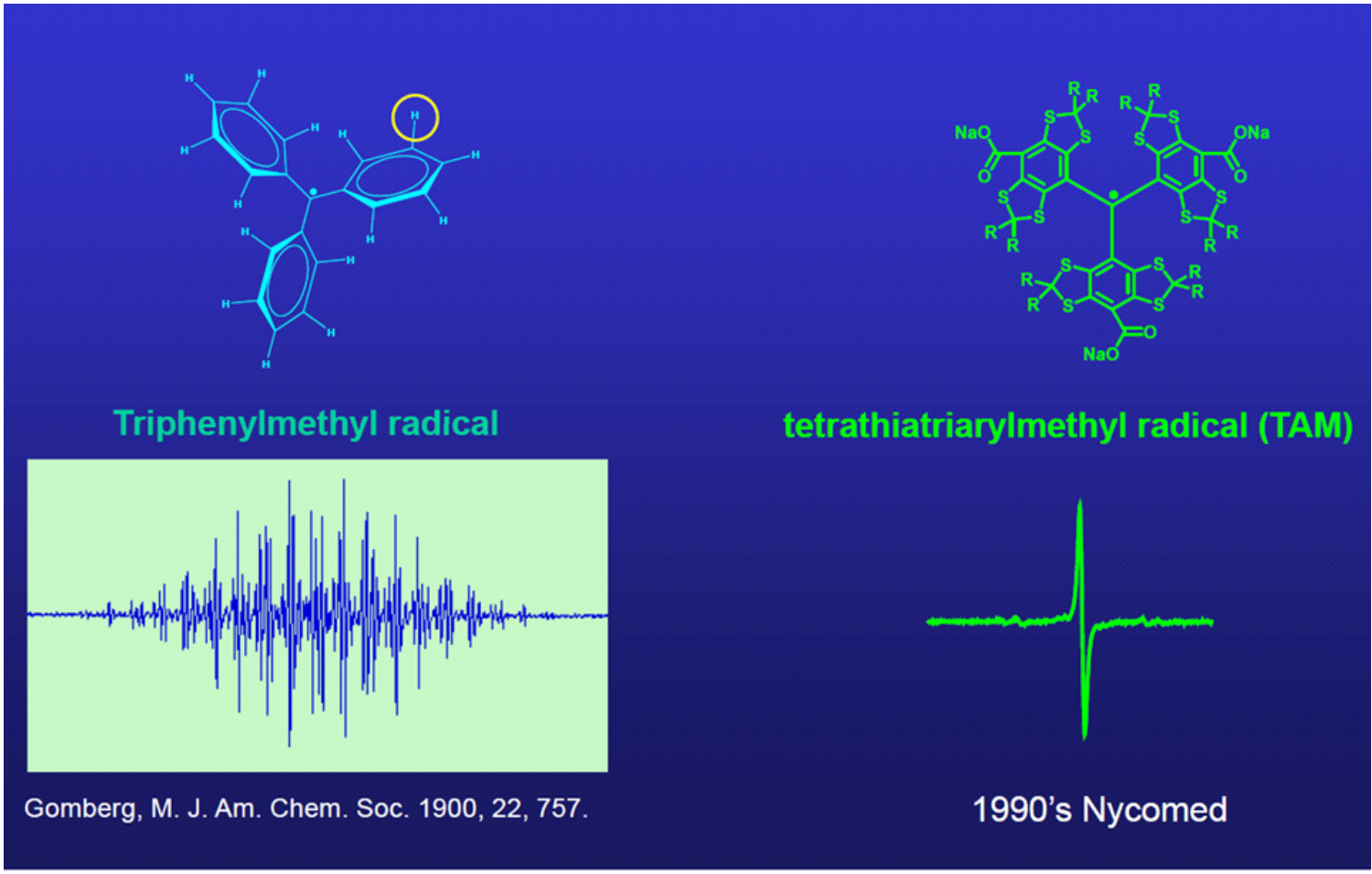
Simulation von EPR Spektren (Flüssig/Fest)



to complex
(many proton couplings)

← from simple (1 line)

Easy Spin Simulationssoftware (free, Matlab program benötigt)
Stefan Stoll (University of Washington, Seattle)

Simulation von
- Flüssig-EPR
- Festkörper EPR
- Slow-Motion EPR
- Puls-EPR

Einfache Skriptfiles zum Erzeugen des Spektrums

```
% EPR von Radikalen in Flüssigkeiten
clear

Sys.g = 2.0;
Sys.lw = [0 0.5];

Sys.Nucs='14N';
Sys.A=[50];
Sys.n=[2];

Exp.mwFreq=9.4;
Exp.Range=[300 370];

garlic(Sys,Exp)
```

