Zinc ions embedded in a dry DNA double helix form a 1D molecular chain of unpaired electron spins

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dnatec09, Dresden 2009

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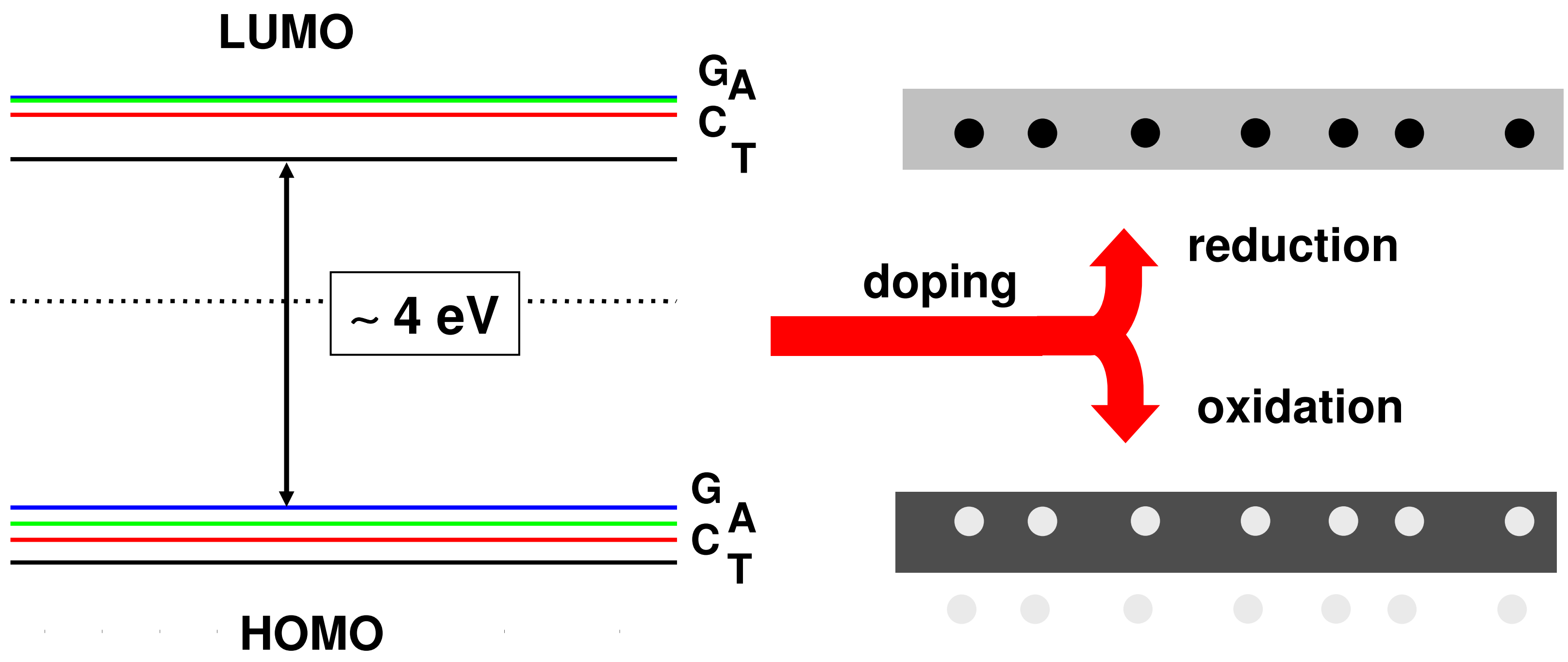
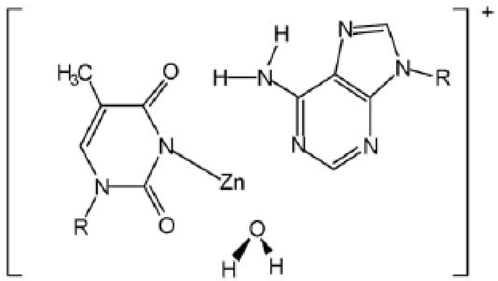
Motivation: DNA electronic doping for better conductivity



