



- Free radicals in solids, liquids or gases
- Paramagnetic ions of transition metals (up to 5 or 9 unpaired e^-)
- localized defects in solids (point defects)
- systems with more than one unpaired e^- :
 - ✓ triplet systems
 - ✓ biradicals
- systems with conduction e^- (semiconductors and metals)

Organic Radicals

- very popular in EPR
- one unpaired e-
- the effect of the spin orbit coupling g_e is very small (in the case of p orbitals)
- the paramagnetism can be considered as exclusively due to e- spin (ESR)
- “free” nomenclature of 1800 to address groups of atoms with one unpaired e- that can migrate from one molecule to another

Organic Radicals

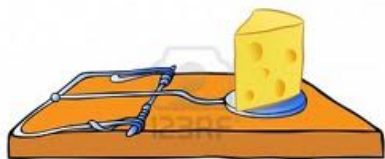
- The first radical that was proved is the triphenylmethyl radical (trytil)
- They are distinguished as σ or π
- The π with an extended π systems are usually both **thermodynamically** more stable
- and have a longer lifetime (kinetics): very important for the ESR study

Organic Radicals

- Neutral radicals (from homolysis)
- Radicalcations +
- Radicalanions -
- Biradicals (triplet state)
also from photoexcitation (ESR proof of the phosphorescence mechanism)
- The stable radicals are used as **spin probes** and **spin labels**

Nitrosyl Radical

- amongst the most diffuse persistent radicals in ESR
- $RR'NO\cdot$
- derivatives of nitric oxide $NO\cdot$
- preparation: by oxidation of the parent secondary amines or oximes by H_2O_2 , peroxides, $Ag(I)$, H_2O_2 and $Ti(III)$
- adducts of transient radicals to nitroso compounds or nitrones (spin trap)



spin trap

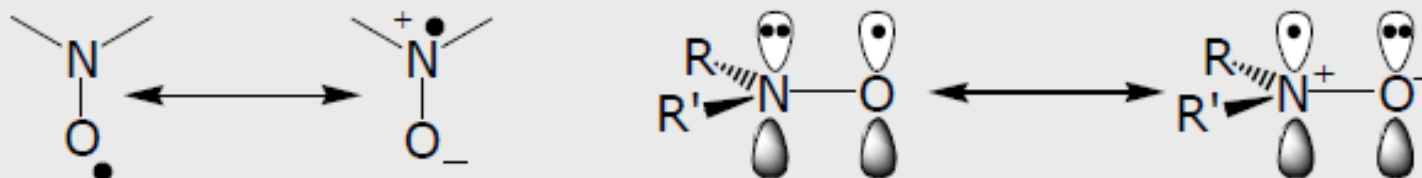


spin adduct

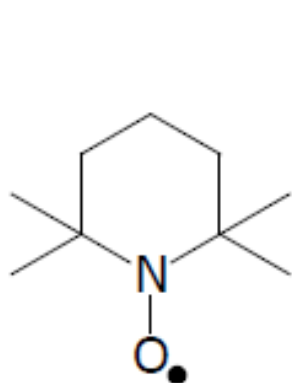


Nitroxide Radicals

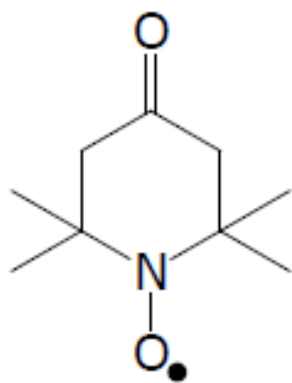
persistent (from months till years), temperature stable,
soluble in water and many organic solvents



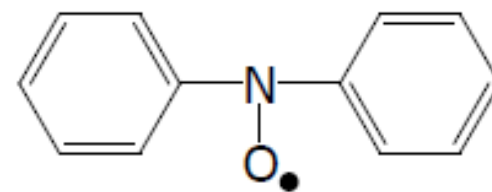
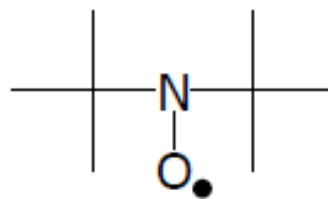
Alcuni esempi



