Perturbed Angular Correlation studies of Hg coordination mechanisms on functionalized magnetic nanoparticles

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ITN, Sacavém, Portugal and ISOLDE-CERN

IO81:
Radioactive probe studies of coordination mechanisms of heavy metal ions from natural waters to functionalized magnetic nanoparticles

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Plan

- Motivation: removal of heavy metals from water
- Microscopic questions: ion coordinations
- Use of hyperfine techniques: PAC
- Results and discussion: local environment
- Conclusions

Removal of heavy metals from water

Water pollution by trace heavy metals (such as mercury, cadmium) is a serious environmental and public health problem.

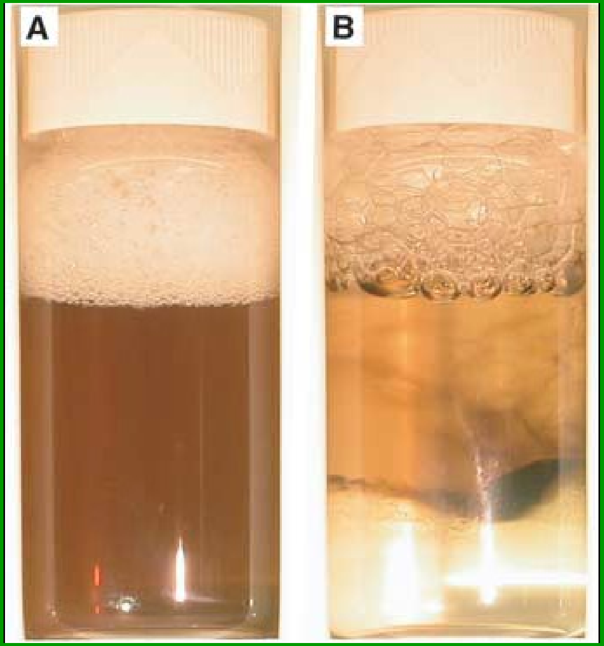
The development of efficient new materials and clean-up technologies for removing those metals from water to within the legal admissible concentrations is urgent.

The threshold for mercury in drinking water potentially causing health problems was set at two parts per billion (microgram of mercury per water liter)

Mercury poisoning on fish and the food chain

Removal of heavy metals from water

Removal of particles from solution with the use of magnetic fields is more selective and efficient (and much faster) than centrifugation or filtration.



Smaller nanometric particles (below 100 nm) provides higher surface/volume ration and increased efficiency (up to 99%)

up to mg of removed ion per kg of material

Chemical functionalization of nanoparticles surfaces improves the efficiency since metal ions can be selectively coordinated by functional groups (e.g. carboxylates or thiolates) attached to the nanoparticles surfaces.

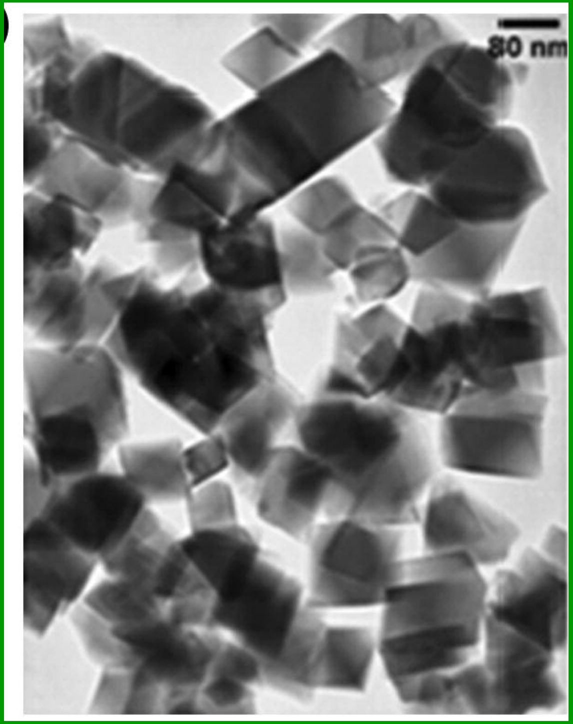
Yavuz et al. "*Low-Field Magnetic Separation of Monodisperse Fe3O4 Nanocrystals*", Science 314, 964 (2006)