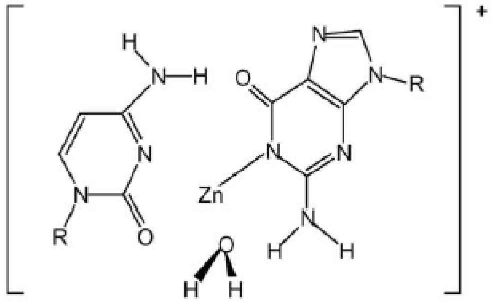
M-DNA

M: Zn^{2+}, Co^{2+}, Ni^{2+}

Imino $H^{+} \leftrightarrow Zn^{2+}$

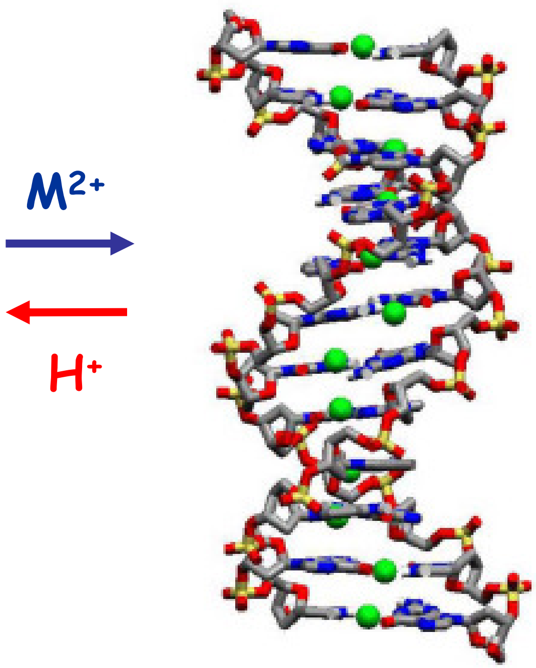


T-A



C-G

at N3 of T **at N1 of G**



- Synthesis in buffered water solutions
- High pH (8-9)
- Moderate temperature (RT ≤ T ≪ T_m)
- Salt concentration c_M > 1 mM
- DNA concentration c_{DNA} ~ 100 μg/ml (150 μM in terms of bp)
- Time t ≥ 1 h

J. S. Lee et al., *Biochem. Cell. Biol.* **71** (1993) 162

M-DNA Conductivity

In Solution

Electrochemical studies

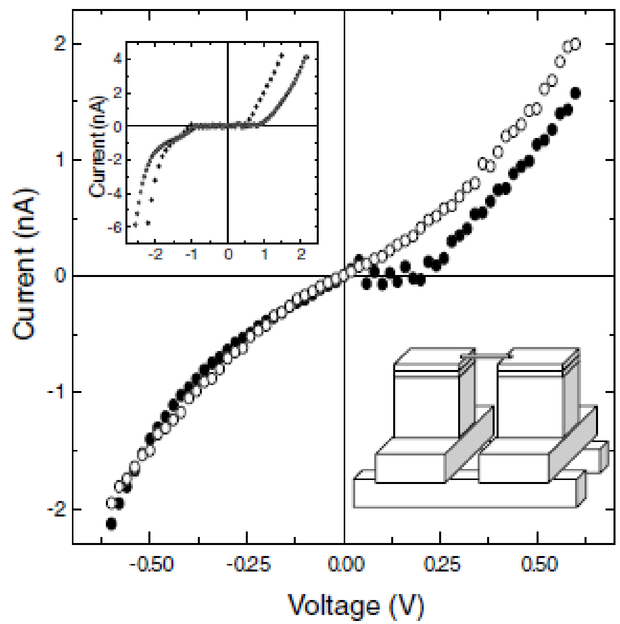
C. Z. Li et al. J. Phys. Chem. ***B*** **107** (2003) 2291

Fluorescence quenching experiments

P. Aich et al., *J. Mol. Biol.* **294**(1999) 477
S. D. Wettig et al., *Nano. Lett.* **3** (2003) 617.

⇒ **High electron-transfer rates**

In Solid State (dry)



A. Rakitin et al., *Phys. Rev. Lett.* **86** (2001) 3670

Free carriers in *M*-DNA?

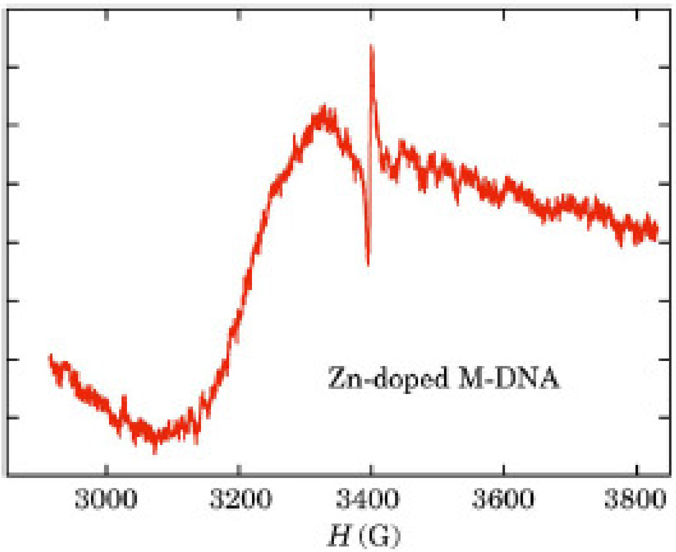


FIG. 5. (Color online) EPR spectrum of Zn-DNA. The signal intensity is much weaker than that for Mn-DNA, as implied by a low *S*/*N* ratio compared with that in Mn-DNA.