TEMPO

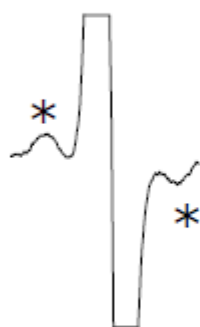
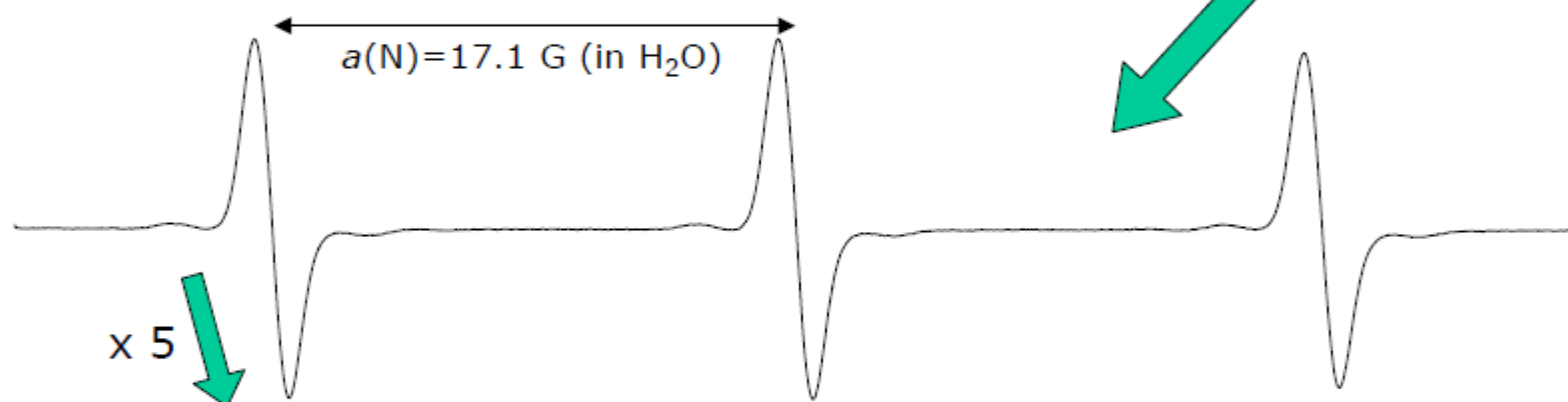
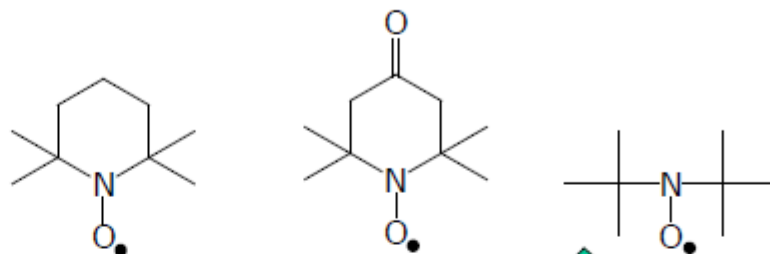


