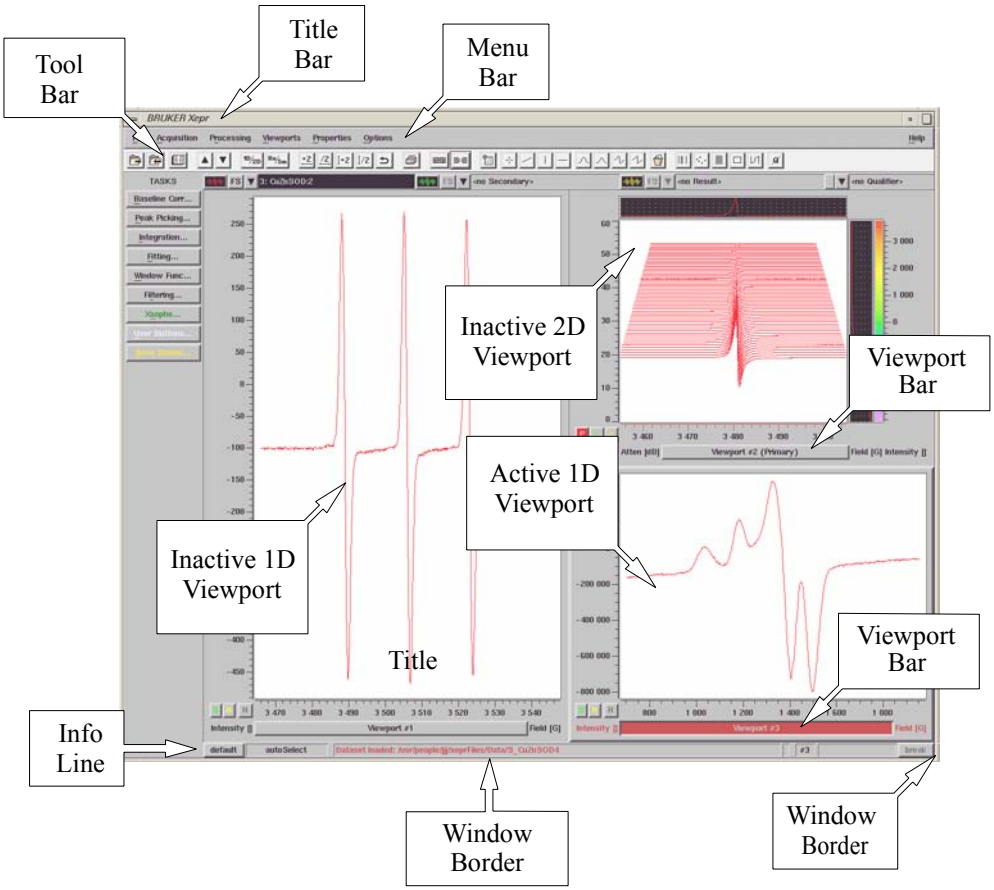


Figure B-17 The parts of an applications window.

Application Window

Most Linux programs operate in an application window. (See Figure B-17.) Xepr displays all its commands and spectra in the application window.

Viewport Each application window has a working area. The working area for Xepr is called a viewport. Acquired spectra are displayed in a viewport. You may have multiple viewports open at the same time, however, only one is active at a time. The active viewport is the one upon which operations will be performed.

Viewport Bar The viewport bar displays the number of the viewport. The active viewport has a red viewport bar at the bottom and the inactive viewports have grey bars. You activate a viewport by clicking the viewport bar.

Title Bar The bar on the top of a window is the title bar. It shows the name of the application. The color of the title bar indicates whether a window is active or not. Moving the mouse pointer inside the window activates that window. You can type in the window only when it is active. By clicking and dragging the title bar, the window may be moved.

Other elements in the title bar are:

Maximize Button The maximize button of the application window expands it to fill the entire screen. You may restore the window to its original size by clicking this button again.

Minimize Button The minimize button of the application window shrinks the window and places it on the desktop. A click on the minimized window icon opens it up to its original size.

Control Menu Button This button is located in the left top corner of the window. A single mouse click opens a drop-down menu. Consult your Linux window manager documentation for further information regarding the commands in the menu.

Close Button Clicking the Close button closes the application window.

The appearances of these buttons may be different depending on which window manager you use and how it is set up.

Menu Bar

The horizontal bar under the title bar of the application window is the menu bar. It displays the names of the available drop-down menus. Choose the desired menu by clicking on it with the left mouse button. The menu consists of a collection of commands. You choose a command by clicking on it with the left mouse button.

Tool Bar

The horizontal bar below the menu bar is the tool bar. It displays buttons to activate the most commonly used commands. Clicking on a button activates the commands.

Info Line

This area of the application window displays program status information including mouse button status, guiding messages or the confirmation line, macro record indicator, and elapsed time.

Window Border

The perimeter of the window is the window border. When the cursor is placed anywhere on the straight edge of a window border, an arrow with a short line replaces the regular cursor. If you click and drag, the window can be resized to the desired size. When the cursor is placed on a corner of a window, a right angle with an arrow replaces the regular cursor. If you click and drag a corner, the two sides that form the corner are resized simultaneously.

Dialog Boxes B.4.1

Many commands open a dialog box. (See Figure B-18.) The dialog box allows you to enter required input for acquisition or processing. What follows is a description of the basic elements of a dialog box and how to use them.