K. Mizoguchi et al., *Phys. Rev.* **B 72** (2005) 033106

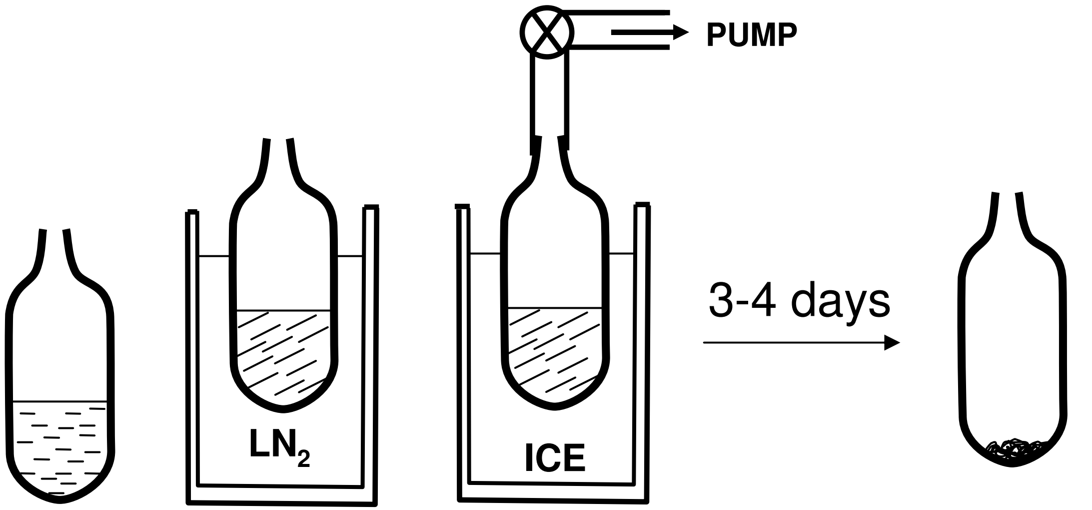
Percipitation with cold (-20°C) EtOH !

Preparation of dry (lyophilised) *M*-DNA

10 mM Tris-HCl buffer
pH 9

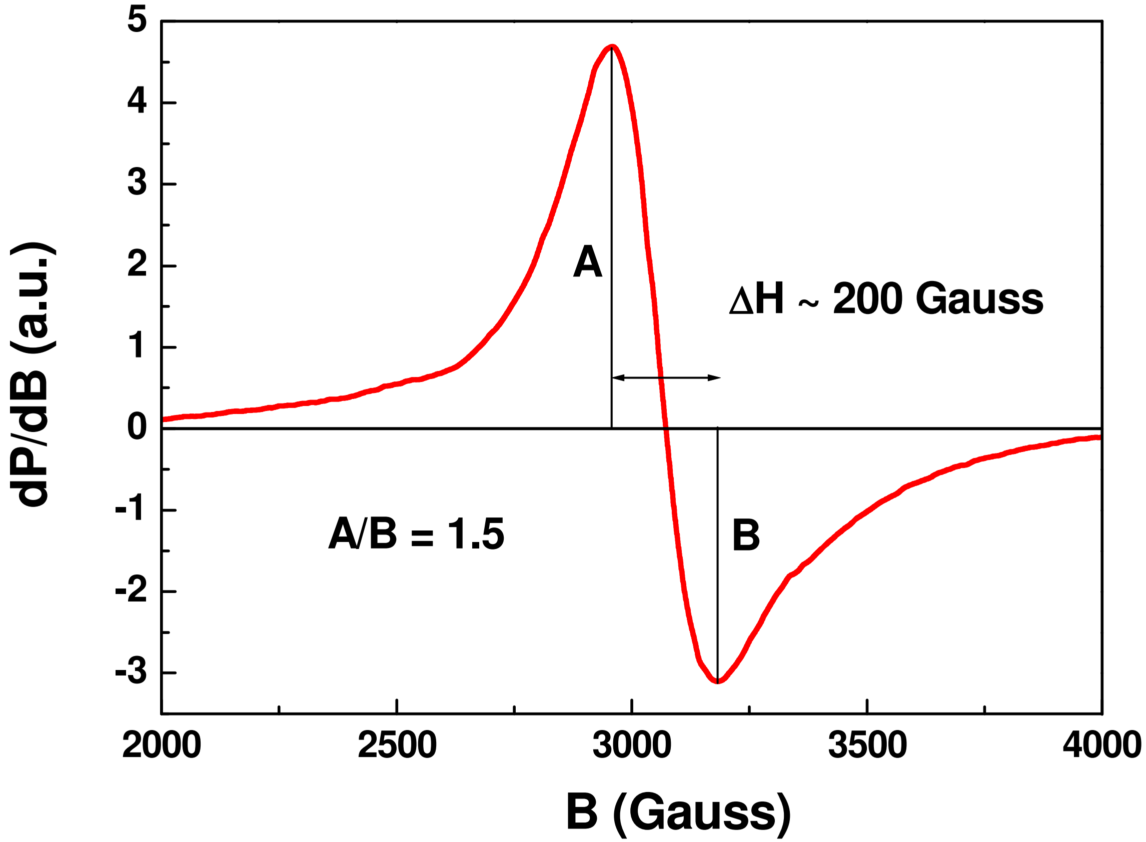
Calf Thymus DNA 100 μg/ml

$ZnCl_2$ ($Zn(ClO_4)_2$) 1.5 mM



Room-temperature ESR signal of *lyophilized* ZnDNA samples

- Strong (0.2-1 spin per bp)
- Broad (~ 200 Gauss)
- Asymmetric (A/B > 1)
- With g-value > 2 (g = 2.2)



Control experiments

ESR signal	Tris-HCl pH 7	Tris-HCl pH 9	DNA	$ZnCl_2$
Yes		✓	✓	✓
No		✓	✓	
No		✓		✓
No	✓		✓	✓

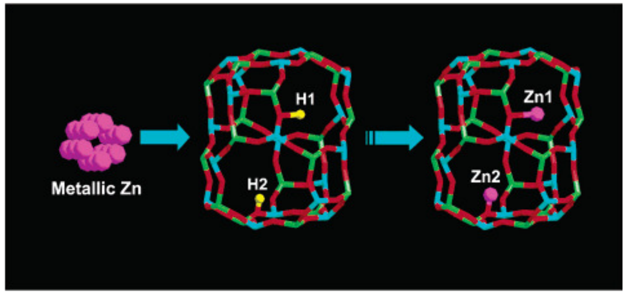
$$\underbrace{DNA + ZnCl_2 + \text{Tris-HCl pH 9} + H_2O}_{\text{diamagnetic}} \xrightarrow{\text{lyophilisation}} \underbrace{Zn@DNA}_{\text{paramagnetic}}$$

Monovalent Zn^{+} ?

