

Simulation of powder EPR spectra with Coupled_ESR software

The software was originally developed for the simulation of biradical spectra [1] with electron-electron (ee), hyperfine (hfc) and nuclear quadrupole (nqc) splittings, the latter due to nuclei with $I > 1/2$. The transition energies and intensities were obtained by diagonalization of the spin Hamiltonian (1). The influence of different relative orientations of radicals forming a pair in a rigid matrix was examined. The method was also used in the analysis of spectra of fluorinated radicals with large hfc splittings, in which case perturbation methods are less accurate. The quality of the simulations in early work with this program was examined by comparison with recently developed software [2].

Developments

- 2000: Original program [1]
- 2000-: Applications in radiation research and surface chemistry
- 2015: Verification using Easyspin [2]

Coupled_ESR theory

To be able to treat single as well as coupled paramagnetic systems containing two or more (N) subunits that interact with each other, the spin Hamiltonian (1) was employed:

$$H = B * \sum_{i=1}^N \mathbf{F}_i \Gamma_i \ell + \sum_{i=1}^N \mathbf{F}_i \mathbf{Q}_i \mathbf{F}_i + \sum_{i < j}^N \mathbf{F}_i \mathbf{A}_{ij} \mathbf{F}_j \quad (1)$$

\mathbf{F}_i is the spin angular momentum operator for electrons (usually denoted \mathbf{S}_i) or nuclei (\mathbf{I}_i). Γ_i is the g-tensor multiplied by the Bohr magneton for an electron or the g-factor times the nuclear magneton for a nucleus, ℓ a unit vector along the magnetic field B. \mathbf{Q}_i is the (electronic) zero-field splitting or (nuclear) quadrupole splitting tensor of magnetic particle i. \mathbf{A}_{ij} is the interaction tensor between particle i and j, e.g., the hyperfine coupling tensor with \mathbf{F}_i = electron spin, \mathbf{F}_j = nuclear spin, or the e-e interaction tensor between two electronic spins. \mathbf{A}_{ij} may contain an isotropic part, e.g. the isotropic hyperfine coupling between electron and nuclear spins or the exchange interaction between two electron spins. The first sum of Zeeman interactions is the only one that depends on the magnetic field strength. The other terms are field-independent. An option for automatic fitting of the spin Hamiltonian parameters included in similar software [2,3] was, however, excluded in the Coupled_ESR program.

Coupled_ESR code

The code was written in Fortran77 except for the memory allocation and computer clock available in Microsoft Fortran Powerstation. Diagonalization of the Hamiltonian matrix (1) with dimensions up to 512x512 was performed in double precision using the Eispack subroutine package. The user interface to produce an input file is still under development as well as possibilities to specify multiple sites in single crystals. Any comments or suggestions on this version may be sent to:

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Input

Input to the program is provided from an input file. The program starts by asking if you want to create a file or not. If the file exists type 'N' and then give the data-file name, e.g. 'Ex1C.txt' as shown below.

```

C:\MSDEV\Projects\Coupled_ESR\Release\Coupled_ESR.exe
Prepare input file(Y/N):n
Input file name:ex1C.txt
ESR spectrum simulation, Link:ping 2015-12-19 fil:ex1C.txt

 0 % finished
10 % finished
20 % finished
30 % finished
40 % finished
50 % finished
60 % finished
70 % finished
80 % finished
90 % finished
Time= 1969.70 seconds
Press any key to clear screen

```

The progress of the calculation can be followed on the screen. Several calculations can be made in one step. To instead create a file type 'Y' and answer the questions given by the program. Save the file by typing **** at the question 'Comment (Stop with ****):'. Follow instructions on the screen to run the simulation.

Output from the run is in two files, e.g. 'Ex1C.out' for the parameters, and 'Ex1C01.plt' for the spectrum. Freeware or commercial software like Gnuplot and Origin have been used to plot the latter file and must be obtained separately.

Input can also be prepared manually with a text editor. Note that the coupling- (records 8-10) and line width (record 11) tensors are in MHz units. Formats are free if not stated.

- ```

Item

1 Text for identification (18A4)

2 LIM,LIZ,LAC,LS
LIM=0 Isotropy
LIM=1 Axial symmetry
LIM=2 No symmetry
LIZ=0 Polycrystal
LIZ=-4 Single crystal
LAC=0 The tensors have no axes in common
LAC=1 The tensors have one axis in common
LAC=2 The tensors have all axes in common
LS=0 Non-equivalence of all nuclei
LS=1 Equivalence of some or all nuclei

```

Records 3A-F are for integration, as in program Maru:

- ```

Powder (LIZ=0):
3A NU,NI: NUxNi= Number of angles ⊙
3B NU,NI: NUxNi= Number of angles ⊕ (LIM=2)

Crystal (LIZ=-4):
3A Number of sites
3B Weights of sites
3C ANGLE ⊙ of static field

```

3D ANGLE Φ of static field
 3E ANGLE Θ of microwave field
 3F ANGLE Φ of microwave field

 4 FREQ=Microvave frequency(MHz)

 5 Nnuc=Number of electron and nuclear spins

 6 Spin,Type
 Spin: S or I value
 Type=T/F for nuclei/electrons

 7A Gn=Nuclear g-factor (Type=T)
 7B G0(I), RG(I,1:3),I = 1:3: g-tensor specified by 3 records,
 principal value, G0(I), followed by direction cosines, RG(I,1:3), of
 principal axis (Type=F)

 (S/I>½)
 8 Q0(I),RQ(I, 1:3), I=1:3: Zero field/Quadrupole tensor(MHz),
 specified by 3 records, principal value, Q0(I), followed by
 direction cosines, RQ(I,1:3), of principal axis

 Records 6-8 repeated Nnuc times

 (Nnuc>1):
 9 Interact(nuc,nuc+1:Nnuc), nuc=1:Nnuc-1
 Interact(nuc,n)=n for interacting spins nuc and n>nuc
 Interact(nuc,n)=0 for noninteracting spins

 10 C0(I), RC(I, 1:3),I=1:3: Interaction tensor (MHz) specified by
 3 records, principal value, C0(I), followed by direction
 cosines, RC(I,1:3), of principal axis

 Record 10 repeated for each spin nuc and n>nuc+1 with
 Interact(nuc,n)>0, see examples

 11 C0(I), RC(I, 1:3),I=1:3: Linewidth tensor (MHz) specified by 3
 records, principal value, C0(I), followed by direction cosines,
 RC(I,1:3), of principal axis

 12 R, SECOND, RANGE, SUPP
 R = 0 for Gauss, R = 1000 for Lorentz, 0<R<20 for Voigt line-shape
 SECOND = 0/1/2 for absorption/1st/2nd derivative
 RANGE: Signals outside [FREQ +/- RANGE] MHz are neglected
 SUPP: Intensities <= SUPP are neglected

 13 BMIN,STEP,BMAX,nnStep,nTh,nFi
 BMIN=Start field (G)
 STEP=Step length (G)
 BMAX=Stop field (G)
 nnSTEP: Exact calculation at every nnstep field, else
 extrapolate
 nTh=1: Exact calculation at every Θ angle;
 nFi=1: Exact calculation at every Φ angle;

14 LADD, PROC, NO PLOT, PRINT, LINES, Kelvin
LADD=0 Single spectrum
LADD=1 Start add spectra
LADD=2 Continue add
LADD=3 Stop add
PROC=Fraction of spectrum added