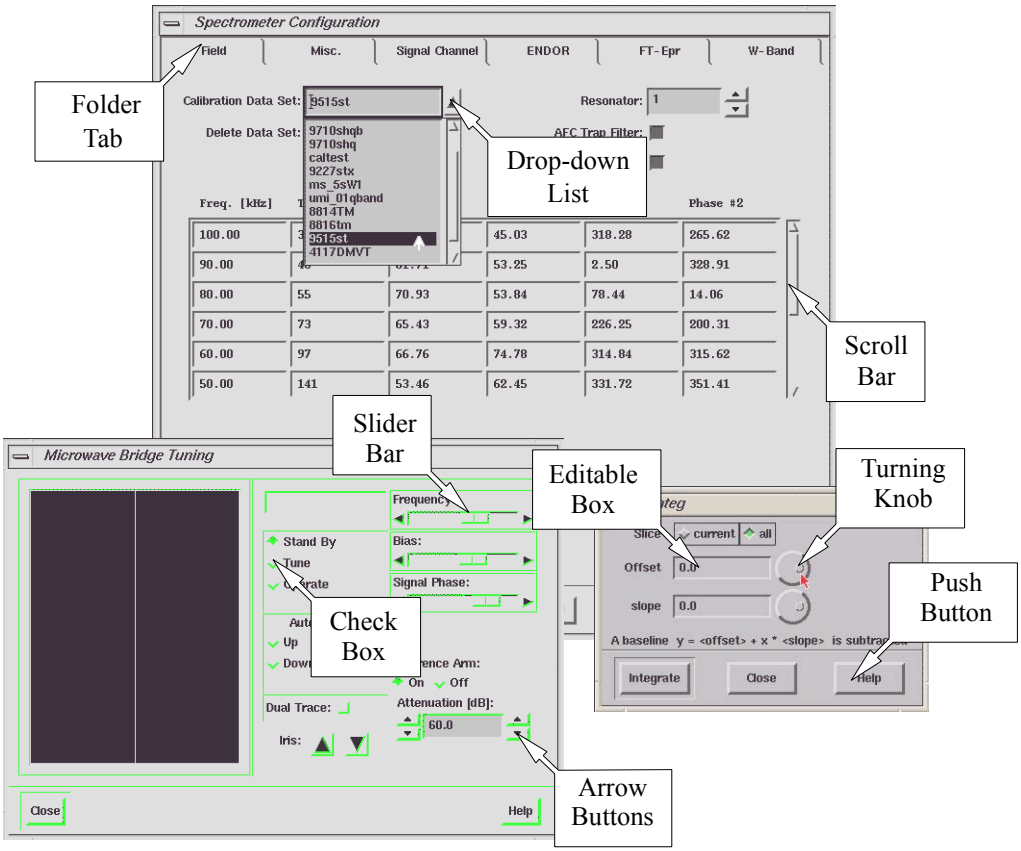


Figure B-18 The parts of a dialog box.

Editable Box

The editable box is a plain box with a white background. As the name suggests, you may edit the value in the box. It is used for the input and display of quantities that are not restricted to specific values but may have a continuum of values such as the center field. After a click with the left mouse button in the text of the box, an insertion marker appears (a vertical line). Any text (or numbers) you type are inserted after the insertion marker. Several characters may be selected or highlighted simultaneously by clicking and dragging over the desired text. Any typed text replaces the highlighted text. The selected text may also be deleted by pressing the Del key. The left and right arrow keys of the keyboard move the insertion marker left and right. Keeping the keys pressed repeats the action automatically.

Drop-down List

This input method is used for parameters that have a limited number of options or choices. After clicking on the downward pointing arrow next to the box, the allowed values appear in a drop-down list and the arrow points upward. The presently active option is highlighted. The highlighted choice is changed by pressing the up and down arrow keys of the keyboard. You may also select the desired choice by clicking the value with the left mouse button. Click the upward pointing arrow. The drop-down list then disappears with the newly selected value or option displayed in the box.

Check Box

The check box acts like a toggle. When clicked, the action turns the option on or off. The color of the box turns green, indicating an on (or active) state.

Push Button

A push button will execute a command when you click it with the left mouse button. The command, such as OK, Cancel, Close, or Help is displayed in the center of the button.

Arrow Buttons The arrow buttons are used to change a variable in a discrete step-wise fashion. If the box has a white background, the values may be edited as in an editable box. Clicking the up or down arrow button increases or decreases the parameter with a fixed step size. For example, the step size for modulation amplitude is 0.1 Gauss. Sometimes there are two sets of arrow boxes. The left arrow buttons allow you change the value in coarse steps while the right arrow buttons change the value in fine steps. The up and down arrows next to the box move you through the allowed values for the variable sequentially. If the background of the box were gray, you are then not able to edit the values, but must change them with the arrows.

Slider Bar The slider bar is used to vary a parameter continuously between its allowed limits. For example, it is used to vary the microwave source frequency from 9.2 to 9.9 GHz. Clicking to the left or right of the rectangular bar acts as a coarse adjustment while clicking the left or right arrows allows fine adjustments. Keeping the mouse button pressed repeats the action automatically. The value of the parameter is indicated graphically by the rectangle to supply you with visual feedback. The parameter may be varied as well by clicking and dragging the rectangular bar.

Scroll Bar The scroll bar looks like a slider bar but functions differently. It is used to view entries in a list. For example, it is used in the Save As dialog box to choose subdirectories. Clicking the up or down arrows scrolls the list up and down. Keeping the mouse button pressed repeats the action automatically. The position of the viewed entry in the list is indicated graphically by the square. The list may be scrolled as well by clicking and dragging the square.

Folder Some dialog boxes have several folders in a dialog box. Clicking on the tab of the folder brings that folder to the front.

Turning Knob

A turning knob is used to change the parameter continuously. Click and hold the left mouse button on the knob and turn it clockwise (increasing the value) or counter-clockwise (decreasing the value).

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