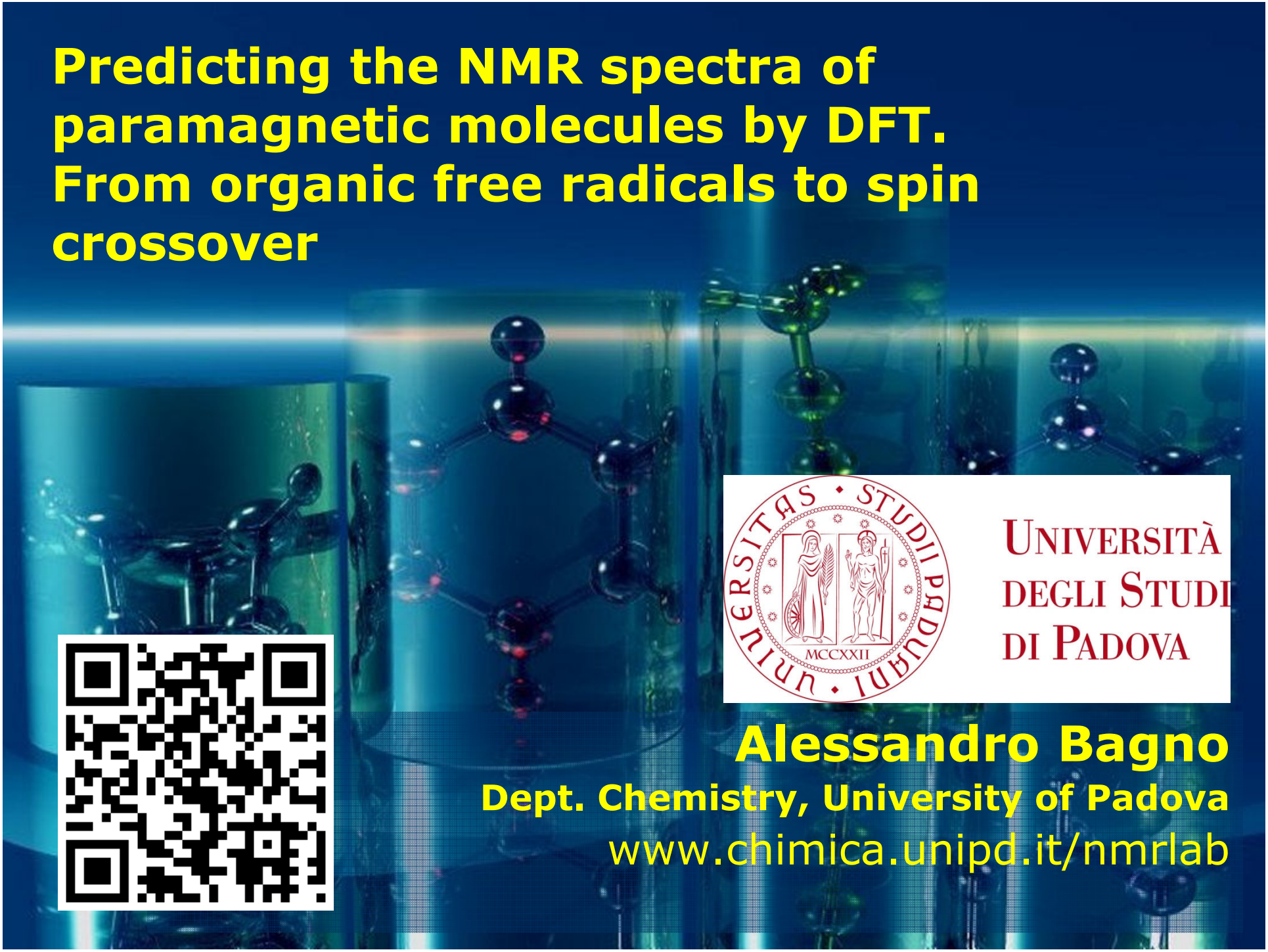
# Predicting the NMR spectra of paramagnetic molecules by DFT. From organic free radicals to spin crossover

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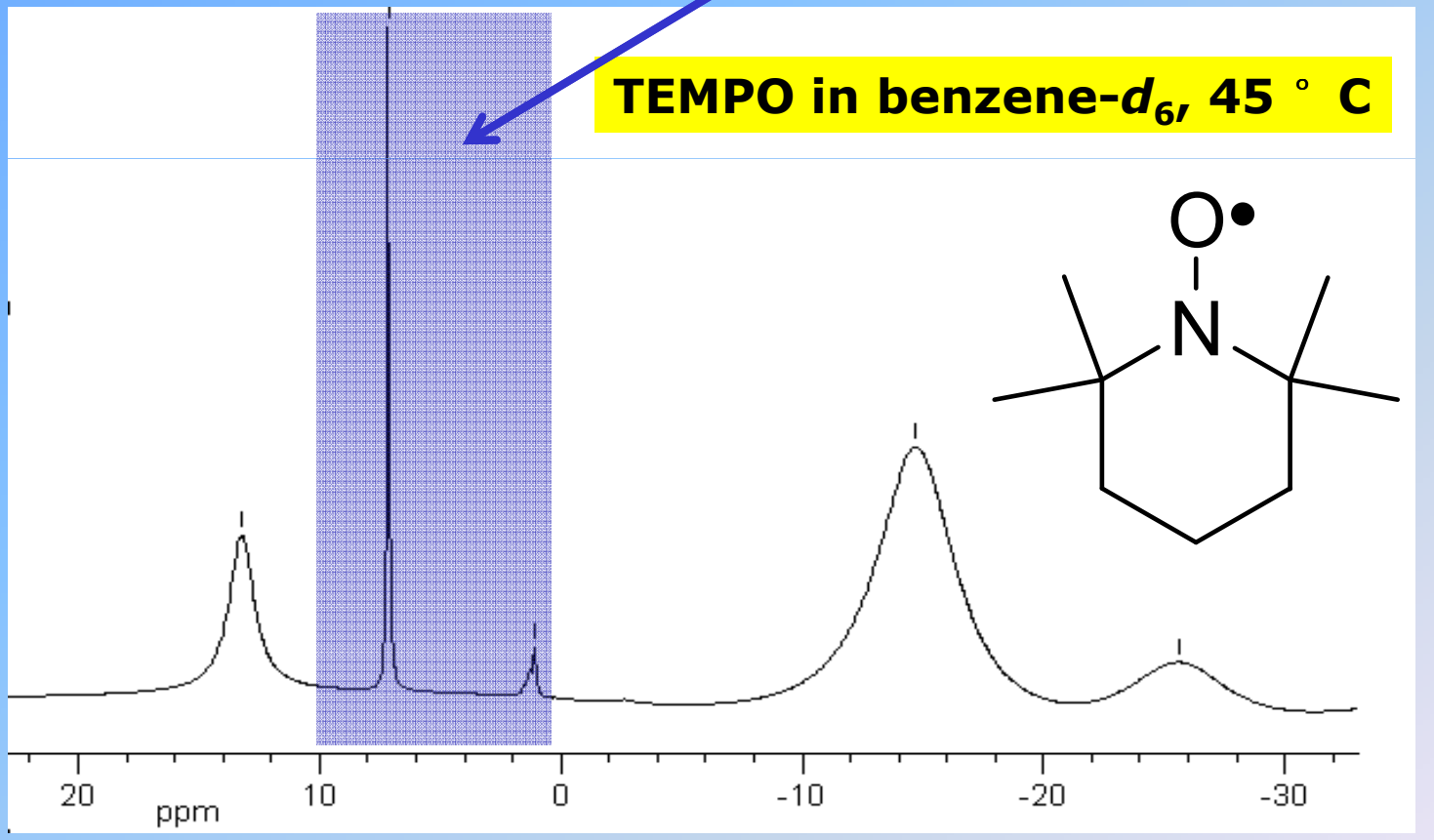
www.chimica.unipd.it/nmrlab