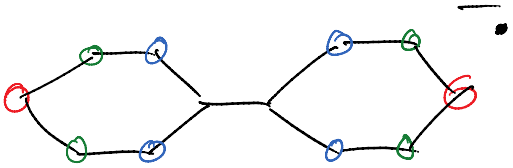
Einheiten und weitere Erklärungen in Online-Dokumentation

Sys beschreibt Molekül

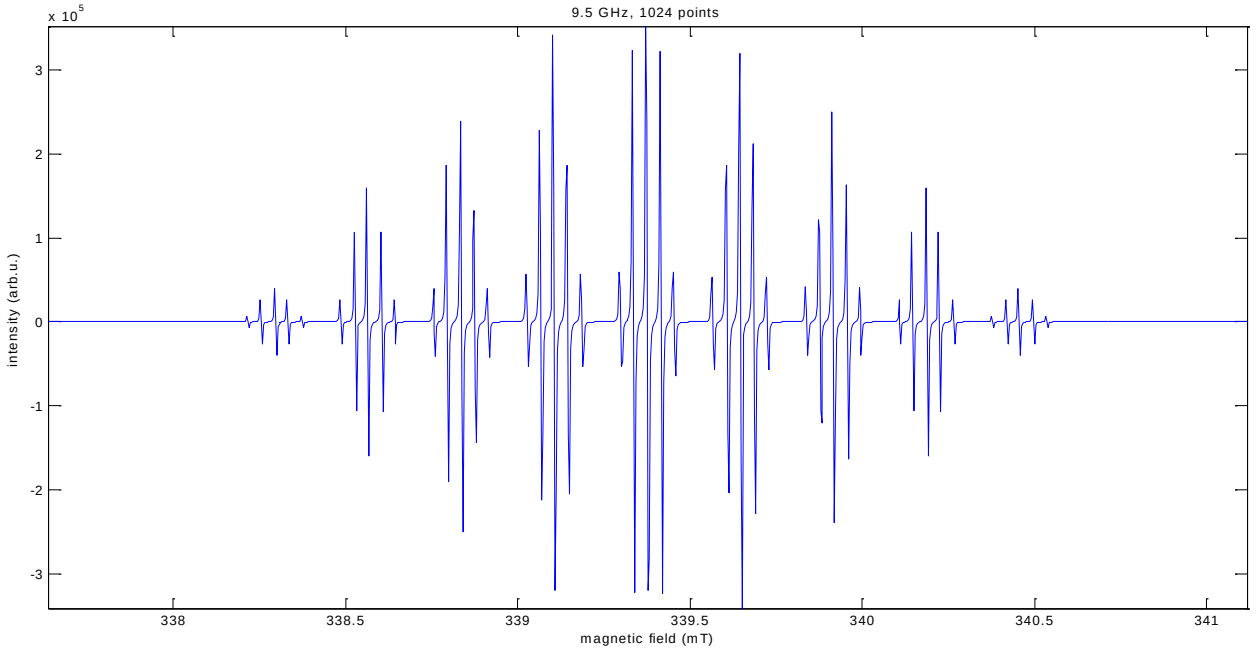
Exp beschreibt Experiment

↳ Programm für Flüssig-Spektren

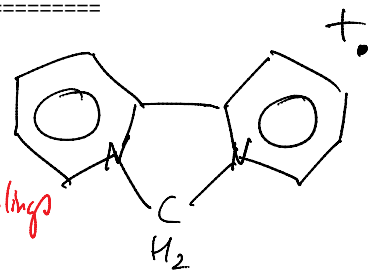
```
% Biphenyl radical anion
%========================================================================
% Hyperfine values taken from Gerson book, p. 114

clear, clf

Sys.g = 2;
Sys.Nucs = '1H,1H,1H';
Sys.n = [2 4 4];
Sys.lwpp = [0,0.001];
Sys.A = [-15.10 -7.59 1.10]; % MHz

Exp.mwFreq = 9.5;

garlic(Sys,Exp);
```



