

NMR study of nano-bio interface

Interaction of metallic nanoparticles with
biothiols



Barbara Pem, mag. pharm.

Nanoparticles

1 – 100 nm

Properties:

- large surface area
- high adsorption capacity
- high reactivity
- optical properties



Bioapplications

AgNPs

Antimicrobials

Wound healing

Food packaging

Cosmetics

Textiles

Air and water disinfection

Anti-inflammation

Drug delivery

Cancer therapy

Biosensors

AuNPs

Diagnostics

Biosensing and bioimaging

Drug delivery

Gene delivery

Photothermal therapy

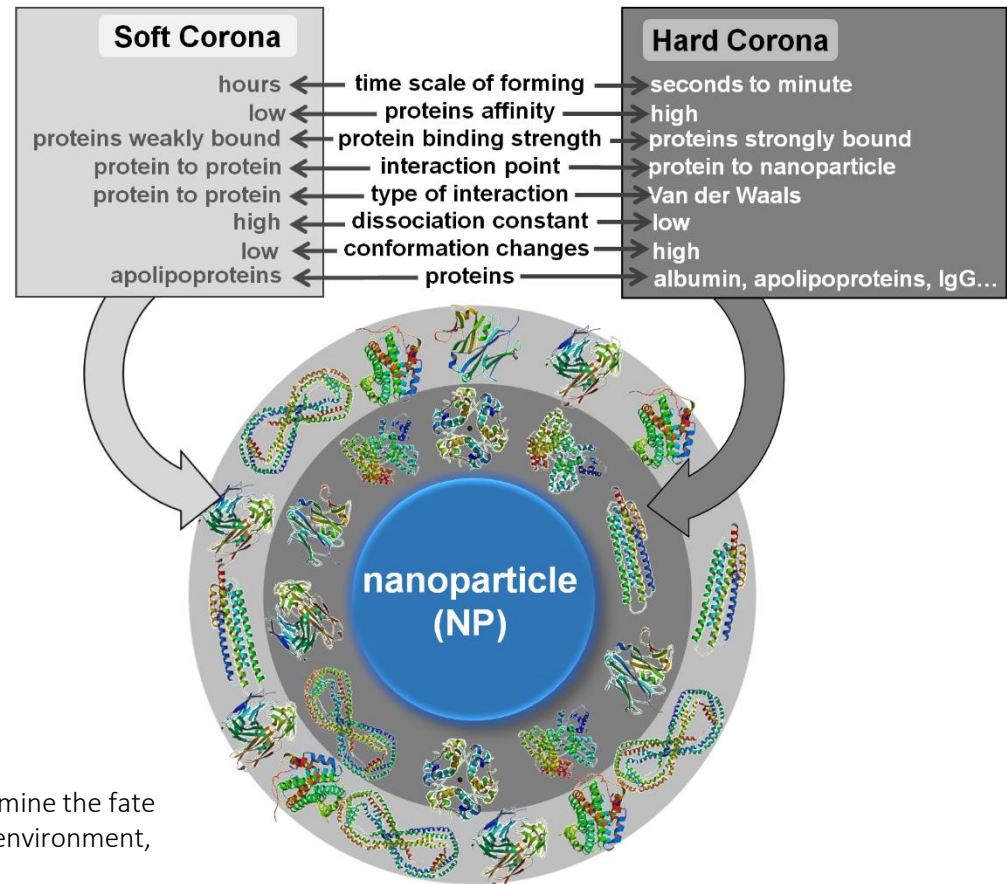
Nano-bio interface

Biomolecule corona

Protein corona

Impact on
physicochemical and
physiological properties
of NPs

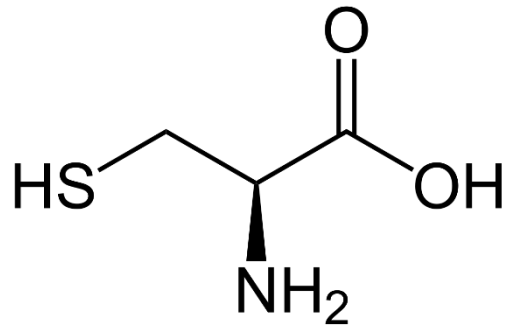
Role of thiol groups



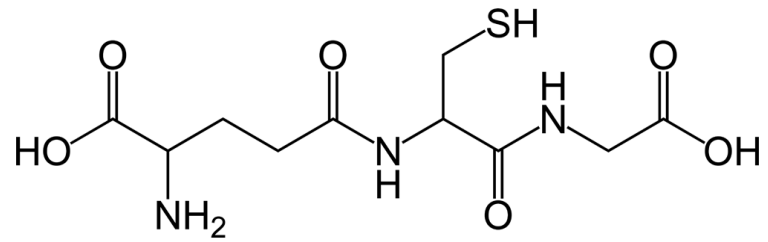
Capjak I, et al. How protein coronas determine the fate of engineered nanoparticles in biological environment, *Arh Hig Rada Toksikol* 2017;68:245-253

Model biothiols

CYSTEINE



GLUTATHIONE



NMR

Nuclear
Magnetic
Resonance



NMR

Identification

Structure determination

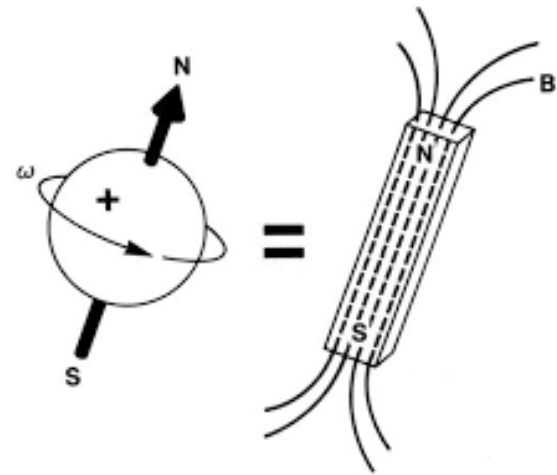
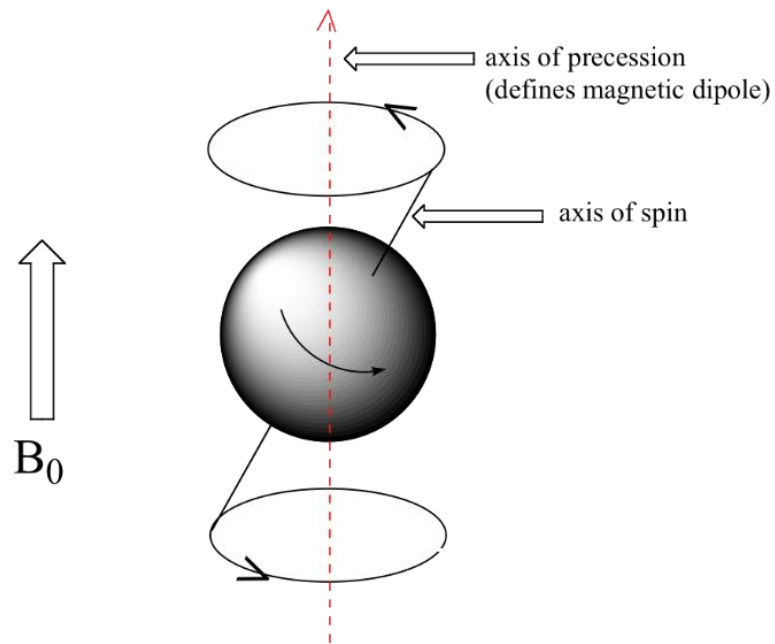
Quality control

