CAESR Training Session

W. Myers, Oct. 2024

Preliminary, have read CAESR User Form Document

Morning ~ 10 am to 12 pm

Explanation of webpage and online resources
Start, Run, \\chem.ox.ac.uk\SRF\ESR *1*… BrukerManuals\ *2*… NewUser_IntrosAndFAQ\
Spectrometer booking: CW by user; Pulsed in booking meeting
General Comments on doing research in ESR (*in CAESR*) … page 2
ESR Research Responsibility statement … page 3

Tour of

F19: clockwise loop of lab, file cabinet drawers, cryostats, resonators, standard samples

F11: lab layout, resonators, special start-up guide, LASER interlock, sign-off

F12: lab layout, magnetic field hazards, resonators, LASER interlock

F13: wet lab resources, Timmel Group resources, clean-up after yourself, COSHH

Services to Facility: helium dewar return manifold, light well lines, chiller locations (control repeaters)

F12 – E680 training

How to
Set up cryogenic flow conditions {liquid N_2, liquid He}
Turn on the spectrometer {N_2 gas, water, power supply, console, mw bridge, software}
Changing samples in Standby
Usage Pause for > 2 hr in your experiments, {TWT off, Magnet power supply off, microwave source in Standby, cryogen low-flow?}
Turn the spectrometer off {software, mw bridge, console, power supply, water, N_2 gas}
Take-down cryogenic flow conditions
StartHere_NewUser folder

Instrumentation, layout of instruments, bridge schematic … page 5-7
GUNN source; ELDOR source;
CW path; LCW; Pulsed EPR path {SPFU; MPFU}

CW-EPR & Pulsed EPR of LiPc … page 8-9

Bruker pulse course 2007, BDPA at X-band and Q-band … page 10

Afternoon ~ 2:30 pm to 5 pm

Transient ESR – Zn(II)TPP *skipped, discussion only* … page 11

Double Electron-Electron Resonance, *discussion only* … page 12

Bruker Pulsed EPR Course 2007 – DEER std. hands-on exercises … page 12

General Comments for Research in ESR:

You should gain familiarity with relevant parts of the Bruker and Oxford Instrument manuals for each spectrometer you use and for transfer lines (LLT600), instrumentation temperature controllers (ITC-503, Mercury, VT-1000) and cryostats (CF-935, ESR-900).

Don't adjust hardware settings or reconfigure console wiring connections without getting help the first few times. Don't change cryostats unless trained by CAESR staff.

If you are unsure of doing something new on the spectrometer software settings, e.g. new PulseSPEL, ProDel, or detection methods, please get help to check that your setup is safe.

1. CW-EPR: Quantification of spin concentration, speciation, g-matrix and large hyperfine values, rapid tumbling room temperature ESR for isotropic values of slowly relaxing spins. Rotational correlation times.

2. Pulse-EPR: Resolve and characterize small anisotropic interactions, e.g. hyperfine, nuclear quadrupole, electron-electron dipole. Measure electron and nuclear relaxation times directly (more easily than in CW-EPR). Exchange correlation spectroscopy.

+	−
Read current and past literature to write a research proposal for publishable results and maintain a realistic plan of samples, experiments, people and publications for your available appointment time. Plan pulsed EPR experiments well in advance of your reservation. . liquid helium order in place five days before . samples prepared and stored as stable (77 K?) . CW-EPR characterization completed, if useful . outline of experiments and what information you want to obtain . do simulations & DFT that will help guide parameter value settings in EPR experiments . know the level of signal-to-noise required for each measurement and so don't waste time During measurements: make plots of your data as soon as possible and render preliminary analysis. Good plotting code will get data to near-publication quality figures with little effort. Start on simulations and report if possible. Make notes of analysis ideas. Keep project participants well-informed, share the results within a few days in a written report with discussion points and possible future work. Explain remaining analysis and questions (it's okay), then follow-up in meetings or on phone. Ask for help if needed. Carefully monitor personal health over multi-day runs.	Don't try to order helium until the day before you start. Assume your collaborators know everything about making a good ESR sample (what you need) and then email them a short list of sample requirements after the measurements fail. Don't start contacting your collaborator about your samples until they have no choice but devote 100% of their time, including evenings and weekends to make certain your samples are good before or during your measurement time. Only use EPR to characterize samples. Talk individually to many people with EPR-expertise who are not on your project about your results and polish the aggregate comments and analysis as your own, for your own exclusive meetings. Collect many EPR data sets and put-off looking at them for months to years (perhaps not until you hear that someone is about to scoop you or collaborators knock on your door or get another person to co-opt your work). Blame the spectrometer, supervisor, or someone else if experiments or analysis don't work. Talk badly about them to other people. Be hyper-independent -- do not ask for help or discuss results with anyone for weeks, months, or years, developing systematic bad habits that end in erroneous data acquisitions, limited analysis, and publications.

ESR Research Responsibilities

As a researcher in CAESR, the measurements you perform, the analysis and reporting in publications and presentations reflect directly on the reputation of yourself, your supervisor(s), the Centre for Advanced ESR, the Department of Chemistry or your Department, and the University of Oxford as a whole. Therefore, maintenance of a high standard of research quality is essential as a singular merit and as the aim of REF2028(?). You are encouraged to learn ESR methods, become capable spectrometer users and ultimately, good ESR spectroscopists; however, please seek *free* consultation in the following, as needed:

Elements of ESR research quality:

1) CW-EPR characterization: non-saturating microwave power, slow-passage field sweep rate --in the limit of no effect on signal shape or field position shift, lower the temperature to the limit of narrow linewidths. Prepare sample concentrations in the limit of narrow linewidths. Choose solvents or solvent combinations that yield a glass (disordered dipoles) when frozen. Choose solvents and sample concentrations that avoid sample aggregation and precipitation in the freezing process. Use a smoothing filter (analog and/or digital) of less than the linewidth. Sweep of the entire ESR signal in a spectrum that includes some baseline beyond the EPR signal, within reason for mostly Lorentzian lineshapes. Separate narrow sweeps over regions with high-detail and/or a change in receiver gain for separate sweeps on large variations of signal intensities. Prepare and measure control samples and check the resonator background under the acquisition conditions of the main sample.
   Spectral subtraction is very useful for discriminating between species, especially in the case of different power saturation dependencies, i.e. relaxation, but extra caution must be applied to avoid over-interpretation and generation of spurious features and signals.

2) A quantitative determination of the number of spins in a sample, the number of molecules intended to have spin, as expected, and the number that do not; know the implications of spin concentration.

3) Discussion of literature for prior EPR measurements of related molecules and theoretical concerns.

4) Accurate EPR simulations and reporting of complete set(s) of simulation parameter values.

5) Correct determination of field-offset between Hall probe and sample, for g-value calculations.