# NMR spectra of paramagnetic molecules

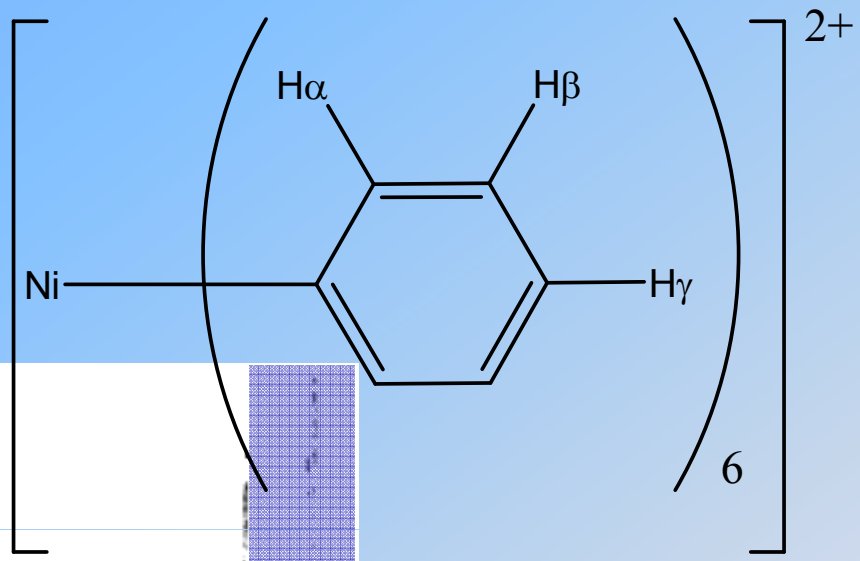
**Broad lines**
**"Unpredictable" shifts**

**Typical range of $^1$H shifts in diamagnetic molecules**

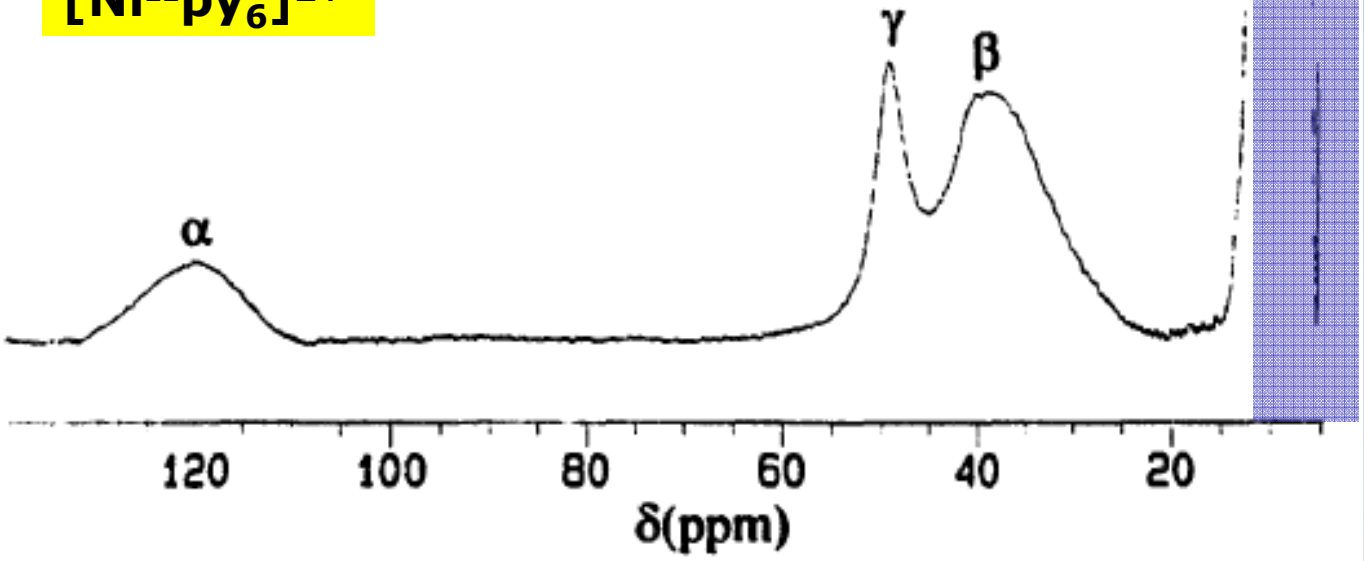


# NMR spectra of paramagnetic molecules

**Even when a spectrum can be obtained, there are serious assignment problems – often based just on relative intensities**




**$[Ni^{II}py_6]^{2+}$**



# Understanding the NMR spectra of paramagnetic molecules

**Two major approaches:**

1. **Determine the relevant parameters empirically from experimental data (Bertini & Firenze school)**
2. **Compute the relevant parameters from first principles**

**Relevant parameters:**

***g* factor**
**Hyperfine couplings *A***
**Magnetic susceptibility $\chi$**

# Modeling the NMR spectra of paramagnetics

$$\delta = \delta_{orb} + \delta_{FC} + \delta_{PC}$$

$$\delta_{FC} >> \delta_{orb}$$

**Fermi contact term: approximate expression depends on *g*, *A*, *S***

$$\delta_{FC} = \frac{2\pi}{\gamma_I} g\mu_B A \frac{S(S+1)}{3kT}$$

**Pseudocontact term: dep. on anisotropy of $\chi$ (negligible w.r.t $\delta_{FC}$ in organic radicals and most transition metal complexes)**

$$\delta_{PC} = \frac{1}{4\pi r^3}\left[(\chi_{zz} - \bar{\chi})\frac{2z^2 - x^2 - y^2}{2r^2} + (\chi_{xx} - \chi_{yy})\frac{x^2 - y^2}{2r^2} + \chi_{xy}\frac{2xy}{r^2} + \chi_{xz}\frac{2xz}{r^2} + \chi_{yz}\frac{2yz}{r^2}\right]$$

$$\chi_{kk} = \mu_0 \mu_B^2 g_{kk}^2 \frac{S(S+1)}{3kT}$$

**Spectra in solution (only isotropic terms)**
**ZFS neglected**
**Only contact term is calculated by DFT: requires *g*, S, *A***