NO PLOT, PRINT, LINES: The parameters do not affect the
calculations. Input F F F to conform with older program versions
Kelvin=T (K) >0: Populations are calculated, ≤0: ignored

15 ****: STOPS EXECUTION

Input/Output files

Ex1C: Chain-end radical RCF₂CF₂ in Nafion perfluorinated membranes exposed to the photo-Fenton reagent

In:

```
NAFION-RADICAL
  2   0   0   1
 48   2
 24   2
 9430.000000
 5
    .500000   F
 2.0017  1.0000   0.0000   0.0000
 2.0032   .0000   1.0000   0.0000
 2.0026  0.0000   0.0000   1.0000
    .500000   T
 5.258000
    .500000   T
 5.258000
    .500000   T
 5.258000
    .500000   T
 5.258000
  2   3   4   5
  0   0   0
  0   0
  0
 96.0  0.9982  0.0563  0.0213
 71.4 -0.0475  0.9540 -0.2959
 42.0 -0.0370  0.2944  0.9550
 82.0  0.9664  0.2355  0.1026
 65.5 -0.1387  0.8141 -0.5639
 83.7 -0.2163  0.5307  0.8195
622.4  0.8996  0.4227  0.1100
 50.4 -0.3470  0.8447 -0.4075
 50.4 -0.2652  0.3284  0.9066
622.4  0.8996  0.4227 -0.1100
 50.4 -0.3470  0.8447 +0.4075
 50.4 -0.2652  0.3284 -0.9066
 54.0  1.0000   .0000   .0000
 46.0   .0000  1.0000   .0000
 46.0   .0000   .0000  1.0000
  0.   1          375.00000   .00100
 3000.000000   1.000000   3750.000000   85   1   1
  0   1.000000   F F F  77.00000
****
```

OUT:

ESR simulation program, Linköping 2015-12- 5 fil:Ex1C.txt

NAFION-RADICAL

Integration procedure

2 0 0 192 96

Microwave frequency= 9430.0 MHz

Spin # 1 S= .5 Electron g-tensor

```
 2.00170          1.00000          .00000          .00000
 2.00320          .00000          1.00000          .00000
 2.00260          .00000          .00000          1.00000
```

```

Spin # 2 I= .5 Nuclear G-value
5.25800
Spin # 3 I= .5 Nuclear G-value
5.25800
Spin # 4 I= .5 Nuclear G-value
5.25800
Spin # 5 I= .5 Nuclear G-value
5.25800
A/J-Tensor (MHz) between spins # 1 and # 2
96.00000 .99820 .05630 .02130
71.40000 -.04750 .95400 -.29590
42.00000 -.03700 .29440 .95500
A/J-Tensor (MHz) between spins # 1 and # 3
82.00000 .96640 .23550 .10260
65.50000 -.13870 .81410 -.56390
83.70000 -.21630 .53070 .81950
A/J-Tensor (MHz) between spins # 1 and # 4
622.40000 .89960 .42270 .11000
50.40000 -.34700 .84470 -.40750
50.40000 -.26520 .32840 .90660
A/J-Tensor (MHz) between spins # 1 and # 5
622.40000 .89960 .42270 -.11000
50.40000 -.34700 .84470 .40750
50.40000 -.26520 .32840 -.90660
Width-tensor (MHz)
54.00000 1.00000 .00000 .00000
46.00000 .00000 1.00000 .00000
46.00000 .00000 .00000 1.00000
Gaussian shape
Intensity treshold= .001
Transition range 9055.00 -- 9805.00 MHz
Bmin= 3000.000 G, Bmax= 3750.000 G
Extrapolation between 85 field points, 1 Fi points, 1 Theta points
Intensity= 1.000 T= 77.000 K
Spectrum file:Ex1C01.plt
Time= 1974.82 seconds

```

Ex2C: Randomly oriented $\dot{C}F_3$ radicals in frozen noble gas matrix

In:

```

CF3, EXP
2 0 0 1
48 2
48 2
9500.000000
4
.500000 F
2.004200 .000000 .000000 1.000000
2.004200 .000000 1.000000 .000000
2.002400 1.000000 .000000 .000000
.500000 T
5.258
.500000 T
5.258
.500000 T
5.258
2 3 4

```

```

0 0
0
737.000000 .952100 .000000 .305700
243.800000 .000000 1.000000 .000000
224.200000 -.305700 .000000 .952100
737.000000 .952100 -.264700 -.152900
243.800000 .000000 -.500000 .866030
224.200000 -.305700 -.824500 -.476100
737.000000 .952100 .264700 -.152900
243.800000 .000000 -.500000 -.866030
224.200000 -.305700 .824540 -.476100
15.000000 1.0000 .000000 .000000
15.000000 .000000 .000000 1.000000
15.000000 .000000 1.000000 .000000
0. 1 200.00000 .00100
2950.000000 1.000000 3800.000000 85 1 1
0 1.000000 F F F 77.00000
****

```

Out:

ESR spectrum simulation, Linköping 2015-12-16 fil:ex2c.txt

CF3, EXP

Integration procedure

2 0 0 192 192

Microwave frequency= 9500.0 MHz

Spin # 1 S= .5 Electron g-tensor

2.00420	.00000	.00000	1.00000
2.00420	.00000	1.00000	.00000
2.00240	1.00000	.00000	.00000

Spin # 2 I= .5 Nuclear G-value

5.25800

Spin # 3 I= .5 Nuclear G-value

5.25800

Spin # 4 I= .5 Nuclear G-value

5.25800

A/J-Tensor (MHz) between spins # 1 and # 2

737.00000	.95210	.00000	.30570
243.80000	.00000	1.00000	.00000
224.20000	-.30570	.00000	.95210

A/J-Tensor (MHz) between spins # 1 and # 3

737.00000	.95210	-.26470	-.15290
243.80000	.00000	-.50000	.86603
224.20000	-.30570	-.82450	-.47610

A/J-Tensor (MHz) between spins # 1 and # 4

737.00000	.95210	.26470	-.15290
243.80000	.00000	-.50000	-.86603
224.20000	-.30570	.82454	-.47610

Width-tensor (MHz)

15.00000	1.00000	.00000	.00000
15.00000	.00000	.00000	1.00000
15.00000	.00000	1.00000	.00000

Gaussian shape

Intensity treshold= .001

Transition range 9300.00 -- 9700.00 MHz

Bmin= 2950.000 G, Bmax= 3800.000 G

Extrapolation between 85 field points, 1 Fi points, 1 Theta points
 Intensity= 1.000 T= 77.000 K
 Spectrum file: ex2c01.plt
 Time= 515.53 seconds

Ex3C: (NO)₂ biradical in Na-LTA zeolite

In:

NO DIMER, angle=0

2	0	1	1				
48	1						
36	1						
34000.000000							
2							
.500000	F						
2.004200		1.000000		.000000		.000000	
1.977000		.000000		1.000000		.000000	
1.912000		.000000		.000000		1.000000	
.500000	F						
2.004200		1.000000		.000000		.000000	
1.977000		.000000		1.000000		.000000	
1.912000		.000000		.000000		1.000000	
2							
-461.000000		1.000000		.000000		.000000	
-775.000000		.000000		1.000000		.000000	
1236.000000		.000000		.000000		1.000000	
112.000000		1.000000		.000000		.000000	
210.000000		.000000		1.000000		.000000	
168.000000		.000000		.000000		1.000000	
0	1	150.000000		.001000			
11750.000000		1.000000	13250.000000	15	1	1	
0	1.000000	F F F	-1.000000				

