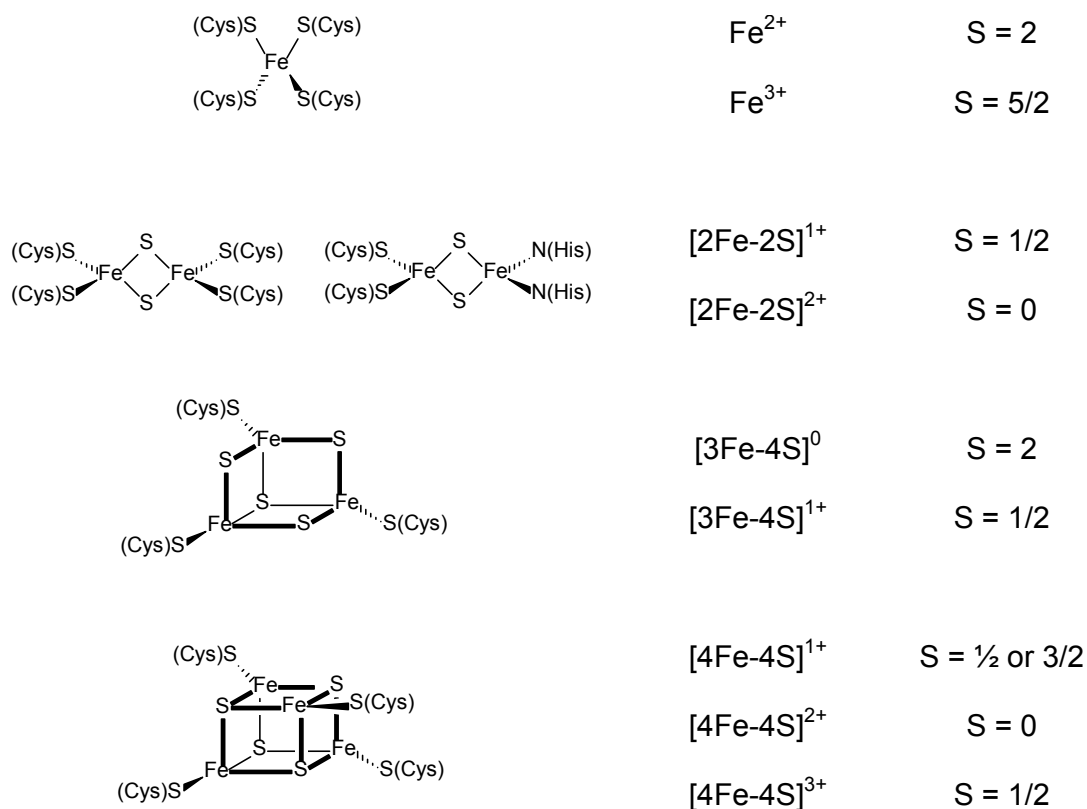
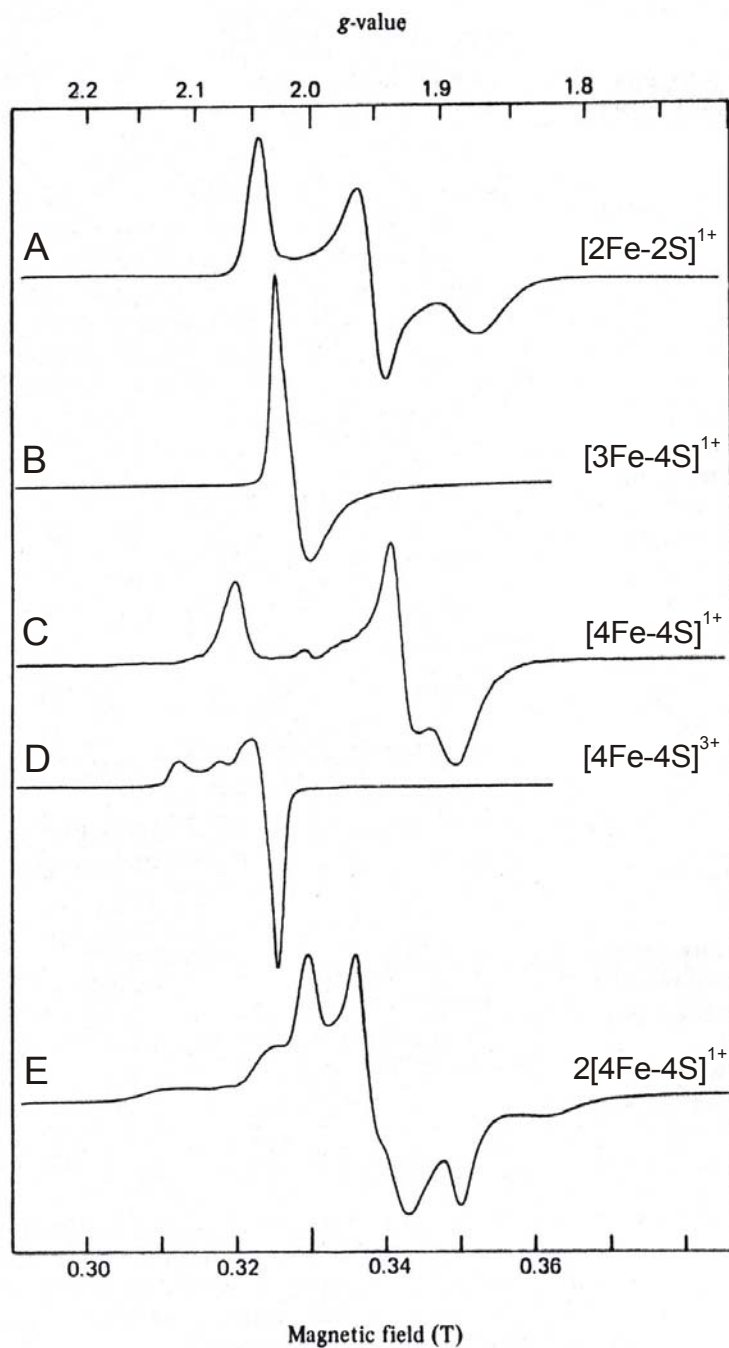


5 Selected
Samples

5.1 Iron sulfur clusters

There are several standard-type iron-sulfur clusters. The figure below gives the basic structure for these clusters, the different oxidation states, and the accompanying spin states.