Zinc Monocation in a Solid State

Electronic structure:

- Zn: $3d^{10}\ 4s^{2}$
- Zn^{+}: $3d^{10}\ 4s^{1}$
- Zn^{2+}: $3d^{10}\ 4s^{0}$



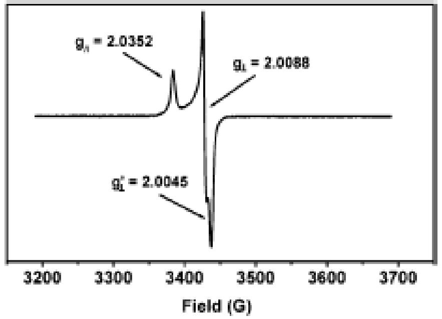
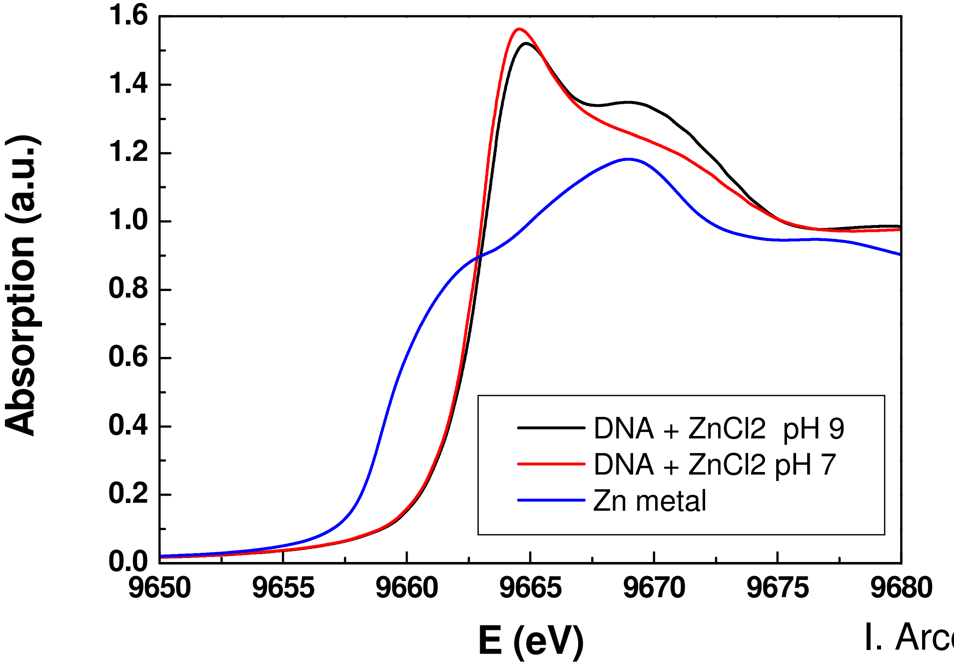


Figure 2. ESR spectrum for Zn@SAPO-CHA at room temperature.