NO DIMER, angle=20

2	0	1	1				
48	1						
36	1						
34000.000000							
2							
.500000	F						
2.004200		1.000000		.000000		.000000	
1.977000		.000000		.984810		-.173650	
1.912000		.000000		.173650		.984810	
.500000	F						
2.004200		1.000000		.000000		.000000	
1.977000		.000000		.984810		.173650	
1.912000		.000000		-.173650		.984810	
2							
-461.000000		1.000000		.000000		.000000	
-775.000000		.000000		0.984810		.000000	
1236.000000		.000000		.000000		1.000000	
112.000000		1.000000		.000000		.000000	
210.000000		.000000		1.000000		.000000	
168.000000		.000000		.000000		1.000000	
0	1	150.000000		.001000			
11750.000000		1.000000	13250.000000	15	1	1	

0 1.000000 F F F -1.00000

OUT:

ESR spectrum simulation, Linköping 2015-12-16 fil:ex3c.txt

NO DIMER, angle=0

Integration procedure

2 0 1 96 72

Microwave frequency=34000.0 MHz

Spin # 1 S= .5 Electron g-tensor

2.00420 1.00000 .00000 .00000

1.97700 .00000 1.00000 .00000

1.91200 .00000 .00000 1.00000

Spin # 2 S= .5 Electron g-tensor

2.00420 1.00000 .00000 .00000

1.97700 .00000 1.00000 .00000

1.91200 .00000 .00000 1.00000

A/J-Tensor (MHz) between spins # 1 and # 2

-461.00000 1.00000 .00000 .00000

-775.00000 .00000 1.00000 .00000

1236.00000 .00000 .00000 1.00000

Width-tensor (MHz)

112.00000 1.00000 .00000 .00000

210.00000 .00000 1.00000 .00000

168.00000 .00000 .00000 1.00000

Gaussian shape

Intensity treshold= .001

Transition range 33850.00 -- 34150.00 MHz

Bmin=11750.000 G, Bmax=13250.000 G

Extrapolation between 15 field points, 1 Φ points, 1 Theta points

Intensity= 1.000 T= -1.000 K

Spectrum file: ex3c01.plt

Time= 28.60 seconds

NO DIMER, angle=20

Integration procedure

2 0 1 96 72

Microwave frequency=34000.0 MHz

Spin # 1 S= .5 Electron g-tensor

2.00420 1.00000 .00000 .00000

1.97700 .00000 .98481 -.17365

1.91200 .00000 .17365 .98481

Spin # 2 S= .5 Electron g-tensor

2.00420 1.00000 .00000 .00000

1.97700 .00000 .98481 .17365

1.91200 .00000 -.17365 .98481

A/J-Tensor (MHz) between spins # 1 and # 2

-461.00000 1.00000 .00000 .00000

-775.00000 .00000 .98481 .00000

1236.00000 .00000 .00000 1.00000

Width-tensor (MHz)

112.00000 1.00000 .00000 .00000

210.00000 .00000 1.00000 .00000

168.00000 .00000 .00000 1.00000

Gaussian shape

Intensity treshold= .001

Transition range 33850.00 -- 34150.00 MHz
 Bmin=11750.000 G, Bmax=13250.000 G
 Extrapolation between 15 field points, 1 Fi points, 1 Theta points
 Intensity= 1.000 T= -1.000 K
 Spectrum file: ex3c02.plt
 Time= 30.77 seconds

Ex4C: Triplet state C(CH₂)₃ in polycrystalline methylene-cyclopropane γ -irradiated at 77 K

IN:

TMM, Ms=2

2 0 2 1

8 1

4 1

9270.000000

7

1.00000 F

2.004200 .000000 .000000 1.000000

2.004200 .000000 1.000000 .000000

2.002400 1.000000 .000000 .000000

-257.0 1.0 0.0 0.0

-240.0 0.0 1.0 0.0

497.0 0.0 0.0 1.0

.500000 T

5.585

.500000 T

5.585

.500000 T

5.585

.500000 T

5.585

.500000 T

5.585

.500000 T

5.585

2 3 4 5 6 7

0 0 0 0 0

0 0 0 0

0 0 0

0 0

0

-14.0 1.0 0.0 0.0

-37.8 0.0 1.0 0.0

-26.3 .0 .0 1.0

-14.0 -.5 -.866 0.0

-37.8 .866 -.5 0.0

-26.3 .0 .0 1.0

-14.0 -.5 +.866 0.0

-37.8 -.866 -.5 0.0

-26.3 .0 .0 1.0

-14.0 1.0 0.0 0.0

-37.8 0.0 1.0 0.0

-26.3 .0 .0 1.0

-14.0 -.5 -.866 0.0

-37.8 .866 -.5 0.0

-26.3 .0 .0 1.0

-14.0 -.5 +.866 0.0

```

-37.8      -.866      -.5      0.0
-26.3      .0      .0      1.0
 17.000000      1.0000      .000000      .000000
 17.000000      .000000      .000000      1.000000
 17.000000      .000000      1.000000      .000000
 0. 1      300.00000      .00100
1600.000000      0.500000      1700.000000      101 1 1
0 1.000000      F F F -1.
****

```

OUT:

ESR spectrum simulation, Link · ing 2015-11-29 fil:ex4C.txt

TMM, Ms=2

Integration procedure

2 0 2 16 8

Microwave frequency= 9270.0 MHz

Spin # 1 S= 1.0 Electron g-tensor

```

2.00420      .00000      .00000      1.00000
2.00420      .00000      1.00000      .00000
2.00240      1.00000      .00000      .00000

```

D-tensor (MHz)

```

-257.00000      1.00000      .00000      .00000
-240.00000      .00000      1.00000      .00000
497.00000      .00000      .00000      1.00000

```

Spin # 2 I= .5 Nuclear G-value

5.58500

Spin # 3 I= .5 Nuclear G-value

5.58500

Spin # 4 I= .5 Nuclear G-value

5.58500

Spin # 5 I= .5 Nuclear G-value

5.58500

Spin # 6 I= .5 Nuclear G-value

5.58500

Spin # 7 I= .5 Nuclear G-value

5.58500

A/J-Tensor (MHz) between spins # 1 and # 2

```

-14.00000      1.00000      .00000      .00000
-37.80000      .00000      1.00000      .00000
-26.30000      .00000      .00000      1.00000

```

A/J-Tensor (MHz) between spins # 1 and # 3

```

-14.00000      -.50000      -.86600      .00000
-37.80000      .86600      -.50000      .00000
-26.30000      .00000      .00000      1.00000

```

A/J-Tensor (MHz) between spins # 1 and # 4

```

-14.00000      -.50000      .86600      .00000
-37.80000      -.86600      -.50000      .00000
-26.30000      .00000      .00000      1.00000

```

A/J-Tensor (MHz) between spins # 1 and # 5

-14.00000	1.00000	.00000	.00000
-37.80000	.00000	1.00000	.00000
-26.30000	.00000	.00000	1.00000
A/J-Tensor (MHz) between spins # 1 and # 6			
-14.00000	-.50000	-.86600	.00000
-37.80000	.86600	-.50000	.00000
-26.30000	.00000	.00000	1.00000
A/J-Tensor (MHz) between spins # 1 and # 7			
-14.00000	-.50000	.86600	.00000
-37.80000	-.86600	-.50000	.00000
-26.30000	.00000	.00000	1.00000
Width-tensor (MHz)			
17.00000	1.00000	.00000	.00000
17.00000	.00000	.00000	1.00000
17.00000	.00000	1.00000	.00000