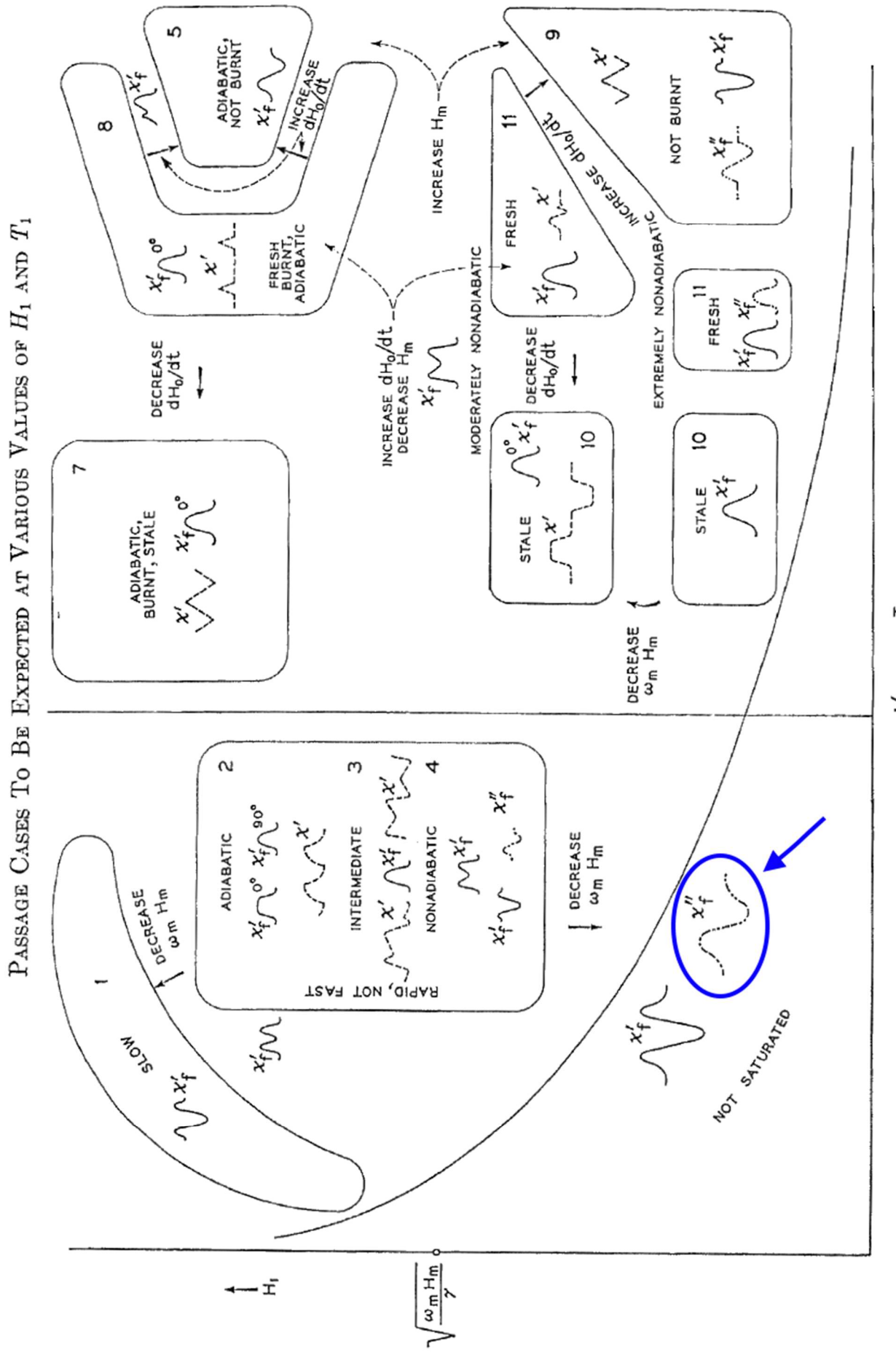
6) Correct mapping of tensor orientations on the molecular frame, *when detail level is appropriate*.

7) Report in experimental section, results section, figures and figure legends with sufficient detail that experiments may be accurately reproduced by other people, elsewhere.

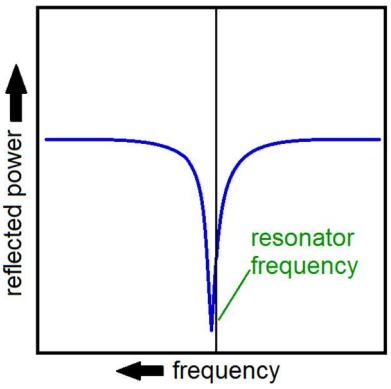
8) ESR figures: Give sufficient figure quality and axes labels that data may be subsequently digitized for comparison in experiment reproduction efforts and simulations. The field values (Magnetic Induction or Magnetic Flux Density) should be in SI units of milliTesla (mT) or Tesla; CGS units, Gauss, kG, remain *okay*. Spectrum regions of fine detail and/or very low relative intensity should be expanded in zoom insets or in supplementary information. These may be separate data acquisitions. Crop excessive baseline to show a bit of baseline, but mostly ESR signal with clear features.

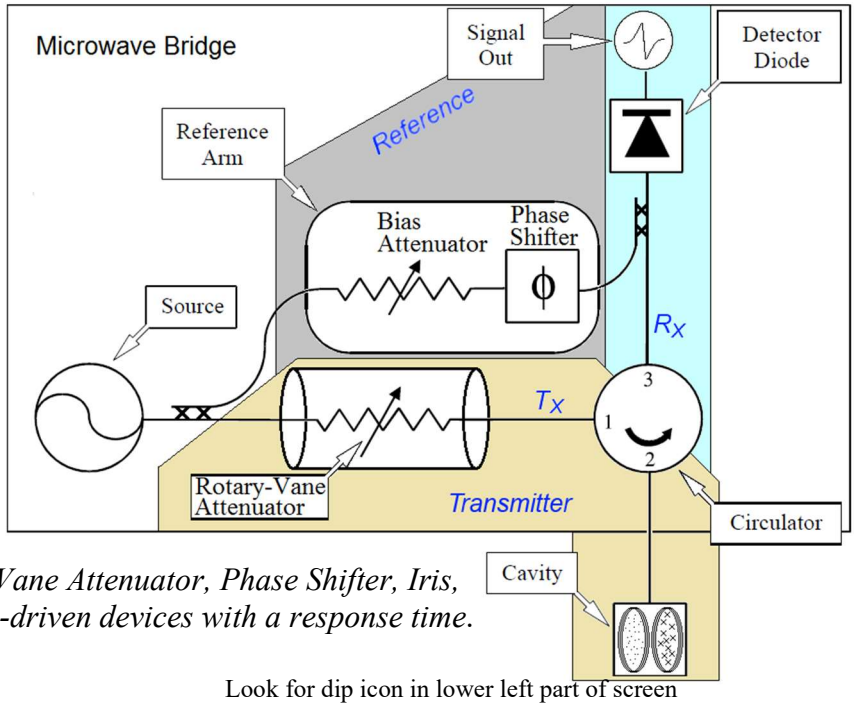
9) Figure legends may include sample concentration, sample solvent, microwave frequency to 100s of kilohertz place, e.g. 9.4136 GHz --depending on source stability, sample temperature, microwave power, sweep rate, time constant (if analog smoothing) and conversion time. Some of this information may rather be included in the Methods section.

You should include somewhere in your paper a line similar to “EPR measurements were performed in the Centre for Advanced ESR (CAESR) located in the Department of Chemistry of the University of Oxford.” And in the acknowledgement, “CAESR is supported by UK EPSRC (EP/L011972/1).”



CW-EPR responses, according to M. Weger, Bell Sys. Tech. J., 1960





CW-ESR Tuning Procedure

Please note that that the Rotary Vane Attenuator, Phase Shifter, Iris, and Frequency are mechanically-driven devices with a response time.

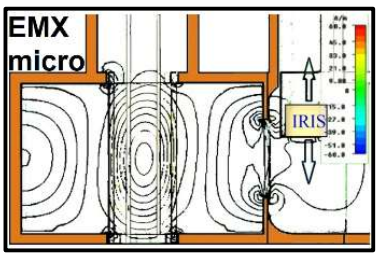
(1*) Switch on Tune Mode — Look for dip icon in lower left part of screen
(2) Set B_0 field off-resonance — Perform tuning at a field position without a strong ESR signal.

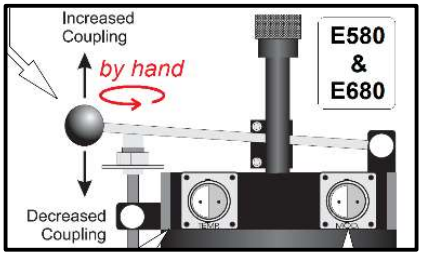
---------- **Coarse Tuning Steps** ----------

(3) Turn Reference Arm off — First, the reflections from the cavity are minimized in isolation from reference.