Multiplizität



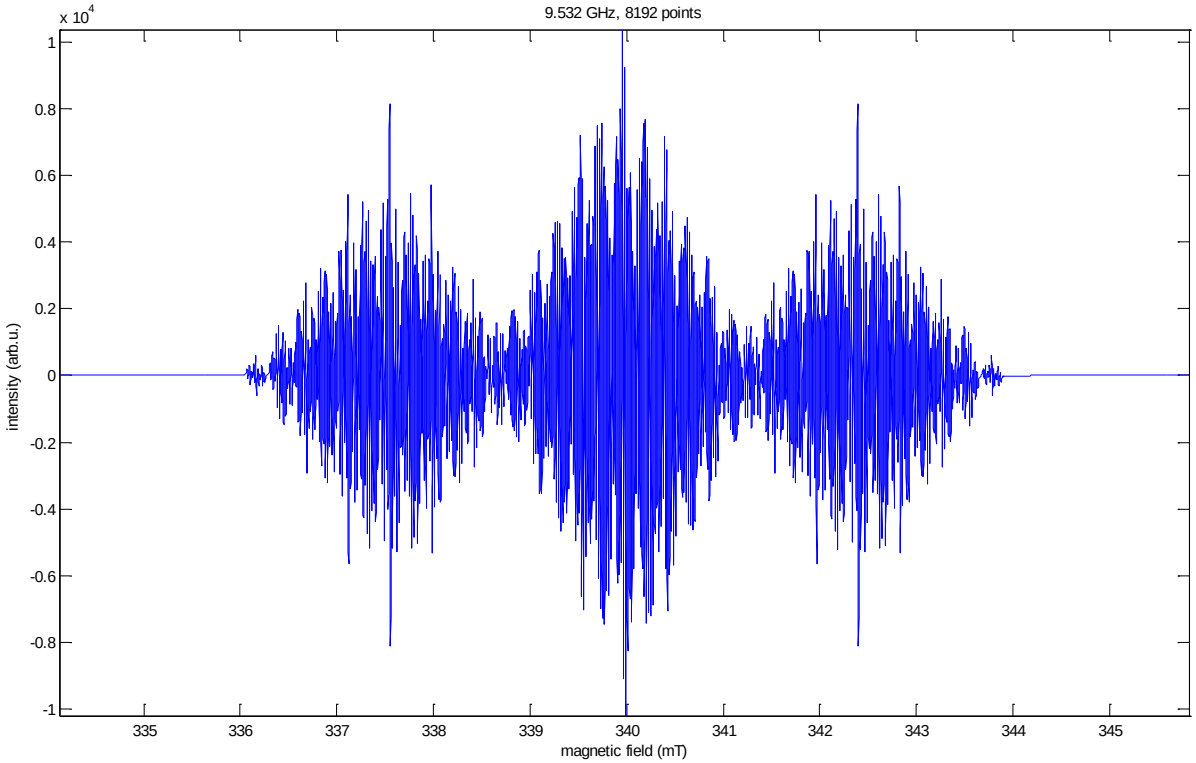
```
% Bridged biaryl cation radical (1000s of lines)
%
================================================================
========
% Cation radical of 6-hydrodipyrido[1,2-c:2',1'-e]-imidazole
% The spectrum contains a total of 9216 resonance lines.

clear, clf

% Hyperfine couplings in units of Gauss (from literature)
A_Gauss = [+4.34,-2.39,-0.65,-2.81,-0.23,+24.24];
A_MHz = mt2mhz(A_Gauss/10,gfree); % xonversion to MHz

% The spin system contains a total of 12 nuclei, in groups of 2
Sys.g = 2.00316;
Sys.Nucs = '14N,1H,1H,1H,1H,1H';
Sys.n = [2 2 2 2 2 2];
Sys.A = A_MHz;
Sys.lwpp = [0,0.01];

Exp.mwFreq = 9.532;
Exp.nPoints = 8192;

% Simulation and plotting of the solution cw EPR spectrum
garlic(Sys,Exp);
```