Gaussian shape
Intensity treshold= .001
Transition range 8970.00 -- 9570.00 MHz
Bmin= 1600.000 G, Bmax= 1700.000 G
Extrapolation between 101 field points, 1 Fi points, 1 Theta points
Intensity= 1.000 T= -1.000 K
Spectrum file: Ex4C01.plt
Time= 526.41 seconds

Ex5C: Radical pairs H...CH3 and D...CD3 in frozen Ar gas at low T
IN:

```

H_CH3_2
  1   0   2   1
12   1
9500.000000
  6
  0.5   F
  2.002320   .000000   .000000   1.000000
  2.002320   .000000   1.000000   .000000
  2.002320   1.000000   .000000   .000000
  0.5   F
  2.002320   .000000   .000000   1.000000
  2.002320   .000000   1.000000   .000000
  2.002320   1.000000   .000000   .000000
  .5   T
  5.585
  .5   T
  5.585
  .5   T
  5.585
  .5   T
  5.585
  2   3   0   0   0
      0   4   5   6
          0   0
              0

```

78.4	1.0	0.0	0.0
78.4	0.0	1.0	0.0
-156.8	0.0	0.0	1.0
1419.0	1.0	0.0	0.0
1419.0	0.0	1.0	0.0
1419.0	.0	.0	1.0
-64.82	1.0	0.0	0.0
-64.82	0.0	1.0	0.0
-64.82	.0	.0	1.0
-64.82	1.0	0.0	0.0
-64.82	0.0	1.0	0.0
-64.82	.0	.0	1.0
-64.82	1.0	0.0	0.0
-64.82	0.0	1.0	0.0
-64.82	.0	.0	1.0
1.000000	1.0000	.000000	.000000
1.000000	.000000	.000000	1.000000
1.000000	.000000	1.000000	.000000
0. 1	300.00000	.000000	
1500.000000	0.100000	1850.000000	101 1 1
0 1.000000	F F F -1.0		
D_CD3_2			
1 0 2	1		
12 1			
9500.000000			
6			
0.5 F			
2.002320	.000000	.000000	1.000000
2.002320	.000000	1.000000	.000000
2.002320	1.000000	.000000	.000000
0.5 F			
2.002320	.000000	.000000	1.000000
2.002320	.000000	1.000000	.000000
2.002320	1.000000	.000000	.000000
1. T			
0.8574			
.000000	.000000	.000000	1.000000
.000000	.000000	1.000000	.000000
.000000	1.000000	.000000	.000000
1. T			
0.8574			
.000000	.000000	.000000	1.000000
.000000	.000000	1.000000	.000000
.000000	1.000000	.000000	.000000
1. T			
0.8574			
.000000	.000000	.000000	1.000000
.000000	.000000	1.000000	.000000
.000000	1.000000	.000000	.000000
1. T			
0.8574			
.000000	.000000	.000000	1.000000
.000000	.000000	1.000000	.000000
.000000	1.000000	.000000	.000000
2 3 0	0 0		
0 4	5 6		

```

      0      0      0
      0      0
      0
    78.4      1.0      0.0      0.0
    78.4      0.0      1.0      0.0
   -156.8     0.0      0.0      1.0
    220.06     1.0      0.0      0.0
    220.06     0.0      1.0      0.0
    220.06     .0      .0      1.0
   -10.08     1.0      0.0      0.0
   -10.08     0.0      1.0      0.0
   -10.08     .0      .0      1.0
   -10.08     1.0      0.0      0.0
   -10.08     0.0      1.0      0.0
   -10.08     .0      .0      1.0
   -10.08     1.0      0.0      0.0
   -10.08     0.0      1.0      0.0
   -10.08     .0      .0      1.0
   -10.08     1.0      0.0      0.0
   -10.08     0.0      1.0      0.0
   -10.08     .0      .0      1.0
    1.000000     1.0000     .000000     .000000
    1.000000     .000000     .000000     1.000000
    1.000000     .000000     1.000000     .000000
    0.      1      300.00000     .000000
    1640.000000     0.100000     1750.000000     101     1     1
    0      1.000000     F F F     -1.0
****

```

OUT:

ESR spectrum simulation, Link - ing 2015-12-16 fil:ex5C.txt

H_CH3_2

Integration procedure

1 0 2 24 1

Microwave frequency= 9500.0 MHz

Spin # 1 S= .5 Electron g-tensor

```

    2.00232     .00000     .00000     1.00000
    2.00232     .00000     1.00000     .00000
    2.00232     1.00000     .00000     .00000

```

Spin # 2 S= .5 Electron g-tensor

```

    2.00232     .00000     .00000     1.00000
    2.00232     .00000     1.00000     .00000
    2.00232     1.00000     .00000     .00000

```

Spin # 3 I= .5 Nuclear G-value

5.58500

Spin # 4 I= .5 Nuclear G-value

5.58500

Spin # 5 I= .5 Nuclear G-value

5.58500

Spin # 6 I= .5 Nuclear G-value

5.58500

A/J-Tensor (MHz) between spins # 1 and # 2

```

    78.40000     1.00000     .00000     .00000
    78.40000     .00000     1.00000     .00000

```

-156.80000	.00000	.00000	1.00000
A/J-Tensor (MHz) between spins # 1 and # 3			
1419.00000	1.00000	.00000	.00000
1419.00000	.00000	1.00000	.00000
1419.00000	.00000	.00000	1.00000
A/J-Tensor (MHz) between spins # 2 and # 4			
-64.82000	1.00000	.00000	.00000
-64.82000	.00000	1.00000	.00000
-64.82000	.00000	.00000	1.00000
A/J-Tensor (MHz) between spins # 2 and # 5			
-64.82000	1.00000	.00000	.00000
-64.82000	.00000	1.00000	.00000
-64.82000	.00000	.00000	1.00000
A/J-Tensor (MHz) between spins # 2 and # 6			
-64.82000	1.00000	.00000	.00000
-64.82000	.00000	1.00000	.00000
-64.82000	.00000	.00000	1.00000
Width-tensor (MHz)			
1.00000	1.00000	.00000	.00000
1.00000	.00000	.00000	1.00000
1.00000	.00000	1.00000	.00000

Gaussian shape
 Intensity treshold= .000
 Transition range 9200.00 -- 9800.00 MHz
 Bmin= 1500.000 G, Bmax= 1850.000 G
 Extrapolation between 101 field points, 1 Fi points, 1 Theta points
 Intensity= 1.000 T= -1.000 K
 Spectrum file: ex5C01.plt
 Time= 73.95 seconds

D_CD3_2

Integration procedure

1 0 2 24 1

Microwave frequency= 9500.0 MHz

Spin # 1 S= .5 Electron g-tensor

2.00232	.00000	.00000	1.00000
2.00232	.00000	1.00000	.00000
2.00232	1.00000	.00000	.00000

Spin # 2 S= .5 Electron g-tensor

2.00232	.00000	.00000	1.00000
2.00232	.00000	1.00000	.00000
2.00232	1.00000	.00000	.00000

Spin # 3 I= 1.0 Nuclear G-value

.8574000

Q-tensor (MHz)

.00000	.00000	.00000	1.00000
.00000	.00000	1.00000	.00000
.00000	1.00000	.00000	.00000

Spin # 4 I= 1.0 Nuclear G-value

.8574000
 Q-tensor (MHz)
 .00000 .00000 .00000 1.00000
 .00000 .00000 1.00000 .00000
 .00000 1.00000 .00000 .00000