(4*) Set Attenuation to 20 dB, find *correct* dip → using the Frequency slidebar. Center dip on center line, using the Mode Zoom Factor as required. — Cryostat + blue or black resonator ~ 9.4 GHz; Empty blue resonator ~ 9.8 GHz; Empty rectangular resonator ~ 9.7 GHz

(5) Use the Iris to minimize reflected power at resonator frequency; E580 & E680 adjust by hand





(6) Turn Reference Arm on, with Bias in middle
(7) Set Attenuation to 30 dB and use Phase to get a symmetric dip

---------- **Fine Tuning Steps** ----------

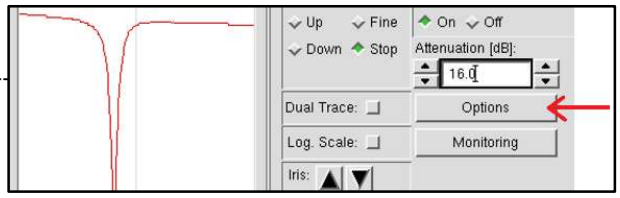
(8*) Set Attenuation to 20 dB and go to Operate Mode

(9*) Center AFC *Lock Offset [%]* within ~ +/-15% w/ Frequency slider

(10) Set Attenuation to 60 dB — This shuts down Transmitter Arm, -60 dB= 1/1,000,000; -3 dB=1/2; -6 dB=1/4.

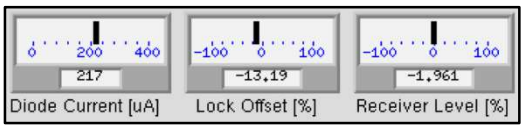
(11) Use Bias to get 200 µA in *Diode Current* — 200 µA is the center of linear detection
(12*) Set Attenuation to 20 dB, center *Diode* with Iris
(13*) Set Attenuation to 10 dB, center *Diode* with Iris
(14) Use Signal Phase to maximize *Diode* — maximize phase coherence of reference and transmitter paths at the diode, possibly skip if (7) is good

(15) Re-center *Diode* at 200 µA w/ the Iris as necessary
(16) Check Tuning at Attenuations from 10 dB to 50 dB in steps of 10 dB Re-center diode with Iris as necessary



---------- **Obtain Q-Value & adjust AFC settings** ----------

(17*) Switch on Tune Mode
(18*) Set attenuation at 33 dB and wait for a green Q-Value, see Options button in Tune window; if Q>3000 DC Gain = 1/10; if Q<3000 DC Gain = 1, AC gain & Mod depth, change 60→90%;
(19*) Set attenuation at 23 dB and switch on Operate Mode, fine adjust Lock Offset with Frequency, … *done*!



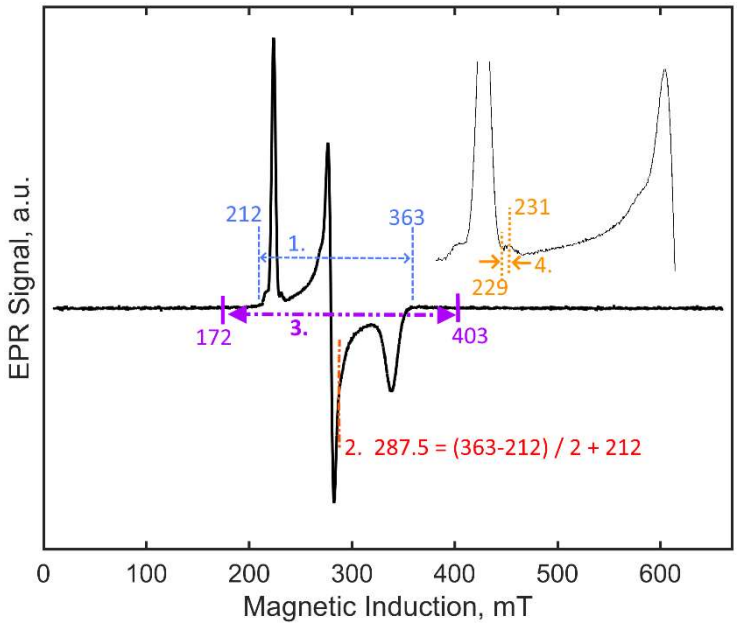
***Next sample in series**: try only steps 1,4,8,9,12,13,17,18,19

========== **Suggested CW-EPR Acquisition Optimization Procedure** ==========

First, complete the previously described Tuning Procedure. Second, determine the extent of the ESR signal in a Zeeman field sweep under moderately high microwave power and modulation amplitude, e.g. ~10 mW and 10 G, respectively, in a field sweep range of 100 to 6600 G, with a sweep time of 120 seconds and a time constant of 20.48 msec (under the Options tab).

Next, carefully determine a number of acquisition parameter values. Some values require iteration.

1. ESR Signal Width (G) _____
High field edge minus low field edge →
2. Center of Signal (G)_____
Field value in middle of the signal →
3. Sweep Width (G) _____
~ **1** + [20 ~ 40] * **4** →
4. Narrowest Feature (G) _____
FWHM or peak-peak width →
5. Mod. Ampl. (G) _____
0.3 * **4**
6. Sweep Time (sec) _____
~10-50 Gauss / sec., or 1-10 min.
7. Time Constant (ms) _____
1 / 10th time to pass narrowest feature

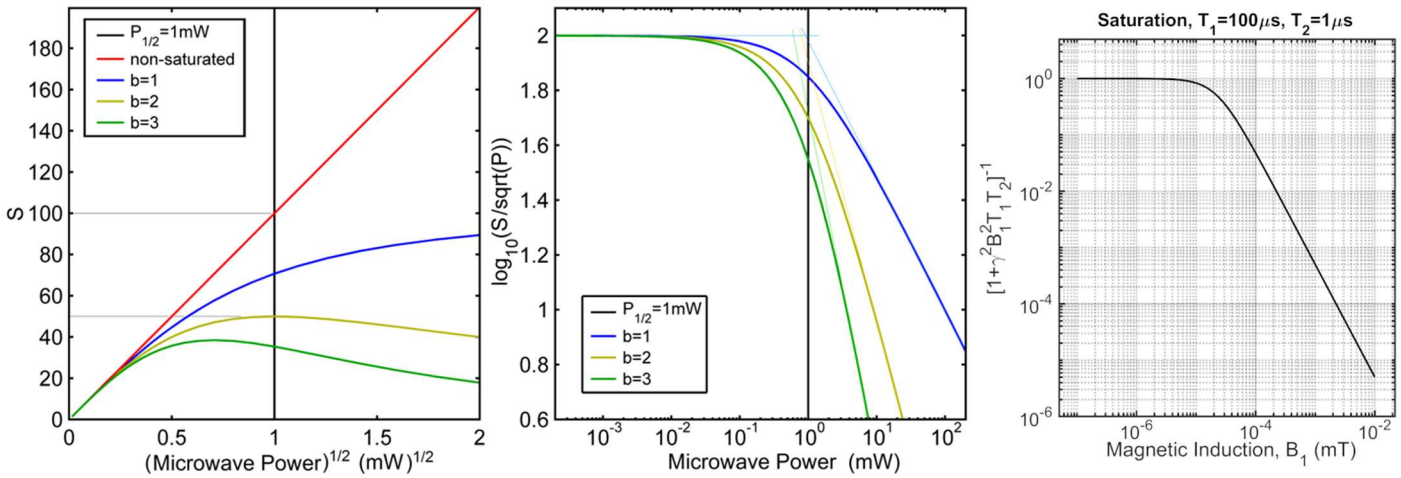


→ Perform a sweep under these conditions. You may need to iteratively change the narrowest feature and modulation amplitude and perform some intermediary sweeps.

8. Microwave Attenuation (dB) _____ Signal is non-saturated at ΔSignal ∝ (ΔPower) ^ 0.5

$$S = K\sqrt{P}\Big/\left[1+\left(P/P_{1/2}\right)\right]^{b/2} \quad \text{or from Bloch,} \quad \text{saturation} \propto [1+\gamma^2 B_1^2 T_1 T_2]^{-1}$$

This relation is of ESR signal amplitude (*S*), which can be defined as the signal amplitude at a single field value, is shown relative to the microwave power (P), using a scalar (K), the value of microwave power for half-saturation ($P_{1/2}$) power, and a homogeneity factor (b). Equation on right has standard definitions.