EPR spectra of Fe-S clusters in ferredoxins:

(A) *Mastigocladus laminosus*;

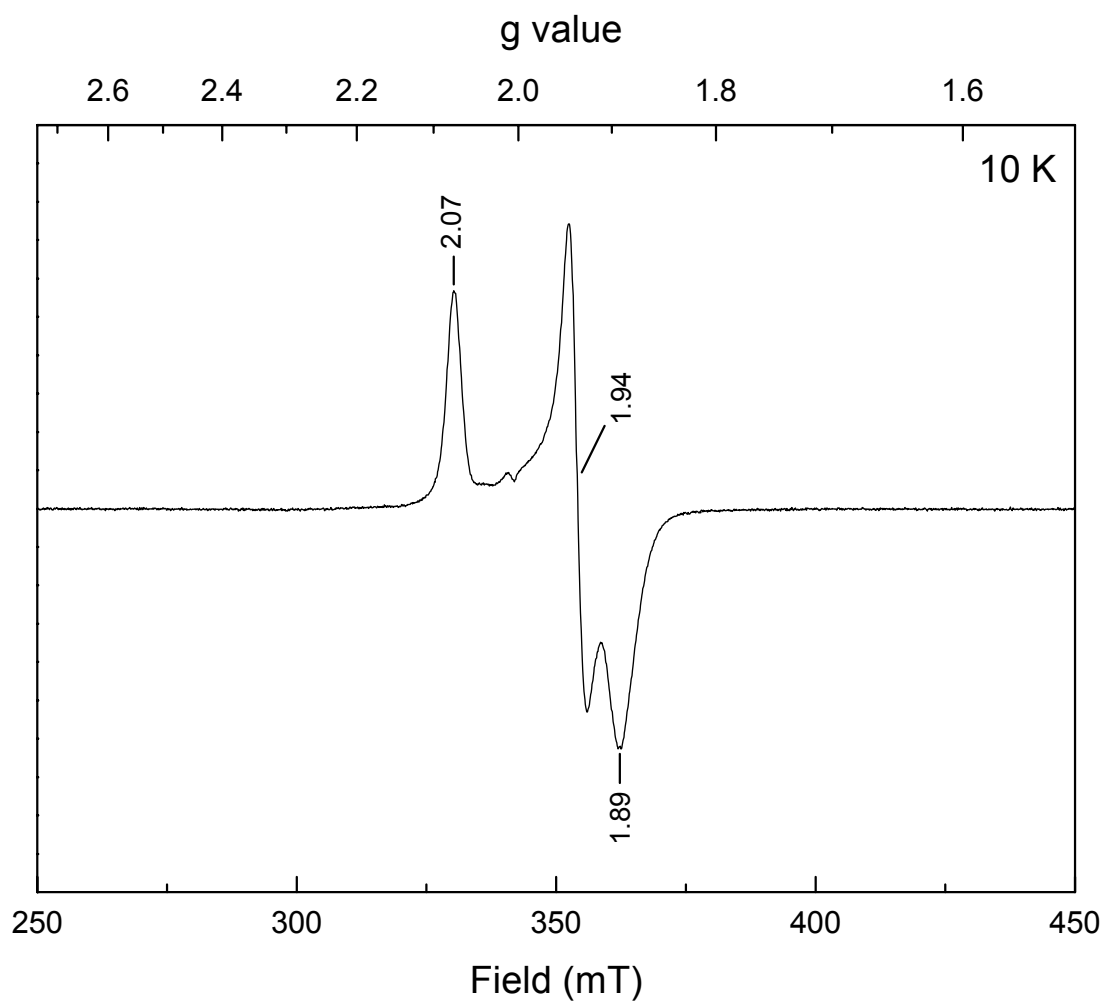
(B) *Desulfovibrio gigas*;

(C) *Bacillus stearothermophilus*;

(D) *Chromatium vinosum* high-potential iron-sulphur protein (HiPIP);

(E) *Clostridium pasteurianum* 8Fe ferredoxin.

Sample A

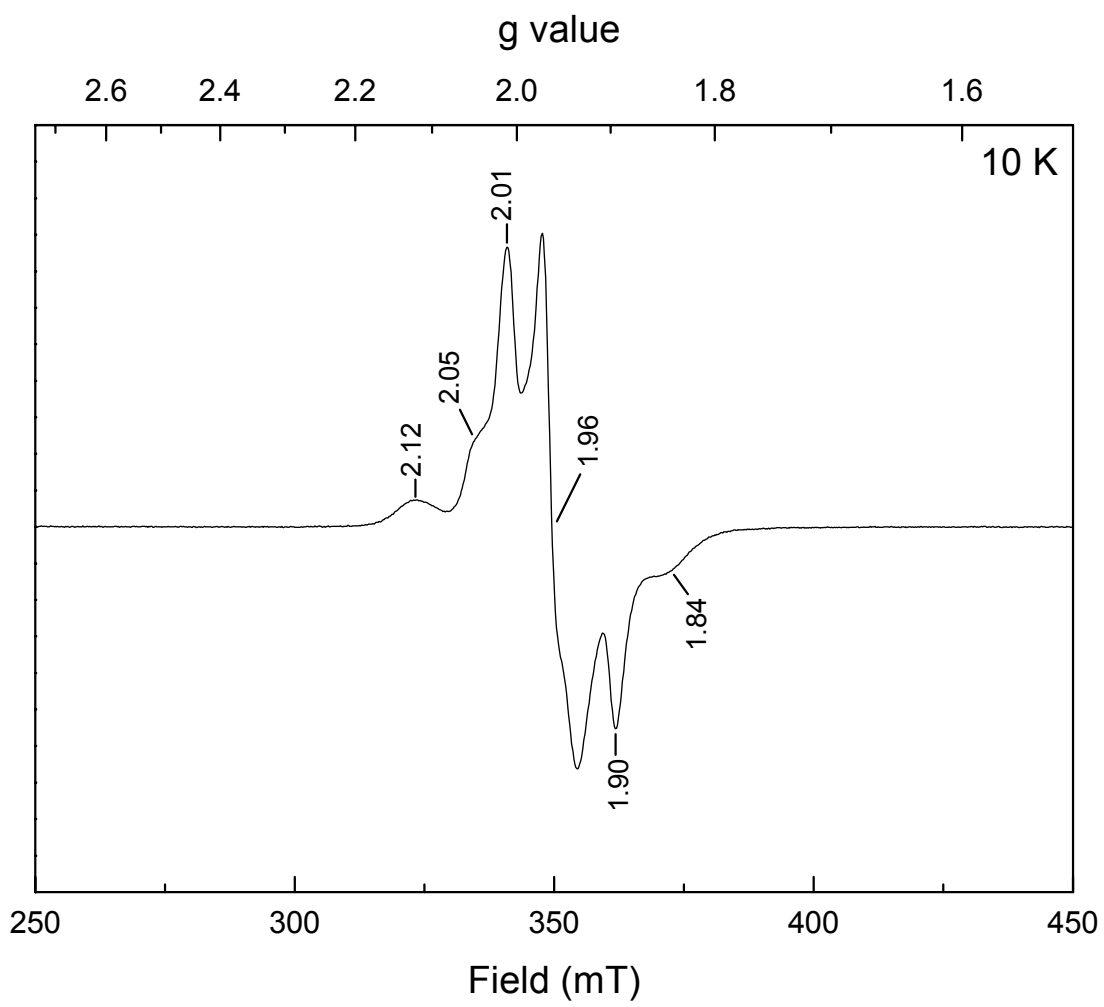


- Rhombic $S = 1/2$
- g values average out close to 2
- g values below 4
- Feature at $g = 2.00$ is due to a radical impurity

Origin: $[4\text{Fe-4S}]^+$

- Signal measured at 10 K, not due to $[2\text{Fe-2S}]$. 4Fe clusters have low-lying excited states causing the signal to show fast relaxation.