Y. Tian et al., *J. Am. Chem. Soc.* **125** (2003) 6622

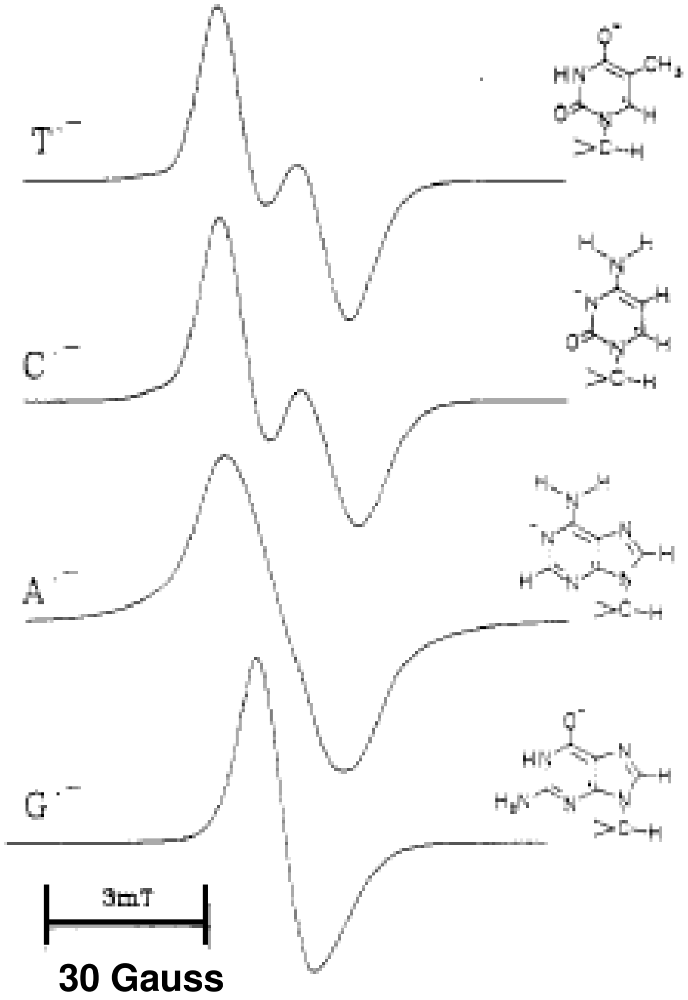
Zn K-edge XANES



I. Arcon, 2009

⇒ **No monovalent Zn^{+}**

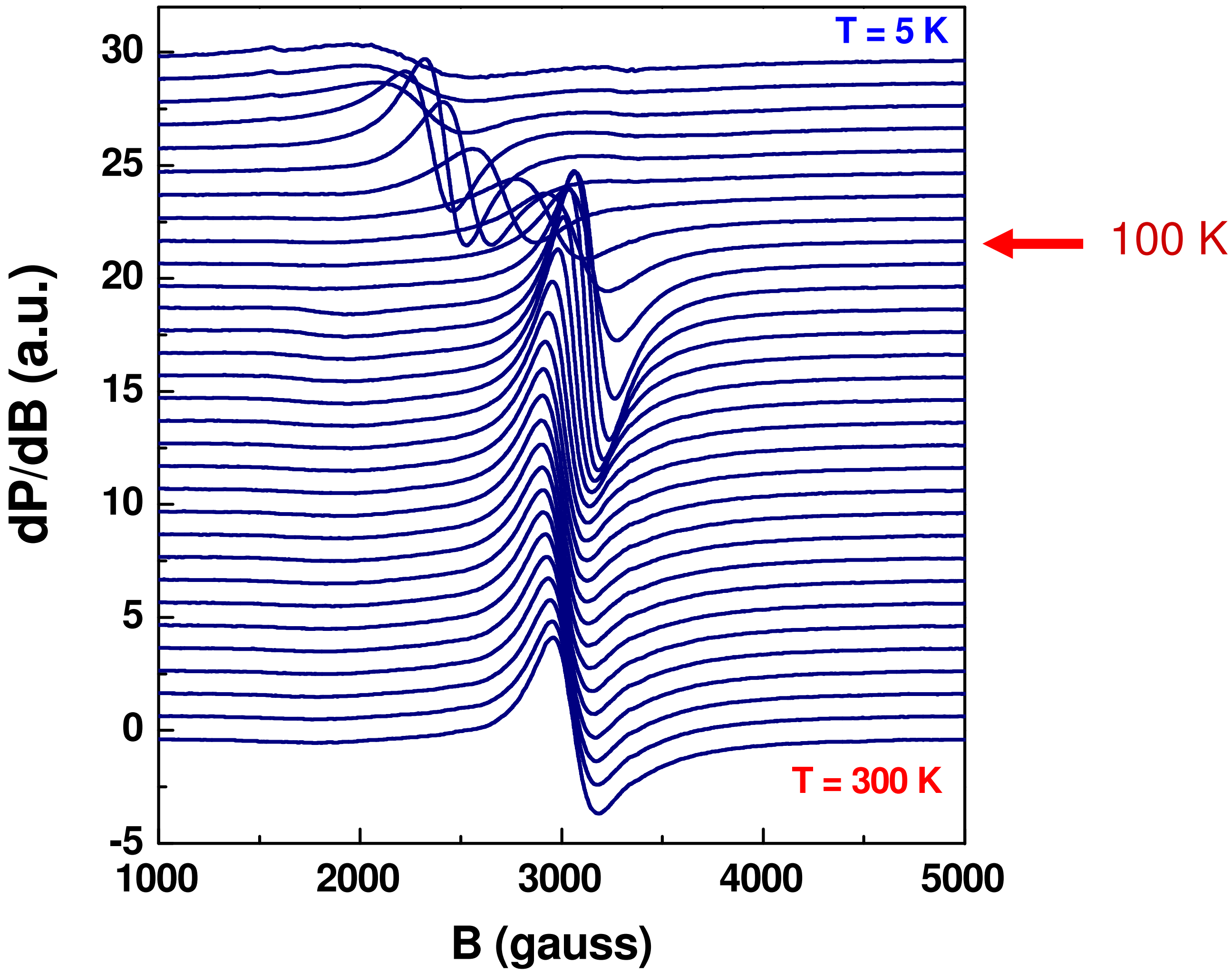
EPR signal of reduced nucleobases at 4 K



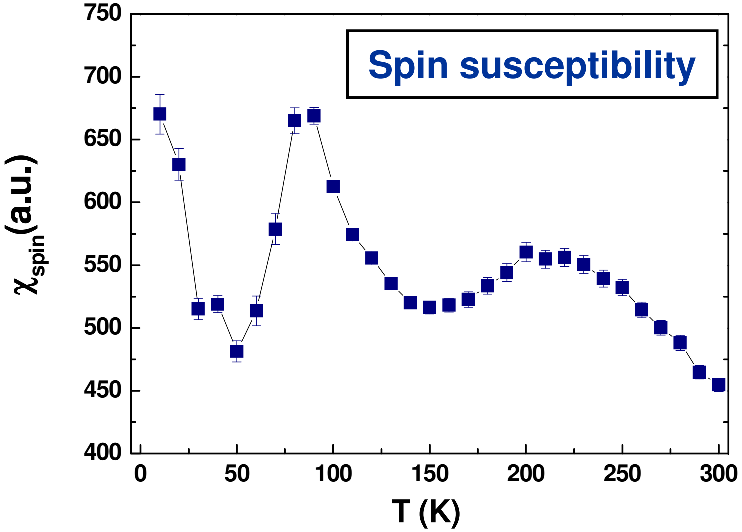
- Measured at low T
- X-ray irradiation in LiCl glass
- Diluted (isolated) spins
- Distinctive & narrow spectra