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also TEMPOLO

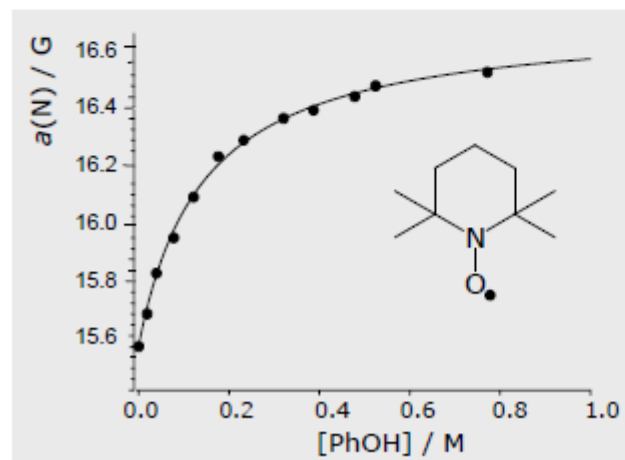
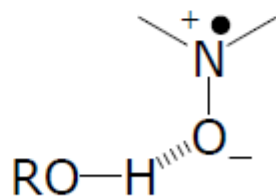
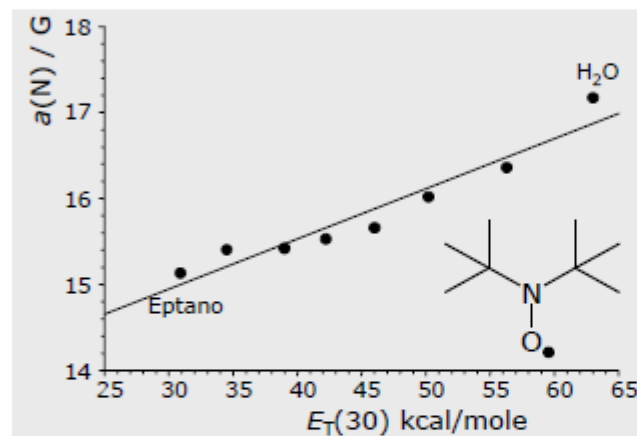
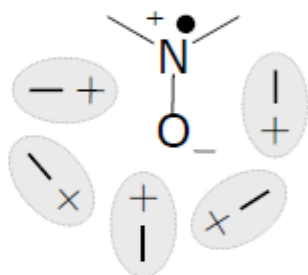
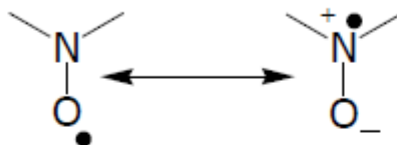
Nitrossidi persistenti