Hrobárik, Reviakine, Arbuznikov, Malkina, Malkin, Köhler, Kaupp, *J. Chem. Phys.* **2007**, *126*, 024107
Rastrelli, Bagno, *Chem. Eur. J.* **2009**, *15*, 7990

# Modeling line widths: Solomon-Bloembergen equations

$$R_2 = 1/T_2 = R_2^{dip} + R_2^{FC}$$

**All dep. on electronic relaxation time $\tau_S$**

**Dipolar term: dep. on *r*, *g*, *S***

**Contact term: dep. on *A*, *S***

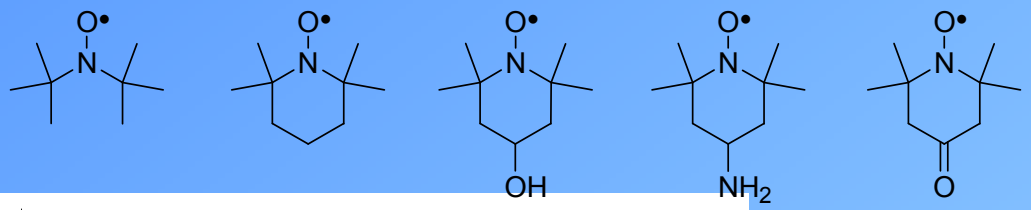
$$R_2^{dip} = \frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 g_e^2 \mu_B^2 S(S+1)}{r^6} \times$$
$$\left[4\tau_c + J(\omega_I - \omega_S, \tau_c) + 3J(\omega_I, \tau_c) + 6J(\omega_I + \omega_S, \tau_c) + 6J(\omega_S, \tau_c)\right]$$

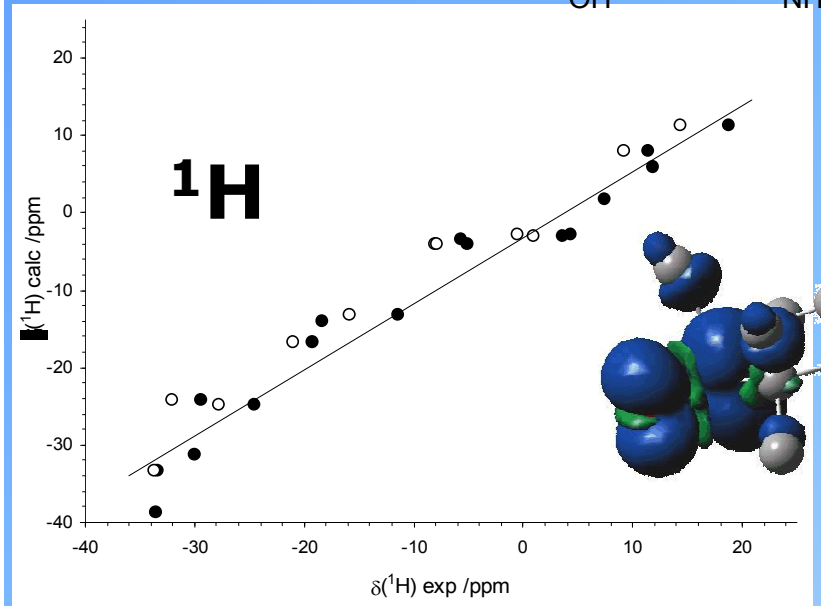
$$R_2^{FC} = \frac{4\pi^2}{3} S(S+1) A^2 \left[\tau_e + J(\omega_S, \tau_e)\right]$$

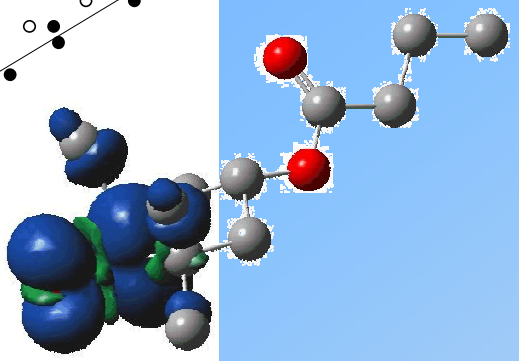
**Geometrical (*r*) and electronic (*g*, *S*, *A*) parameters can be predicted by DFT**
**Useful for qualitative predictions (relative line widths)**

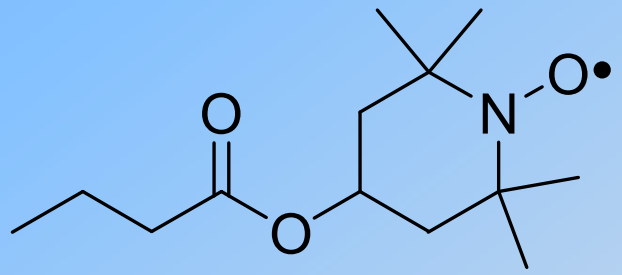
Rastrelli, Bagno, *Chem. Eur. J.* **2009**, *15*, 7990