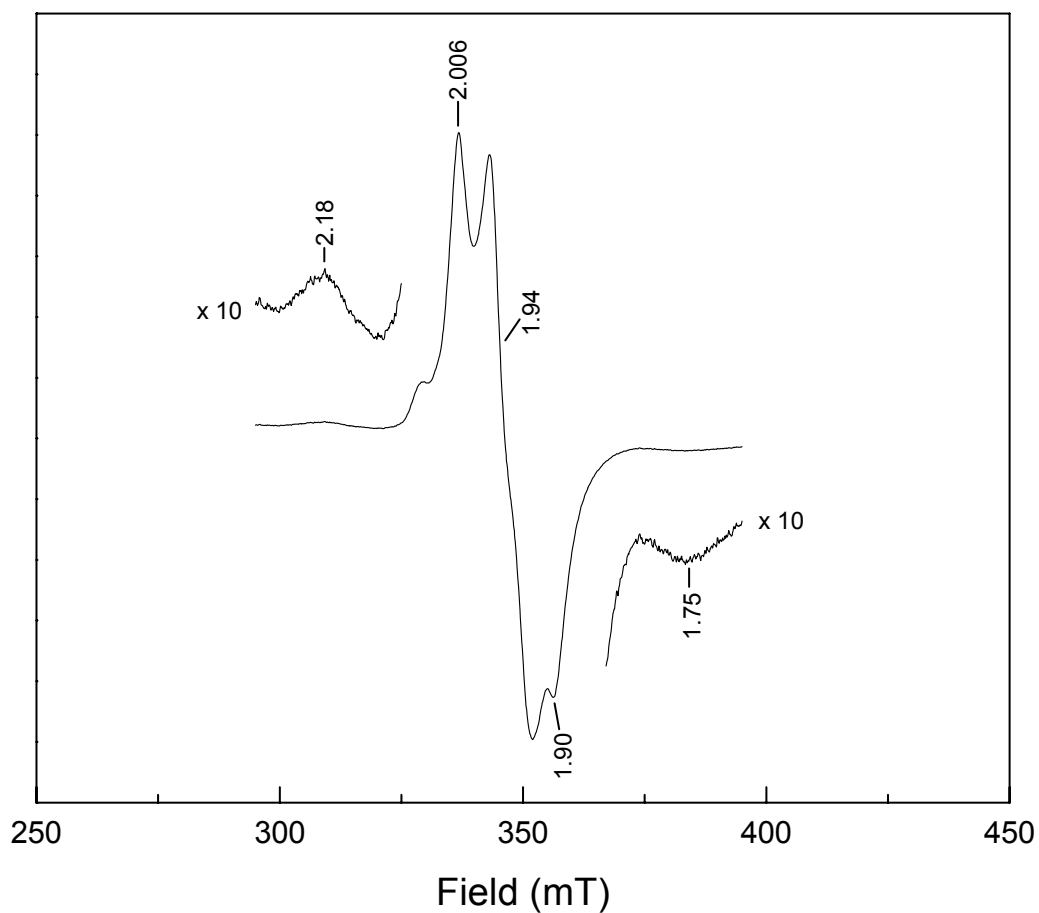
Sample B



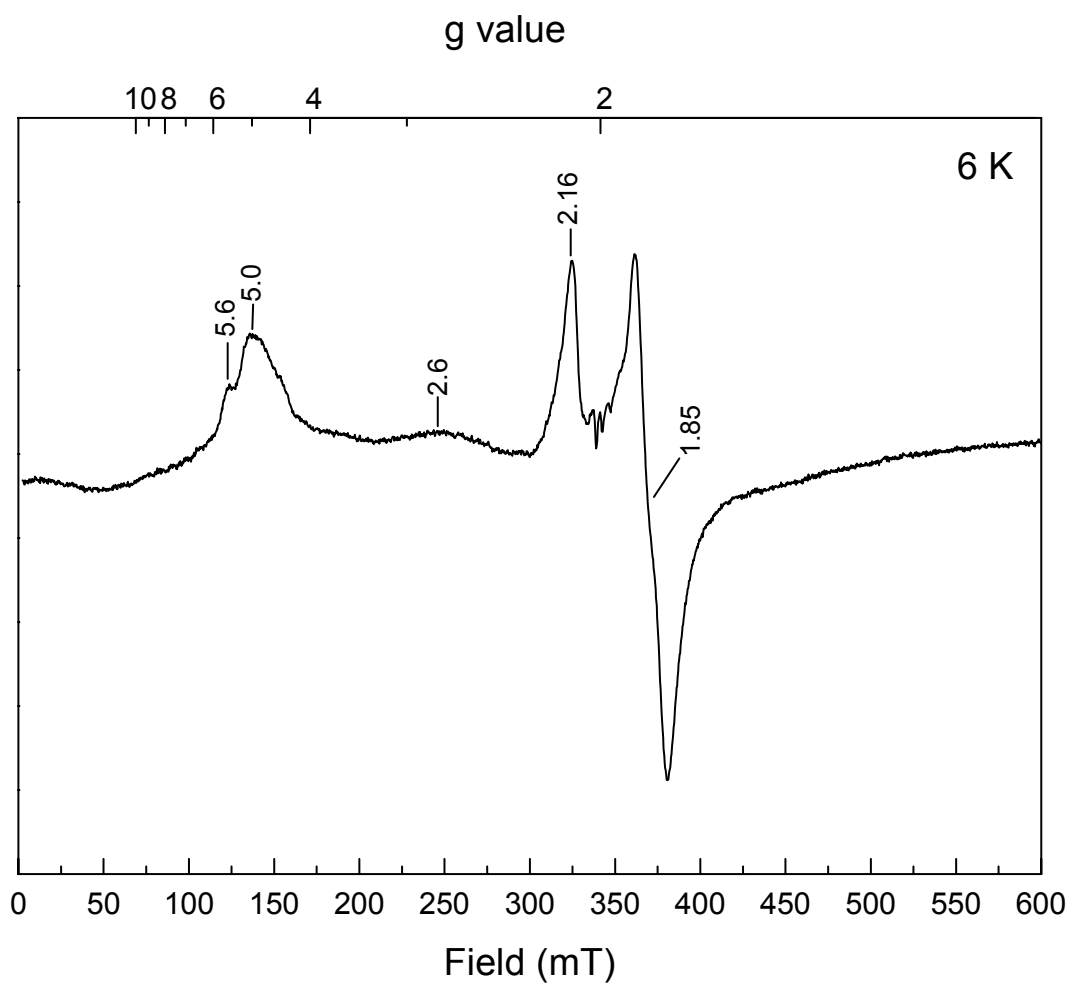
- $S = 1/2$ (g_{av} close to 2)
- 2 clusters?