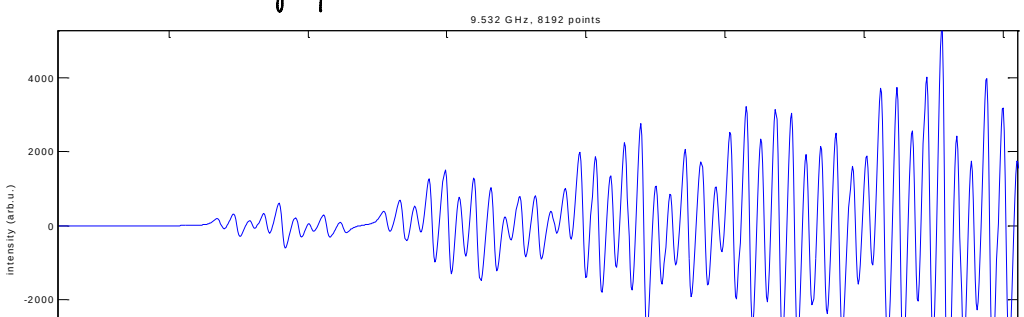
} hf couplings

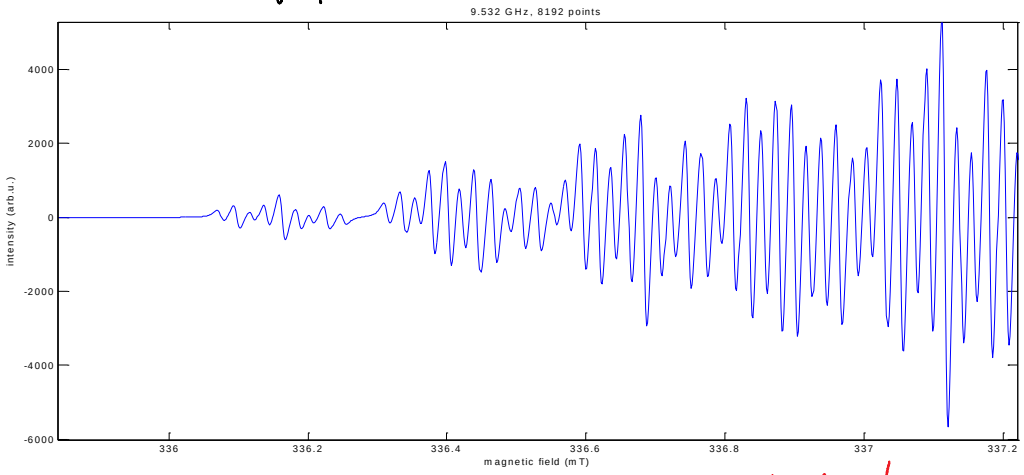
type of nucleus
multiplicity

Run Simulation

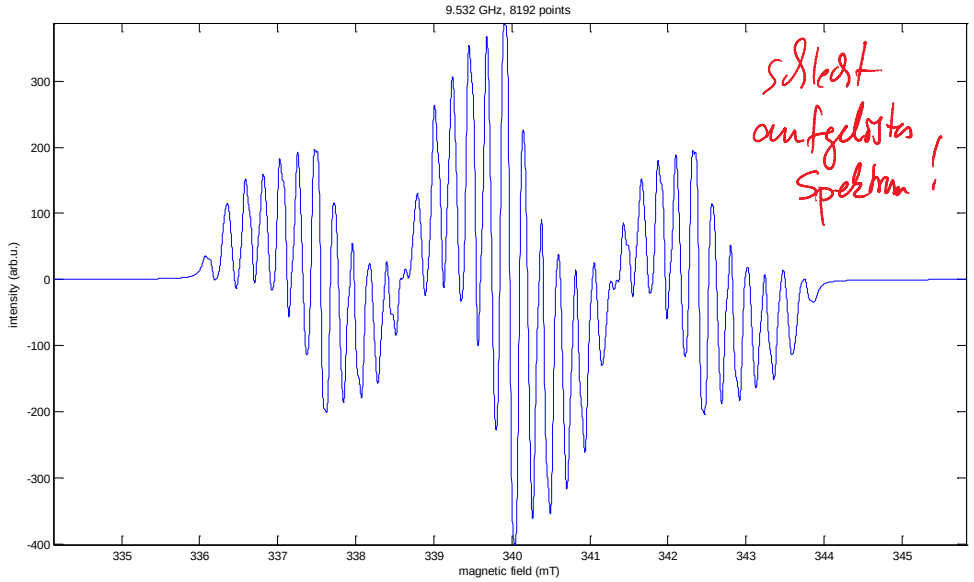


Vergrößerter Ausschnitt:





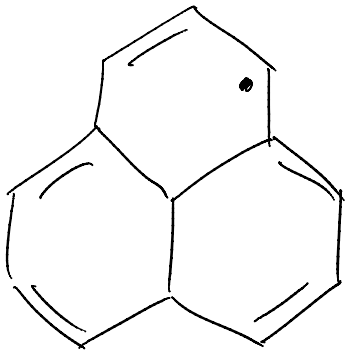
Sys.lvpp = [0,06] → falls Lösemittel nicht Sauerstoffrei!



schlecht aufgelöstes Spektrum!