Saturation Figure. Plots of the microwave power saturation at limits of b = 1 for inhomogenous broadening of ESR lines, an intermediate case of b = 2 and at a limit of b = 3 in the case of homogeneous broadening. The plot on the centre shows a graphical means of estimating the half-saturation power; the Bloch relation is right.

Thorough Process for microwave power optimisation: Measure a two-dimensional data set of field and microwave power and check that all parts of the spectrum are not saturation, such as in the case of anisotropic relaxation behaviour.

Expedient Process for microwave power optimisation: Set the field to the maximum signal intensity point in the spectrum by clicking and dragging the green vertical field marker in the spectrum. Temporarily set the time constant to 655 ms. Go to 10 dB attenuation and set the receiver gain such that the receiver level is somewhere between +/- 60-80%. Find a point in the field sweep range where there is no ESR signal intensity and make sure that the signal level is at zero by using the offset. An attenuation increase of 6 dB = ¼ relative; as Signal = $1/\sqrt{(P)} = ½$, expect a factor of two reduced signal level. Choose the highest power in this case.

Selected Microwave Power Optimizations (*receiver level %*)						
Microwave attenuation (dB)	10	16	22	28	34	40
Microwave power (mW)						
Signal Intensity						

9. Receiver Gain (dB) _____ Max |Signal| to +/- 60-80% Receiver Level [%]

n.b., under the Options Tab, you will have the choice of the Field Settling. The Default is Wait LED off, but for many sweeps of narrow lines or wide sweeps to low field, the better choice is a Given Delay. The delay might be as long as 20-60 seconds for a wide sweep starting at 50-100 Gauss or very narrow lines.

==========

EPR Acquisition Controls

Consider that a microwave resonator and on the EMX with inserted cryostat, the cryostat, may be contaminated with paramagnetic debris and may contain evanescent fields that overlap with metal components of the cryostat. Standard grade chemicals can contain paramagnetic transitions metals and other components that would be problematic. Hence background signals may underly you signal. Here is a prioritisation.

1. Empty Resonator (& cryostat) — Do this early-on to verify signal before other samples/tests
2. Solvent / Buffer minus analyte — Best control for subtracting bkgd, acquire 4x in this case
3. Sample with & without $^3O_2$ — Signals of $^3O_2$ are at all fields, esp. < 15 K, ~550 mT
4. Change concentration by a factors of 10 — Sample might be aggregated
5. Change solvent system, H/D — Sample might be aggregated, Δ conformers
6. Change pH, ionic strength, % glycerol of buffer — Sample might be aggregated
7. Change freezing method — Sample might be aggregated
8. Try turbo-pumping of powder / film sealed sample — O_2 / H_2O might be very difficult to remove
9. Change wavelength, irradiance, light on / light off — Additional controls for light-induced signals

========== **Brief Notes on Pulsed EPR Acquisition Optimization** ==========

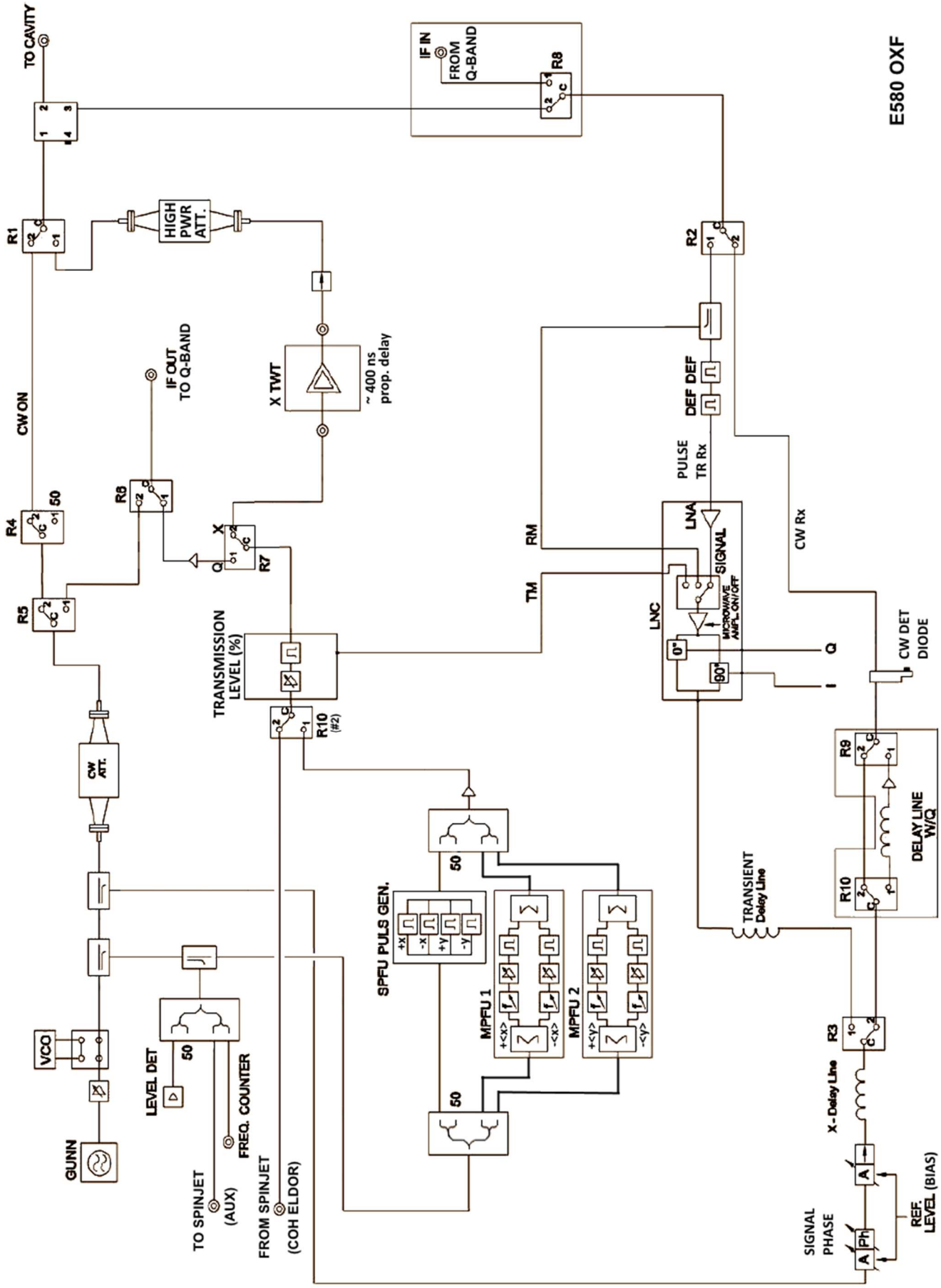
I. After completing relevant CW-EPR studies, in Tune Mode, ***Over-Couple the Resonator***.