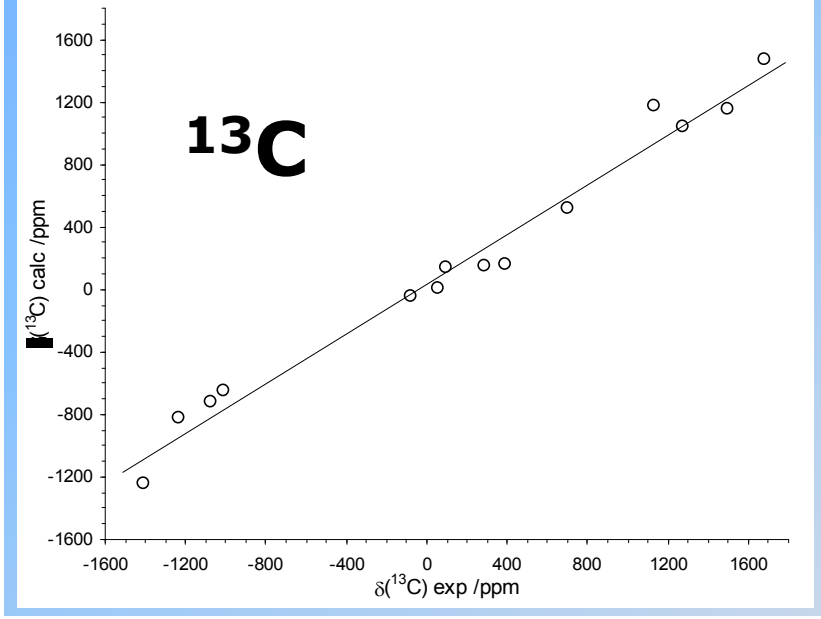
# Nitroxides, *S* = ½



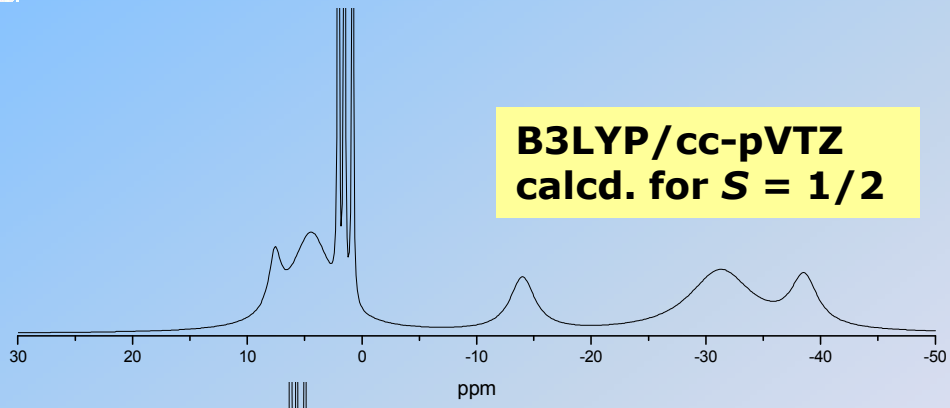



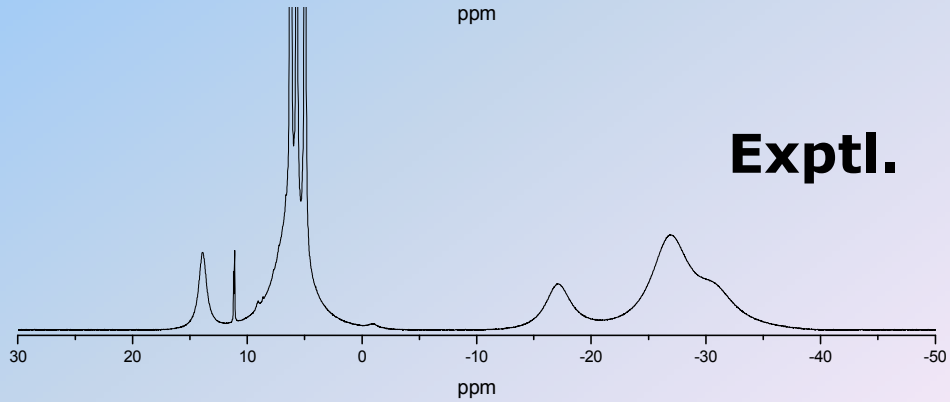



**B3LYP/cc-pVTZ calcd. for *S* = 1/2**

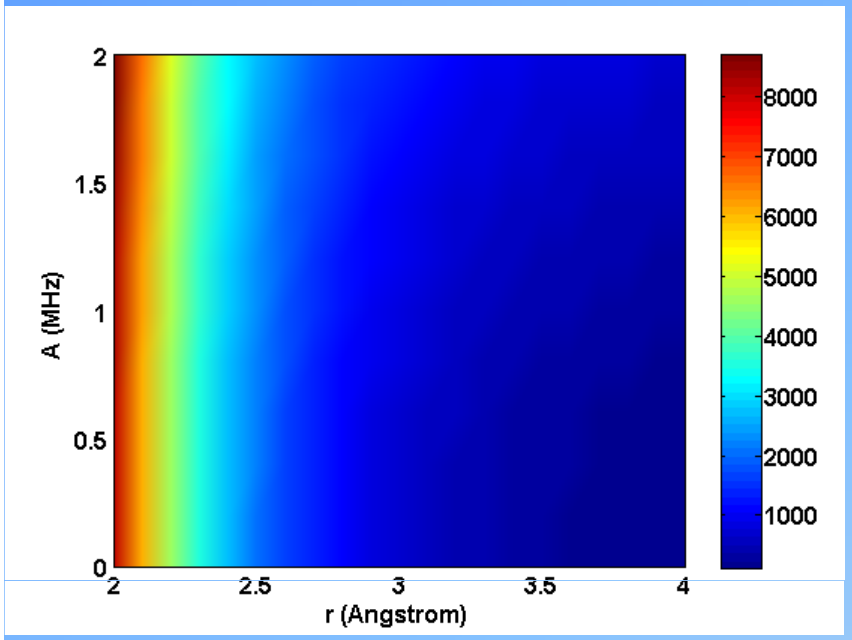


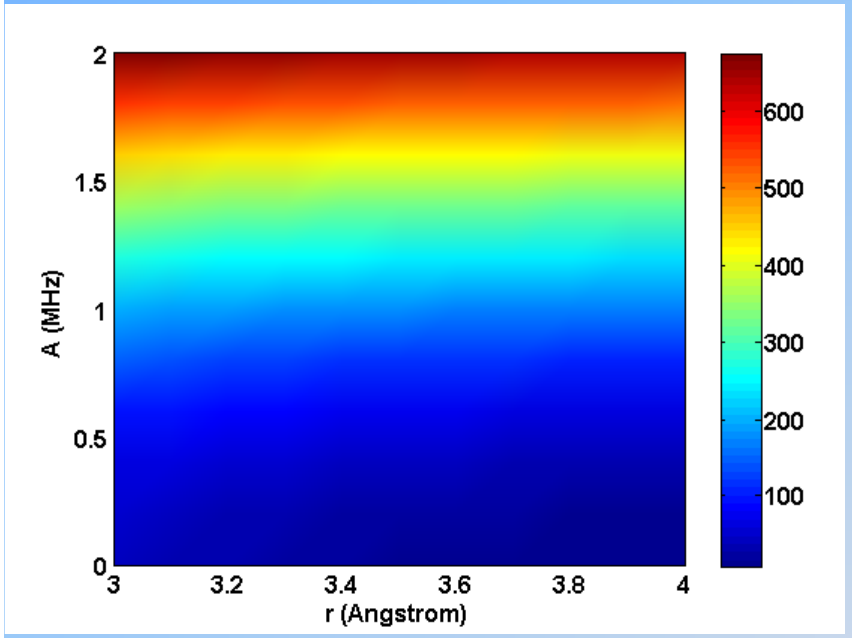

**Exptl.**




Rastrelli, Bagno, *Chem. Eur. J.* **2009**, *15*, 7990