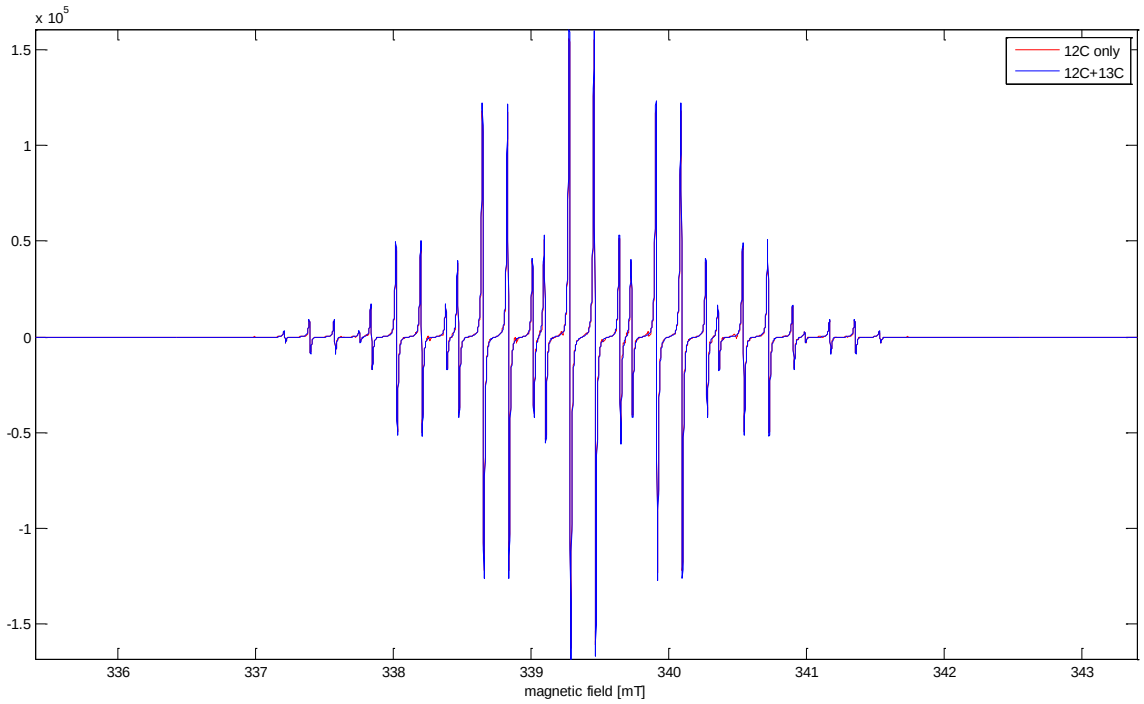
```
% Phenalenyl radical anion, including 13C satellite lines
%==========================================================================
% EasySpin can automatically simulate the spectra resulting from
% isotope mixtures. Here, we simulate the spectra of the phenalenyl
% radicals with (a) pure 12C and (b) natural-abundance 13C. The small
% 13C contents leads to small satellite peaks.

% Hyperfine values taken from Gerson book, Table 8.4, page 225

clear, clf

% Parameters
%--------------------------------------------------------------------------
A_H = [-0.629 +0.181]; % in mT
A_C = [+0.966 -0.784 -0.784]; % in mT
Sys.g = 2;
Sys.n = [6 3 1  1  1];
Sys.A = mt2mhz([A_H A_C]);
Sys.lwpp = [0, 0.01];  % Lorentzian line shape

Exp.mwFreq = 9.5;
Exp.CenterSweep = [339.4 8];
Exp.nPoints = 10000;

% Simulations
%--------------------------------------------------------------------------
% Spectrum of species with all 12C
Sys.Nucs = '1H,1H,12C,12C,12C';
[x,y0] = garlic(Sys,Exp);

% Spectra with species containing natural-abundance 13C
Sys.Nucs = '1H,1H,C,C,C';
[x,y1] = garlic(Sys,Exp);

% Plotting
%--------------------------------------------------------------------------
plot(x,y1,'r',x,y0,'b');
xlabel('magnetic field [mT]');
axis tight
legend('12C only','12C+13C');
```

