Electron paramagnetic resonance (EPR) spectroscopy

A versatile and little-known tool

in life sciences and related applications

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Nano Innovation 2020 Conference & Exhibition
Rome, 15-18 September

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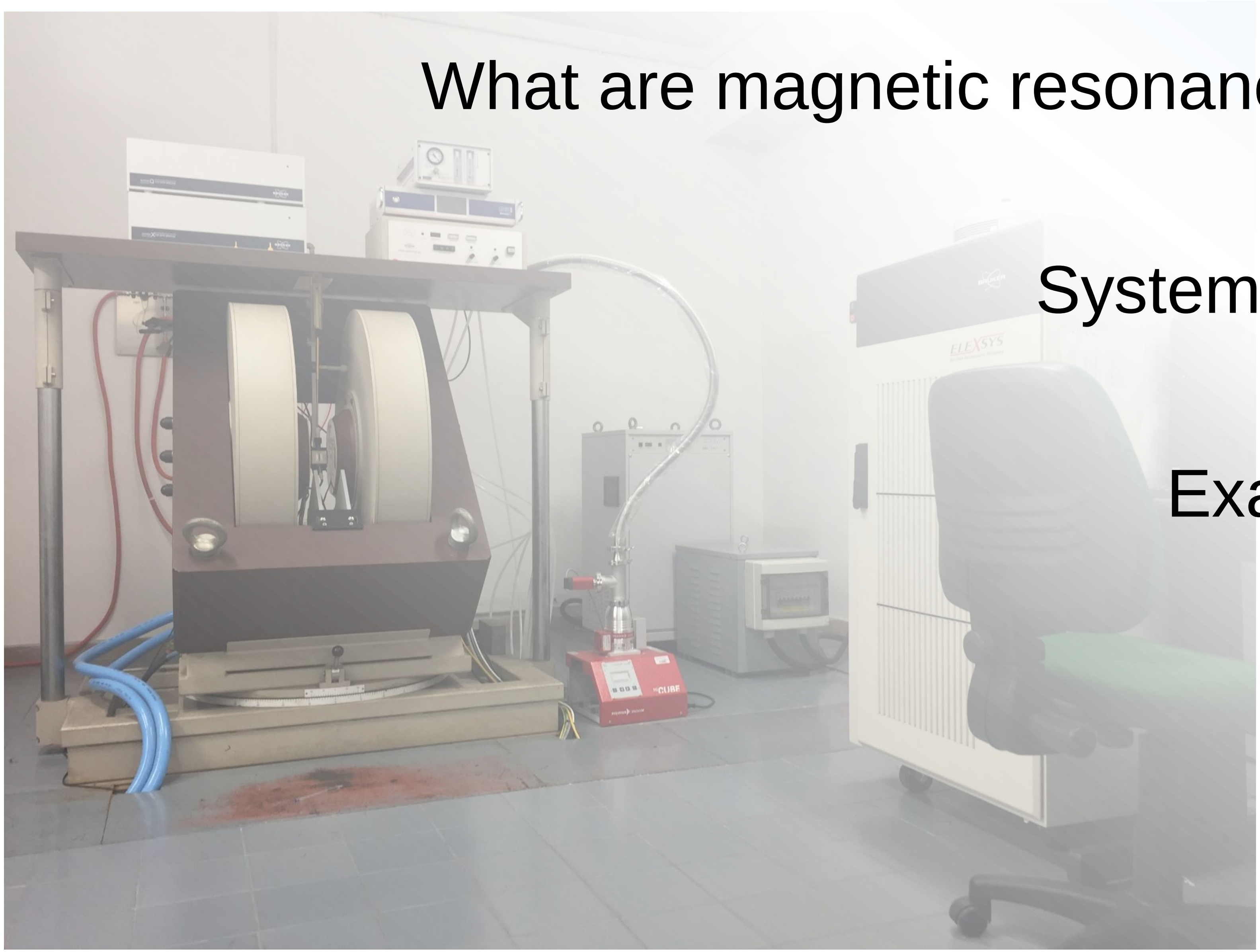


What are magnetic resonances and what is EPR?