# Predicting line widths: nitroxides, $S = 1/2$



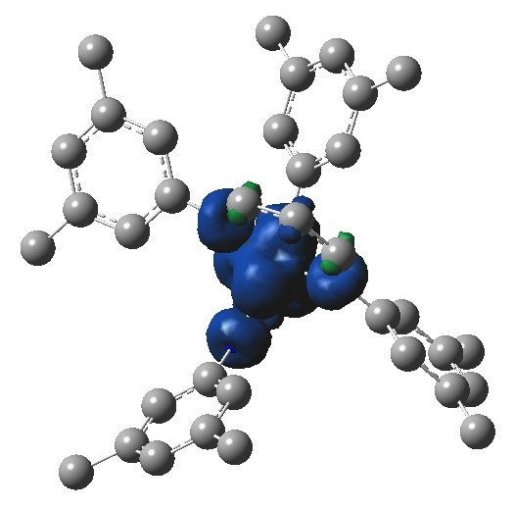

**Very slow el. relaxation**
**$\tau_S = 10^{-7}$ s**

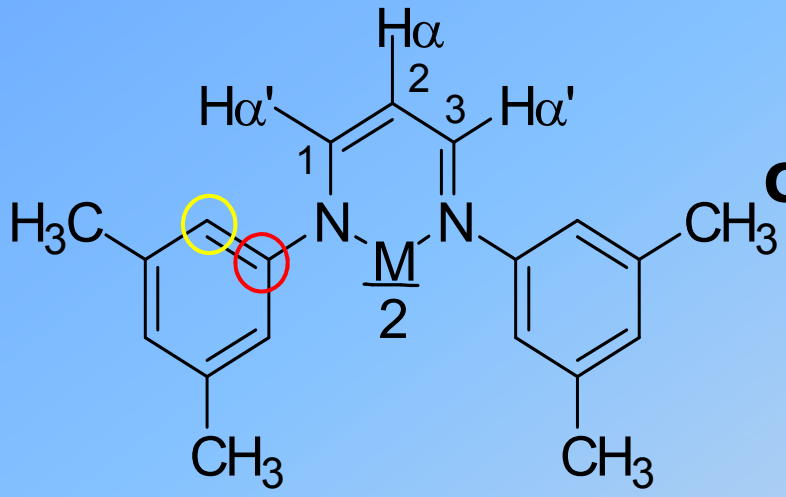
**$^1$H: mostly dipolar**

***g* = 2 is assumed**

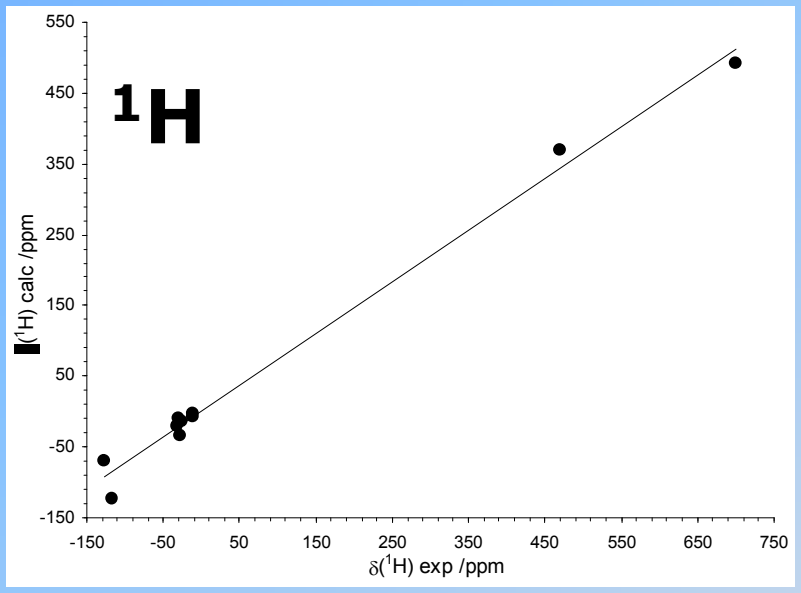
**$^{13}$C: mostly contact**

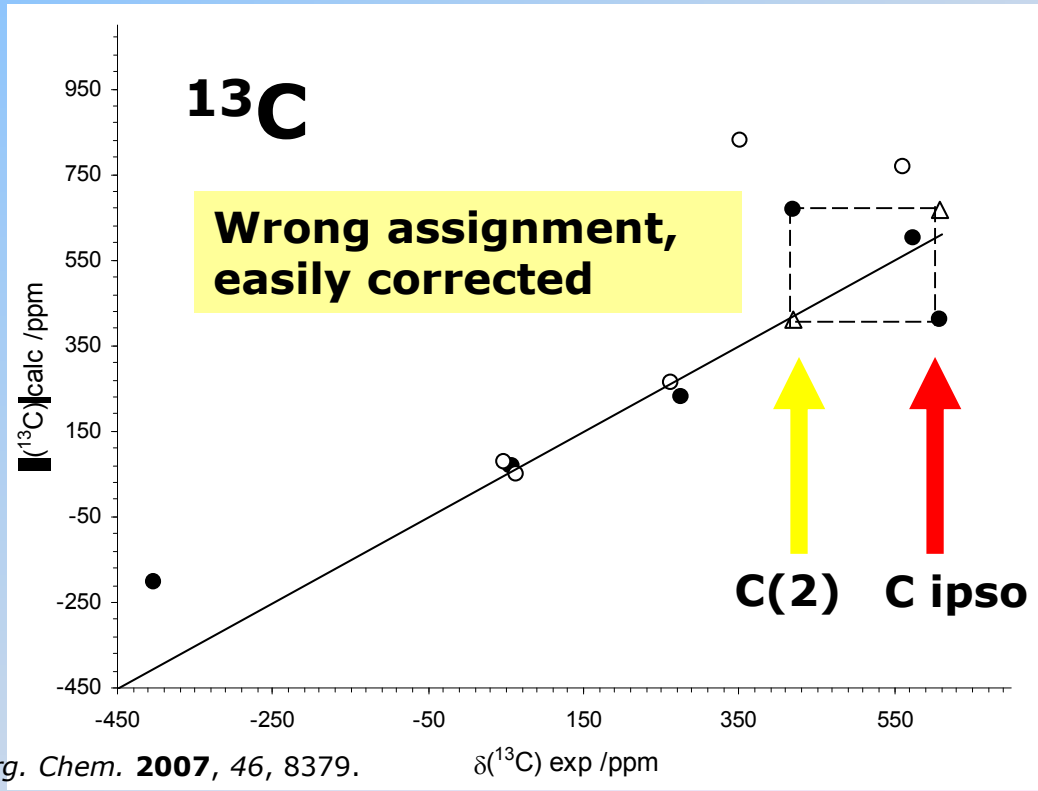