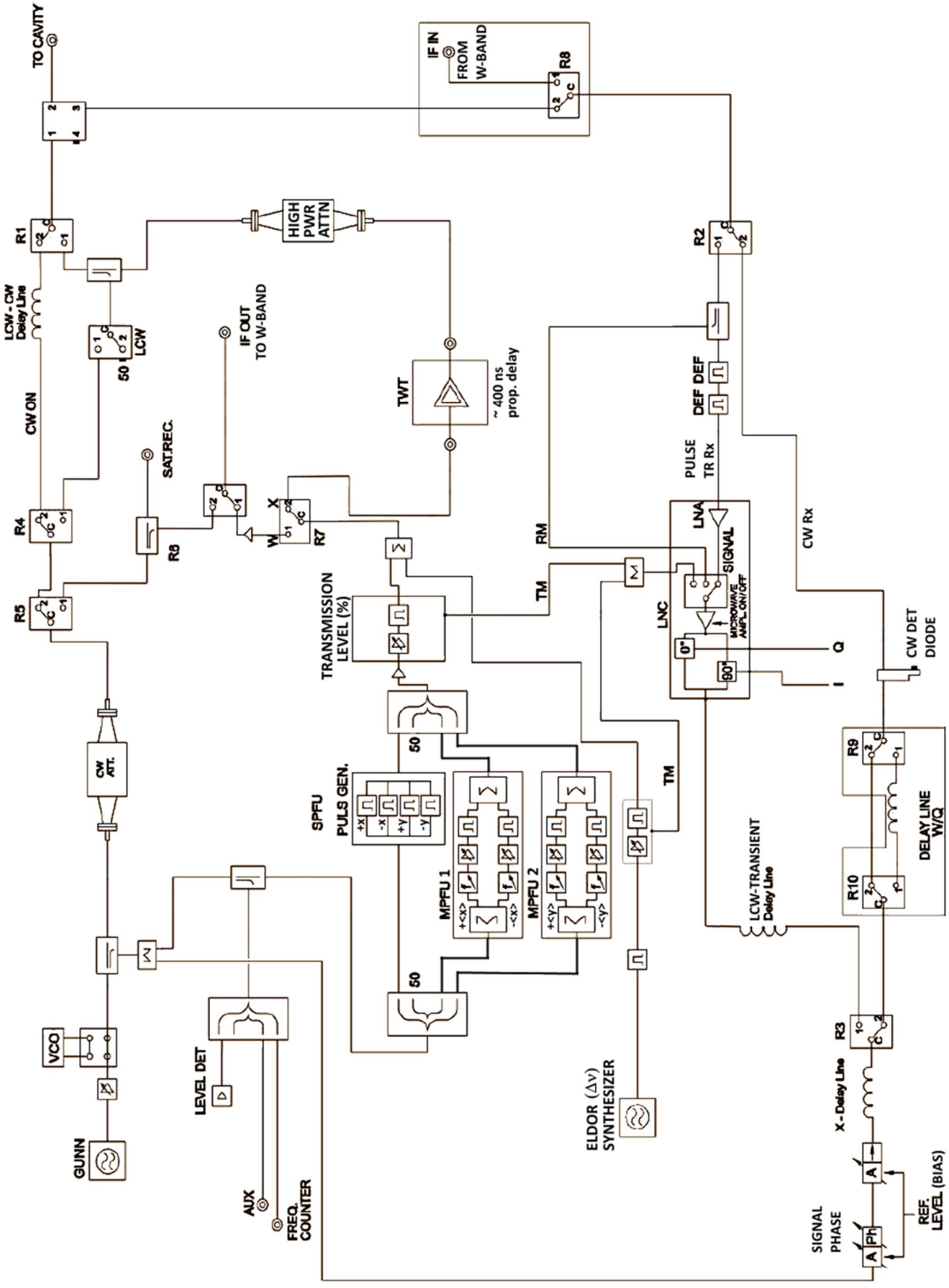
II. Double-check FT-Epr PDCH setup in Spectrometer Configuration and Turn on the TWTA in Standby mode for 3-10 minutes. Meanwhile, do the ***Safety Test***. Make a 16 ns pulse on a functioning channel and give the Acquisition 40 ns length at position 0 ns. Set 48 dB Video Gain, Set HPA to 60 dB, and SpecJet averages to 1024. See Defense pulses and verify with Signal Phase. Stop sequence in Tables.

III. Check that HPA is at 60 dB and put TWTA in Operate, Start a 16 ns-300 ns-32 ns-300 ns-[echo] sequence. Acquisition should be ca. 700 ns so you can see the end of the Defense pulse. Slowly decrease HPA from 60 dB by 3-10 dB to 0 dB. ***Check for ringing*** caused by a higher Q-factor than expected. If ringing occurs, *STOP*. Increase the Protection Pulse in Spectrometer Configuration & repeat, or ask for help.

IV. If an echo is seen, decrease HPA attenuation to the 1st echo maximum, achieving optimized pulses.

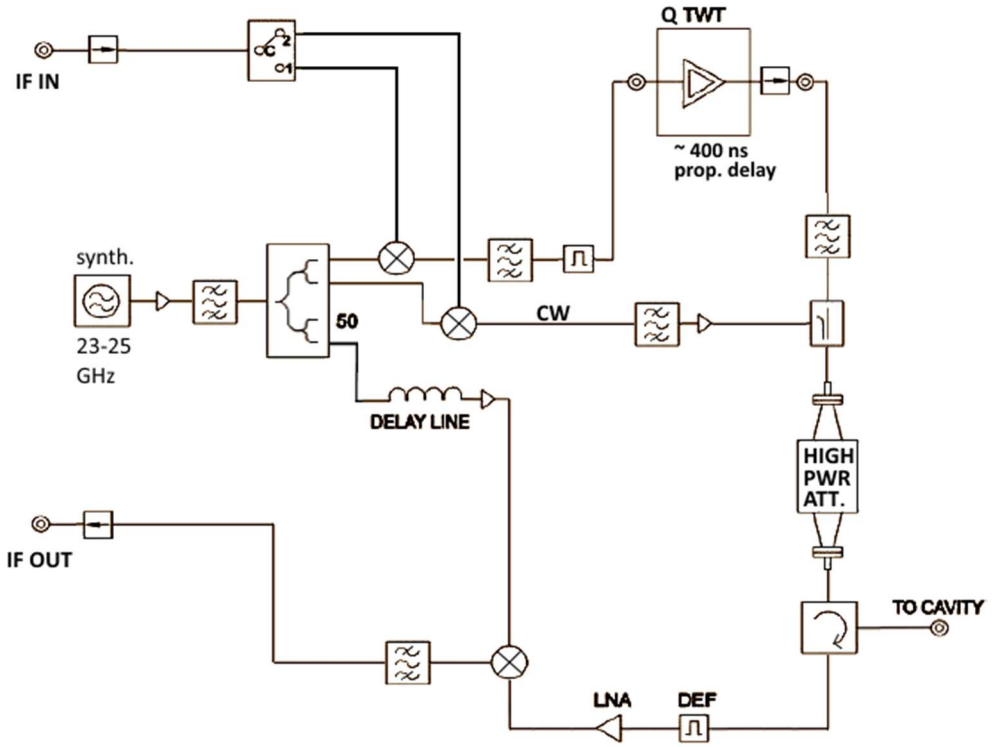
As in NMR, canonical pulse sequence elements are [preparation]…[mixing]…[detection], where the mixing step can involve changes to coherence, e.g. HYSCORE, and/or populations, e.g. ENDOR. Pulses of a sequence should be as accurate as possible in amplitude and phase. A sufficiently long phase-memory time (T_M) is required, or Pulsed EPR won't be possible. You should read in detail the respective literature of the sequence you are using to ensure the phase cycle is correctly selected and programmed; furthermore, considerations on sample preparations must be carefully optimized for the expected sequence sensitivity.


E580 OXF
TO CAVITY
IF IN
FROM
Q-BAND
R8
R1
HIGH
PWR
ATT.
R2
CW ON
IF OUT
TO Q-BAND
X TWT
~ 400 ns
prop. delay
DEF DEF
PULSE
TR Rx
R4
50
R6
X
Q
R7
RM
LNA
SIGNAL
CW Rx
R5
TM
LNC
MICROWAVE
AMPL ON/OFF
0°
90°
Q
I
TRANSMISSION
LEVEL (%)
R10
(#2)
CW DET
DIODE
CW
ATT.
R9
DELAY LINE
W/Q
TRANSIENT
Delay Line
R10
50
SPFU PULS GEN.
+X
-X
+Y
-Y
MPFU 1
MPFU 2
+<X>
-<X>
+<Y>
-<Y>
VCO
LEVEL DET
50
R3
X - Delay Line
GUNN
TO SPINJET
(AUX)
FREQ. COUNTER
FROM SPINJET
(COH ELDOR)
SIGNAL
PHASE
A
Ph
REF.
LEVEL (BIAS)