Reaction monitoring

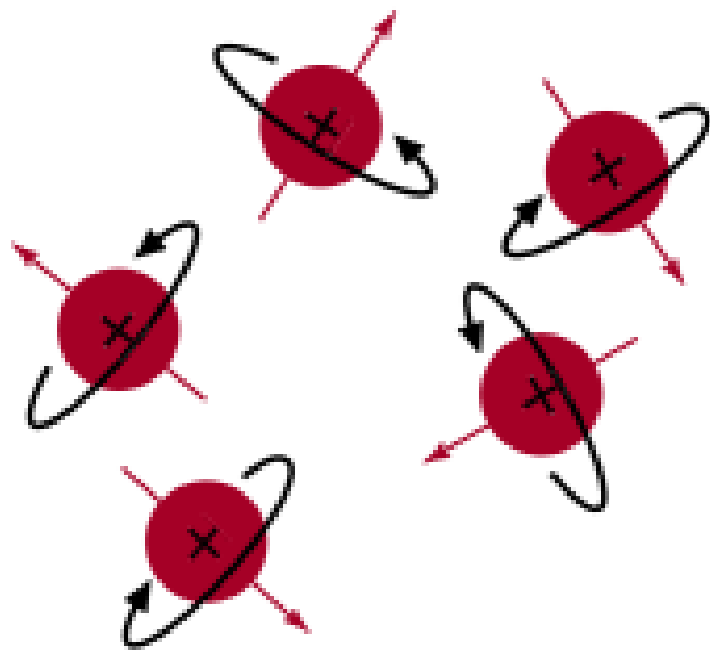
Quantification

Kinetics

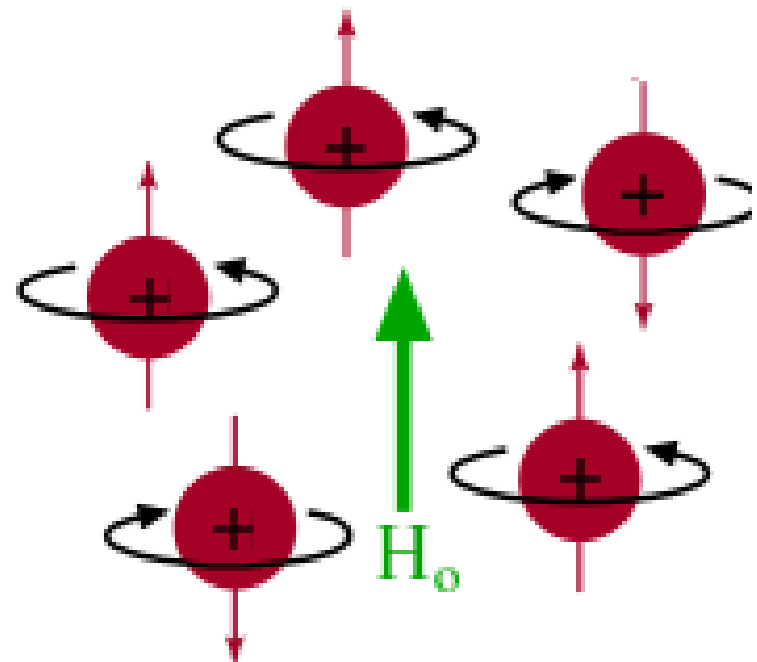
Nuclear



Magnetic

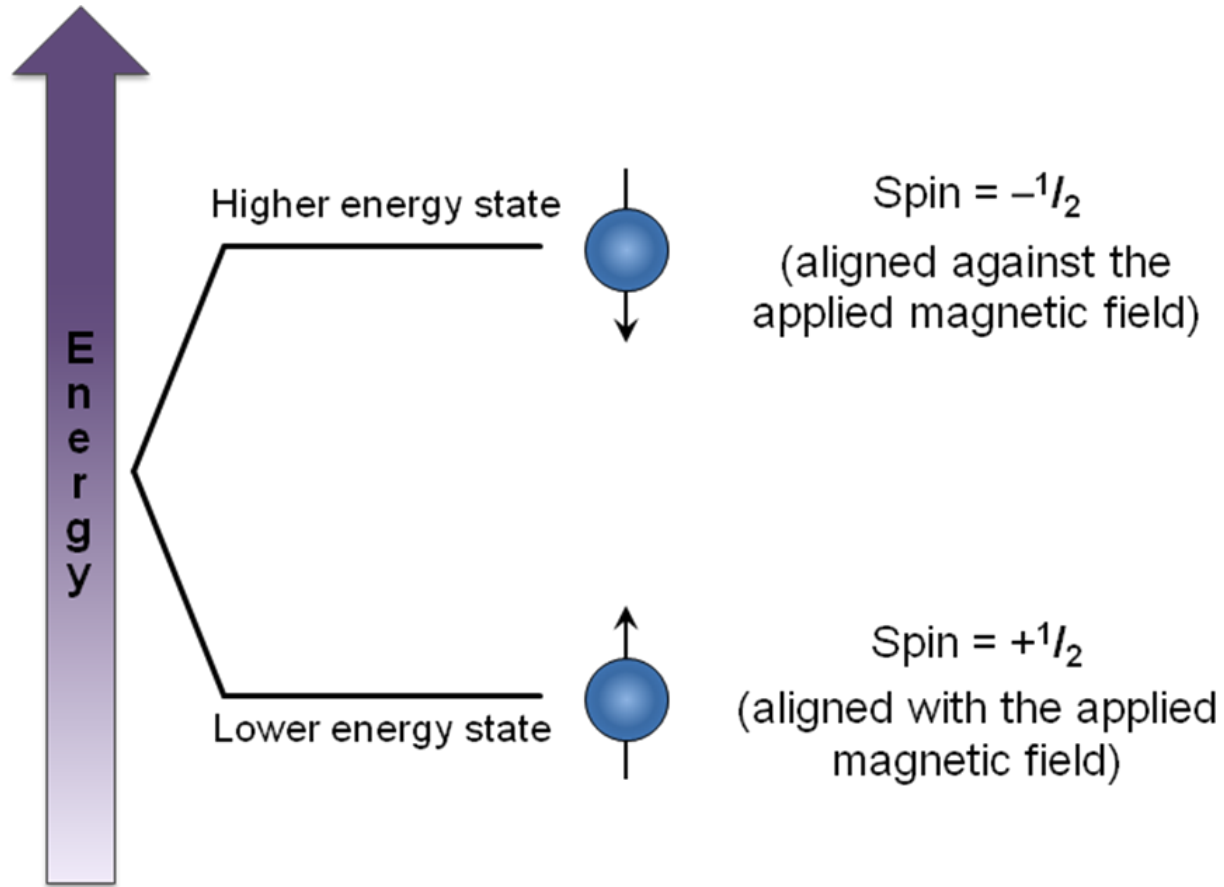


No field

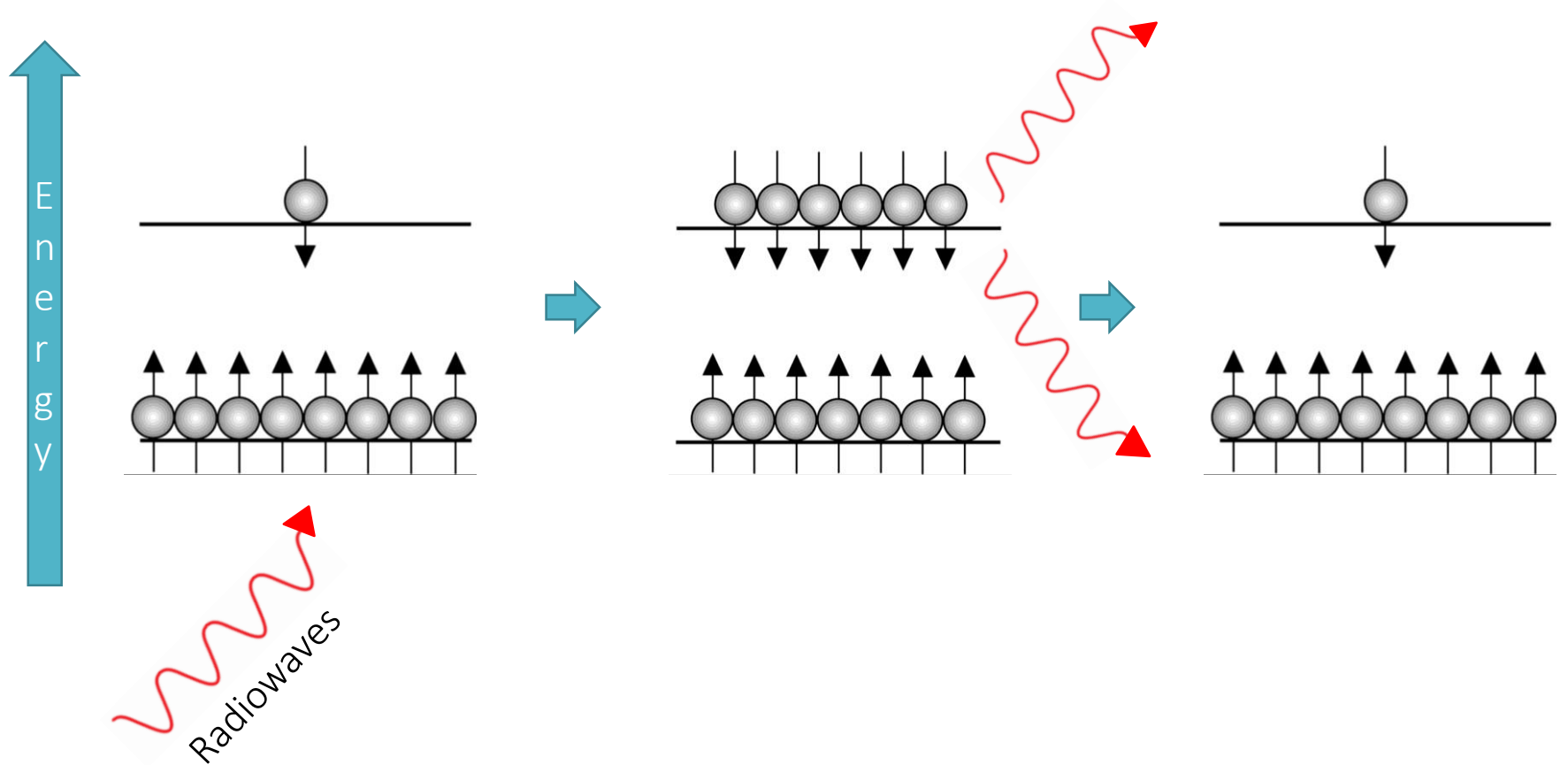