Origin: 8Fe ferredoxin containing two $[4Fe-4S]^+$ 12 Å apart.

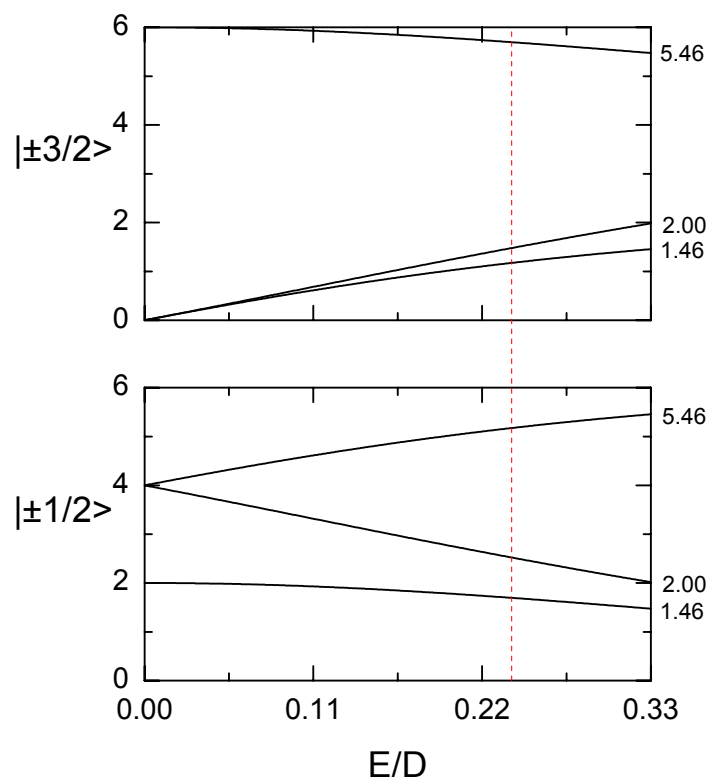
- Next step would be to run different temperatures, powers etc.,
- to do a simulation of the EPR signal,
- to run the same sample at Q or S-band. (If this is an interacting species the g values will change.)



Sample C



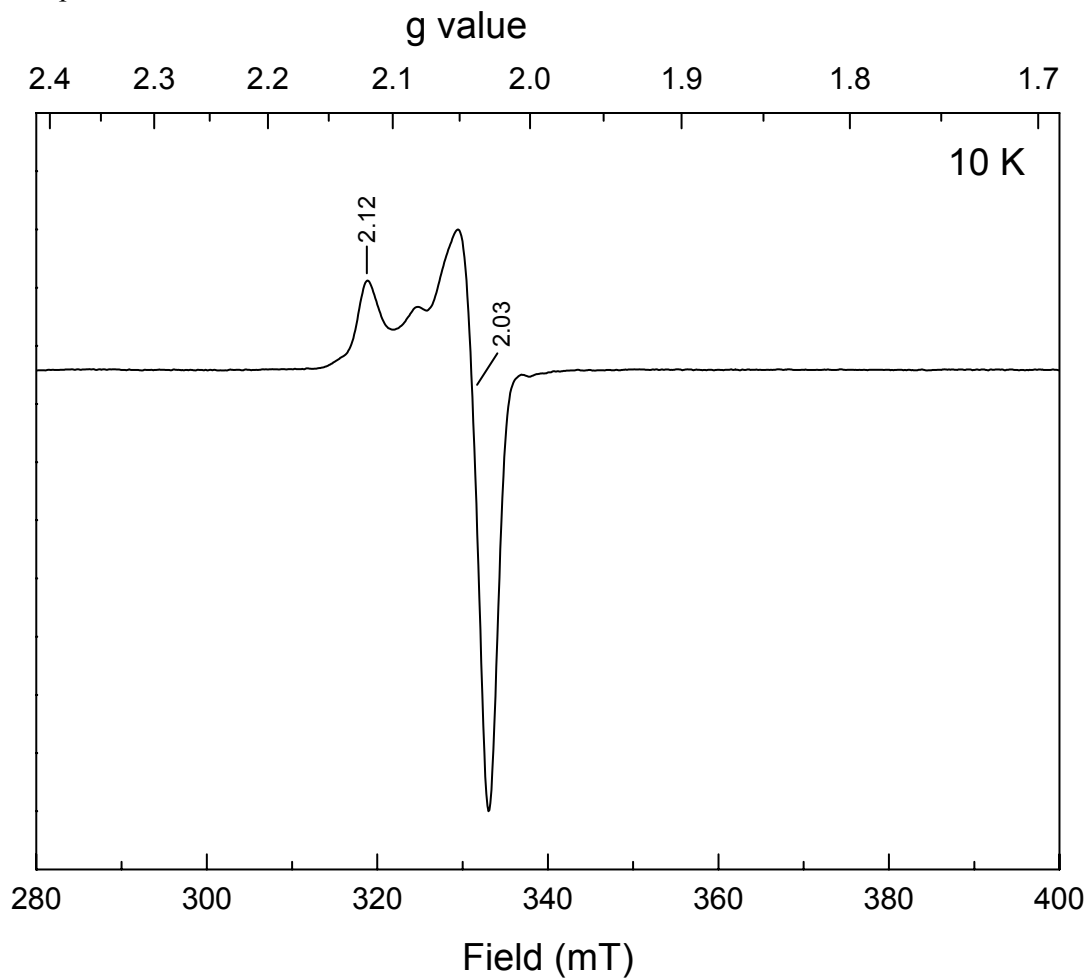
Rhombogram for $S = 3/2$



- $S = 3/2$ (all g values below 6)
20% $S = 1/2$, 80% $S = 3/2$
- $E/D \approx 0.24$
- $D > 0$