* Righe satelliti dovute all'isotopomero contenente un nucleo ^{13}C

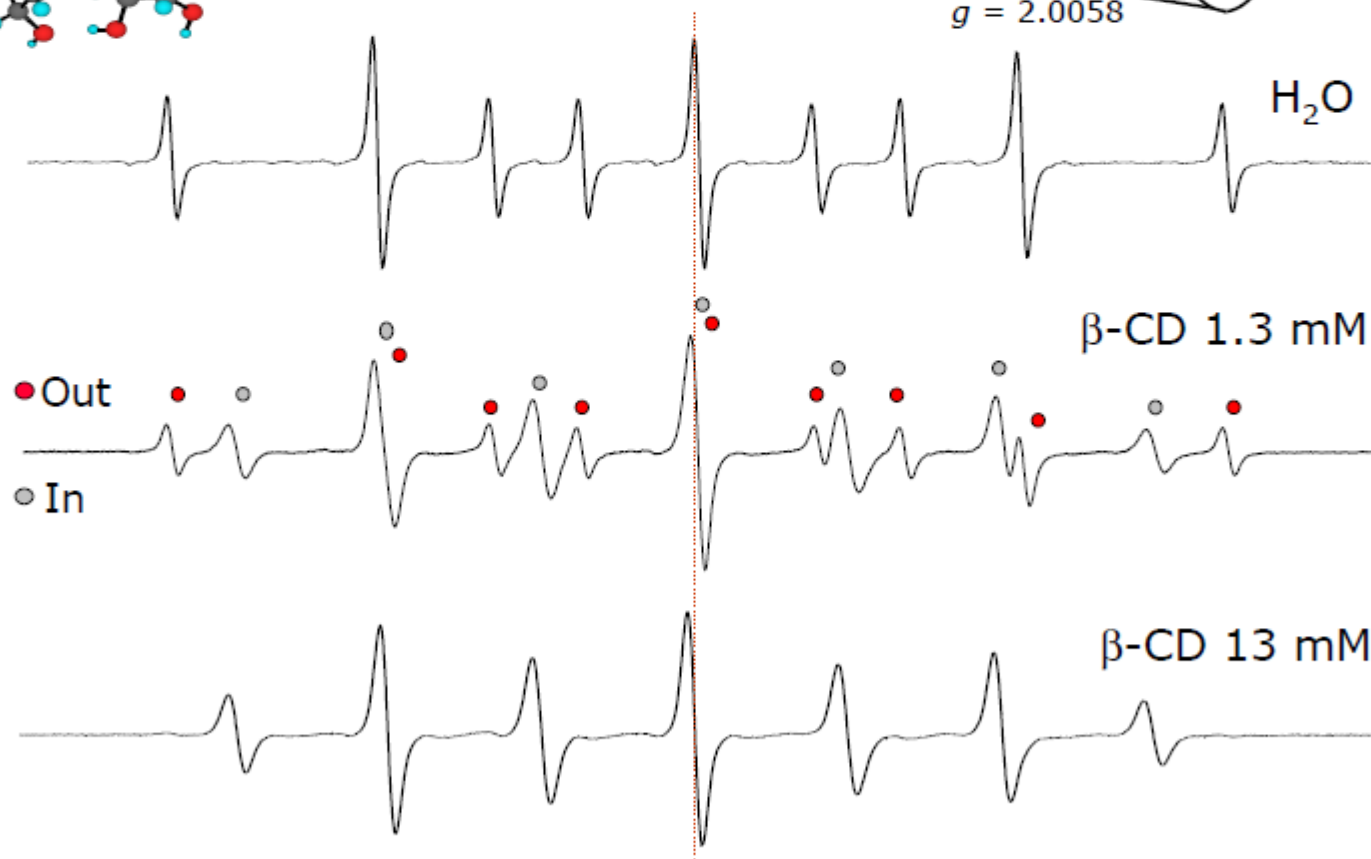
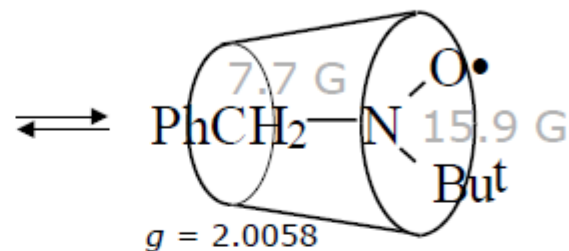
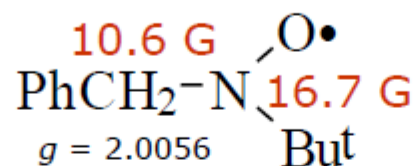
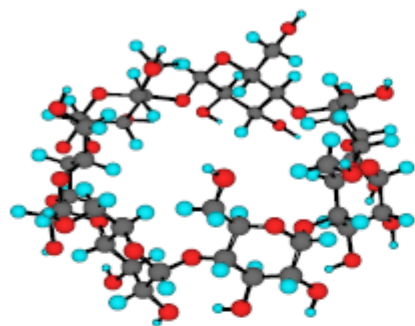
Spin probe