With field

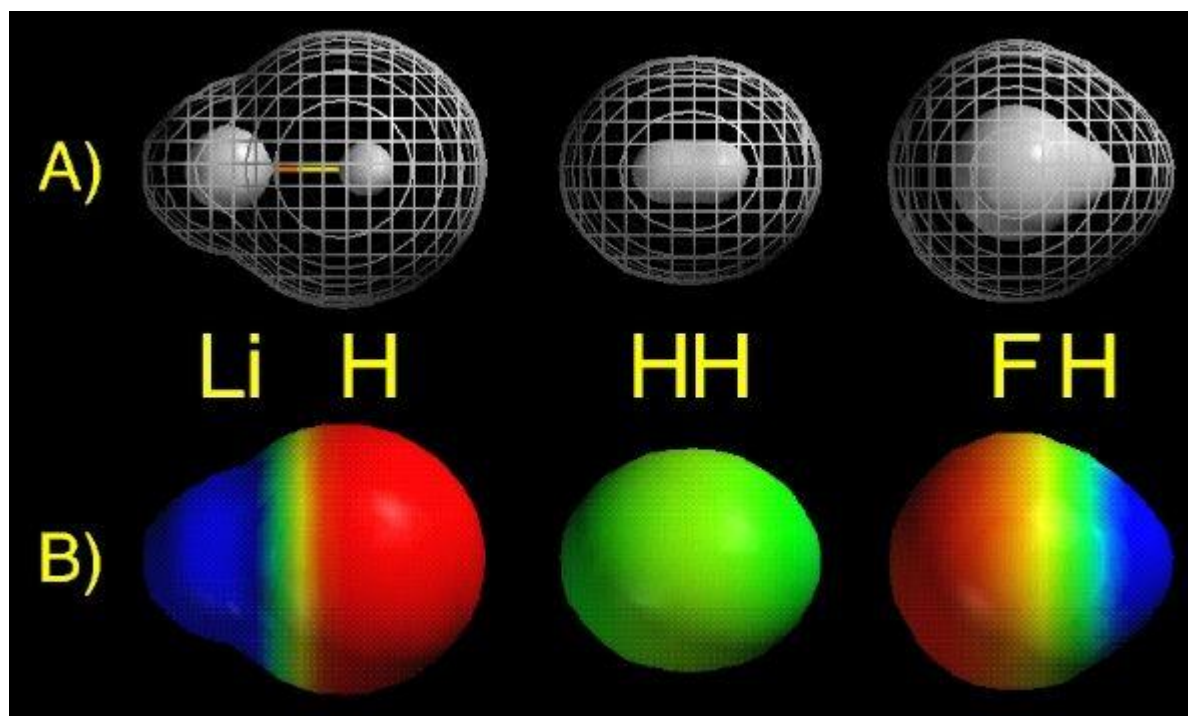
Magnetic



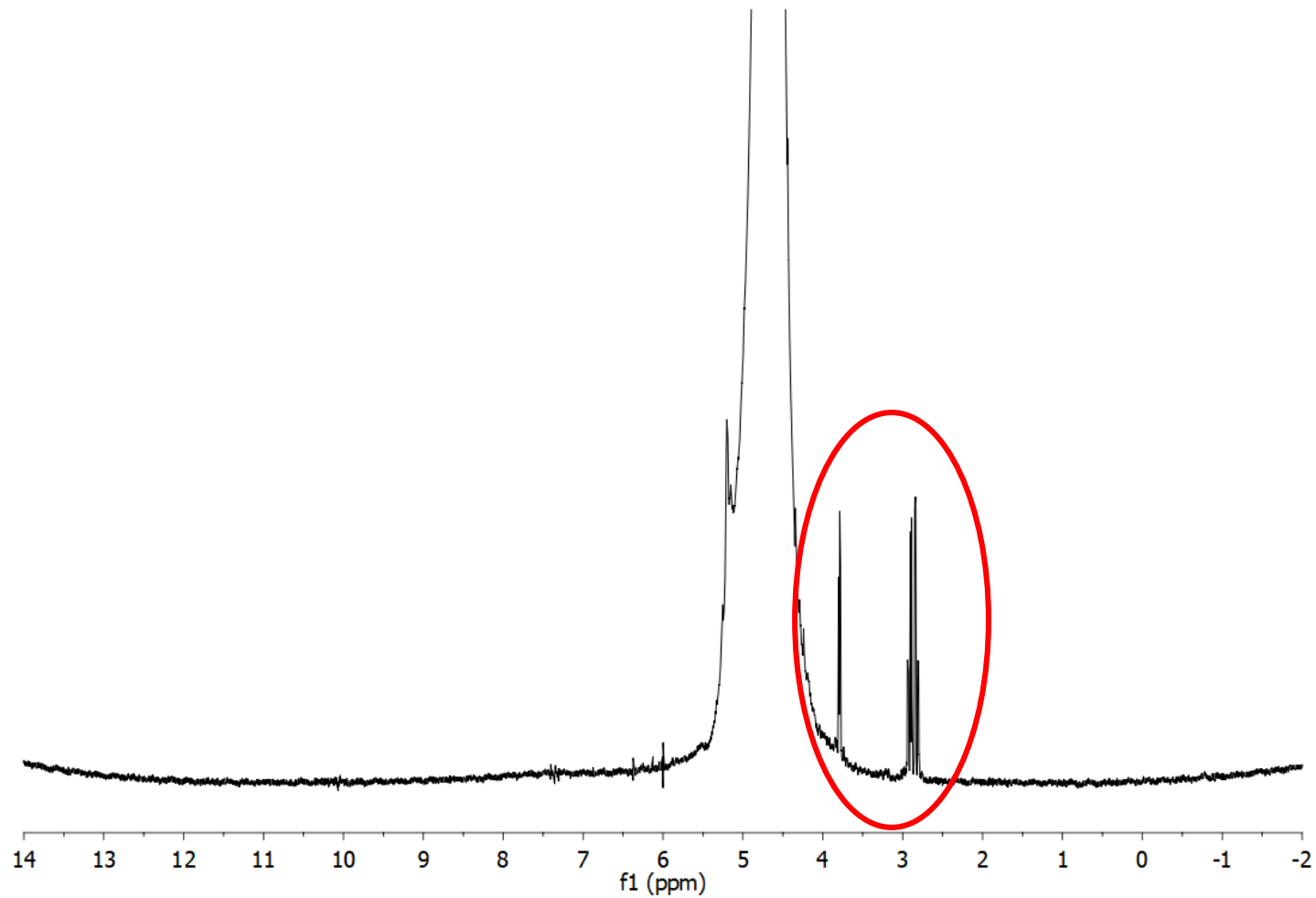
Resonance



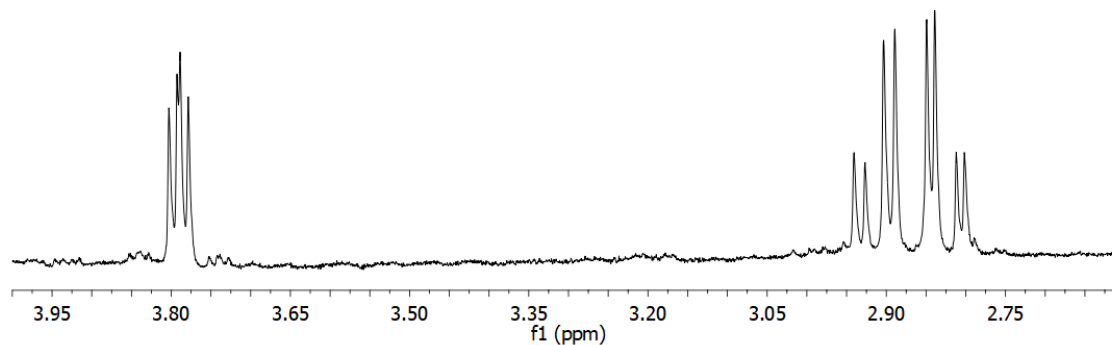
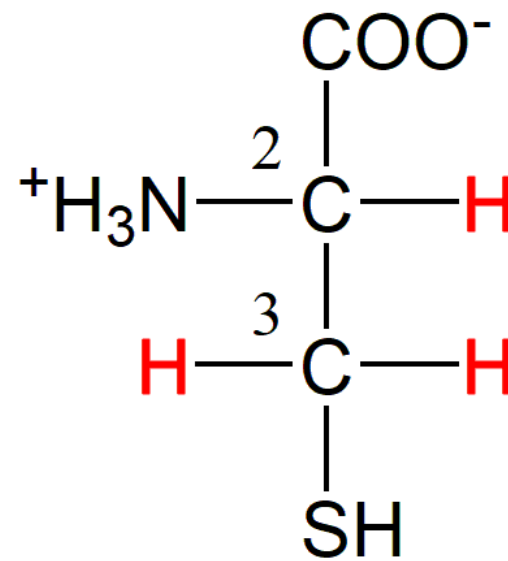
Shielding