Systems measurable by EPR

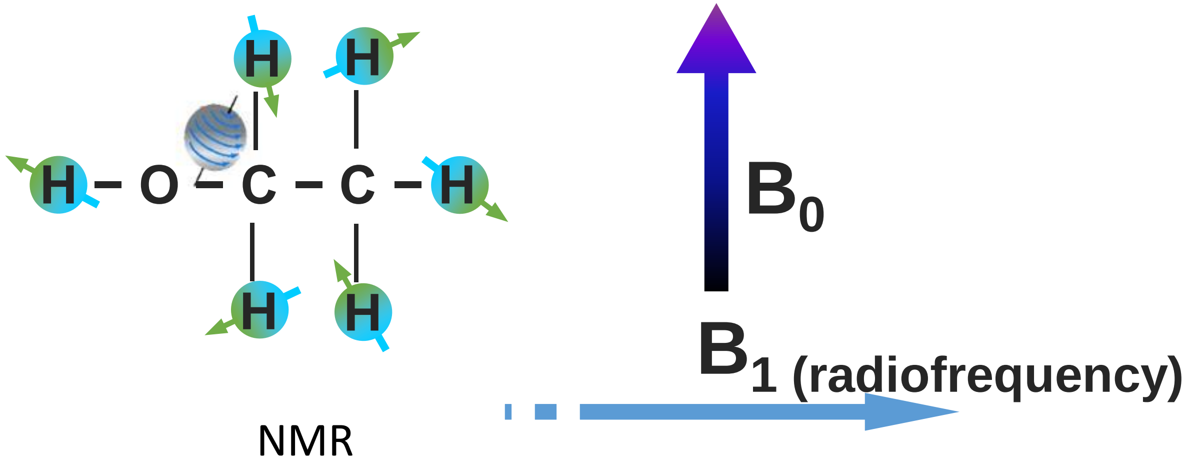
Examples of applications

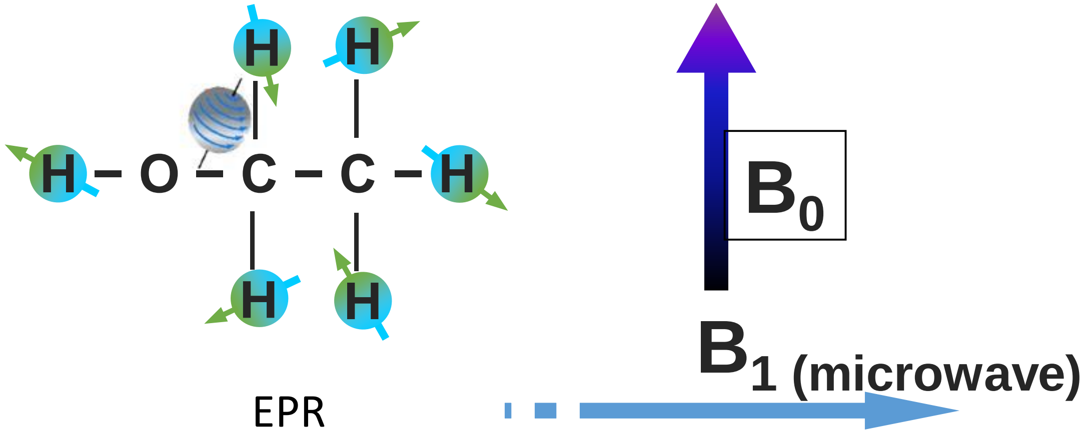
Practical weak points

What are magnetic resonances and what is EPR?

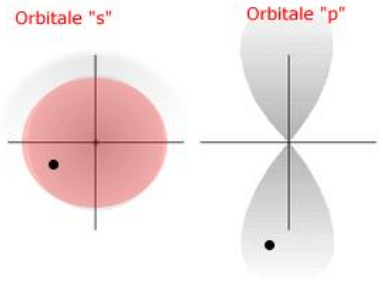
EPR and NMR share the same physical principle.

The rotating spin of electrons or nuclei interact with external magnetic (static and alternate) fields.





Only unzero electron spins are detectable by EPR. This are present only in atoms or molecules with one unpaired electron (instead of two) in one or more orbitals (paramagnetic species).



EPR – the twin sister of NMR

Electron Paramagnetic Resonance
&
Nuclear Magnetic Resonance

A parallel story

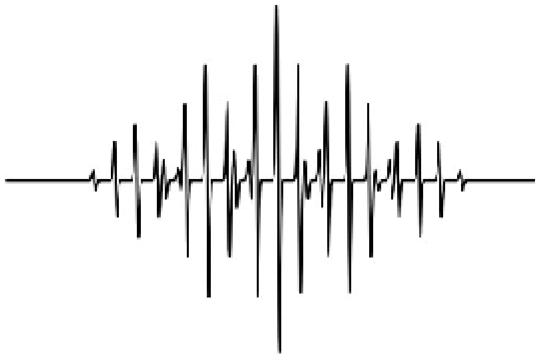
1938	1st description and measurements of NMR by Isidor Rabi (Nobel Prize in Physics in 1944).
1944	1st observation of electron spin resonance by Yevgeny Zavoisky
1946	Felix Bloch and Edward Mills Purcell expanded NMR (shared Nobel Prize in Physics in 1952).
1952	Varian Associates developed the first NMR unit.
1957	First commercialized EPR by JEOL Ltd.

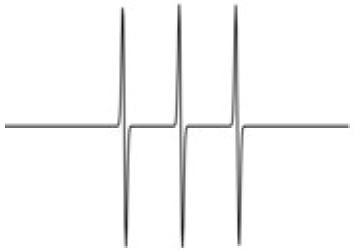
Why is EPR less known and less spread than NMR?

1. Because most stable molecules have all their electrons paired.

This weakness is also its strength because it makes EPR specific for unpaired electrons: if a signal is detected, it certainly comes from an unpaired electron.

2. Because a single species is not described by a single line, but by a complex profile





Which systems contain unpaired spins?