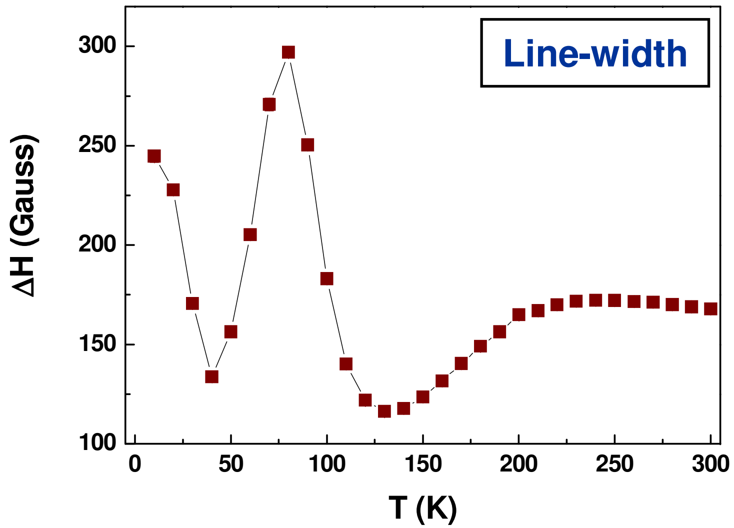
W. A. Bernhard, *J. Phys. Chem*. **1989**, 93, 2187

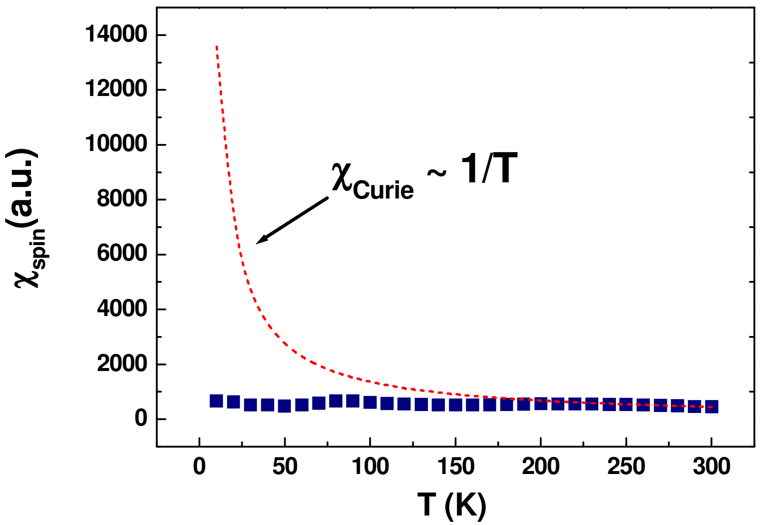
Temperature evolution of Zn@DNA ESR signal