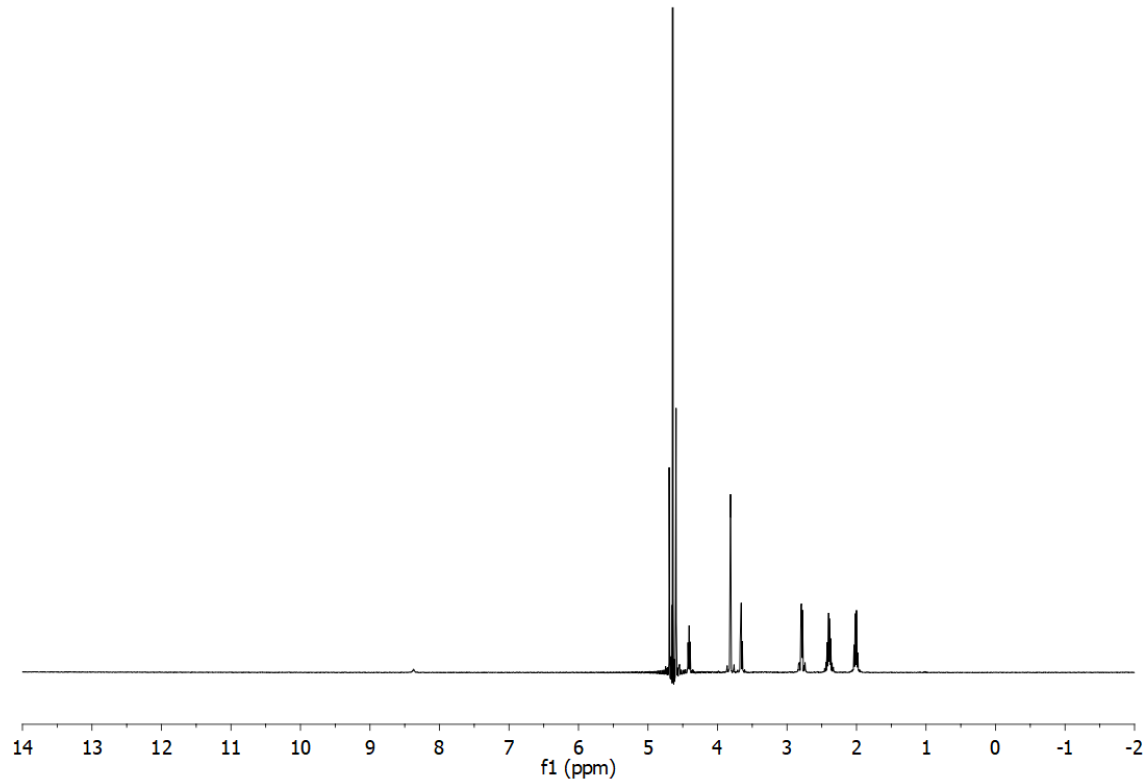
Spectrum of cysteine



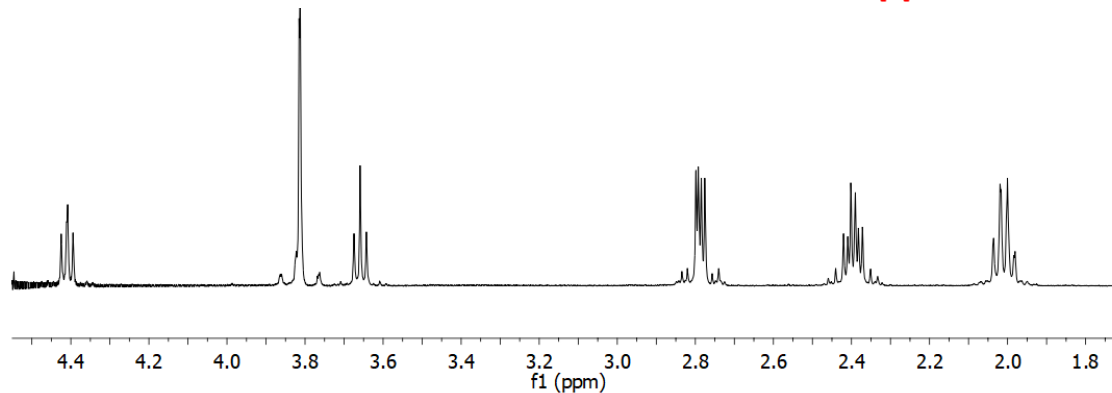
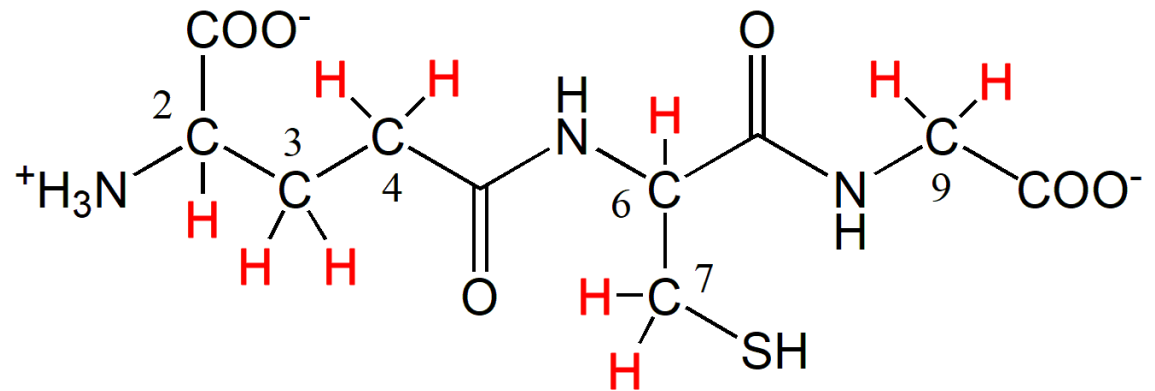
Spectrum of cysteine



Spectrum of glutathione



Spectrum of glutathione



Methods

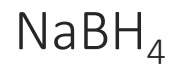
AuNP SYNTHESIS



+

CYS/GSH

+



1

:

1

:

10

AgNP SYNTHESIS