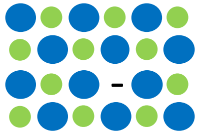
A surprisingly large number of compounds have unpaired electrons, such as:

biological systems

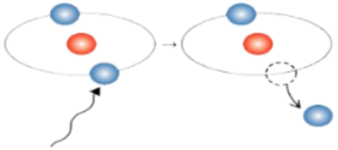
free radicals

transition metals in metalloproteins

inert materials

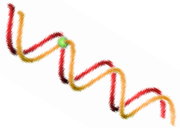


localized defects and conduction electrons



radiation induced defects

non-paramagnetic systems



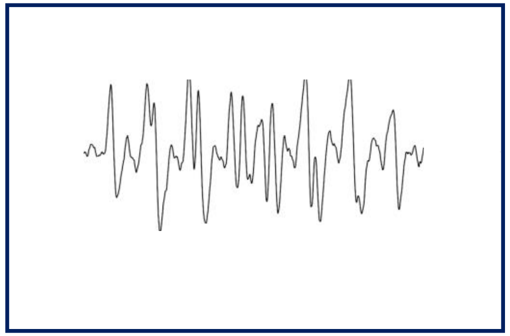
macromolecules

Many more applications possible in various branches of science, from pharmacology to cultural heritage, from material science to geology, from clinical diagnostic to dating.

Free radicals in biological systems (cells, tissues)

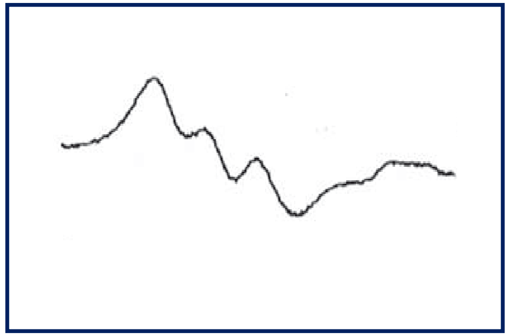
A free radical is a paramagnetic molecule which is extremely reactive, capable of engaging in rapid chain reactions that destabilize other molecules and generate many more free radicals.