# $Ni^{II}$ and $Co^{II}$ vinamidines






**Ni(II), *S* =1**
**Co(II), *S* = 3/2**

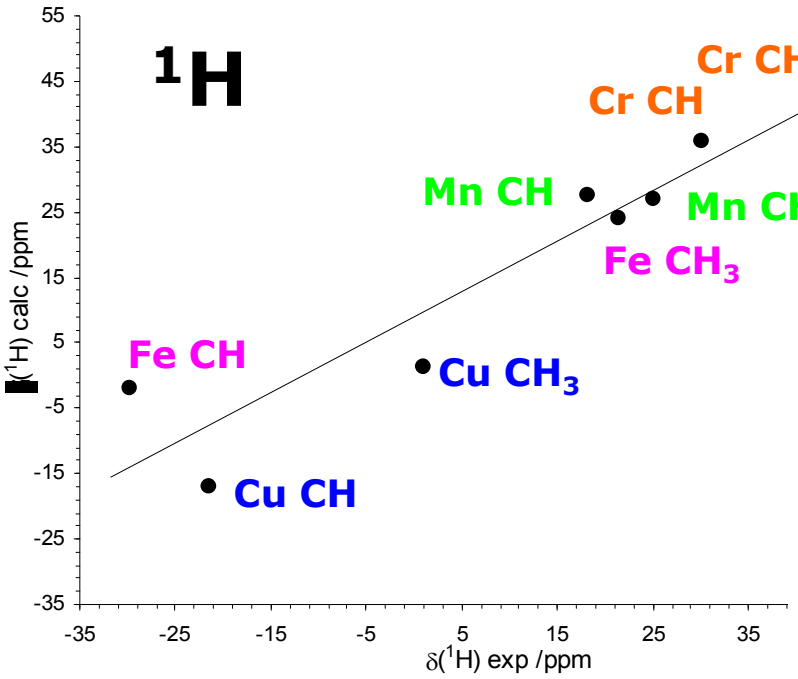


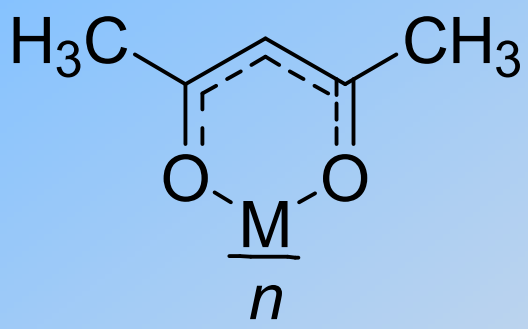



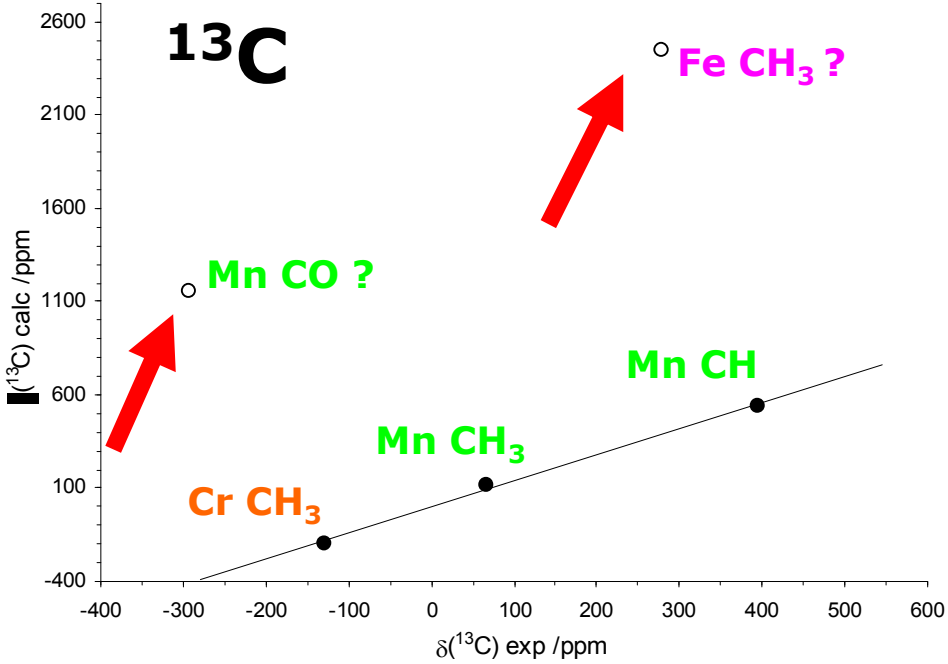


Rastrelli, Bagno, *Chem. Eur. J.* **2009**, *15*, 7990
Knorr, Hauer, Weiss, Polzer, Ruf, Löw, Dvortsák, Böhrer, *Inorg. Chem.* **2007**, *46*, 8379.