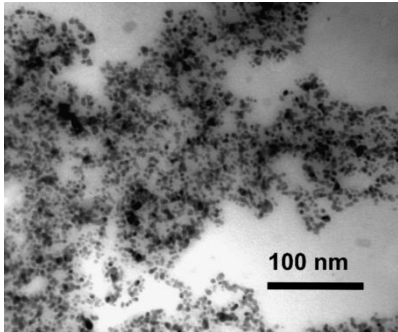
+

CYS/GSH

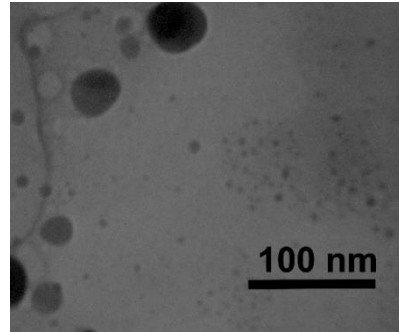
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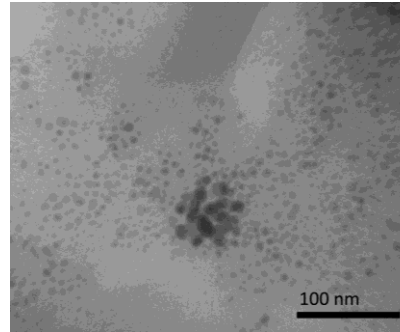
Characterization



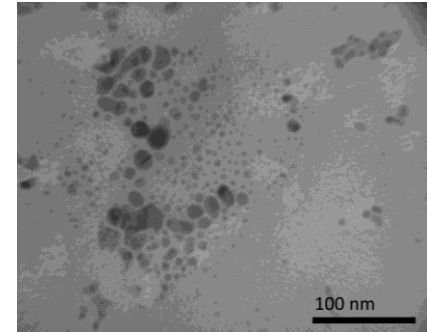
CYS-AuNP



GSH-AuNP



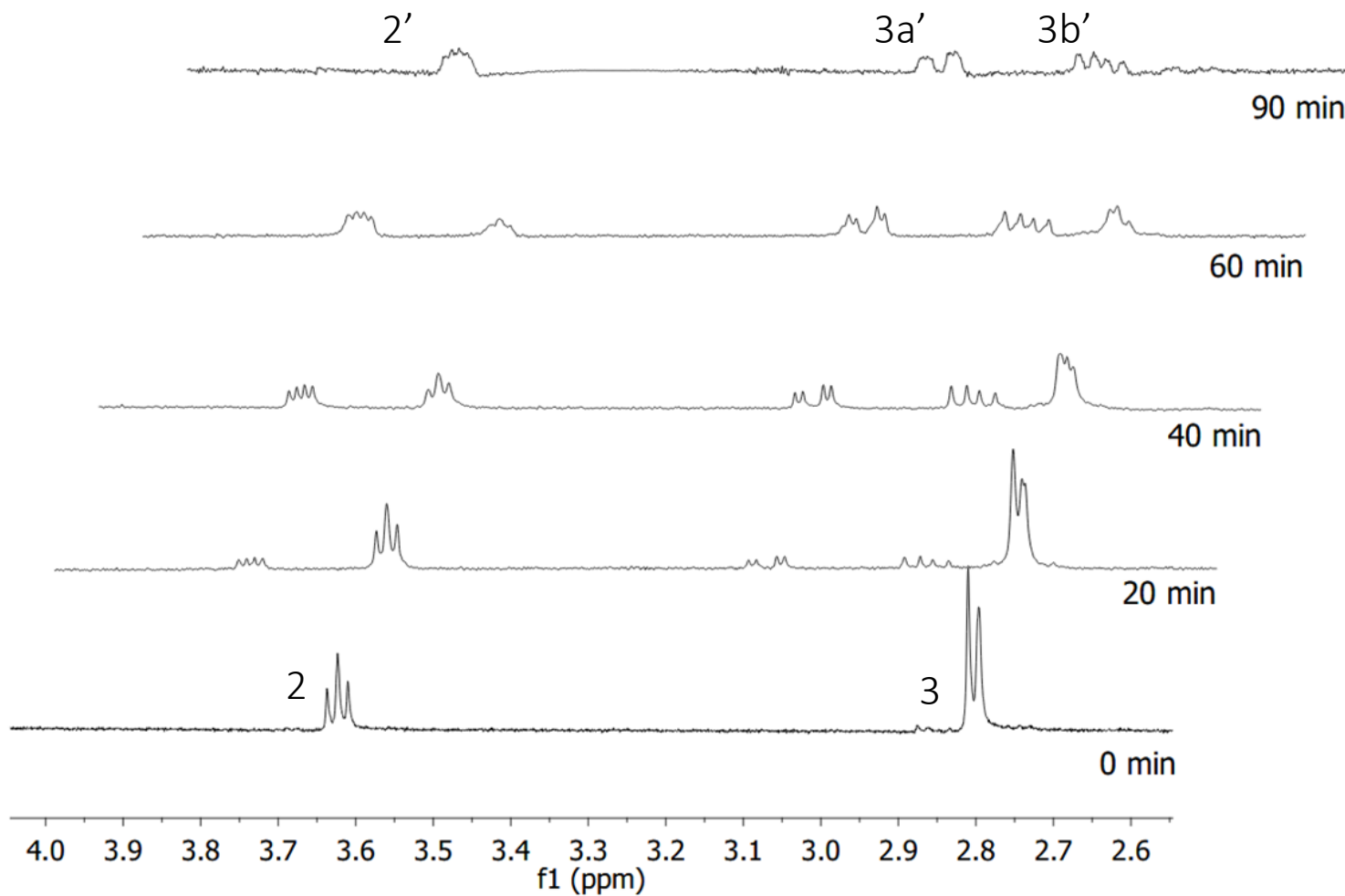
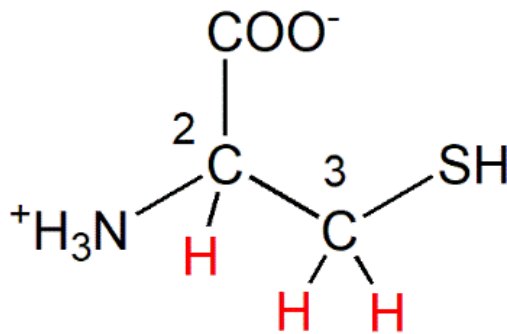
CYS-AgNP