Superoxide anion



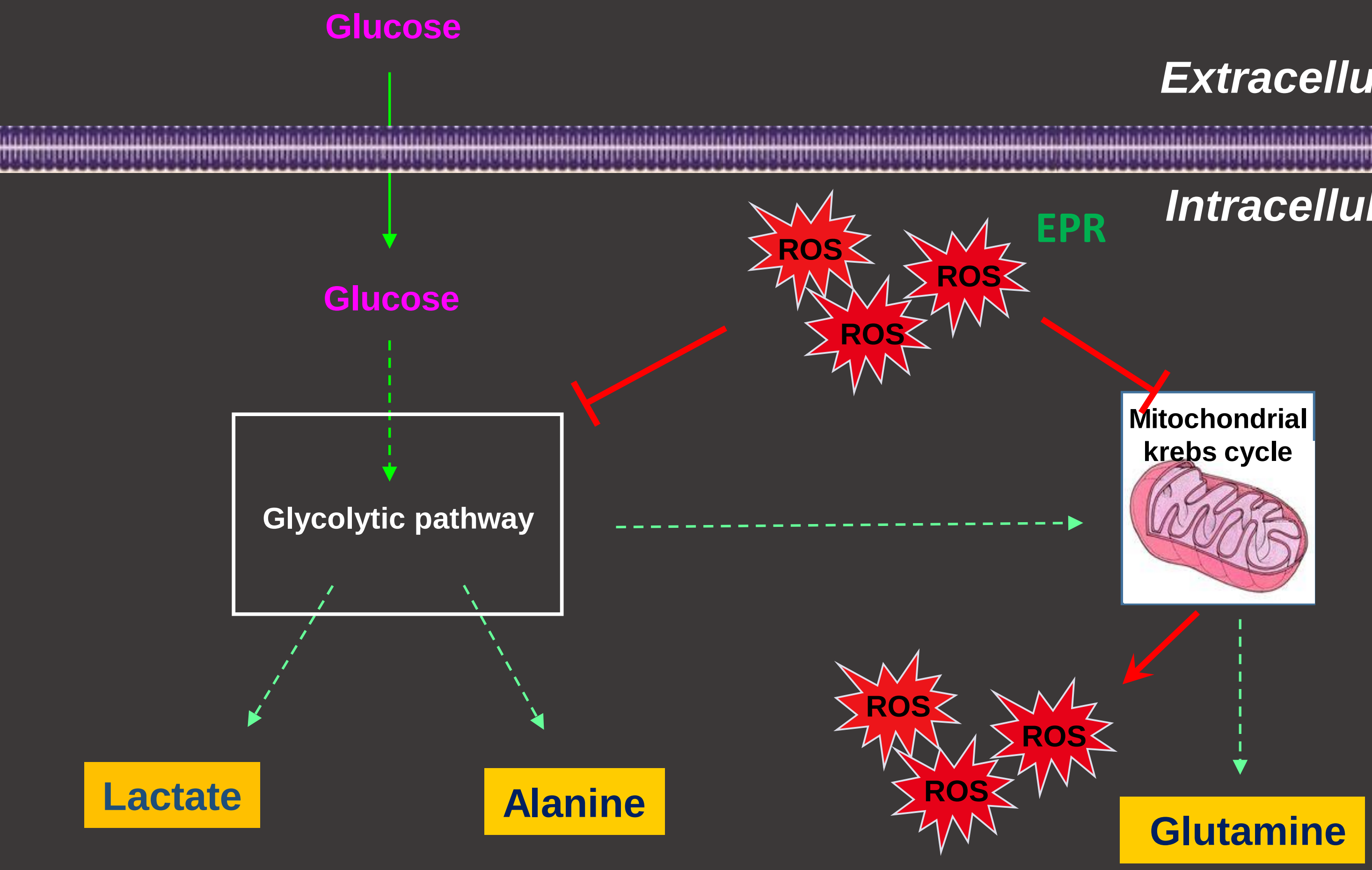
Hydroxyl radical

Nitric oxide

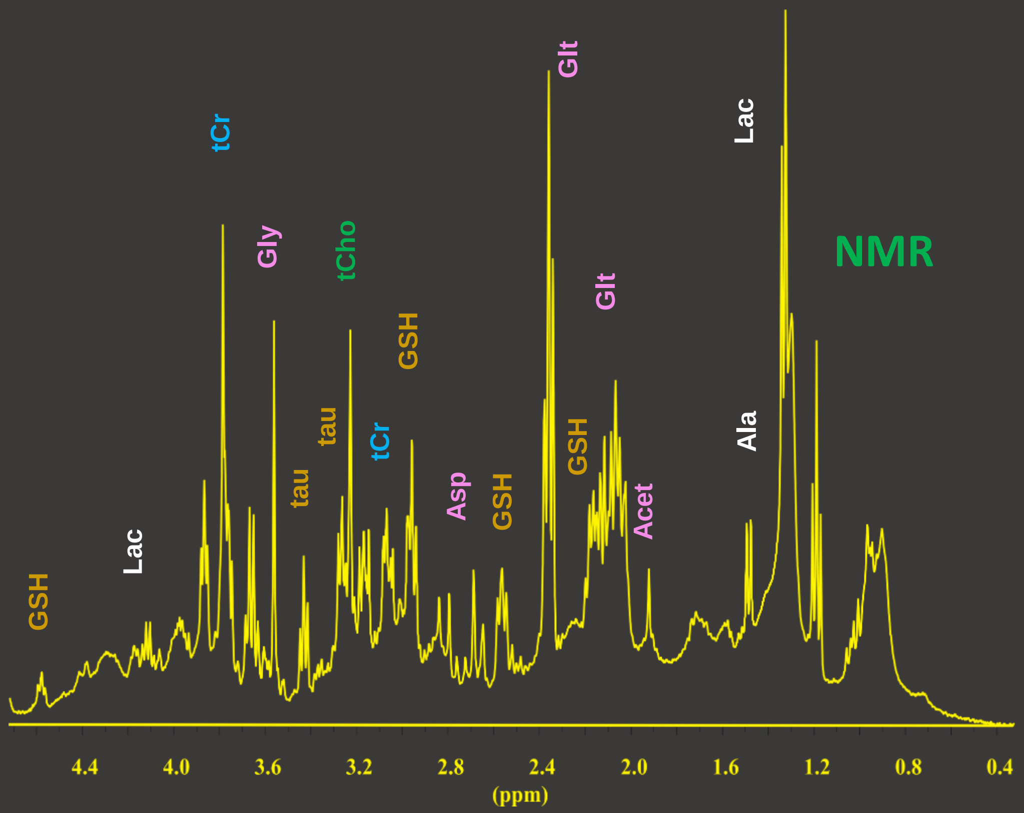


The signal line shape clearly indicates the free radical present in the system.