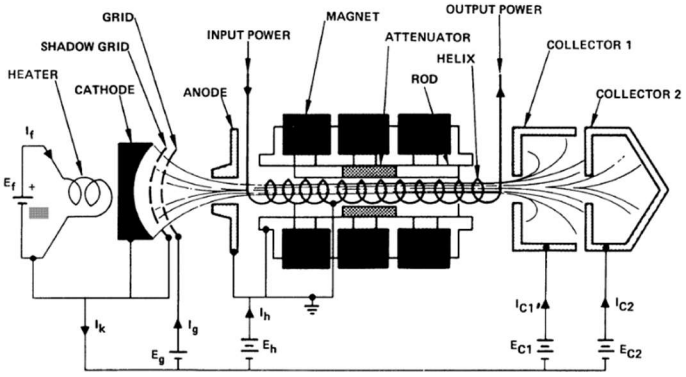


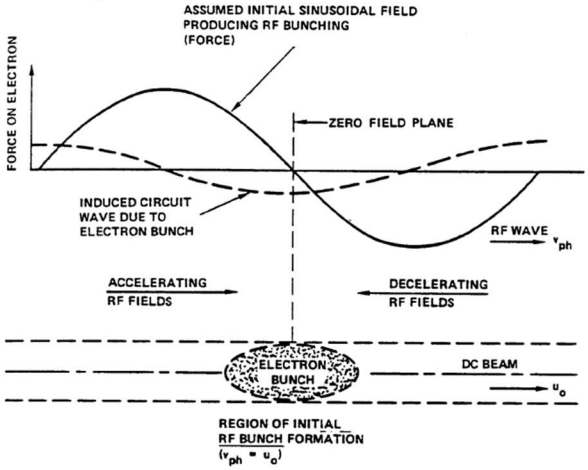
E680 X-band Bridge Schematic

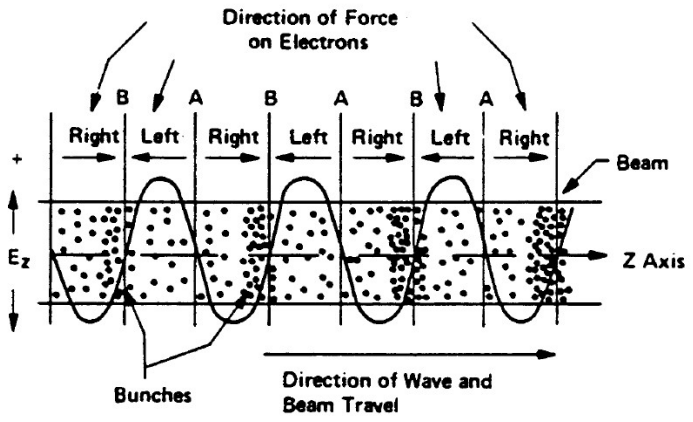
Q-band IF Bridge Schematic, E580 Oxford

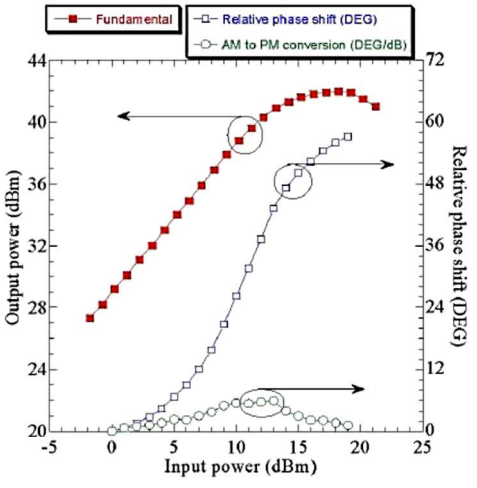


TWT-A, briefly: The electrons traveling through the helix continuously drift toward the decelerating electric field of RF causing an increase in wave amplitude. The electrons will lose kinetic energy and gain potential energy, thereby adding energy to the retarding field. The modulated electron beam close to a slow wave circuit induces an image current, 90 deg. out of phase, acting as capacitive RF load to slow down wave.









EPR standard: clear fused, γ-irradiated SiO_2

Wilmad cat.# WG-R-E01; 4mm O.D. fused quartz rod
Irradiated by NIST to a dose of 261 Gy with ^{60}Co gamma source. X-band reference standard for pulsed EPR: 100M. E'_1 centres are set by heating at 575 K and are annealed by heating the above 700 K.

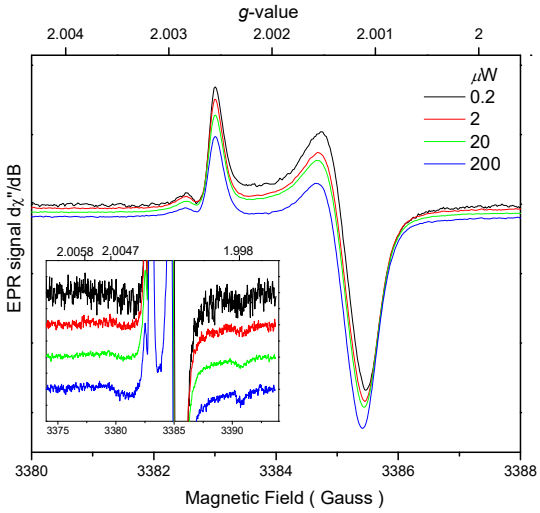


Figure. EPR tube exposed to synchrotron beamline as measured at room temp., above, and 5K, below. (what's wrong with this plot?). $A(^{29}Si) \sim 420$ G.

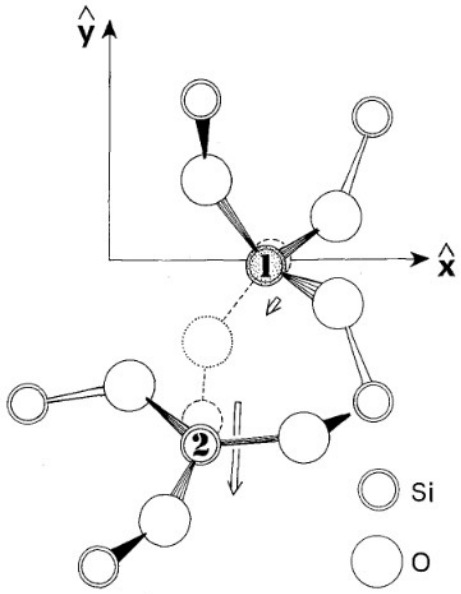
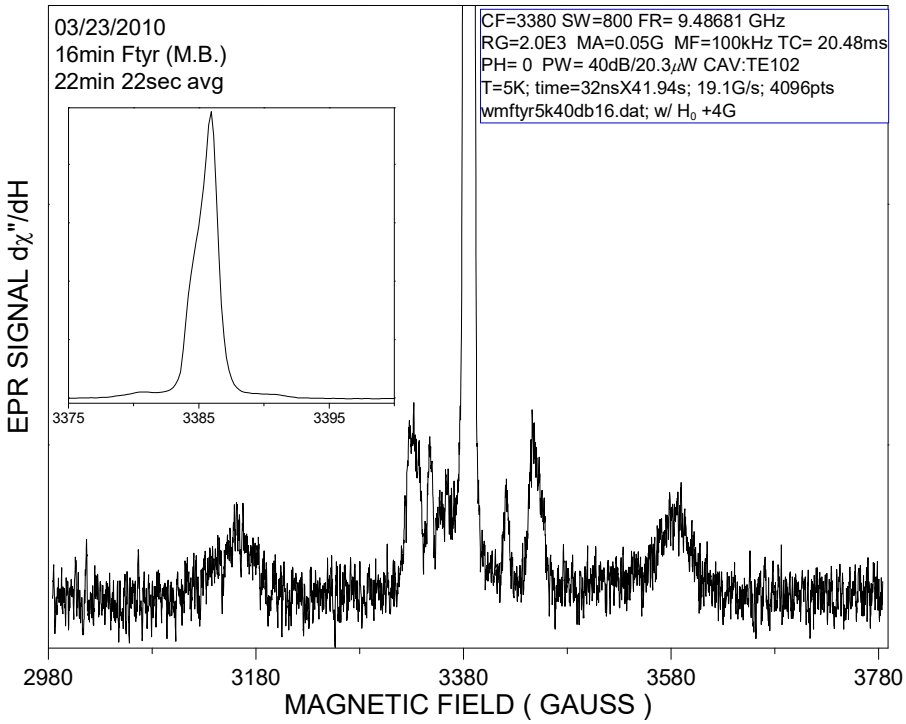


Fig. 11. Model of the E'_1 centre, showing the missing bridging oxygen ion between Si(1) and Si(2) as a dotted circle. The optic axis ê is perpendicular to the plane of the figure. The open arrows indicate computed asymmetric relaxation of the two silicon positions. The unpaired electron is predominantly located on Si(1). Reference: Isoya et al. 1981



1. CW-EPR detection
(mw power, dB_0/dt, mod. Ampl.)

2. Pulsed FID and Echo FT-EPR

3. On-res. vs. Off-res. Echoes

4. Echo-det. Field sweep
(pulse length, $\Delta E_s \Delta t \geq \hbar/2$.)

5. FID det. Field sweep

The following value will prove useful: $\frac{h}{\mu_B} \equiv \frac{4\pi m_e}{e} = 71.447735\ \text{mT GHz}^{-1}$.