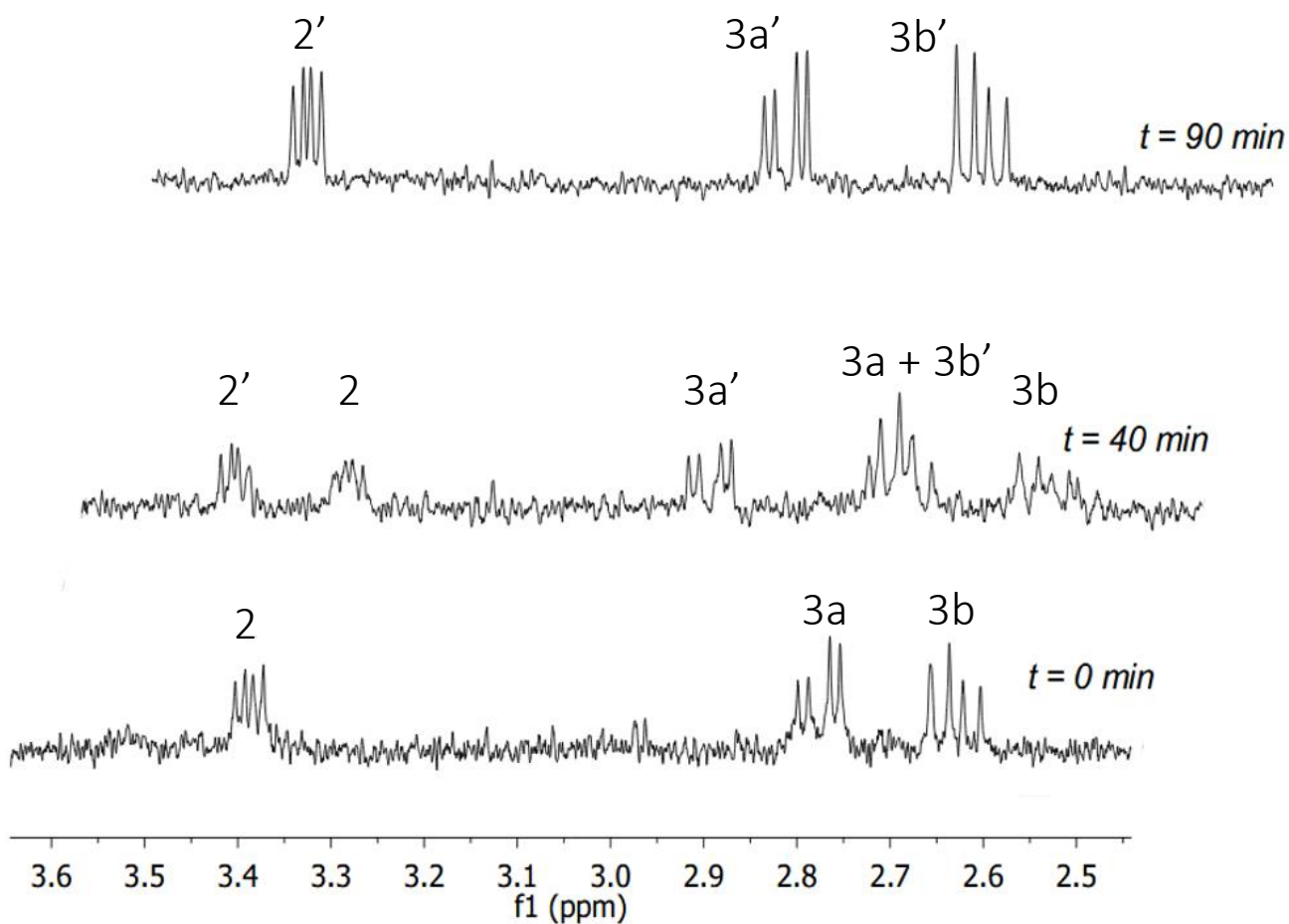
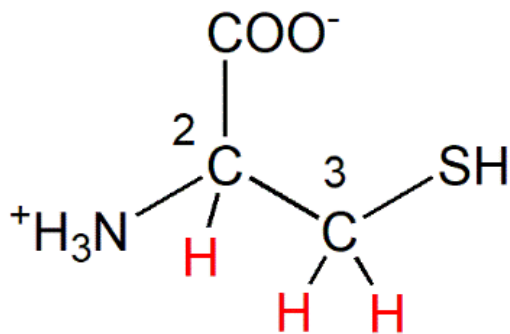
GSH-AgNP

NP	d_H (nm)	% Volume	ζ (mV)
CYS-AuNP	$24,2 \pm 3,4$	54,3%	$-46,8 \pm 2,1$
	$80,0 \pm 2,1$	10,4%	
	$219,7 \pm 48,9$	35,3%	
GSH-AuNP	$6,4 \pm 0,8$	64,9%	$-58,0 \pm 3,8$
	$65,1 \pm 3,8$	35,1%	
CYS-AgNP	$8,0 \pm 0,9$	99,7%	$-56,9 \pm 7,5$
GSH-AgNP	$6,0 \pm 1,2$	99,9%	$-50,9 \pm 2,3$