Origin: $[4\text{Fe-4S}]^+$ cluster

Sample D

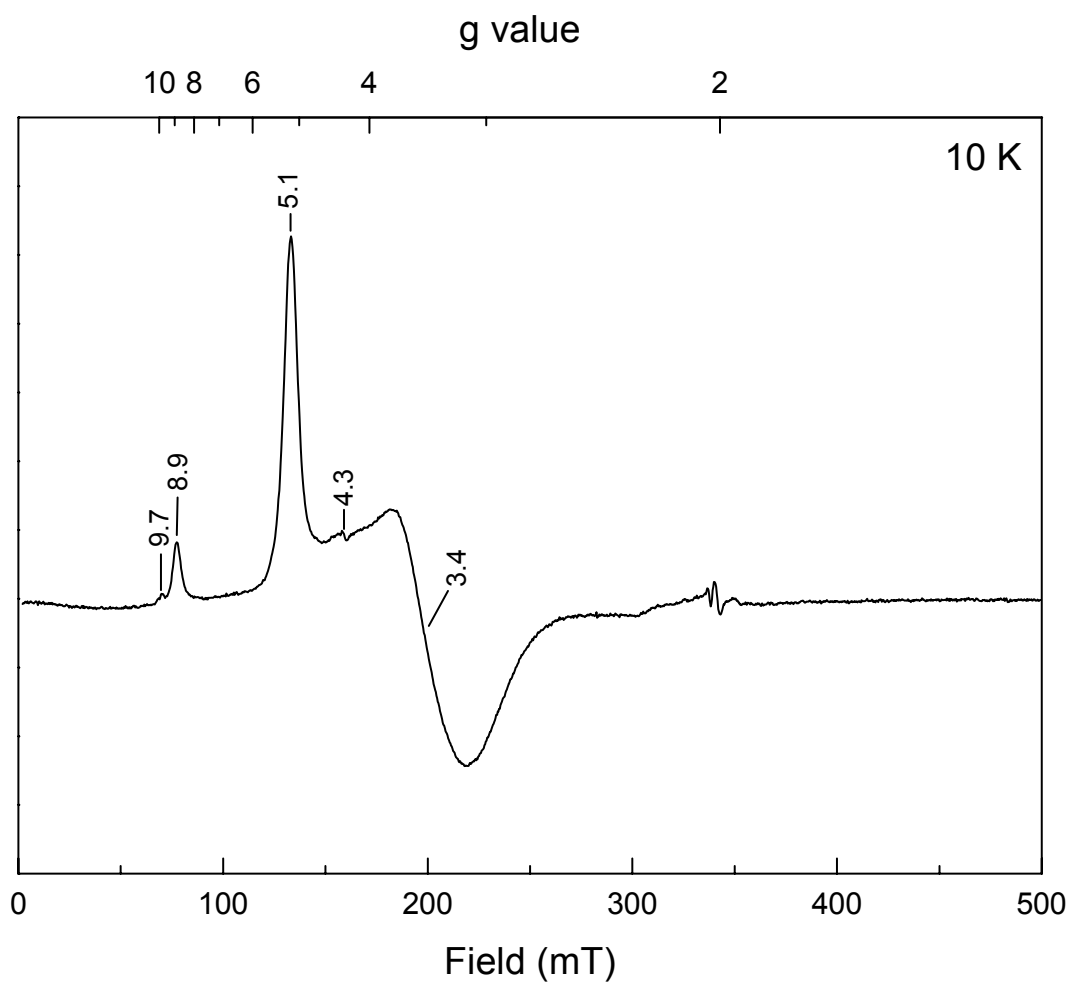


- Rhombic $S = 1/2$
- g values average out close to 2
- g values below 4
- Feature at $g = 2.00$ is due to a radical impurity

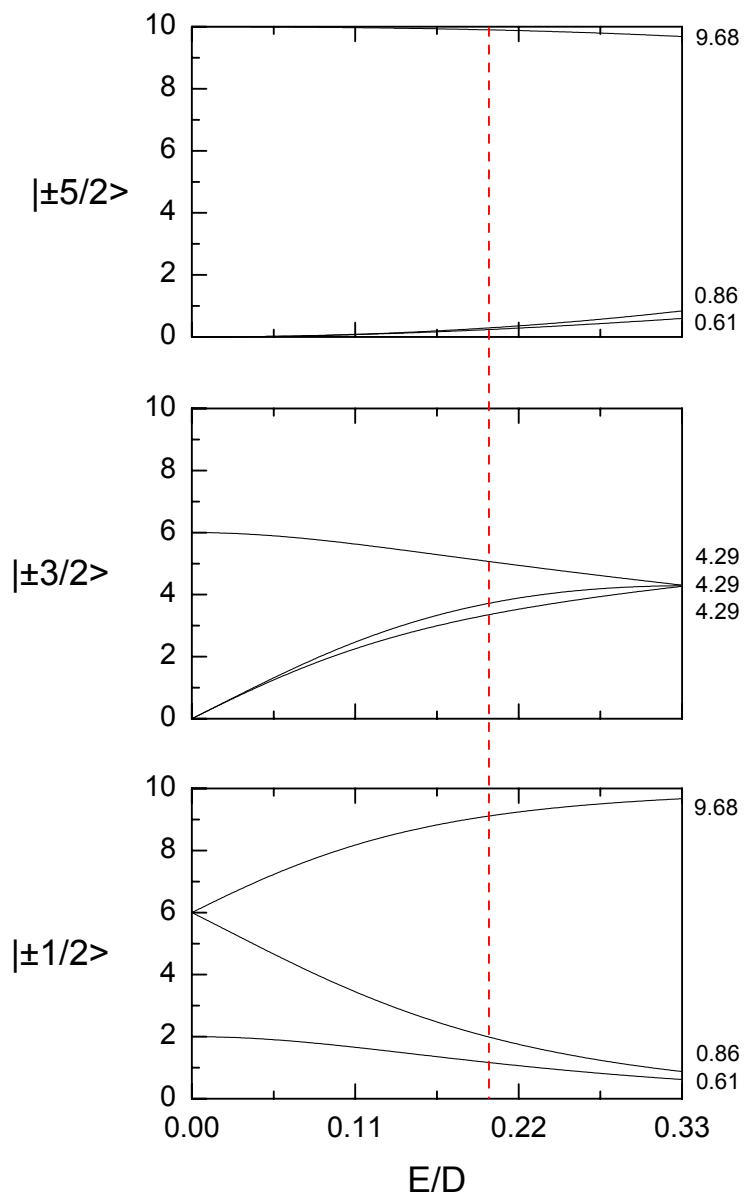
Origin: $[4\text{Fe-4S}]^{3+}$ (HiPIP)

- Signal measured at 10 K, not due to $[2\text{Fe-2S}]$. 4Fe clusters have low-lying excited states causing the signal to show fast relaxation.