Matlab Programmsprache

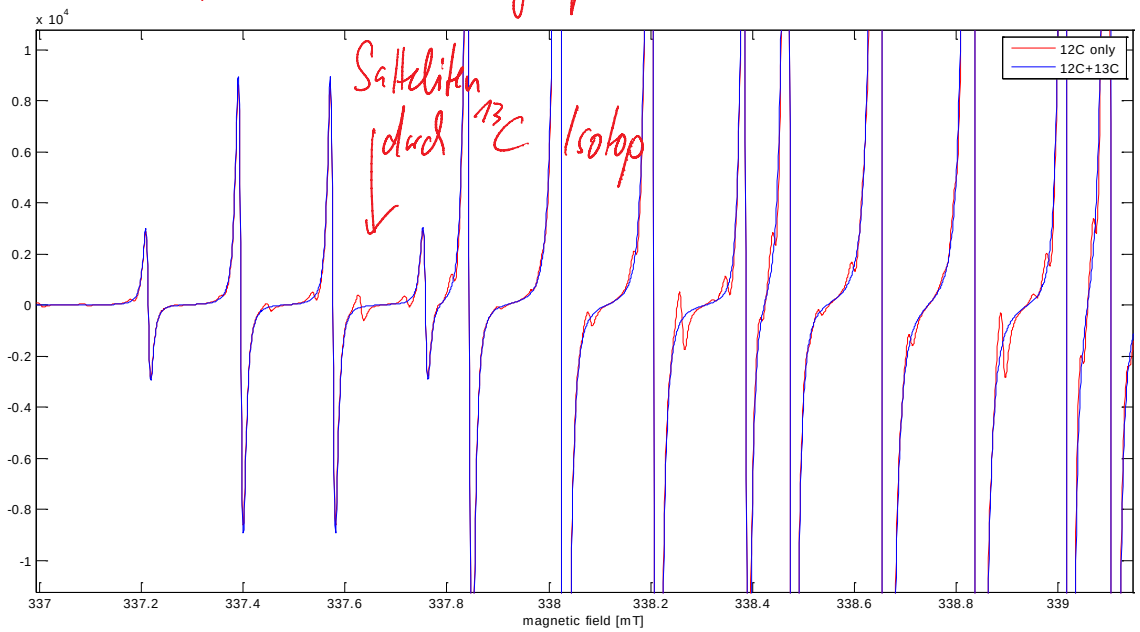


Durch Pyrolyse von Petrolium mit O_2 und Proton-Abspaltung kann zu diamagnetischem Dimer reagieren

Durch Erhitzen wieder Monomer Anion-Radikal



Ausschnitt Vergrößert:



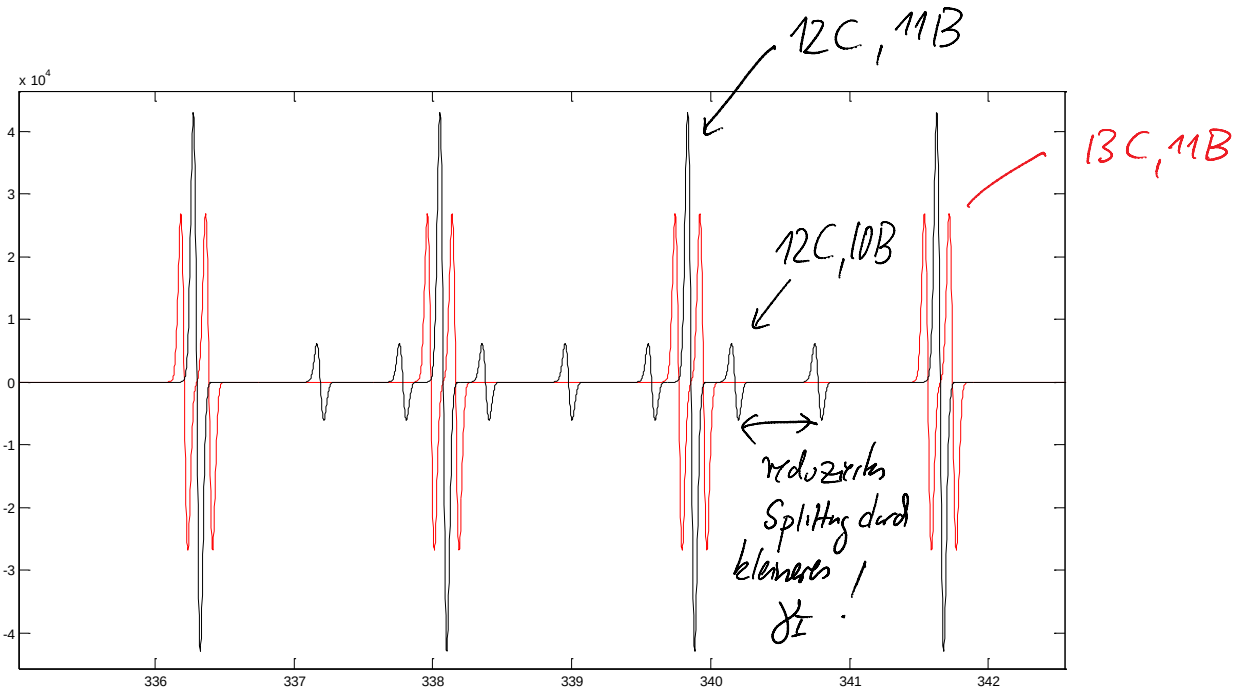
```
% Simple isotope mixture
%========================================================================

clear
Sys.A = [5 50];
Sys.n = [1 1];
Sys.lwpp = 0.05;
Exp.mwFreq = 9.5;
Exp.Range = [330 348];
Exp.nPoints = 1e4;

Sys.Nucs = '13C,11B'; [x,y1] = garlic(Sys,Exp);
Sys.Nucs = '12C,B';  [x,y0] = garlic(Sys,Exp);

plot(x,y1,'g',x,y0,'k');
```