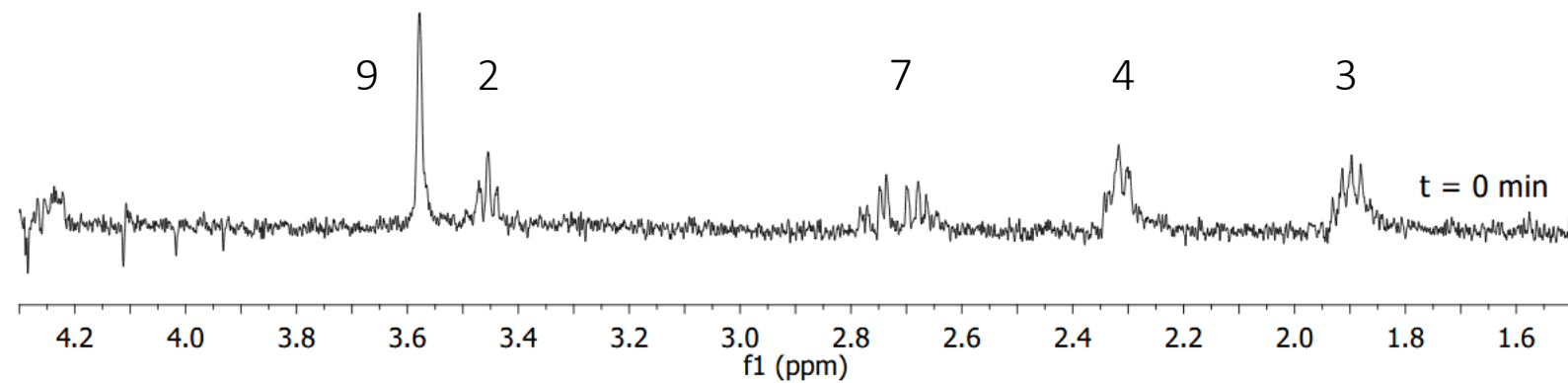
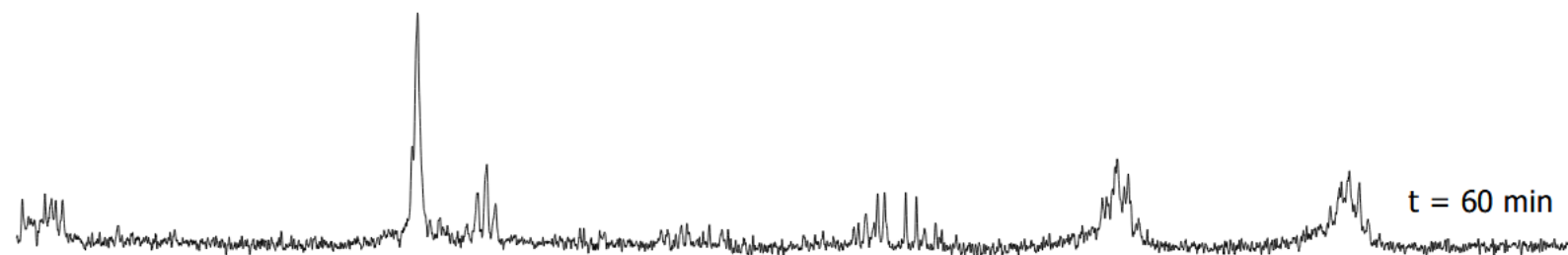
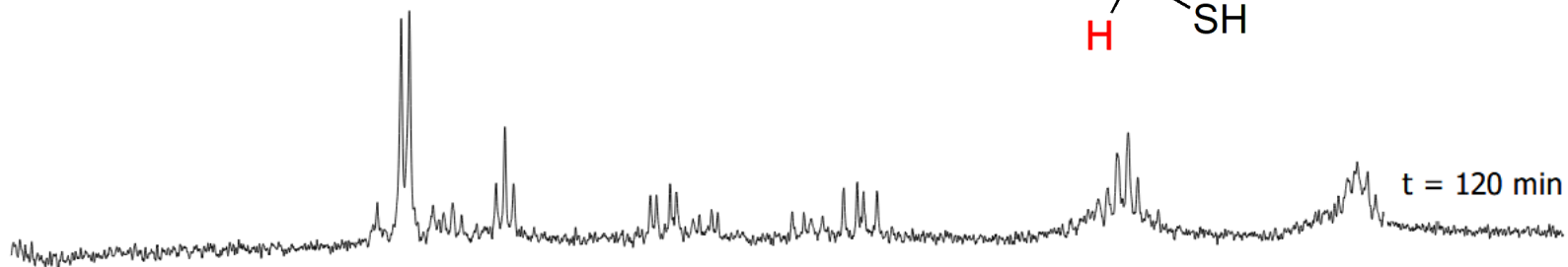
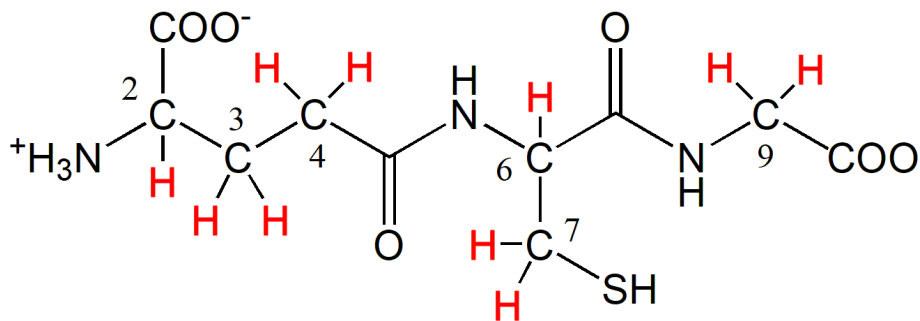
CYS-AuNP



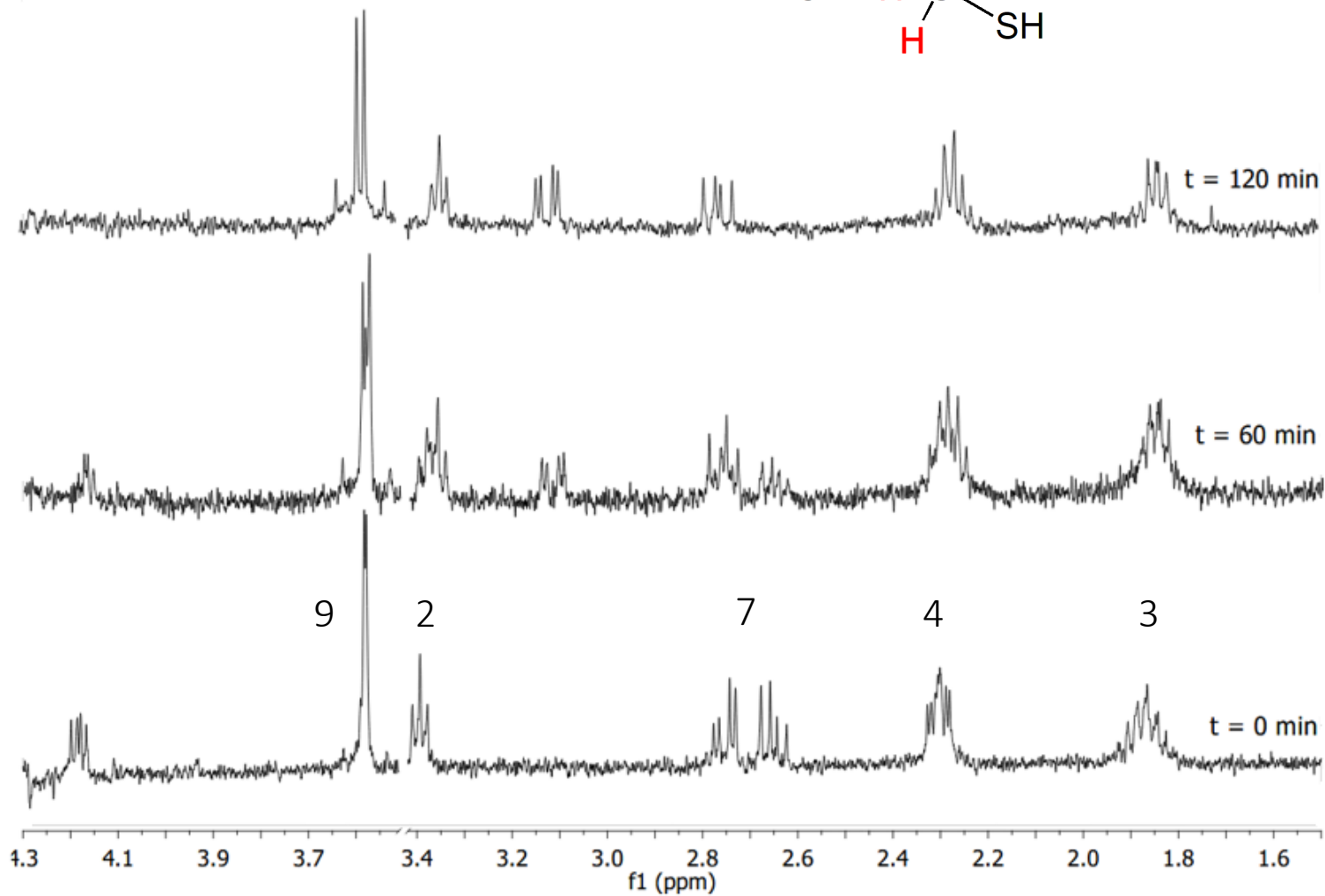
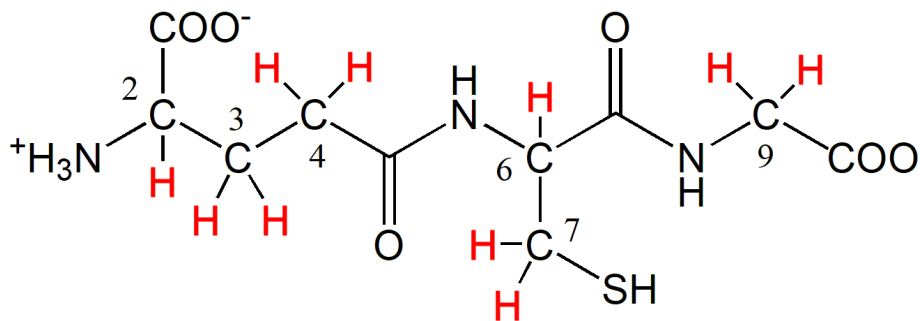
CYS-AgNP