Spin # 5 I= 1.0 Nuclear G-value

.8574000
 Q-tensor (MHz)
 .00000 .00000 .00000 1.00000
 .00000 .00000 1.00000 .00000
 .00000 1.00000 .00000 .00000

Spin # 6 I= 1.0 Nuclear G-value

.8574000
 Q-tensor (MHz)
 .00000 .00000 .00000 1.00000
 .00000 .00000 1.00000 .00000
 .00000 1.00000 .00000 .00000

A/J-Tensor (MHz) between spins # 1 and # 2
 78.40000 1.00000 .00000 .00000
 78.40000 .00000 1.00000 .00000
 -156.80000 .00000 .00000 1.00000

A/J-Tensor (MHz) between spins # 1 and # 3
 220.06000 1.00000 .00000 .00000
 220.06000 .00000 1.00000 .00000
 220.06000 .00000 .00000 1.00000

A/J-Tensor (MHz) between spins # 2 and # 4
 -10.08000 1.00000 .00000 .00000
 -10.08000 .00000 1.00000 .00000
 -10.08000 .00000 .00000 1.00000

A/J-Tensor (MHz) between spins # 2 and # 5
 -10.08000 1.00000 .00000 .00000
 -10.08000 .00000 1.00000 .00000
 -10.08000 .00000 .00000 1.00000

A/J-Tensor (MHz) between spins # 2 and # 6
 -10.08000 1.00000 .00000 .00000
 -10.08000 .00000 1.00000 .00000
 -10.08000 .00000 .00000 1.00000

Width-tensor (MHz)
 1.00000 1.00000 .00000 .00000
 1.00000 .00000 .00000 1.00000
 1.00000 .00000 1.00000 .00000

Gaussian shape

Intensity treshold= .000

Transition range 9200.00 -- 9800.00 MHz

Bmin= 1640.000 G, Bmax= 1750.000 G

Extrapolation between 101 field points, 1 Fi points, 1 Theta points

Intensity= 1.000 T= -1.000 K

Spectrum file: ex5C02.plt

Time= 2795.60 seconds

Input data are also attached in separate folders.

Simulations

Simulated spectra obtained with Easyspin, (version 5.0.9) and Coupled_ESR were compared with experimental data, when available, in examples 1-5. Unless otherwise stated, Easyspin spectra were simulated exactly using the 'matrix' option. The theory employed in Coupled_ESR is summarized in the theory section and further described in [1,3].

Ex1C: Chain-end radical $\text{RCF}_2\dot{\text{C}}\text{F}_2$ detected in Nafion perfluorinated membranes exposed to the photo-Fenton reagent:

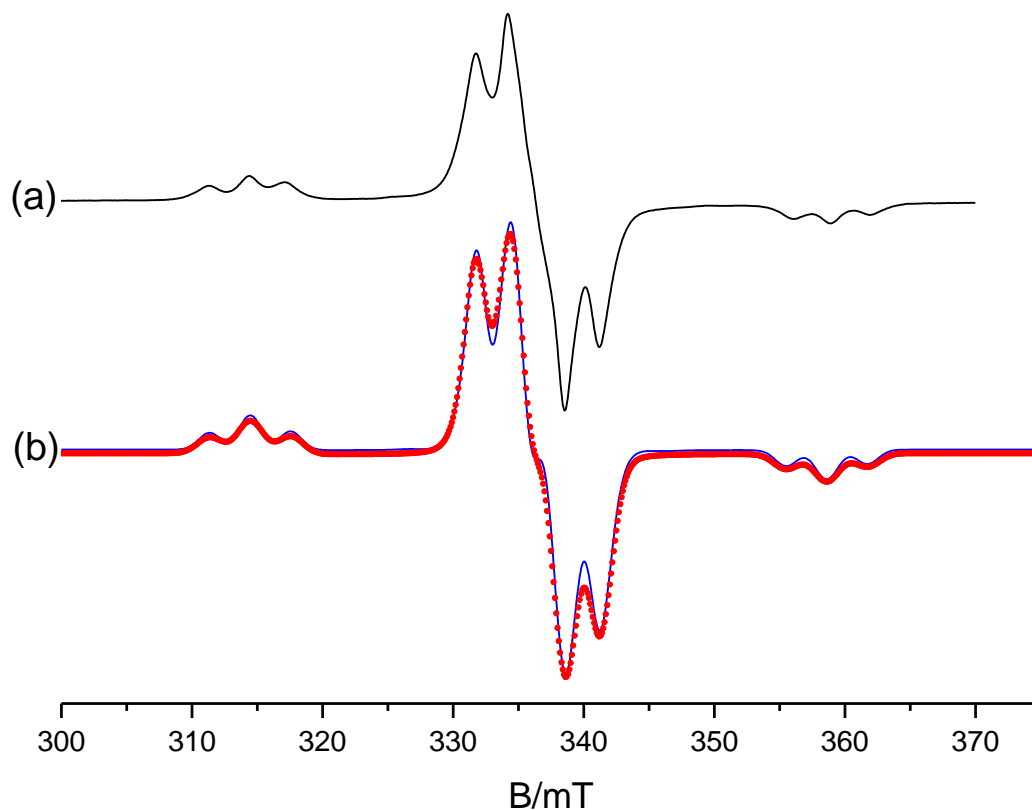


Figure 1. Experimental (a) and simulated (b) X-band ESR spectra at 77 K of the radical $\text{RCF}_2\dot{\text{C}}\text{F}_2$ in a UV-irradiated Nafion/Fe(III) sample. (•) Coupled_ESR. (—) Easyspin with spin Hamiltonian parameters from [4], reproduced in Ex1C above.