Sample E



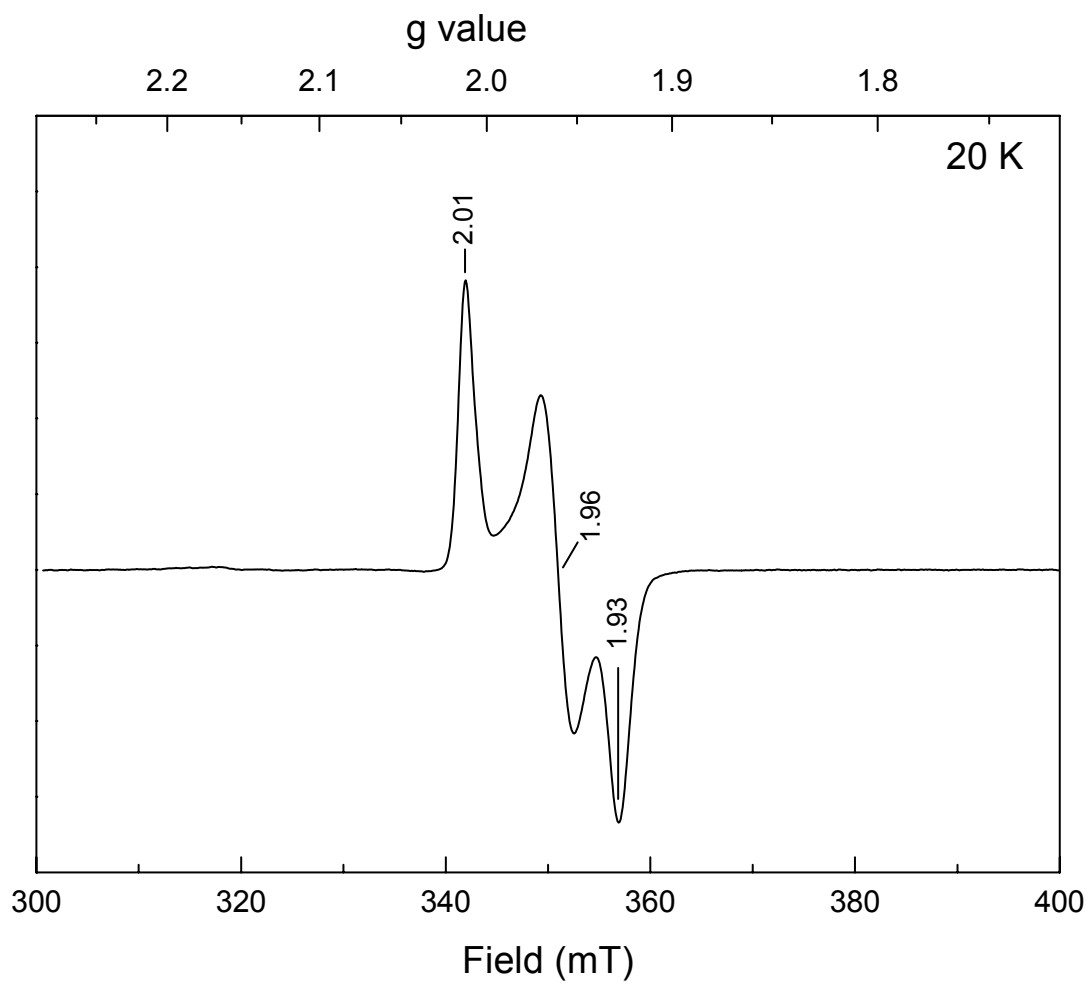
Rhombogram for $S = 5/2$



- $S = 5/2$ (all g values below 10)
- $E/D \approx 0.2$ ($g = 9.67$ is due to a different species)
- $D < 0$

Origin: $[\text{Zn-3Fe-4S}]^+$ cluster

Sample F

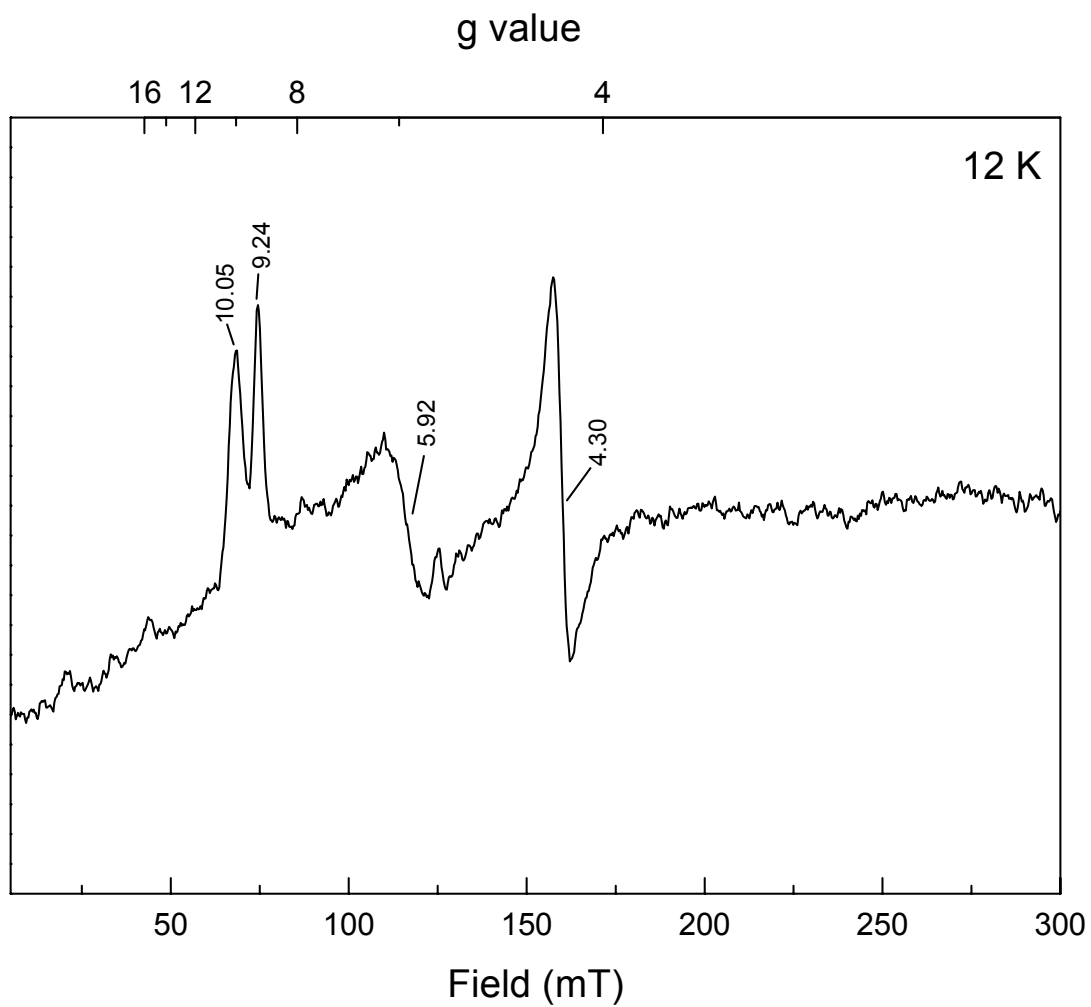


- Rhombic $S = 1/2$
- g values average out close to 2
- g values below 4

Origin: $[2\text{Fe-2S}]^+$ (*Clostridium pasteurianum* 2Fe Fd)

- Signal measured at 20 K, not due to $[4\text{Fe-4S}]$. 4Fe clusters have low-lying excited states causing the signal to show fast relaxation.