Dipendenza di $a(N)$ dall'ambiente circostante



Spin probe

Un esempio: ciclodestrine



Origin of Polarity Dependence of Nitroxides

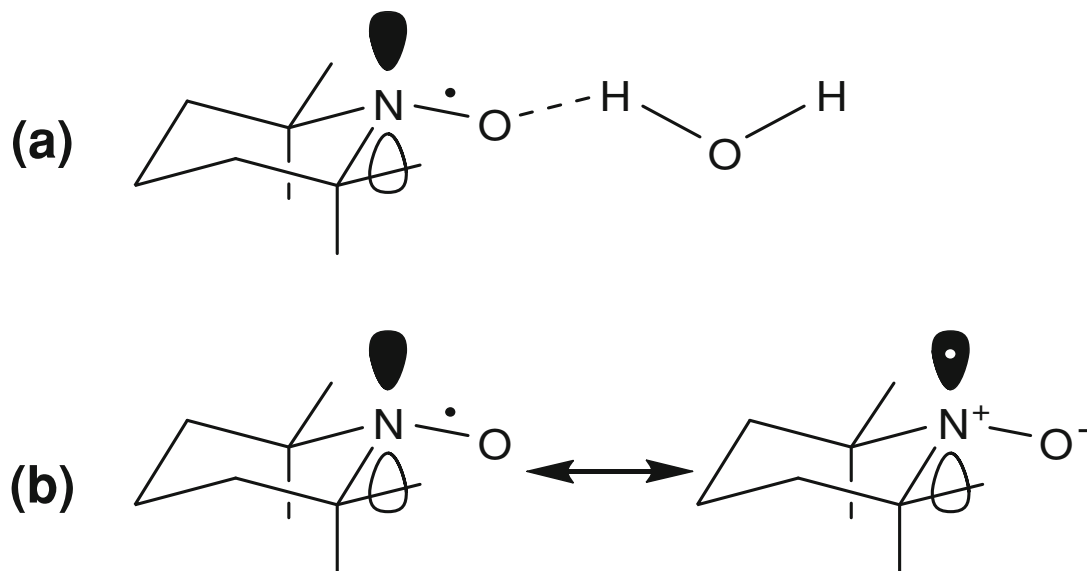


Fig. 2.14 Origin of the polarity and proticity dependence of nitroxide spectra. **a** Hydrogen bonding leads to a decrease of the spin-orbit coupling. **b** A stabilization of the zwitterionic resonance structure causes an increase of the spin density at the nitrogen atom. The combined effects lead to a decrease of g_{iso} and to an increase of a_{iso}

Zeeman Interaction

ESR spectroscopy is based on the interaction of the magnetic moment of e⁻ with the magnetic field

$$\alpha \text{ ————— } E_{\alpha} = \frac{1}{2}g_e\mu_B B$$

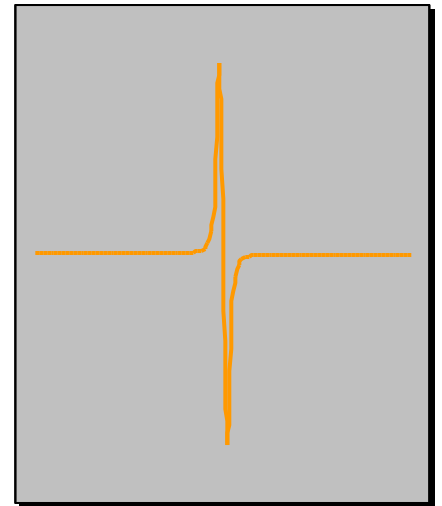
$$\Delta E = h\nu = g_e\mu_B B$$

$$\beta \text{ ————— } E_{\beta} = -\frac{1}{2}g_e\mu_B B$$

e⁻ gyromagnetic ratio

$$\gamma_e = \nu/B = g_e\mu_B/h = 2.8024 \cdot 10^{10} \text{ s}^{-1}\text{T}^{-1}$$

considering the g_e of the free e⁻



Electron-Nuclear Magnetic Interaction

Hyperfine and Superhyperfine Interactions

Hyperfine interaction for the hydrogen atom

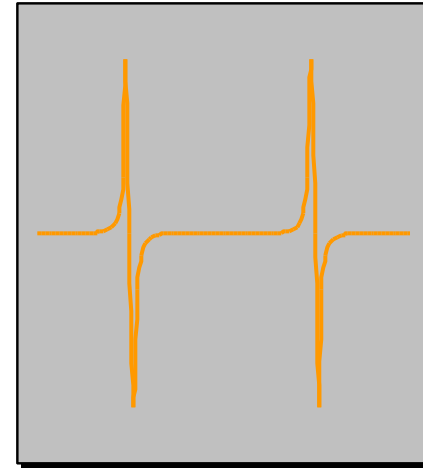
$$a(\text{H}) = 506.8 \text{ G}$$

selection rules

$$\Delta M_s = \pm 1$$

$$\Delta M_l = 0$$

Fermi contact mechanism



$$m_l = +1/2$$

$$m_l = -1/2$$

$$B - a/2$$

$$B + a/2$$