# Acetylacetonates: $Cr^{III}$, $Mn^{III}$, $Fe^{III}$, $Cu^{II}$



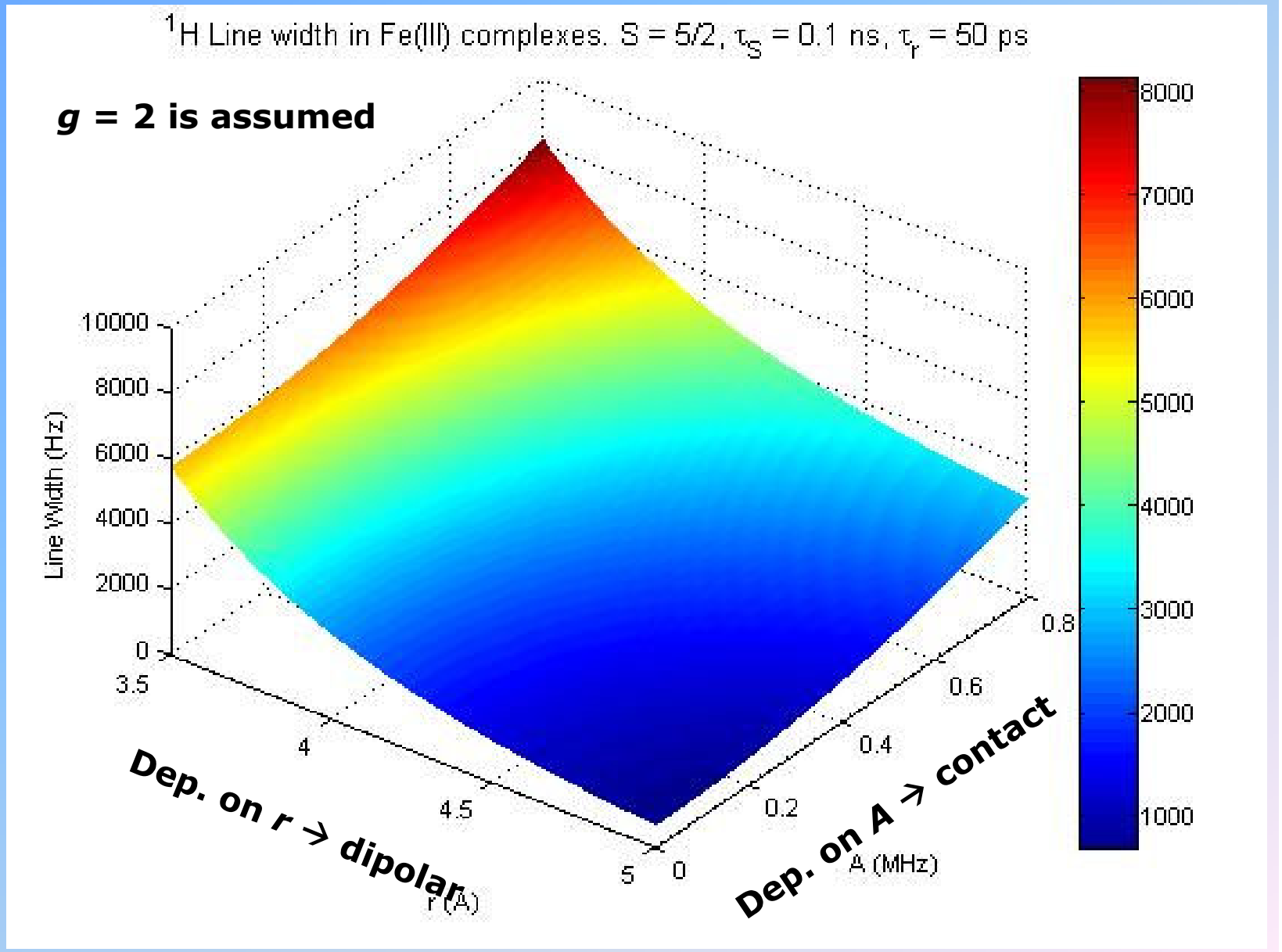



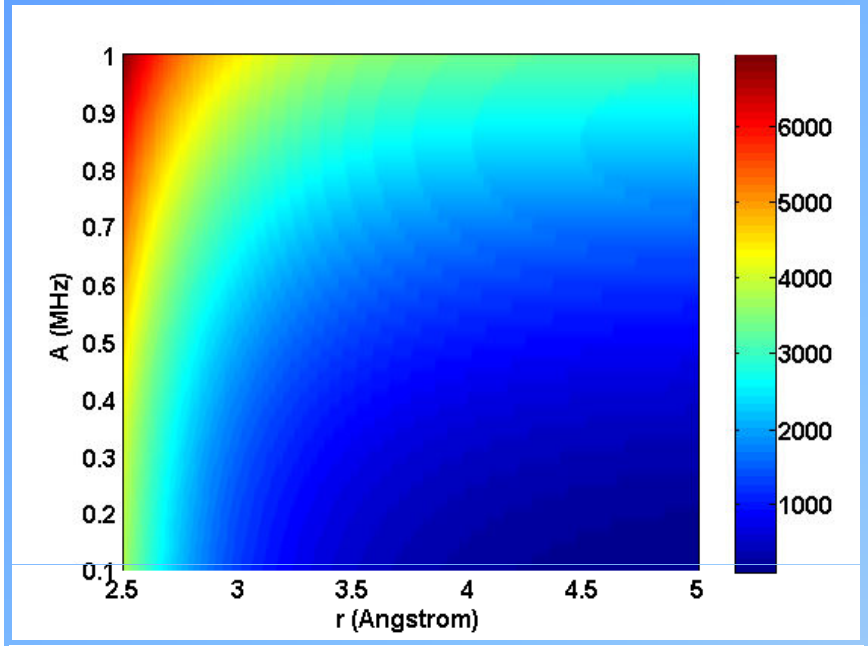

**Calculated line widths too large for detection**

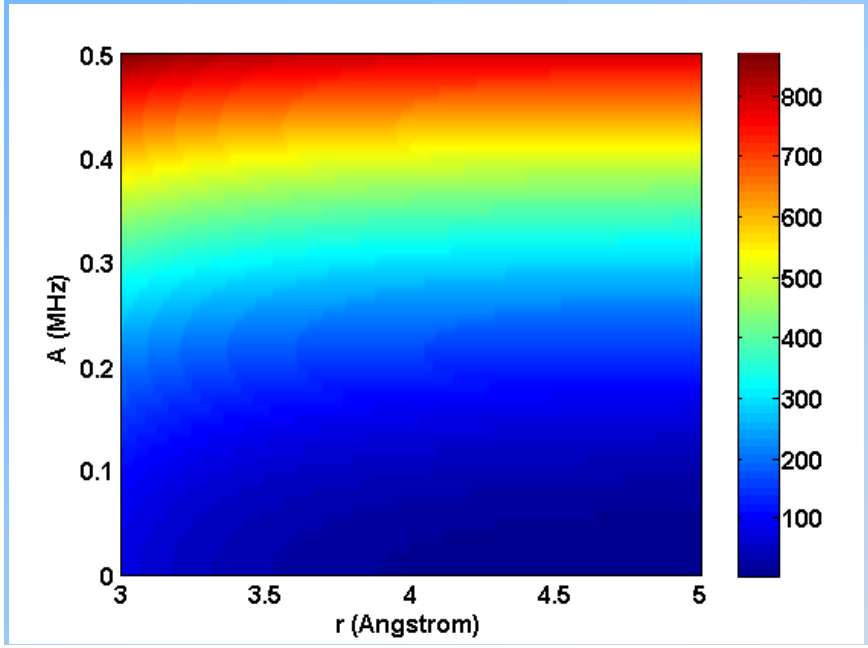
Rastrelli, Bagno, *Chem. Eur. J.* **2009**, *15*, 7990