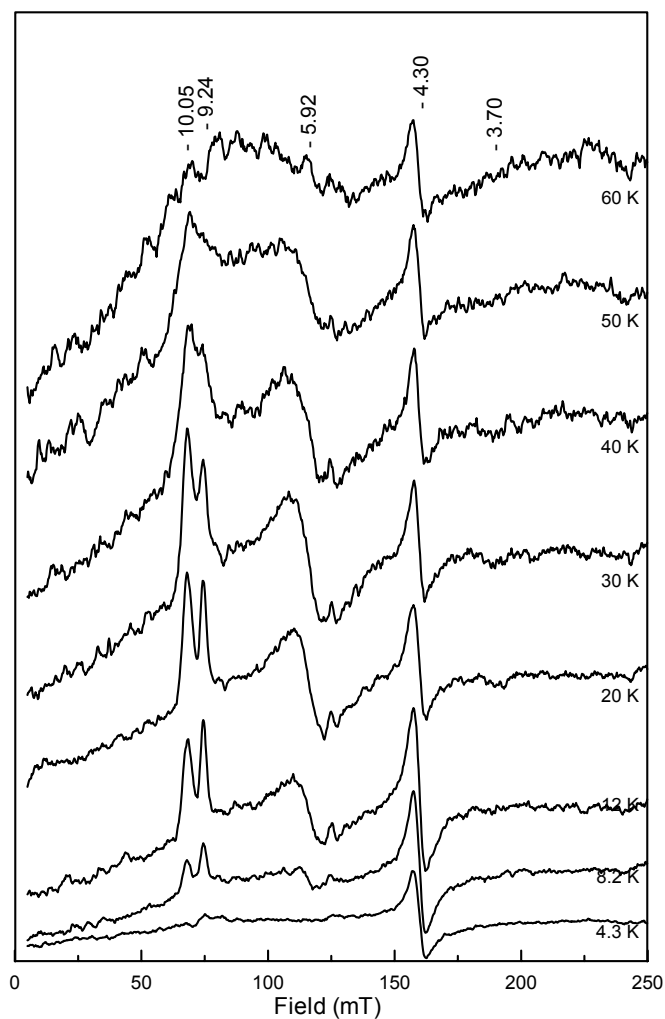
Sample G



Origin $[2\text{Fe}-2\text{S}]^+$ cluster with $S = 9/2$ (*Clostridium pasteurianum* 2Fe Fd, C60S mutant)

(Compare with $S = 9/2$ complexes)

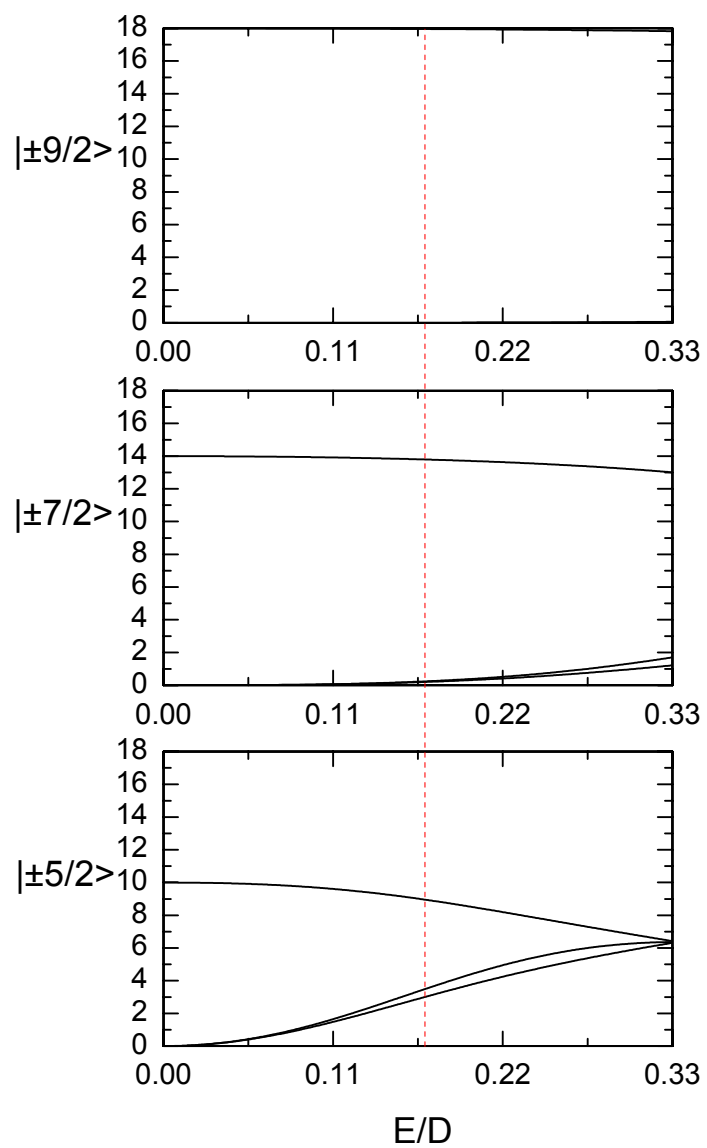
Sample is clearly a species with $S > 1/2$. Temperature studies needed to get correct spin state:

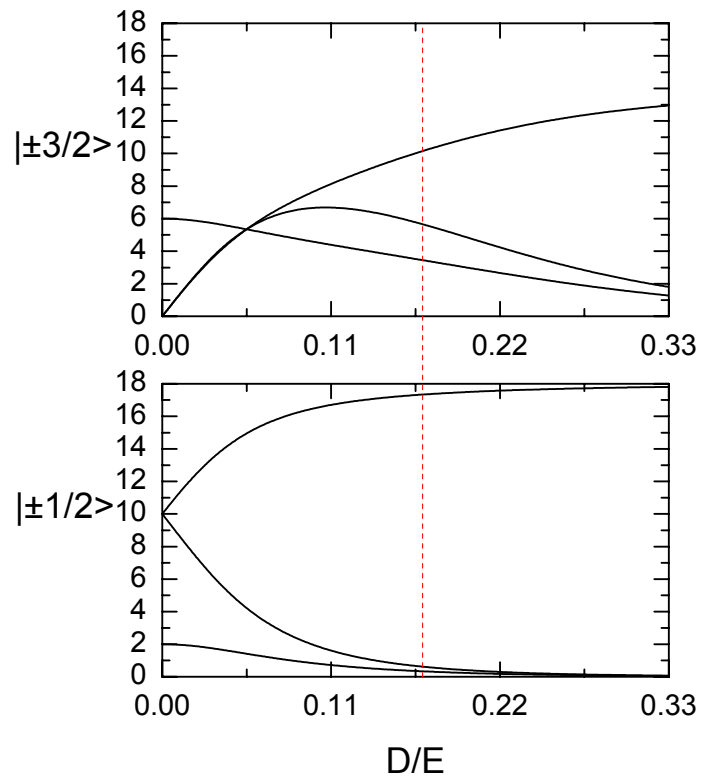


$E/D = 0.17, g = 2.00$			
$ \pm 1/2\rangle$	0.35	17.32	0.66
$ \pm 3/2\rangle$	3.51 (3.70)	10.05 (10.05)	5.75 (5.92)
$ \pm 5/2\rangle$	9.00 (9.24)	2.91	3.37
$ \pm 7/2\rangle$	13.80	0.19	0.22
$ \pm 9/2\rangle$	17.96	0.003	0.003