Example: free radicals and metabolomics



Processes for energy supply to cells

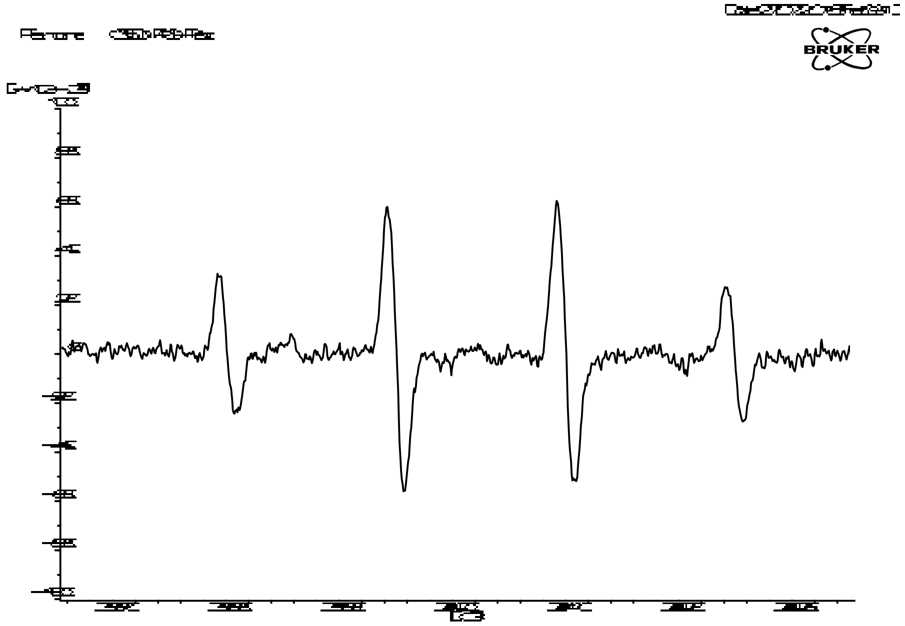


1H NMR spectrum on cell extract of A549 cells

M.R. Pascucci et al, Ageing Cell (2012)

Example: free radicals and nanoparticles

nanoparticles	EPR detects
release free radicals/induce oxidative stress	increase of free radicals
act as free radical scavenger	decrease of free radicals

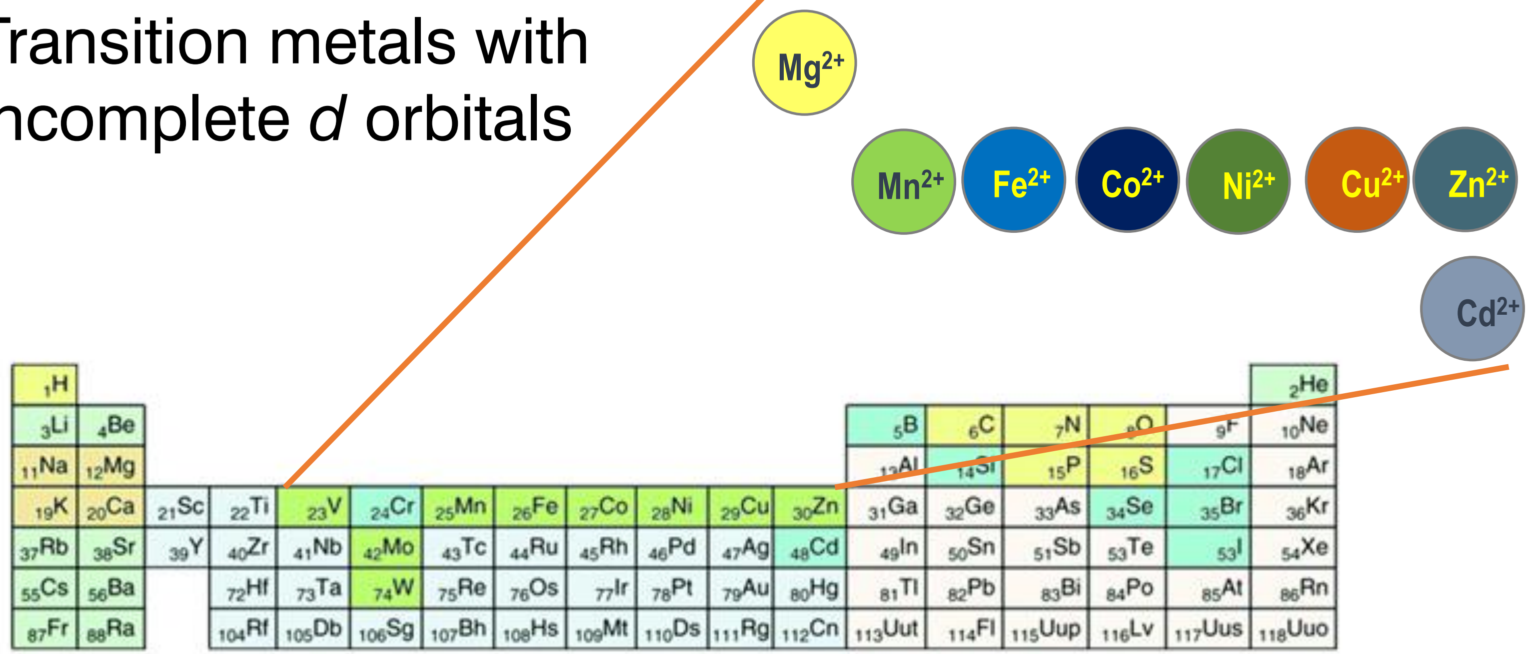


Collaboration with F. Barone and coworkers (ISS)

EPR signal of reactive oxygen species in nanoparticles in solution

Metals: what does EPR measure?