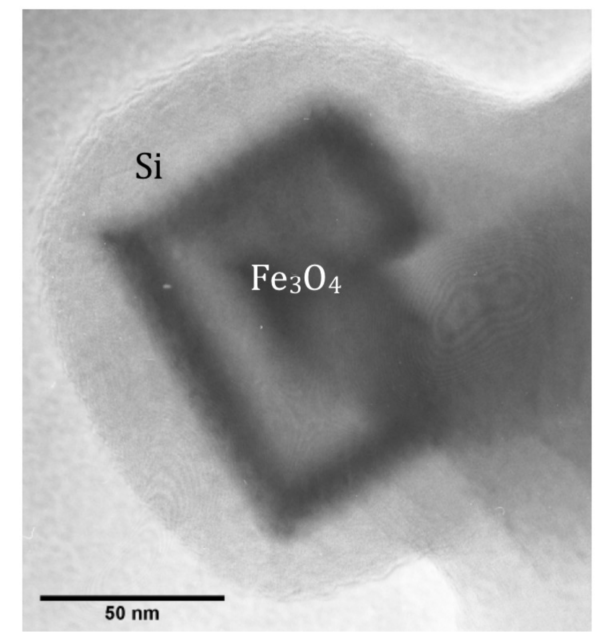
Removal of heavy metals from water

We have been investigating the synthesis, surface modification (with amorphous SiO2) and functionalization of magnetite Fe3O4 nanoparticles, by grafting dithiocarbamate (DTC: NS_2) groups to the particles surface.

Surface functionalization process introduced DTC groups without destroying the morphological characteristics of the magnetite nanoparticles.

magnetite nanoparticles

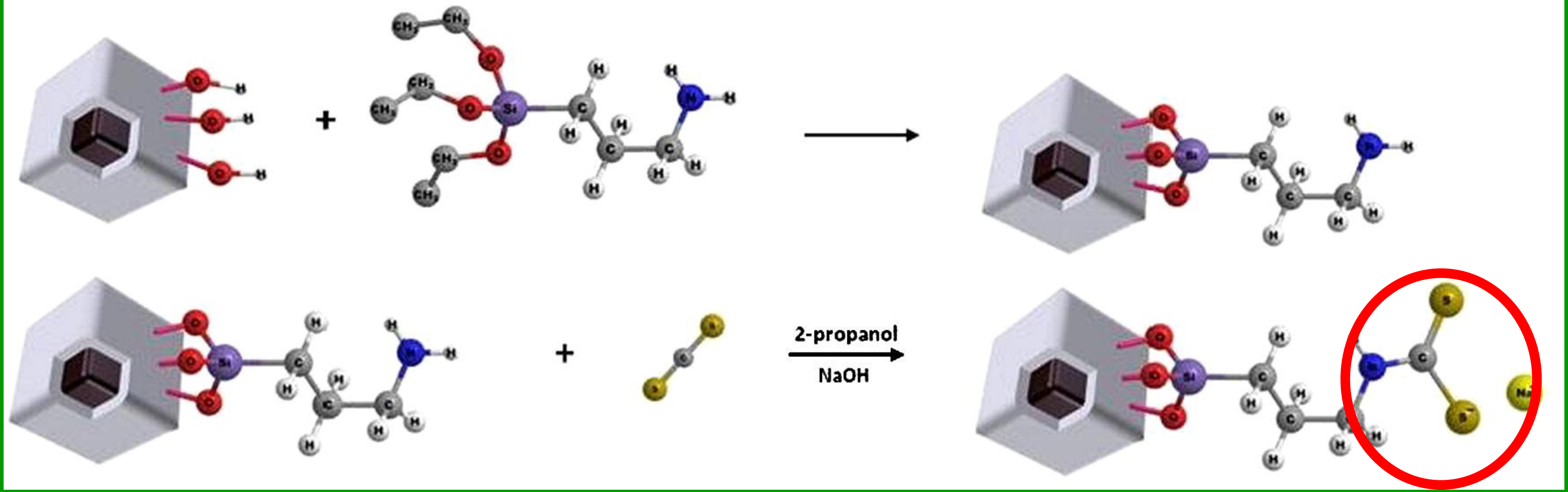




Silica-coated Fe_3O_4 nanoparticle

Removal of heavy metals from water

Surface functionalization process with DTC (N S_2)