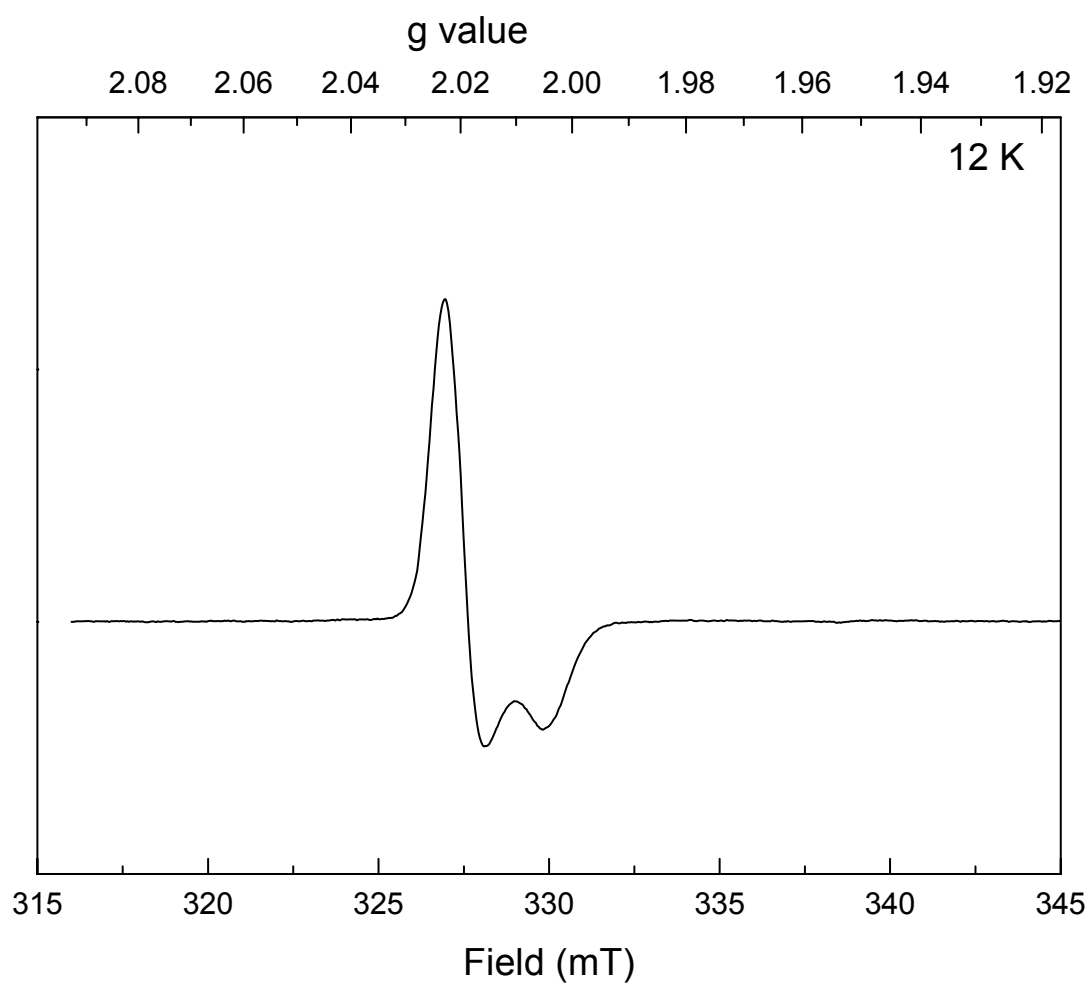
$D = -1.4 \text{ cm}^{-1}$ (log $[I_{10.05}/I_{9.24}]$ versus $1/T$)

Rhombogram for $S = 9/2$





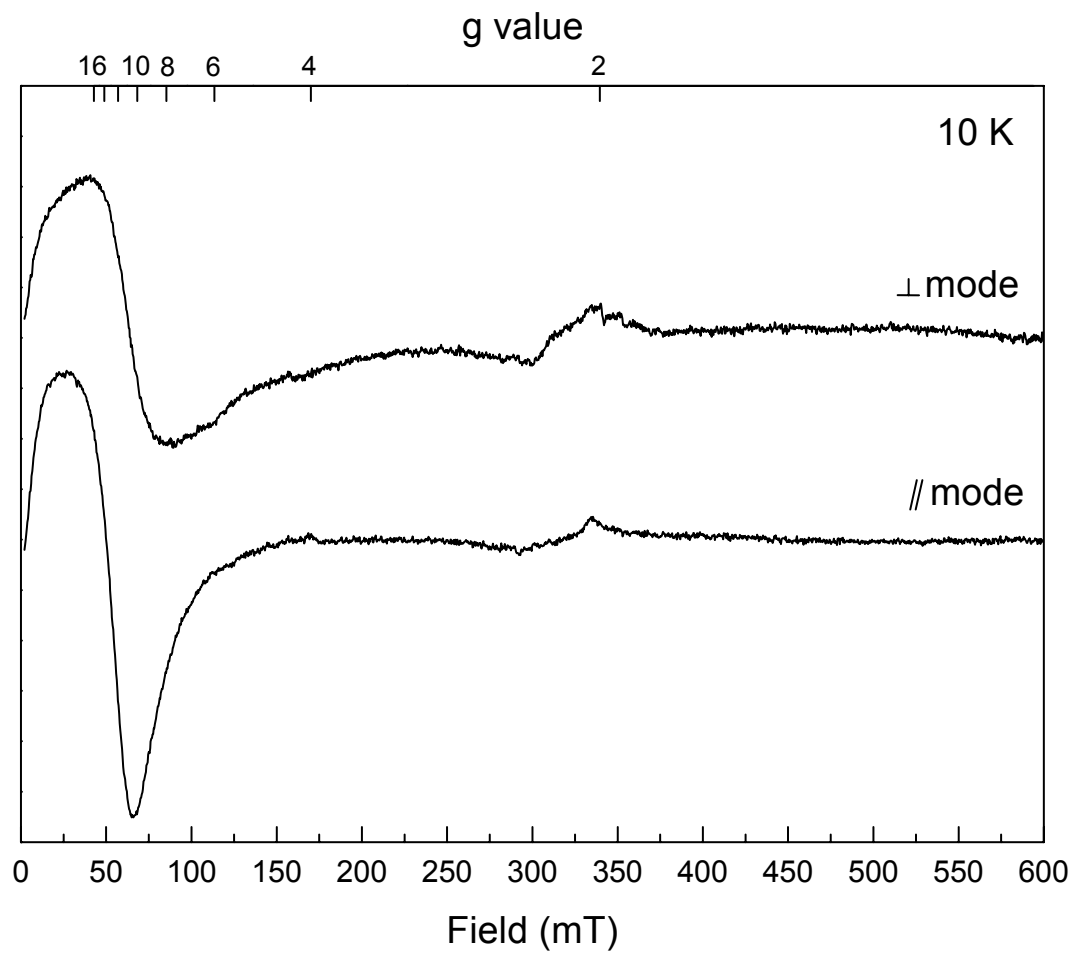
Sample H



- Axial $S = 1/2$
- g values average out close to 2
- g values below 4

Origin: $[3\text{Fe-4S}]^+$ (*Chromatium vinosum* Hydrogenase)

Sample I



Origin: $[3\text{Fe-4S}]^0$, $S = 2$