Transition metals with incomplete *d* orbitals



Presence of metal

Metal concentration

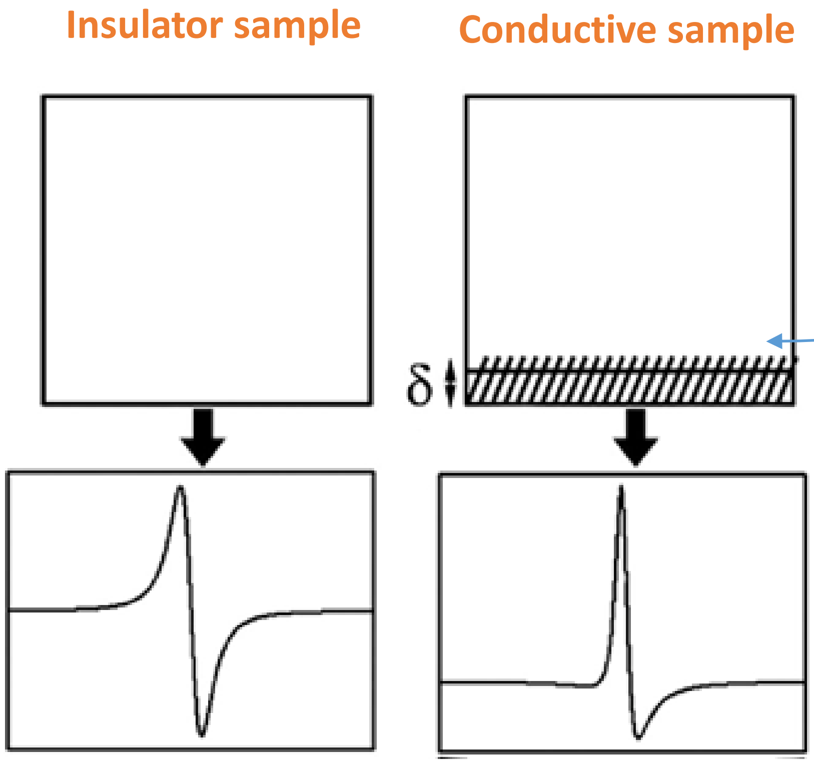
Redox state

Depending on valence state, the spin is zero (EPR silent) or unzero (EPR active). Redox reaction switches between active and silent states.

Metal Ion	Spin State
Fe^{2+}	S = 0 (ls) or S = 2 (hs)
Fe^{3+}	S = 5/2 (hs)
Ni^{1+}	S = ½
Ni^{2+}	S = 0 or S = 1
Ni^{3+}	S = ½
Cu^{1+}	S = 0
Cu^{2+}	S = ½

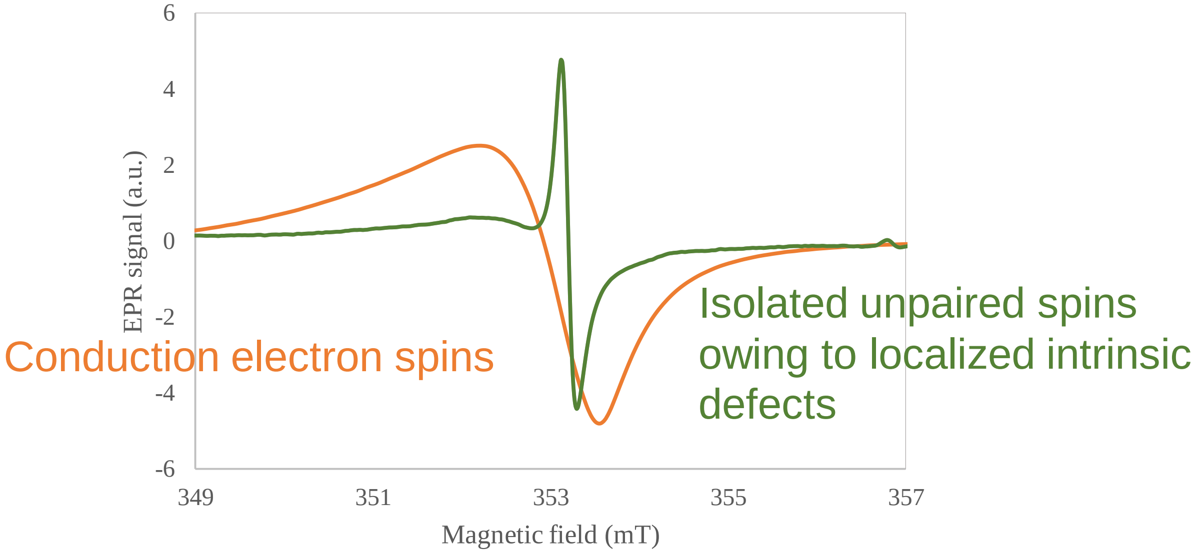
Conduction electron spin resonance

EPR of conduction electrons in metal, semiconductors and carbon samples.



Because the alternate magnetic field does not penetrate in the conductive material, EPR takes place only at the skin depth.