# Predicting Line Widths



# Predicting Line Widths: Cu(II), $S$ = ½




**Slow el. relaxation**
**$\tau_S = 10^{-9}$ s**
**NMR is difficult**

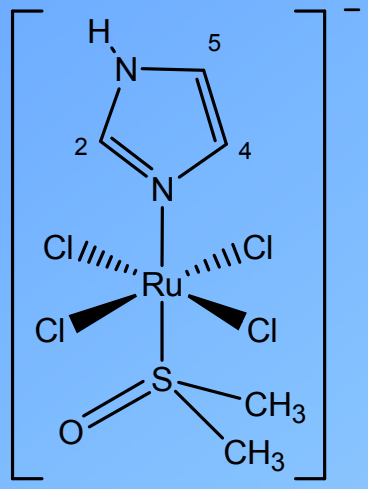
**$^1$H: dipolar + contact**

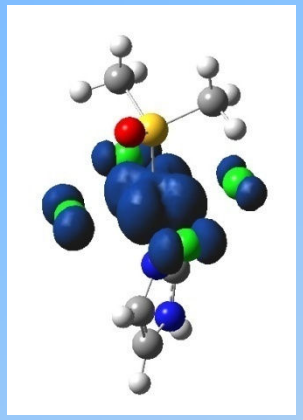
***g* = 2 is assumed**

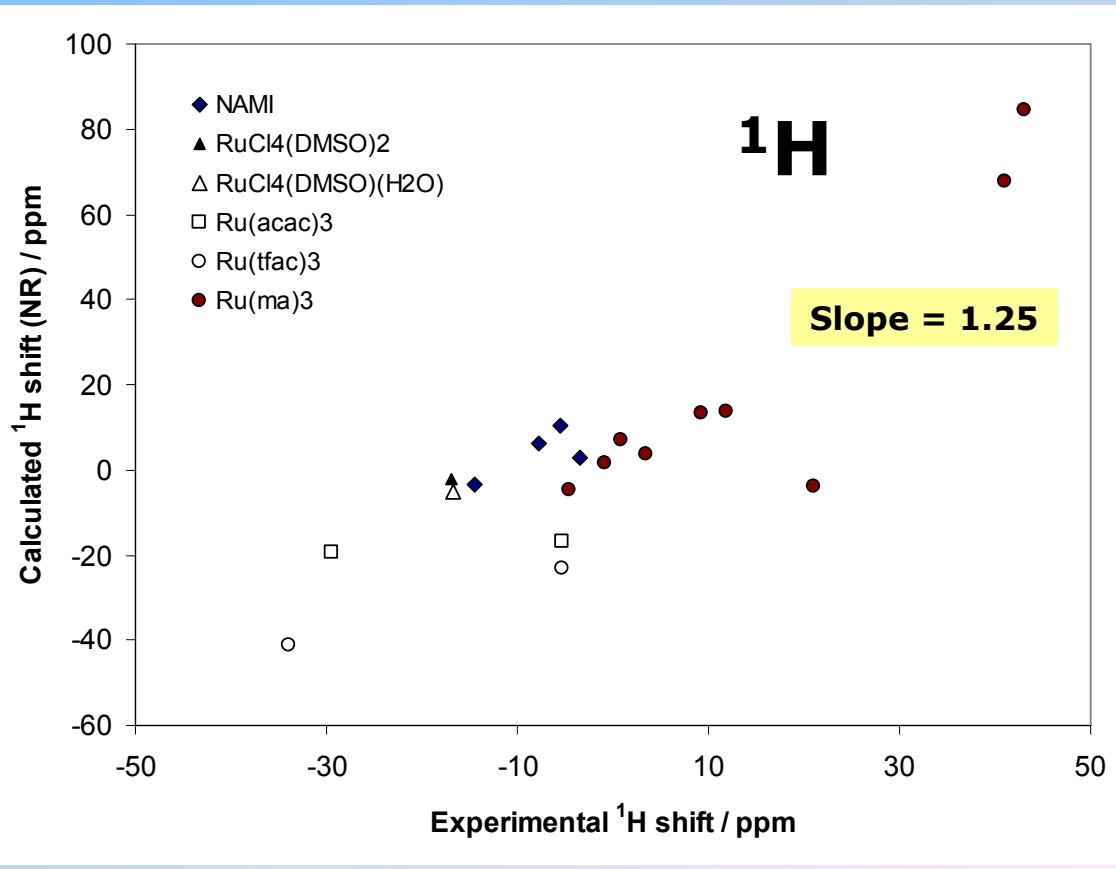
**$^{13}$C: mostly contact**

# $Ru^{III}$ complexes, S = 1/2

**Many important catalysts and anticancer drugs (NAMI)**
**Very fast electronic relaxation: $\tau_S = 5 \times 10^{-12}$ s → NMR relatively easy**
**Often, very complex equilibria in solution → spectra difficult to interpret**

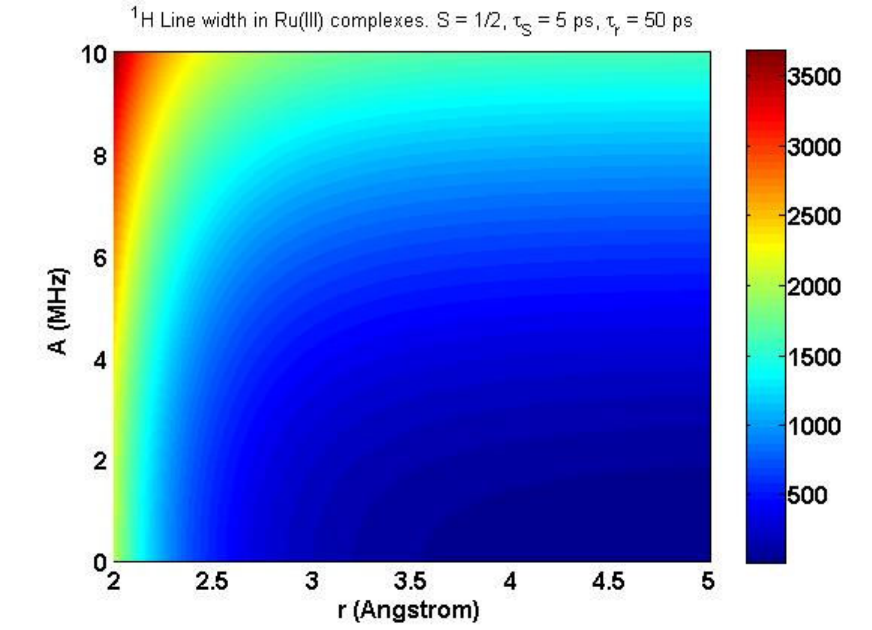


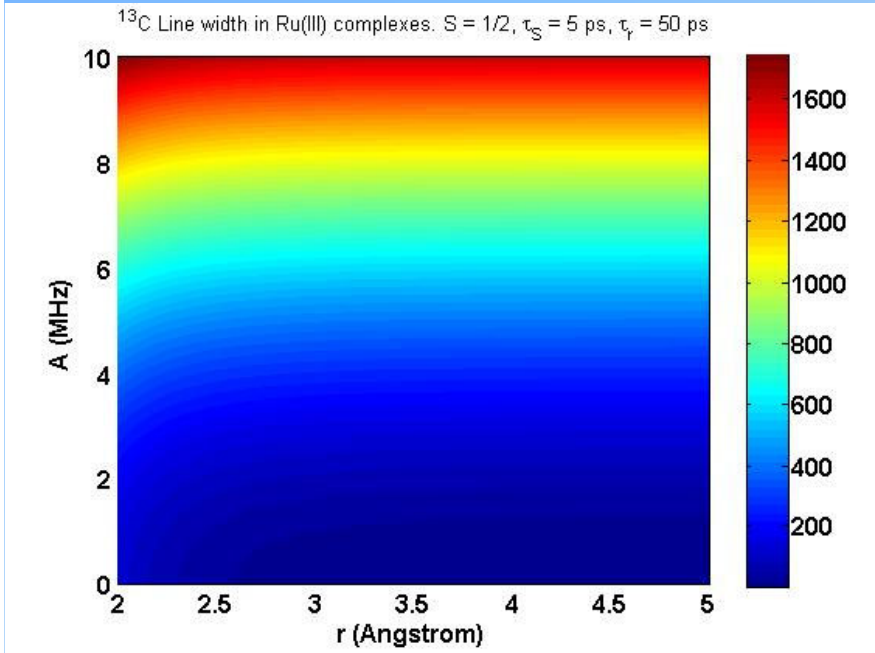






F. Rastrelli, A. Bagno, *Magn. Reson. Chem.* **2010,** *48*, S132-S141.

# Predicting line widths: Ru(III), $S = 1/2$




**Very fast el. relaxation**
**$\tau_S = 5 \times 10^{-12}$ s**

**$^{1}$H: dipolar + contact**

***g* = 2 is assumed**

**$^{13}$C: mostly contact**

# Conclusions

DFT calculations allow for prediction and assignment of NMR spectra of paramagnetics, including spin-crossover complexes and reactive intermediates

Lower accuracy than for diamagnetics (also of experimental data)

# Acknowledgments


Andrea Borgogno

Federico Rastrelli