GSH-AuNP



GSH-AgNP



Conclusions

Interaction of CYS and GSH with NPs happens through the thiol group

Thiols are stably bound to the NP surface – no fast exchange

AgNP synthesis with GSH

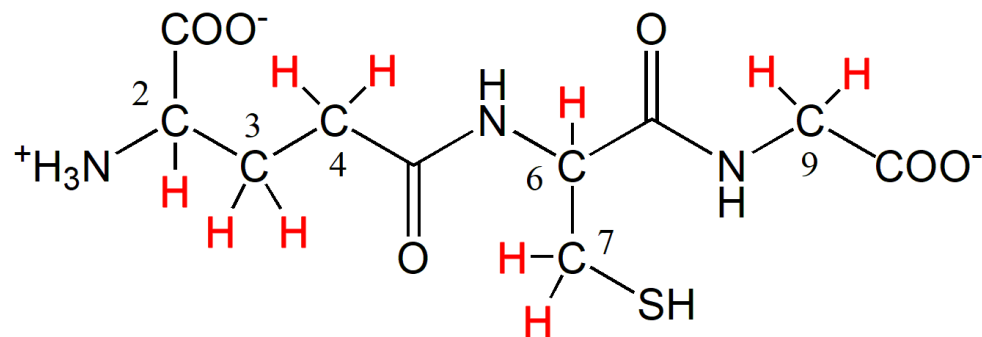
Model of *in vivo* synthesis of AgNPs from ionic silver
GSH as a reducing/stabilising agent

$\text{AgNO}_3 : \text{GSH} = 2 : 1$

Room temperature

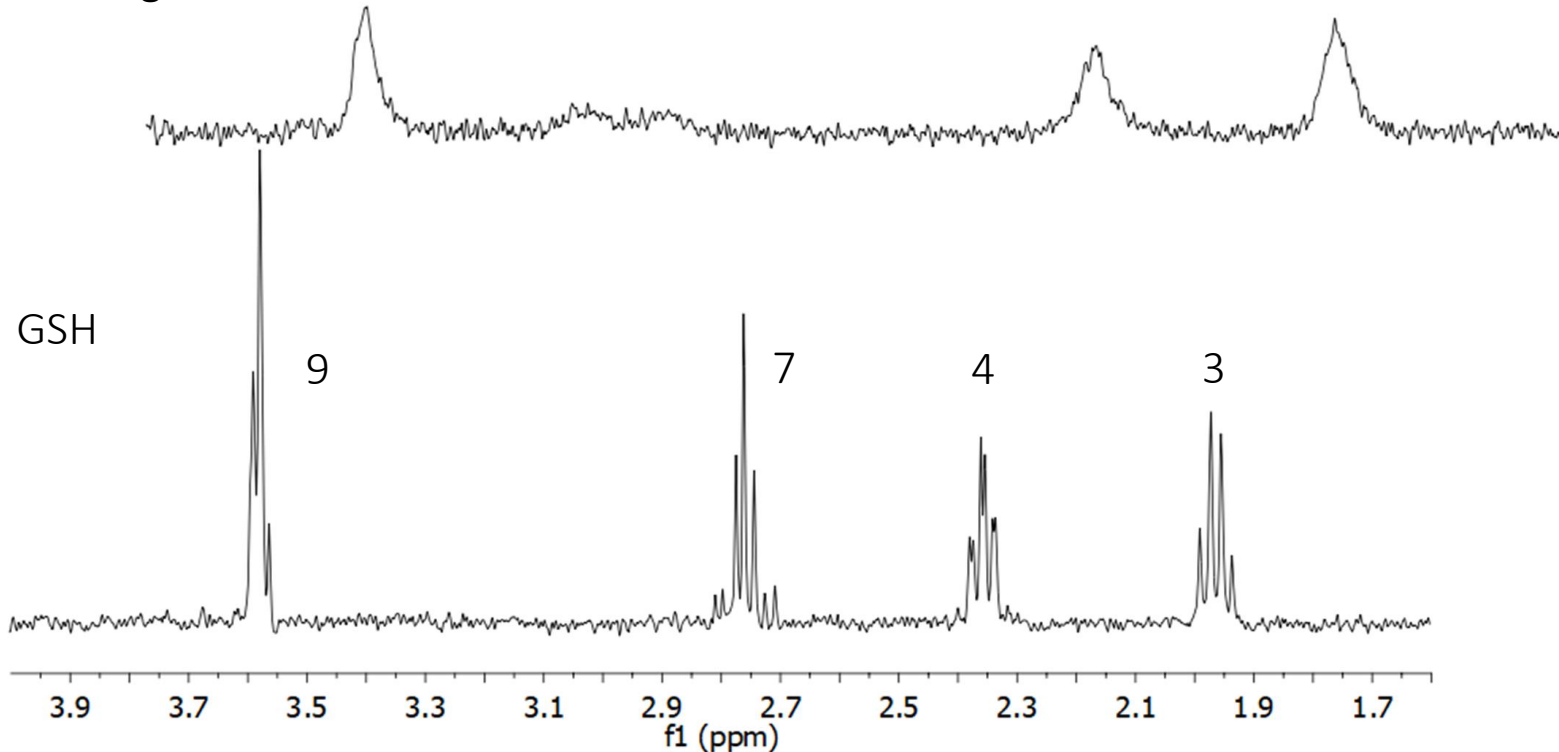
Neutral environment - Phosphate buffer 25mM pH 7

GSH-AgNP in PB pH 7



GSH-AgNP

GSH



Problems

Non-homogenous sample

Cannot track fast reactions

Interference from NaBH_4

What next

Temperature studies

Peak integral analysis

Kinetics

^{13}C NMR