Simulations and analysis of crystalline right-hand α-SiO_2

Spin Hamiltonian $\mathcal{H}_0 = \mu_B \vec{B}' \cdot g \cdot \hat{S}_z + \sum_{j=1}^{3} \hat{I}'_j \cdot A_j \cdot \hat{S}$ $\mathcal{H}_1 = \mu_B \vec{B}'_1 \cdot g \cdot \hat{S}_x$

Electron Zeeman

$g_e = 2.00231930436$

$g_{iso} = 2.0008$

Δg (g_{eff}-g_e) principle values; [-6 -18 -20] x10^{-4}; Silsbee 1961

[-6 -18 -21] x10^{-4}; Feigel, Anderson 1970

Hyperfine Interactions { ^{29}Si (4.685% natural abundance), I=1/2, Silsbee 1961}

1 cm^{-1} = 29,979.2458 MHz, values in 10^{-4} cm^{-1}

$A_1(1) = 424$; $A_{2,3}(1) = 364$; (orientations omitted here…)

$A_1(2) = 8.61$; $A_{2,3}(2) = 6.89$;

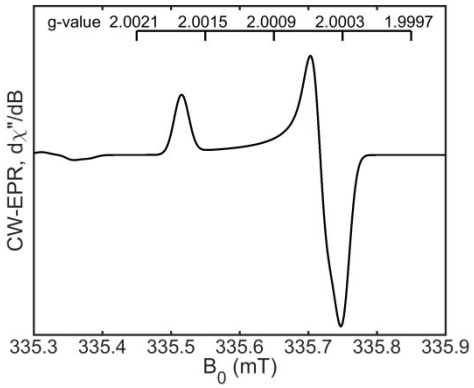
$A_1(3) = 9.15$; $A_{2,3}(3) = 7.34$;

EPR Simulation outline

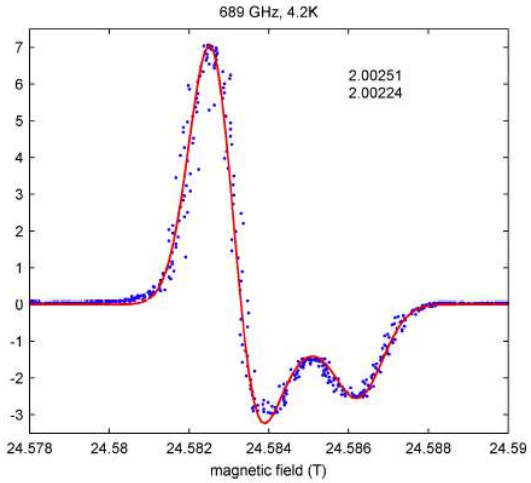
1. Build Hilbert space spin matrices, separate isotropic and anisotropic terms
2. Make orientational grid in lab frame and determine geometric weights
3. For each sample orientation in magnet find resonance field:
   a. Rotate anisotropic G-matrix into new position
   b. Solve eigenvalues vs. field, possibly with optimized sparsity
   c. Find field positions where transitions (Ei-Ej) = microwave frequency
   d. Calculate transition intensity: $geom.weight \times (\rho_j - \rho_i) \left| \langle i | \hat{S}_x | j \rangle \right|^2$
4. Interpolation over orientational grid, f(intensity, field)
5. Construct spectrum with lineshape convolved at each resonance field position
6. Interpolation to desire field range and number of points
7. Convolution to field derivative

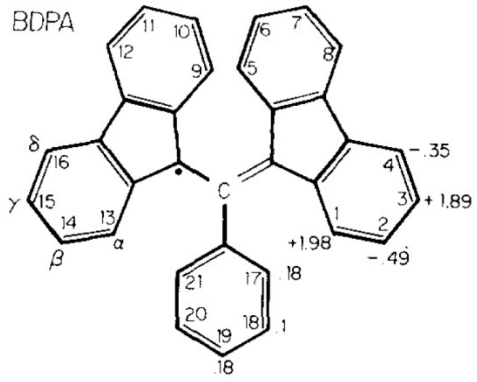
<u>simulation input and plotting</u>

```
clear all; clc; fs = 12; lw = 1.25;
sys.g = [-6 -18 -20]*1e-4 +2.00231930436;
sys.lw = [0.05 0.1];
sys.Nucs = 'Si,Si,Si';
sys.A = [424 364 364;8.61 6.89 6.89; 9.15 7.34 7.34].*1e-4*29979.2458;
sys.lw = [0.025 0];
exp.mwFreq = 9.4;
exp.nPoints = 65536;
exp.Harmonic = 1;
exp.Range = [-1 1]*50+71.447735*exp.mwFreq/mean(sys.g);
opt.GridSize = 96;
opt.Method = 'matrix';
[x,y,trans] = pepper(sys,exp,opt);
figure(1); clf;
plot(x,y,'k','LineWidth',lw); hold on;
xtick = (335.45:0.1:335.85);
ylev = [1.15*max(y) 1.25*max(y)];
for ii = 1:numel(xtick)
    plot([xtick(ii) xtick(ii)],[ylev(1) ylev(2)],'k','LineWidth',lw-1); hold on;
    text(xtick(ii)-0.04,1.35*max(y),num2str(71.447735*exp.mwFreq./xtick(ii),'%1.4f'));
end
plot([xtick(1) xtick(end)],[ylev(2) ylev(2)],'k','LineWidth',lw-1);
text(xtick(1)-0.13,1.35*max(y),'g-value');
pbaspect([1.25 1 1]); axis tight; box on;
xlim([335.3 335.9]); ylim([1.05*min(y) 1.5*max(y)]);
xlabel('B_0 (mT)','FontSize',fs,'FontName','Arial');
ylabel('CW-EPR, d\chi"/dB','FontSize',fs,'FontName','Arial');
title(' \alpha-SiO_2','FontSize',fs,'FontName','Arial');
set(gca,'ytick',[],'LineWidth',lw,'FontSize',fs,'FontName','Arial');
```



BDPA, 0.5% by weight in polystyrene





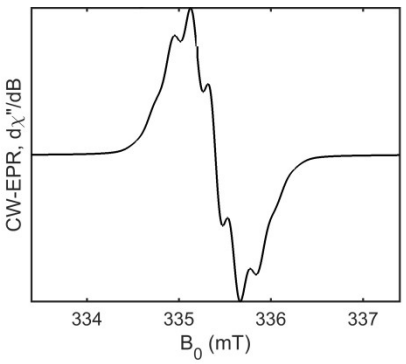
α,γ-bisdiphenylene-β-phenylallyl, hyperfine values in Gauss