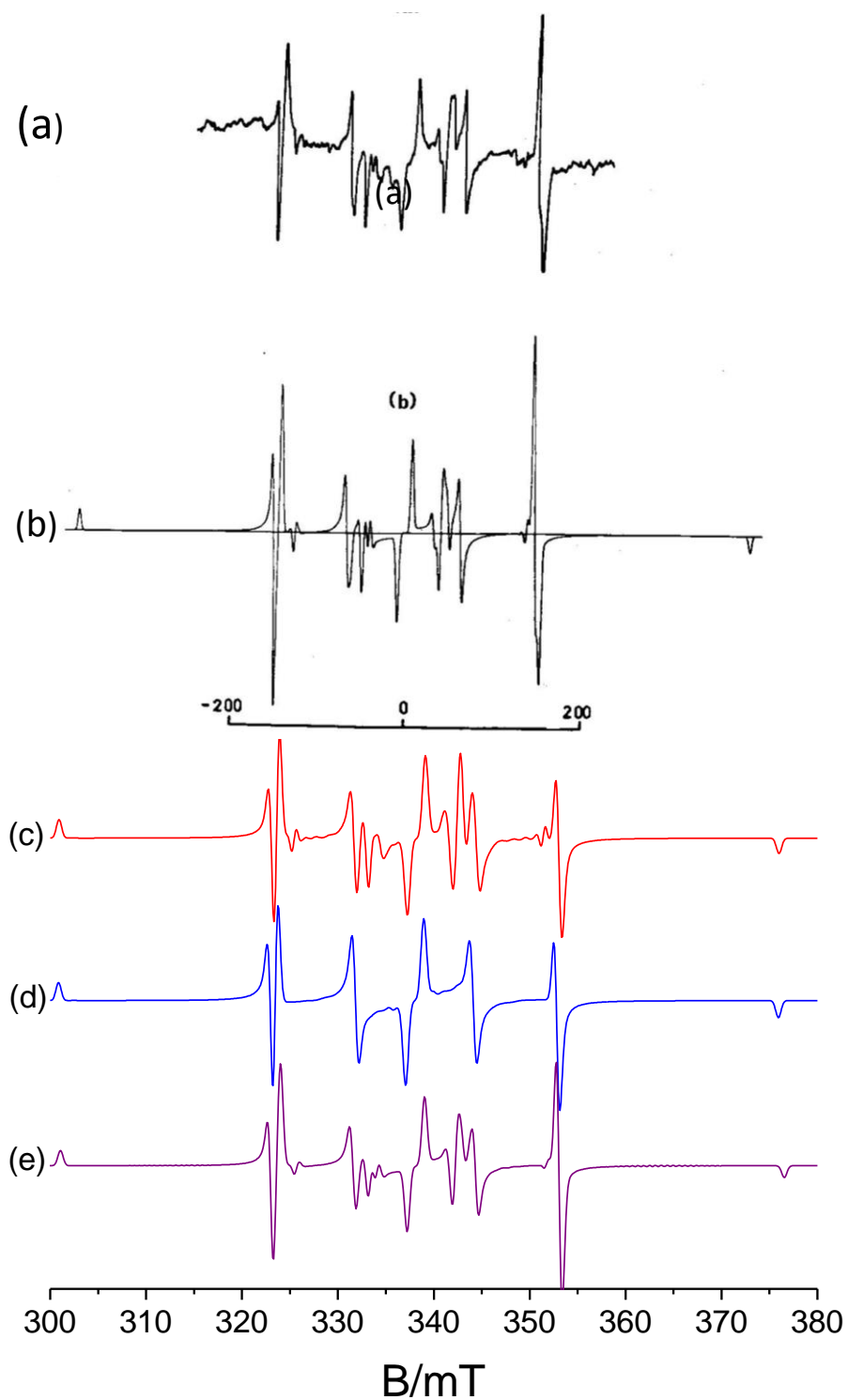
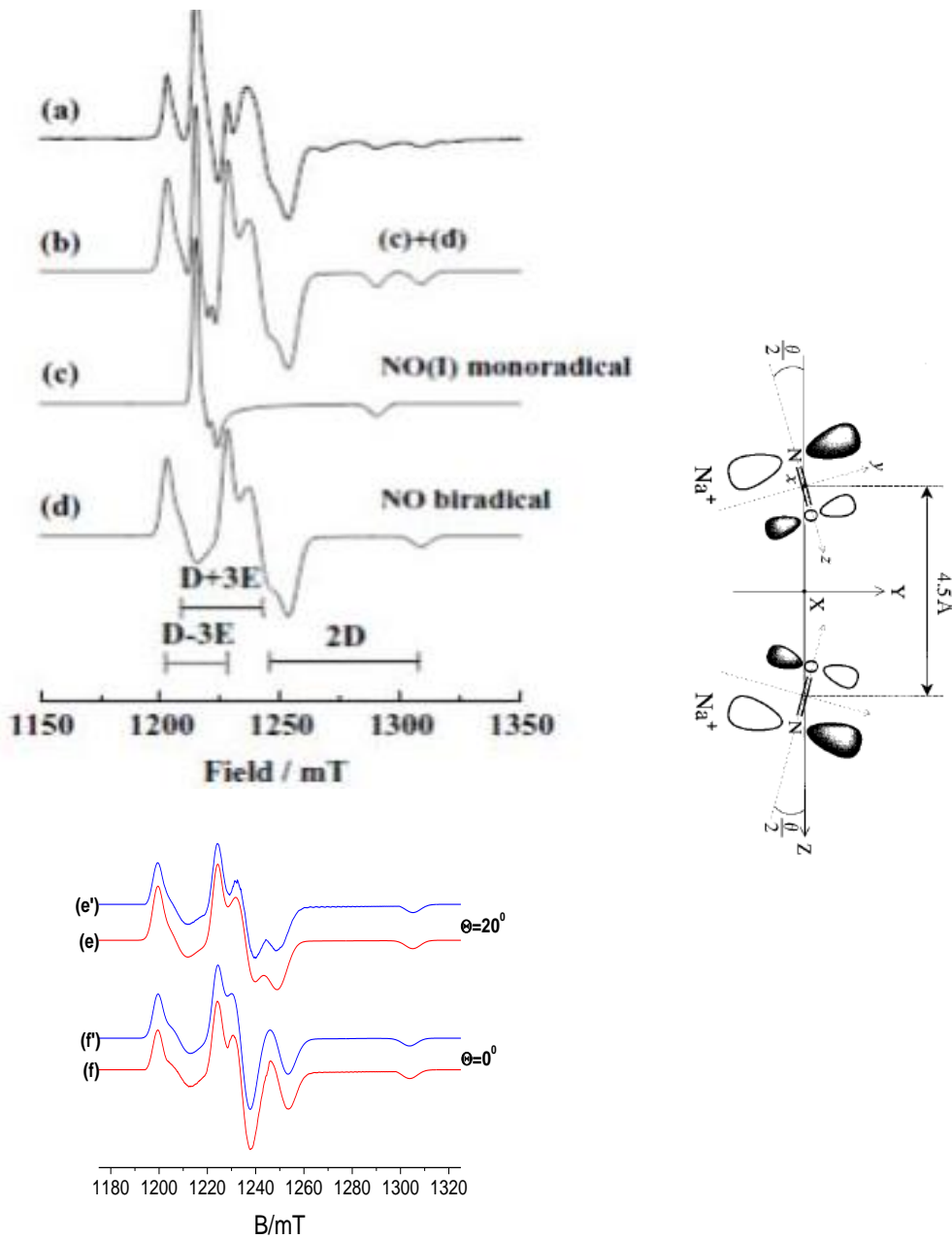


Figure 2. (a) Experimental X-band ESR spectrum of randomly oriented $\dot{C}F_3$ radicals in a frozen noble gas matrix, (b) simulation obtained from Dr J.A.R. Coope, (c) simulation with Easyspin using matrix option, (d) perturb2 option, (e) simulation with Coupled_ESR using parameters from [5]

Ex3C: $(\text{NO})_2$ biradical by introducing NO in Na-LTA zeolite



2+
 Fig. 3. Experimental (a) and simulated Q-band EPR spectra at 5 K of NO (13.2 kPa) introduced in Na-LTA [1,6]. The theoretical spectra (c) for NO(I) and (d) for the $(\text{NO})_2$ biradical were calculated using Simfonia [7]. Trace (b) is a superposition of (c) and (d) in the ratio 1:1. Simulations were obtained with Easyspin (red line) and Coupled_ESR (blue line) for the $(\text{NO})_2$ biradical with $\Theta=0^\circ$ in (e), (e'), $\Theta=20^\circ$ in (f), (f')

Ex4C: Triplet state trimethylene-methane in γ -irradiated methylene-cyclopropane polycrystal at 77 K.