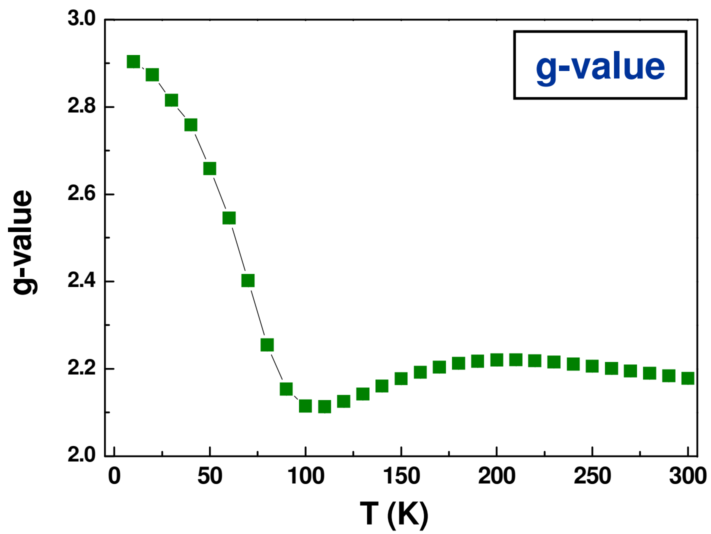


Temperature dependence of ESR parameters



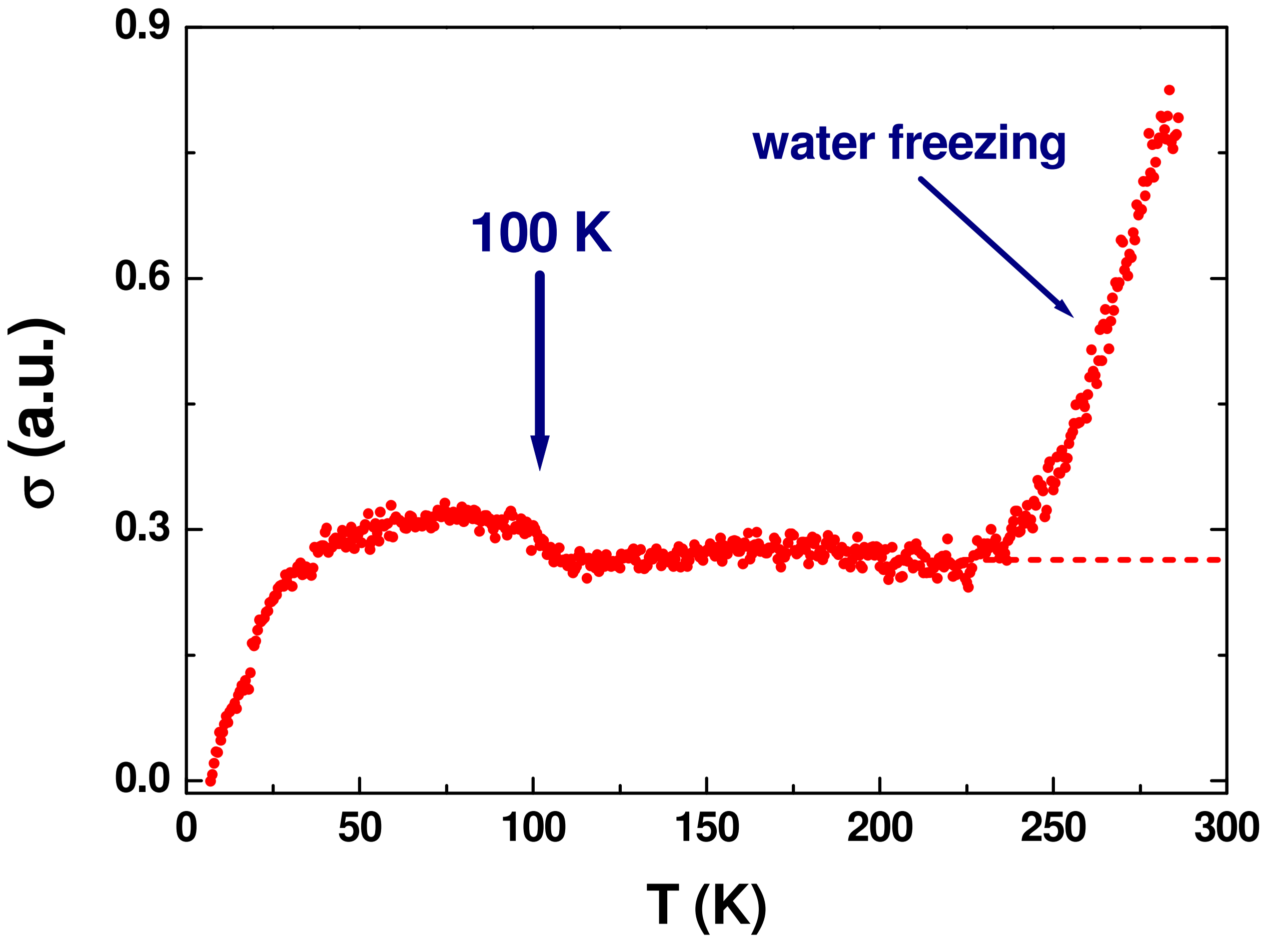






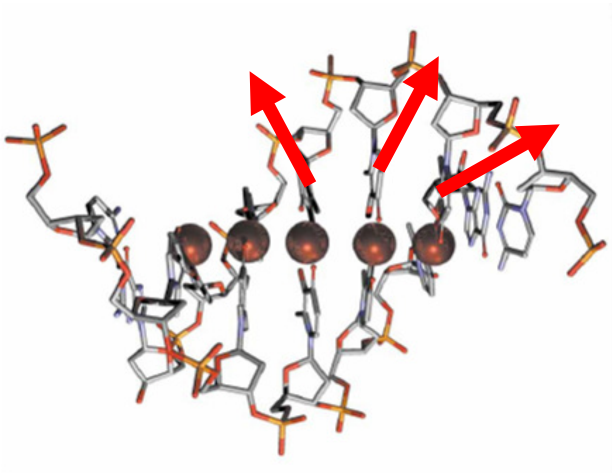
Microwave conductivity

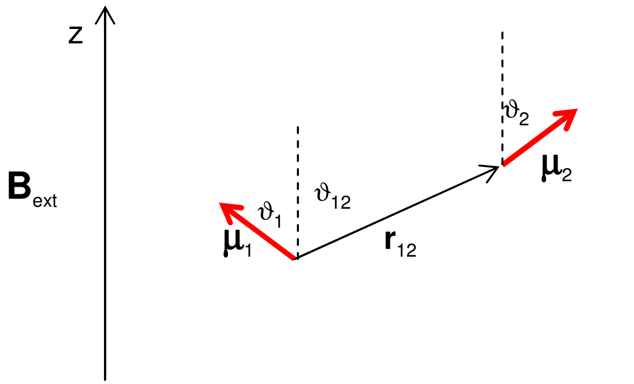
Method: Cavity perturbation technique at 16 GHz (contactless)