Lösung 1
Lösung 2

Bor hat 20 unterschiedl. magn. Isotope

^{10}B $I = 3$ 20 % 7 Linien $\nu_{Zeeman}^{I} = 32\,MHz$ (bei 7 T B_0)

^{11}B $I = 3/2$ 80 % 4 Linien $\nu_{Z}^{I} = 96\,MHz$ (bei 7 T B_0)

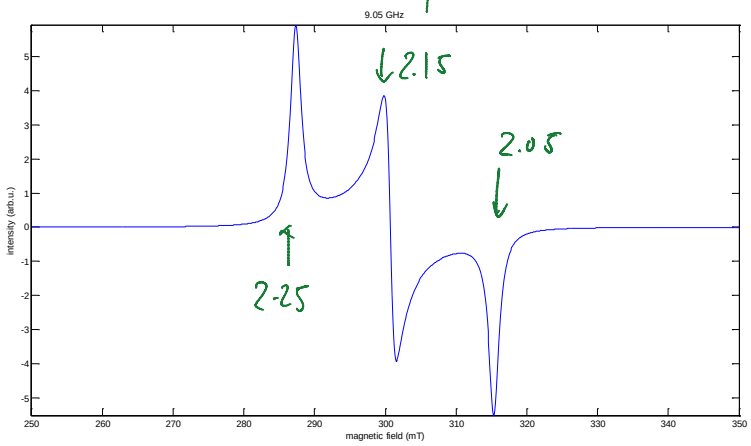


Simulation von Festkörper-Spektren ()

g-Tensor

```
clear

Sys.g = [2.05 2.15 2.25];

Sys.lwpp = [0 1];

Exp.mwFreq = 9.05;
Exp.Range = [250 350];


pepper(Sys,Exp);
```

Pulver-Spektrum



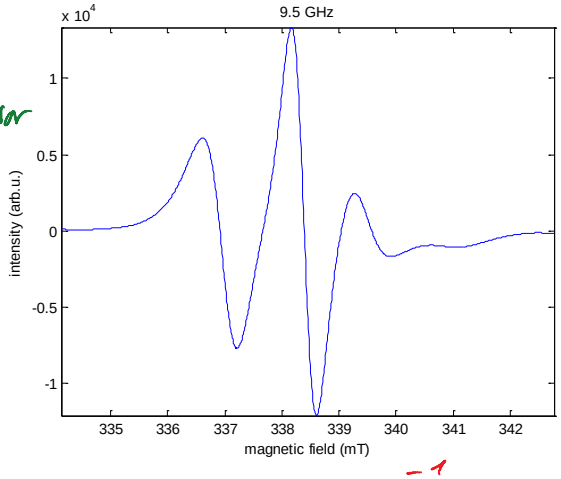
↑ statisches Pulverspektrum – Simulations programm

```
% Simple slow-motional cw EPR spectrum simulation of a nitroxide radical
%=========================================================================
clear, clf

% Parameters
%-------------------------------------------------------------------------
% Static parameters
Nitroxide.g = [2.008,2.006,2.003];
Nitroxide.Nucs = '14N';
Nitroxide.A = [20,20,85];

% Dynamic parameters
Nitroxide.lw = 0.3;
Nitroxide.tcorr = 5e-9;

% Experimental parameters
Experiment.mwFreq = 9.5;


% Simulation and graphical rendering
%-------------------------------------------------------------------------
chili(Nitroxide,Experiment);
```