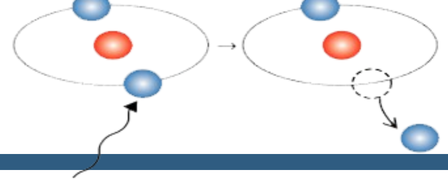
(skin depth: depends on material conductivity and field frequency)



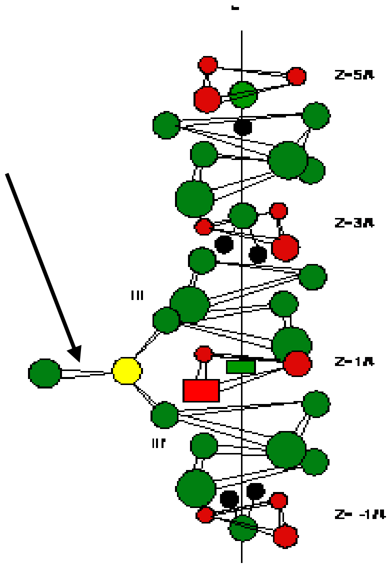
Collaboration with University of Tor Vergata, Rome (Federica Valentini)

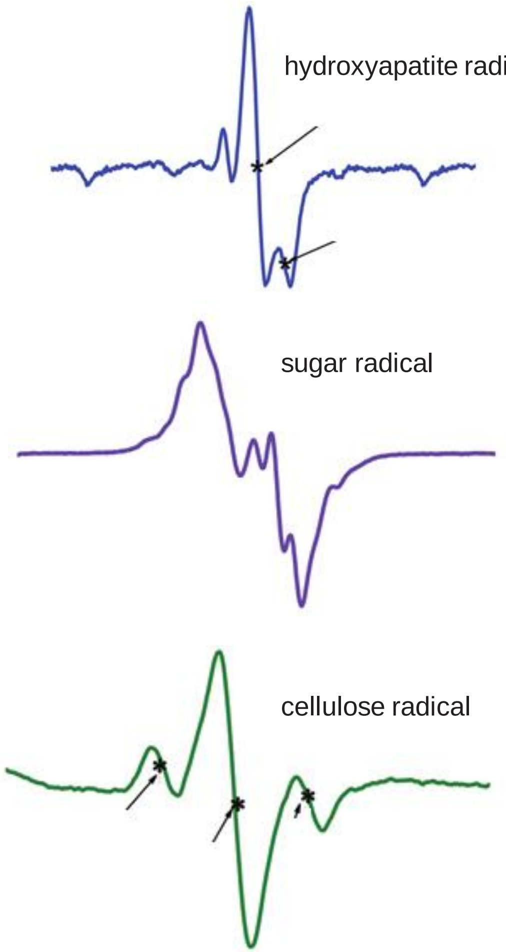
Tadyszak et al. Magn. Res. Chem. 2015

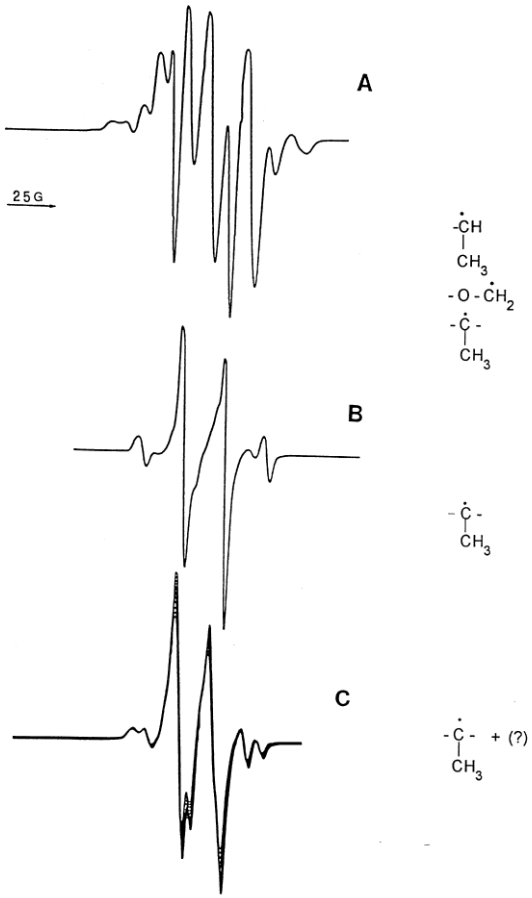
Ionizing radiation induced defects



EPR detects and identifies radiation induced defects in solid matter.







poly(lactide-co-glycolide) microspheres

- radiation induced changes in the properties of “old” and “new”plastics and other materials
- radiation sterilization for
  foods, medical, pharmaceutical and cosmetics products, human tissues (bone, skin, cartilage) for grafts, preservation of cultural heritage
- dosimetry for radiation therapy and industrial beams