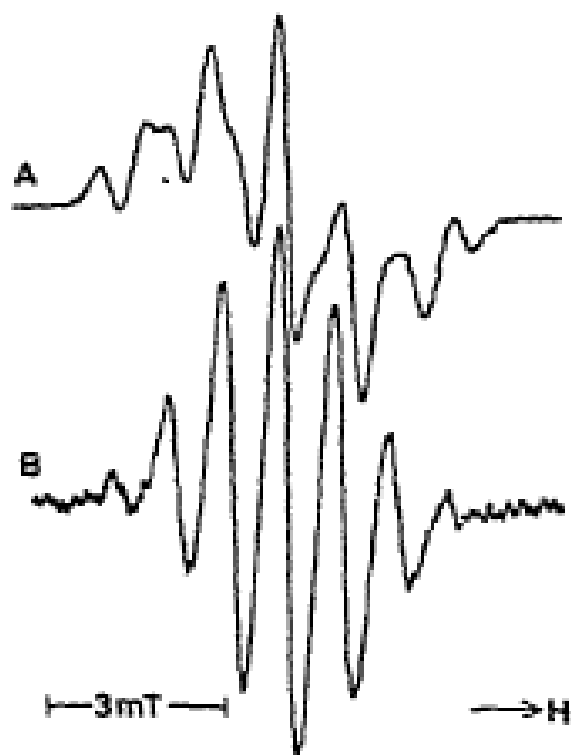
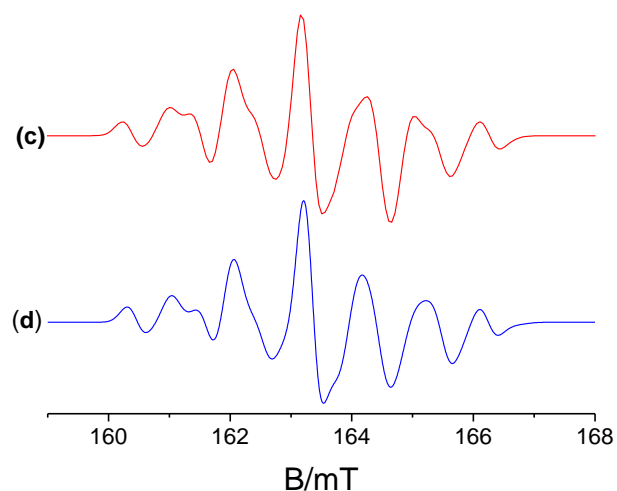


Fig. 4. EPR spectra of the $\Delta M_S = 2$ transition recorded at (A) 77 K and (B) 121 K for triplet state $C(CH_2)_3$ generated in polycrystalline methylene-cyclopropane irradiated by γ -rays at 77 K [8]. The simulated spectra, (c) obtained with Coupled_ESR (red line) and (d) Easyspin (blue line) were calculated with parameters in [9]

Ex5C: Radical pairs $H\cdots CH_3$ and $D\cdots CD_3$ in frozen Ar gas at low T

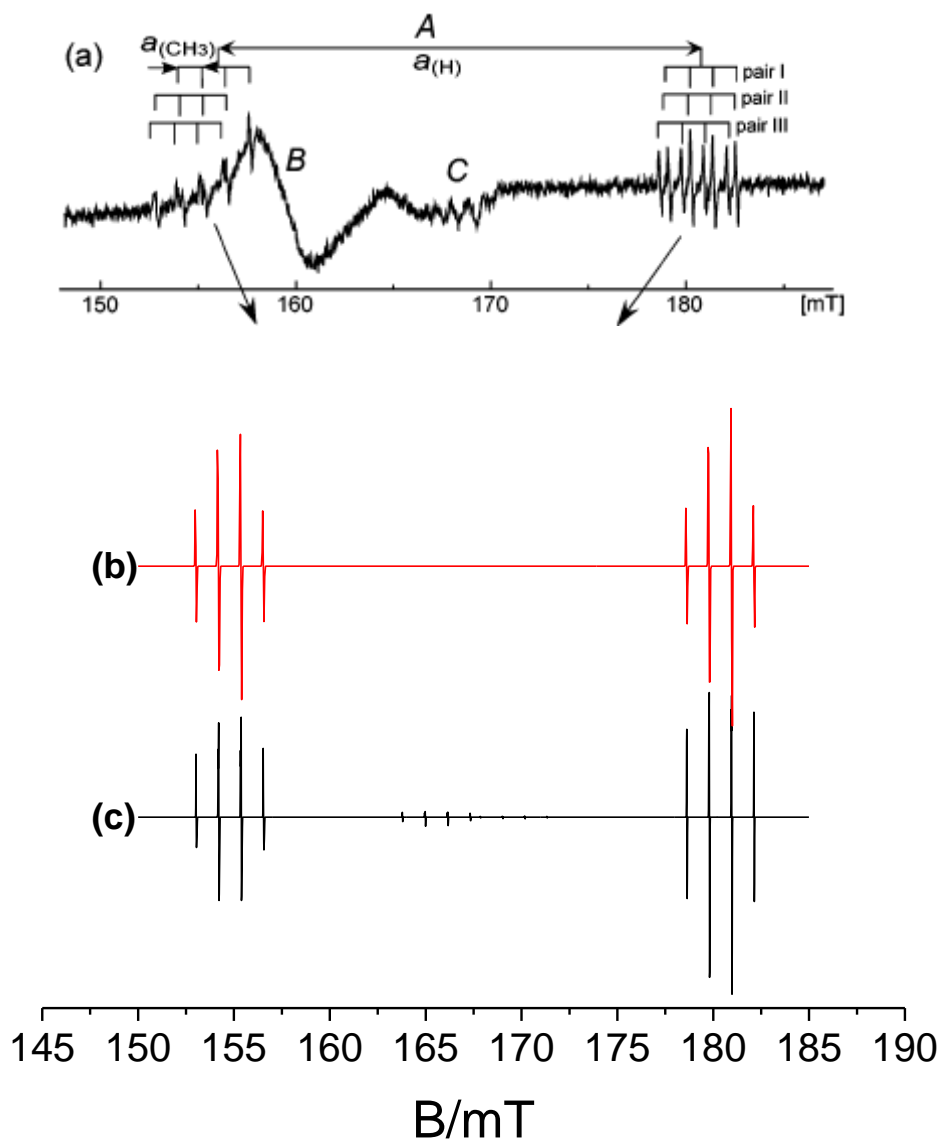


Fig.5. (a) Experimental $\Delta M_S = 2$ powder spectrum of $H \cdots CH_3$ in frozen argon gas at 4 K. (b) Simulations (b) with Easypin (red trace), (c) with Coupled_ESR (black trace) were obtained with experimental data in [10].