← anisotroper $\tilde{G}$-Tensor

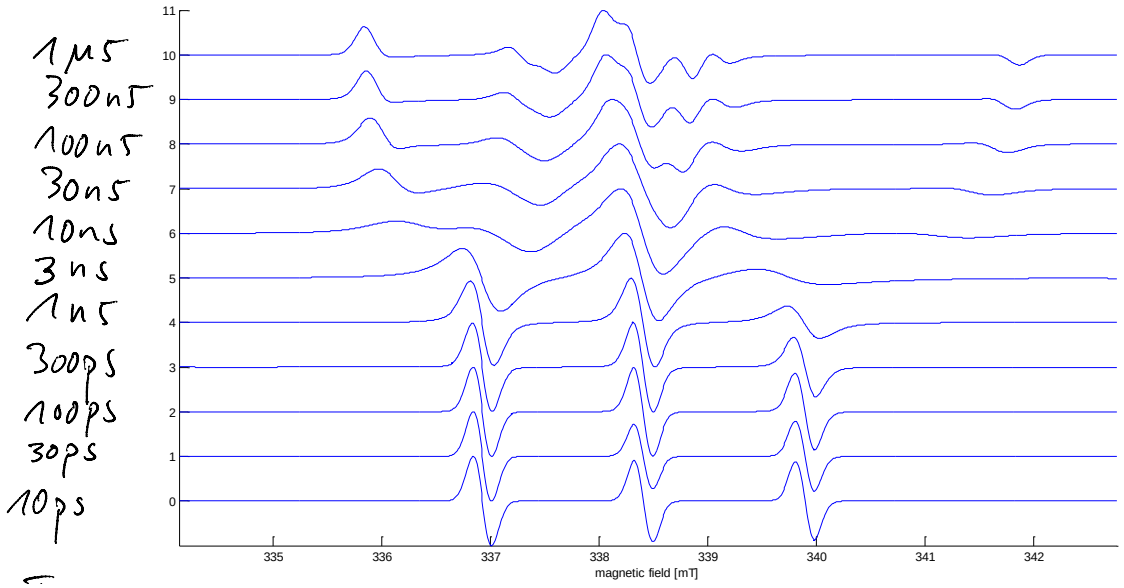
← anisotrope Hf-WW ($\tilde{A}$)

← rotations-Korrelationszeit



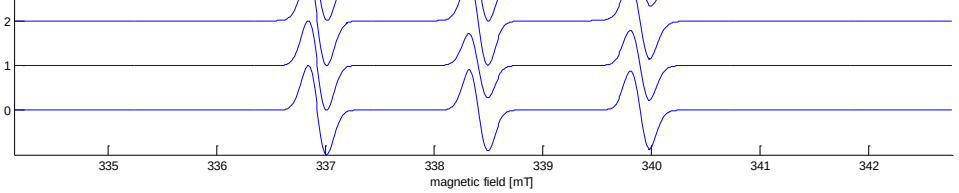
↑ Programm zur Simulation von langsamen Dynamiken

$\tau_c > \Delta\omega^{-1}$ anisotrope WW



Solid
$\tau_c \Delta\omega \gg 1$

liquid
$\tau_c \Delta\omega \ll 1$



10 ps

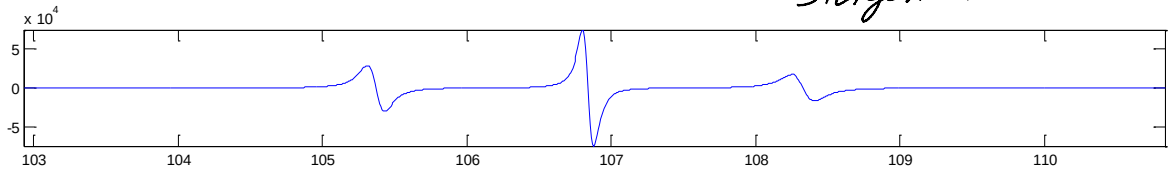
τ_c

$\tau_c \Delta\omega \ll 1$

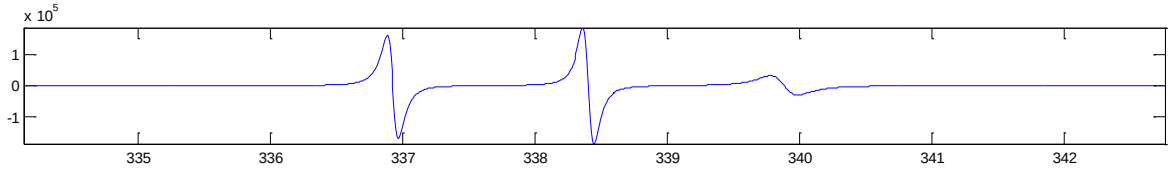
Da $\Delta\omega$ mit B_0 steigt, von liquid → solid mit steigendem Feld

$\tau_c = 1$ ns

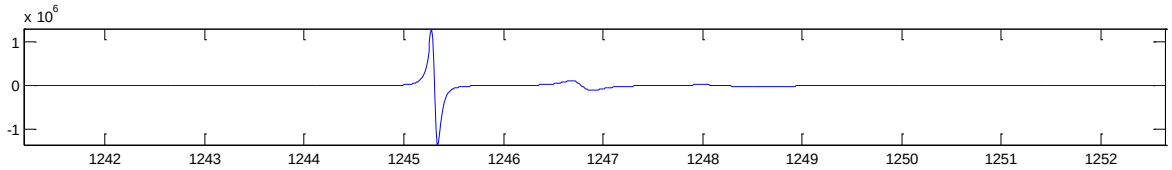
0.1T
3GHz
(S-band)



0.3T
9 GHz
(X-band)



1T
35 GHz
(Q-Band)



3.4T
95 GHz
(W-band)