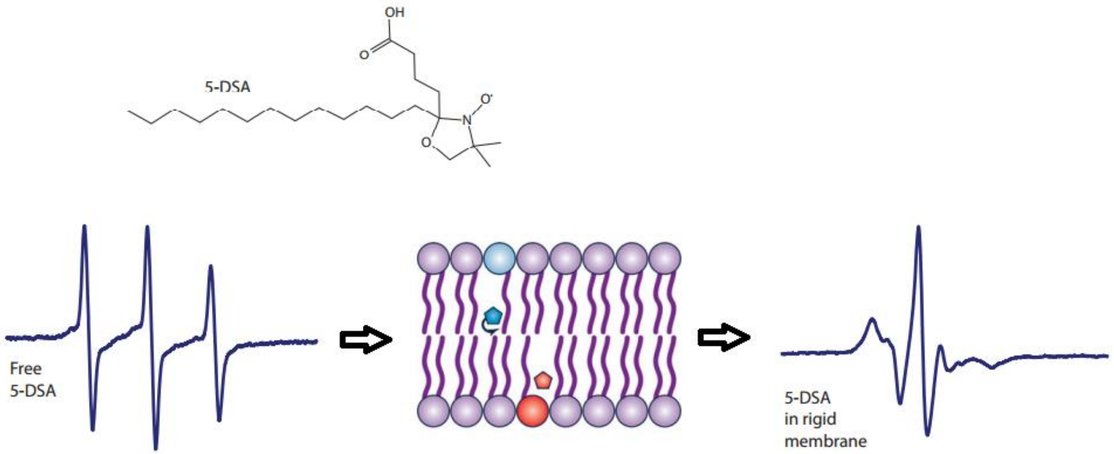
Ionizing radiation may play a role in nanotechnologies.

Joong-Ho Kwon et al. 2014
Montanari et al. 1998

Not only paramagnetic systems

Diamagnetic atoms or molecules may be marked by paramagnetic labels («spin labels») and be measured by EPR. Applications are mainly in the study of dynamics and structure of membranes, proteins and nucleic acids.

Example: membrane fluidity

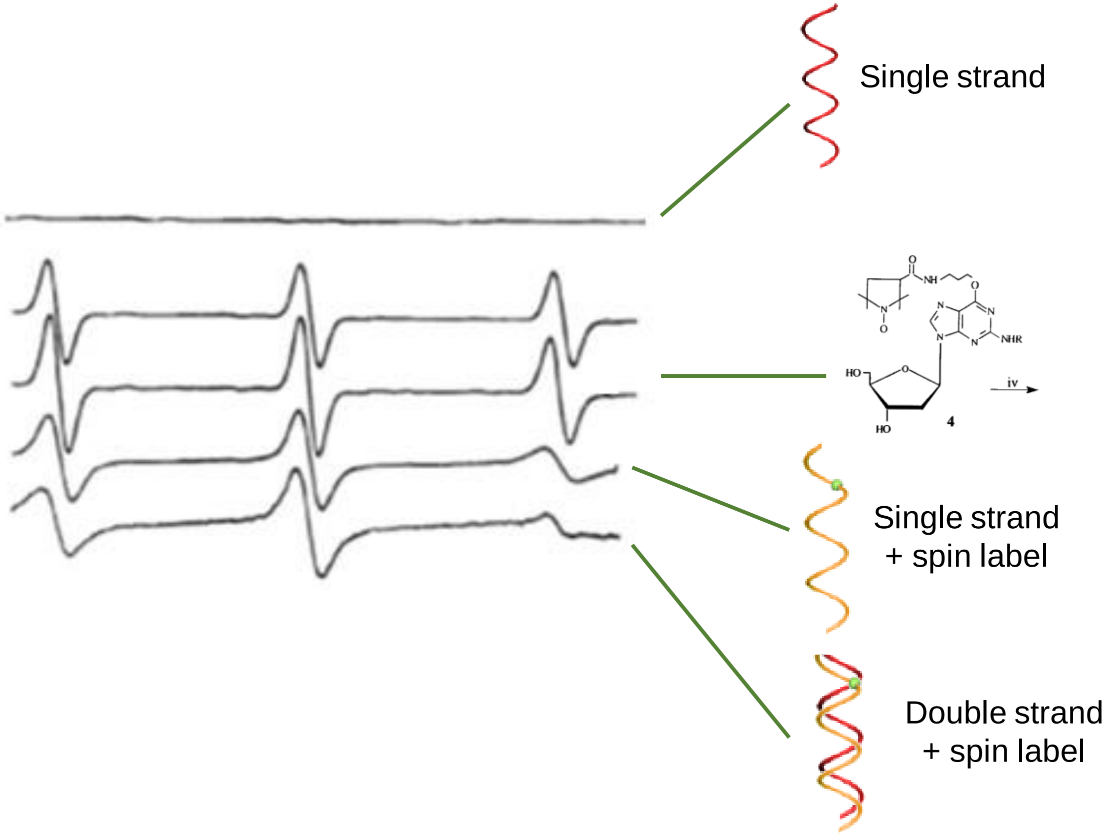


Free spin label

Membrane phospholipidic layer

Rigid motion spin label

Example: nucleic acid dynamics



Giordano et al, Nucleosides, Nucleotides and Nucleic Acids, 2000
E.A. Abdel-Rahman et al. J Physiol. 2016

Practical limits

- Paramagnetic properties of the system
- Available amount of sample
- System resistant to cryogenic temperatures
- Available budget (cryogenic measurements)

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Rossella Canese (next talk)

https://www.iss.it/servizio-grandi-strumentazioni-e-core-facilities