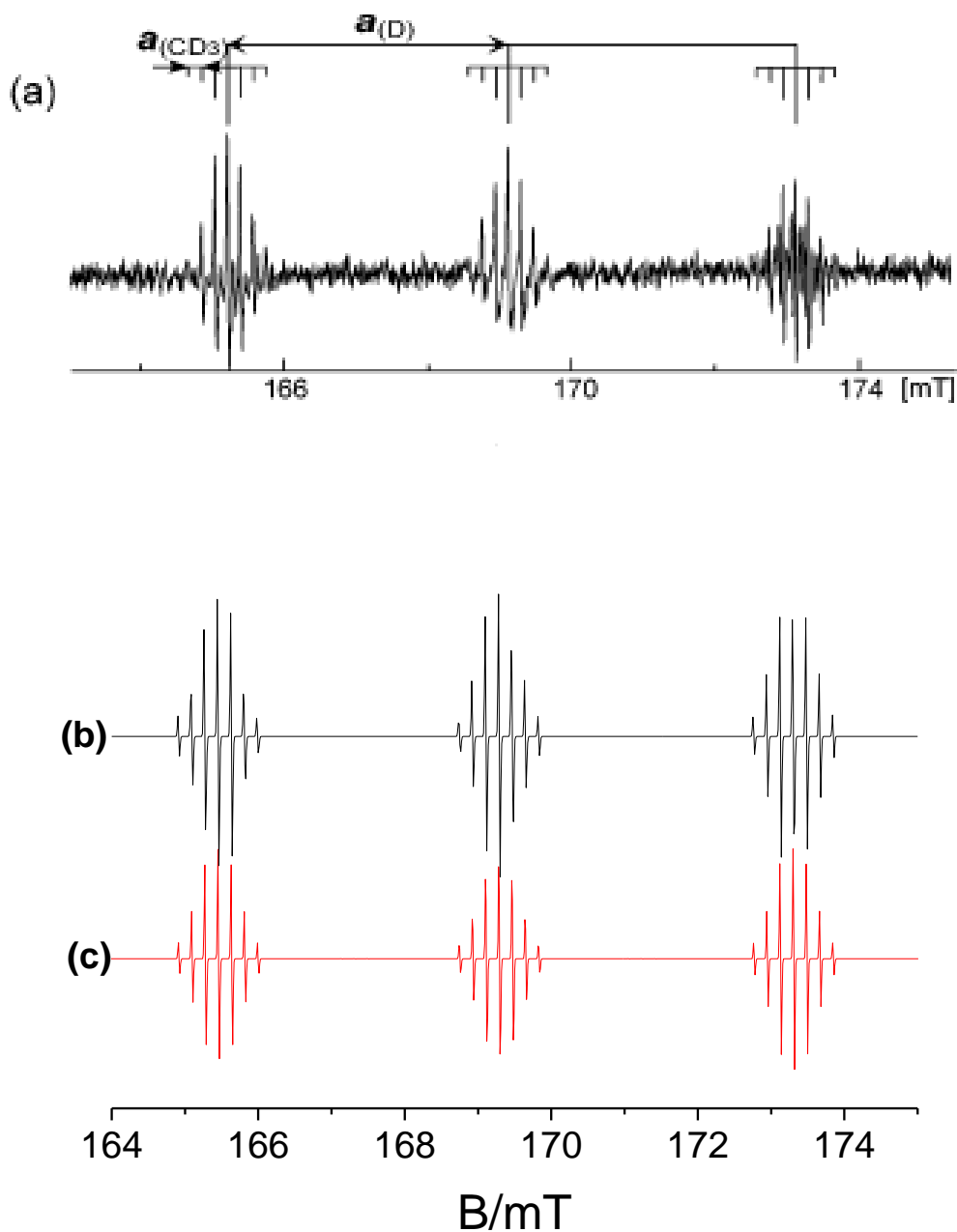


Fig.6. (a) Experimental $\Delta M_S = 2$ powder spectrum of $D \cdots CD_3$ in frozen argon gas at 4K, Simulations (b) with Easyspin (red trace), (c) with Coupled_ESR (black trace) were obtained with experimental data in [10].

Coupled_ESR performance in comparison with Easyspin

The simulations of the X-band spectra in Figs. 1 and 2, obtained with Coupled_ESR and Easyspin were in better agreement with the experimental spectra, attributed to the radical $R\dot{C}F_2CF_2$ in a UV-irradiated Nafion/Fe(III) sample, and CF_3 in frozen noble gas, than obtained earlier using Simfonia and Maru for the simulations [4,11]. The central features of the experimental $\dot{C}F_3$ spectrum could not be reproduced with the

2nd order option in [2], however. The lack of agreement between experimental and simulated spectra, observed previously for RCF₂CF₂, was attributed to a nonplanar radical structure [4], leading to the observed broadening of the central features in Fig. 1(a). The method employed in Coupled_ESR seems to be applicable for radicals containing a few magnetic nuclei, but became time-consuming for S=½ species with several hfc couplings, e.g. of ¹⁹F nuclei [12]. Computations with Easyspin were faster.

The EPR spectra observed by introducing NO in Na-LTA zeolite were analyzed using the geometric model for the (NO)₂ biradical shown in Fig.3. A conformation with an angle $\Theta \approx 0^\circ$ between the two NO bonds was proposed based on simulations [1,6] for two interacting NO molecules. The simulations in Figs. 3 (e), (e'), (f) and (f') obtained with Easyspin (red line) and Coupled_ESR (blue line) support the assignment. The $\Delta M_S = 2$ transition was weak and not observed in the Q-band spectra or in simulations. The $\Delta M_S = 2$ spectrum of triplet state C(CH₂)₃ generated in γ -irradiated methylene-cyclopropane at 77 K [8], Fig4A. was simulated with Coupled_ESR (Fig. 4(c), red line) and Easyspin (Fig. 4(d) blue line, The 2nd order option in Easyspin and Simfonia [12] (not shown) did not account for the $\Delta M_S = 2$ transitions. Those methods are therefore unsuitable for the simulation of spectra containing $\Delta M_S = 2$ features. The simulated hfc pattern of the $\Delta M_S = 2$ spectrum in Fig. 4(c), agrees quite well with experiment and with Easyspin simulation, Fig.4(d), supporting the assignment in [9]. The corresponding calculation with this method of the $\Delta M_S = 1$ spectrum was very time-consuming (several days), however. The hybrid option in Easyspin [2] and the Triplet program [13] seem to be better suited for the analysis of complex hyperfine patterns of the $\Delta M_S = 1$ spectra in the triplet state.

High-resolution ESR spectra of radical pairs of a hydrogen atom that couples with a methyl radical (H··CH₃, H··CHD₂, D··CH₂D, and D··CD₃) were observed in X- irradiated solid argon containing selectively deuterium-labeled methanes at 4.2 K [10]. The $\Delta M_S = 2$ spectra of H··CH₃ and D··CD₃ in Fig. 5 and 6 were simulated by treating the hydrogen atom and methyl radical as two units coupled by the e-e interaction between the unpaired electrons. The resolution was extremely good due to the absence of e-e coupling in the $\Delta M_S = 2$ spectra. The line-shapes predicted by simulations with Easyspin and Coupled_ESR are displayed in Figs 5 and 6 together with the experimental spectra. Calculations of the $\Delta M_S = 1$ spectra using Simfonia were reported in [10]. The hybrid method in [2] is of interest in case higher accuracy is needed for the $\Delta M_S = 1$ spectra, while simulation with Coupled_ESR is expected to be time-consuming.

Conclusions

Accurate simulations were obtained for powder spectra of S=½ systems containing a few magnetic nuclei using Coupled_ESR. Previous studies have shown that the simulation of c-alkane radical anions with appreciable hfc splittings of up to eight ¹⁹F were tedious, however. The relative orientation of the N—O bonds was found to affect the shape of the (NO)₂ biradical spectrum. Hfc patterns of I=½ and I=1 nuclei in radical pairs and triplet states could be accounted for by simulations of the $\Delta M_S = 2$ spectra. The quality was comparable with that obtained using Easyspin [2]. The computer times were, however, longer especially for the $\Delta M_S = 1$ EPR spectra. Further developments seem to be needed to match the performance of Easyspin [2] and other software [14] in such calculations.

Files at <http://www.liu.se/simarc/downloads?l=en>

- Data: Input data for the simulation of powder spectra are in files Ex1C.txt, Ex2C.txt, Ex3C.txt, Ex4C.txt and Ex5C.txt.
- Programs: Source and executable codes are in files Coupled_ESR.for and Coupled_ESR.exe.
- References: Copies of [1], [3], and [4] are in files Ref_1.pdf, Ref_3.pdf, and Ref_4.pdf.
- Manual: This document.

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