H. Matsui, 2009

Dipolar interactions I





Dipolar field

$$\Delta \vec{B}_1 = \frac{3(\vec{\mu}\cdot\hat{r}_{12})\hat{r}_{12} - \vec{\mu}}{r_{12}^3}$$

Random spin orientations

1st moment
(centre of the resonant field)

$$\langle \Delta \vec{B}_1 \rangle = 0 \quad \Rightarrow \quad B_{res} = B_0 \equiv \frac{\omega}{\gamma}$$

2nd moment
(resonant line-width)

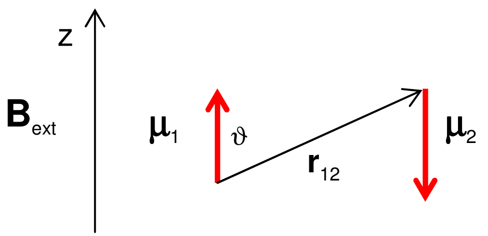
$$\langle |\Delta \vec{B}_1|^2 \rangle = \frac{5\,\mu^2}{2\,\ldots}$$

$\mu = \mu_B \quad r_{12} = a \sim 3$ Å

$$\sqrt{\langle |\Delta \vec{B}_1|^2 \rangle}$$

Dipolar interactions II

Antiferromagnetic correlations

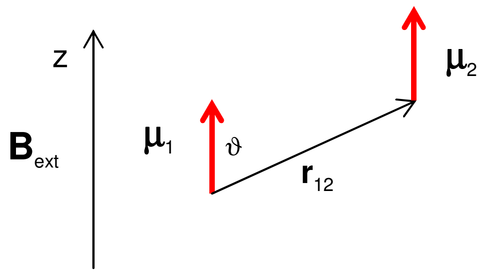


$$\Delta B_1^z = -\frac{\mu\,(3\cos^2\vartheta - 1)}{r_{12}^3}$$

$$\langle \Delta B_1^z \rangle = -\frac{\mu}{2 r_{12}^3} \Rightarrow B_{res} = B_0 + \Delta B$$

$$\Rightarrow \quad = \quad \rightarrow \quad <$$

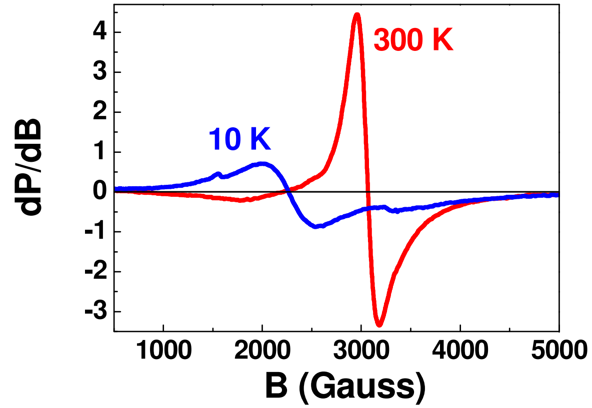
Ferromagnetic correlations



$$\Delta B_1^z = \frac{\mu\,(3\cos^2\vartheta - 1)}{r_{12}^3}$$

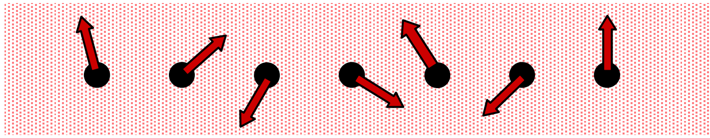
$$\langle \Delta B_1^z \rangle = \frac{\mu}{2 r_{12}^3} \Rightarrow B_{res} = B_0 - \Delta B$$

$$\Rightarrow \quad = \quad \rightarrow \quad >$$



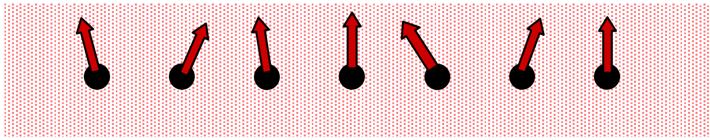
Conclusions

• Temperature independent spin susceptibiliy & MW conductivity between 100 K and 300K



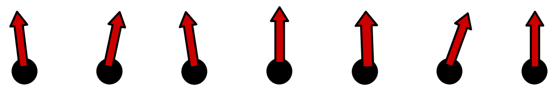
T = 300 K : delocalized electrons, uncorrelated spins

• Divergence of spin susceptibility and ESR linewidth, g-value starts to increase + step increase in MW conductivity at 100K



T ~ 100 K : delocalized electrons, onset of FM spin correlations

• T $\rightarrow$ 0 , MW conductivity $\rightarrow$ 0, g-value $\rightarrow$ 3



T $\rightarrow$ 0`: localized electrons, FM correlated spins

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Than you for your attention !

$ZnCl_2 + DNAbp \rightarrow Zn^{2+} + 2Cl^- + DNAbp^- + H^+$ — dissociation in Tris-HCl buffer at pH 9

$Zn^{2+} + 2Cl^- + DNAbp^- + H^+ \rightarrow Zn(II)DNAbp^+ + HCl + Cl^-$ — Zn^{2+} pushes into DNA

$2Zn(II)DNAbp^+ + 2Cl^- \rightarrow 2Zn(II)DNAbp + Cl_2$ — Cl^- releases an e^- to the complex and turns into a molecular Cl