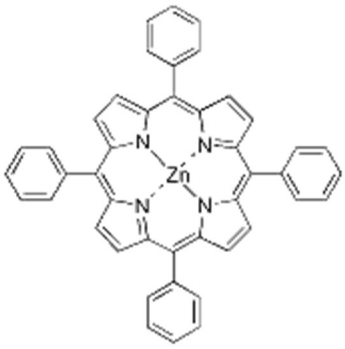
X-band		Bruker Pulse Course 2007	
0.	CW-EPR to verify signal	3-1 to 3-25	(*E500 basic manual*)
1.	Find and optimize echo signal	4-13 to 4-24	5-37 to 5-39
2.	Do an echo-detected field sweep	5-40 to 5-43	
3.	Set field to max of signal		
4.	Davies-ENDOR	14-1 to 14-8; 7-1 to 7-10	14-21 to 14-25 (*E560 ENDOR manual*)
5.	Mims-ENDOR	14-11 to 14-13; 8-11 to 8-18	(*E560 ENDOR manual*)
6.	*ELDOR-detected NMR*	*10-13 to 10-14;*	

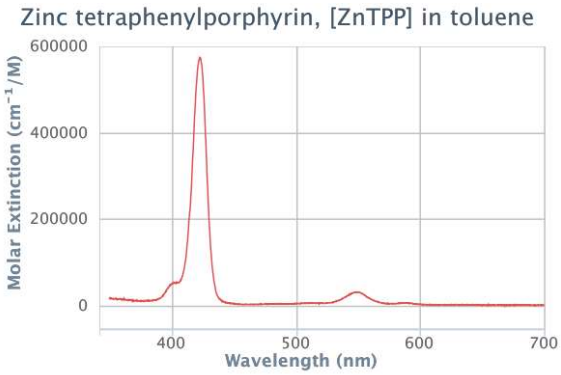
simulation input and plotting

```
clear all; clc;
fs = 12; lw = 1.25;

sys.g = [2.00251 2.00251 2.00224];  % Stoll 689 GHz data, isotropic value 2.00242
sys.Nucs = '1H,1H,1H,1H,1H,1H,1H,1H'; %,1H,1H,1H,1H,1H,1H,1H,1H,1H,1H,1H,1H,1H';
sys.A = [1.98;1.98;1.98;1.98;1.89;1.89;1.89;1.89].*2.8025; %;...
%-0.49;-0.49;-0.49;-0.49;-0.35;-0.35;-0.35;-0.35;0.18;0.18;0.18;0.1;0.1].*2.8025;
sys.lw = [0.20 0.1];
exp.mwFreq = 9.4;
exp.nPoints = 2048;
exp.Range = [-1 1]*2+71.447735*exp.mwFreq/mean(sys.g);
opt.GridSize = 64;
opt.Method = 'perturb';
[x,y,trans] = pepper(sys,exp,opt);
figure(1); clf;
plot(x,y,'k','LineWidth',1.25);
pbaspect([1.25 1 1]); axis tight; box on;
xlabel('B_0 (mT)','FontSize',fs,'FontName','Arial');
ylabel('CW-EPR, d\chi"/dB','FontSize',fs,'FontName','Arial');
title('BDPA, g = 2.00254 +/- 0.000032','FontSize',fs,'FontName','Arial');
set(gca,'ytick',[],'LineWidth',lw,'FontSize',fs,'FontName','Arial');
```

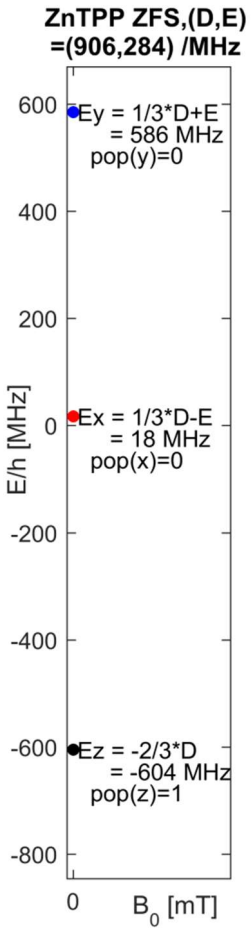






http://omlc.org/spectra/PhotochemCAD/html/100.html

A LASER flash of ca. 7 ns length produces an excited singlet state (S=0) that leads to the formation of an excited triplet state (S=1) via inter-system crossing (ISC). Typically, this would be at 355 nm or 532 nm with a Nd:YAG LASER, but with an Optical Parametric Oscillator (OPO) now in CAESR, 410-1700 nm are presently available via fibre coupling to any of the three magnets in F11 & F12. This allows selection of the $S_0 \rightarrow S_2$, Soret band, a.k.a. B-band, at ca. 423 nm and $S_0 \rightarrow S_1$, Q-band, ca. 550 nm.



1) Soret: $\epsilon_{423nm} = 572.6\ cm^{-1}\ mM^{-1}$
2) Q-band: $\epsilon_{550nm} = 29.5\ cm^{-1}mM^{-1}$

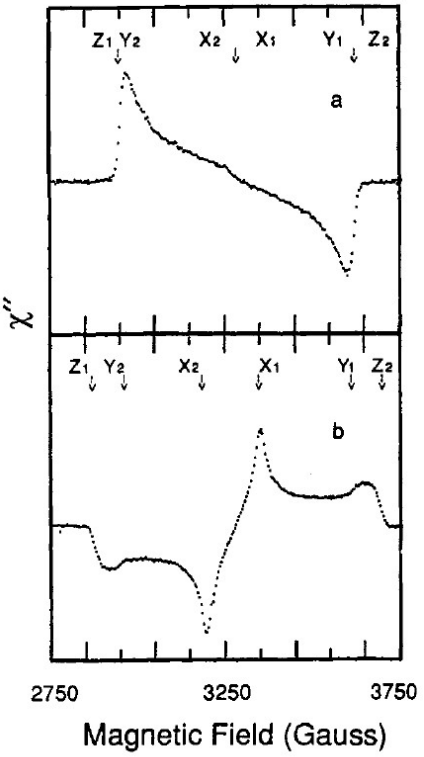


Figure 7. Direct detection time-resolved triplet EPR spectra of porphyrins in toluene glass: ZnTPP (a), H_2TPP (b), Spectra were recorded at 140 K

The inner diameter of the EPR tube is 2.5 mm, so for photoexcitation at 550 nm and an objective of an Absorbance of 2, the concentration would be ~0.27 mM. Choice of photoexcitation with a lower molar extinction has the advantage of allowing higher sample concentrations. However, higher sample concentrations may lead to aggregation and additional photophysical considerations like triplet-triplet quenching. In porphyrins, the Q-band region is also complicated by photoselective properties of molecular orientation.

	Zero-Field Splitting (ZFS)		g-value			ISC ratio	
	D/MHz	E/MHz	g_x	g_y	g_z	Px-Py:Pz-Py	Ref. (DOI)
ZnTPP	906	284	2.0020	2.0024	1.9968	0:1	10.1021/jp1023197

Based on Discussion: DEER, with AWG, using PulseSPEL (see NotesOnDEER.txt)

Hands-on Instrument Use

Bruker DEER standard, bis-nitroxide, 22 Å apart.

85 Kelvin *Not a Coal sample!*

Bruker Pulse Course 2007

0.	CW-EPR to verify signal (optional, skip)	3-1 to 3-25	(*E500 basic manual*)
1.	Find and optimize echo signal; SRT ~ 200 us Variation of high power attenuator setting, field position	4-13 to 4-24	5-37 to 5-39
2.	Do an echo-detected field sweep Centre at g~2.005, sweep width 150 Gauss, 300 points, 100 shots Acquisition from Tables		5-40 to 5-43
3.	Set field to max of signal Check SpecJet with 1 shot. If it clips the window, then optimize Video Gain and go back to step 2.		
4.	Inversion recovery with echo detection (T_1) Load program, defs in PulseSPEL (button at bottom of Expt window) Acquisition from PulseSPEL, compile program & defs in PulseSPEL	6-1 to 6-23;	8-5 to 8-11
5.	2-pulse decay of phase memory time (T_M) x-axis label should be 2 tau.	6-8 to 6-10;	8-15 to 8-17
6.	2-pulse ESEEM x-axis label should be tau.	7-1 to 7-9;	9-1 to 9-9
7.	3-pulse ESEEM x-axis label should be tau + T.	7-9 to 7-11;	9-14 to 9-28
		Background Reading	**Straight Procedure** ***See print-out***