Removal of heavy metals from water

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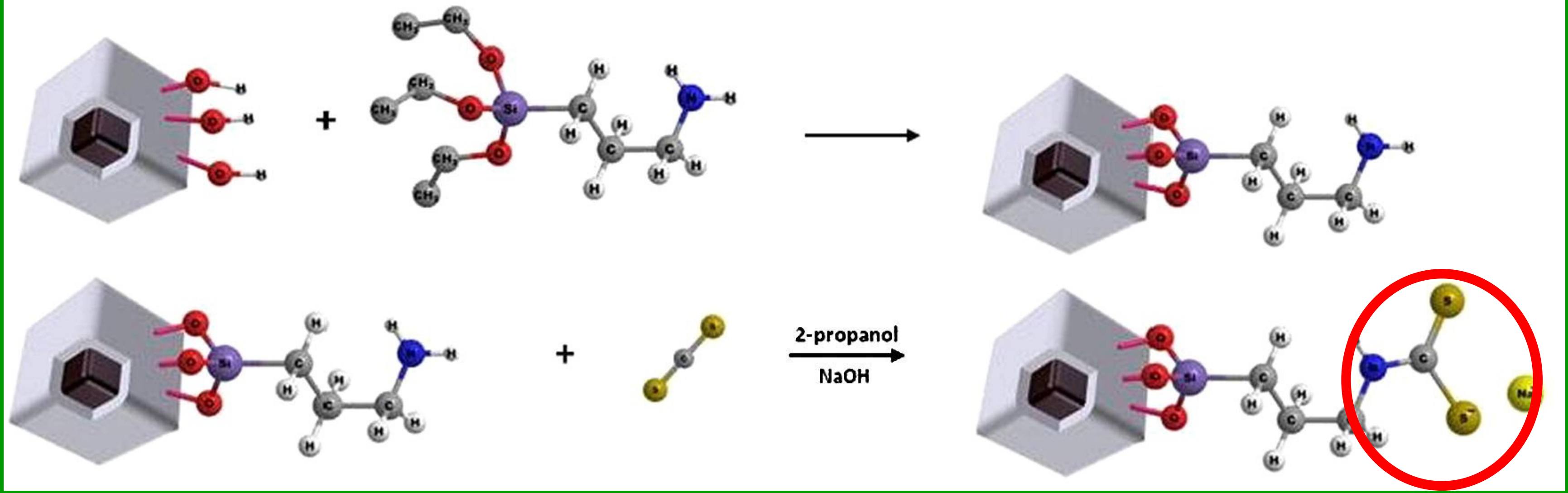
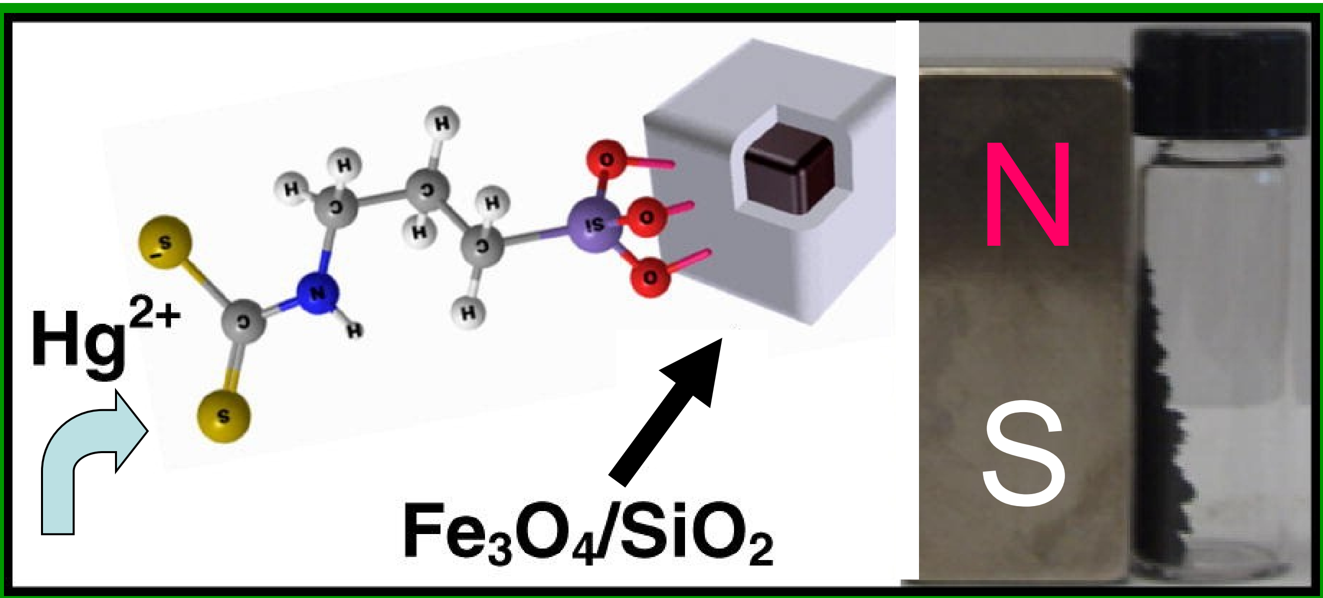
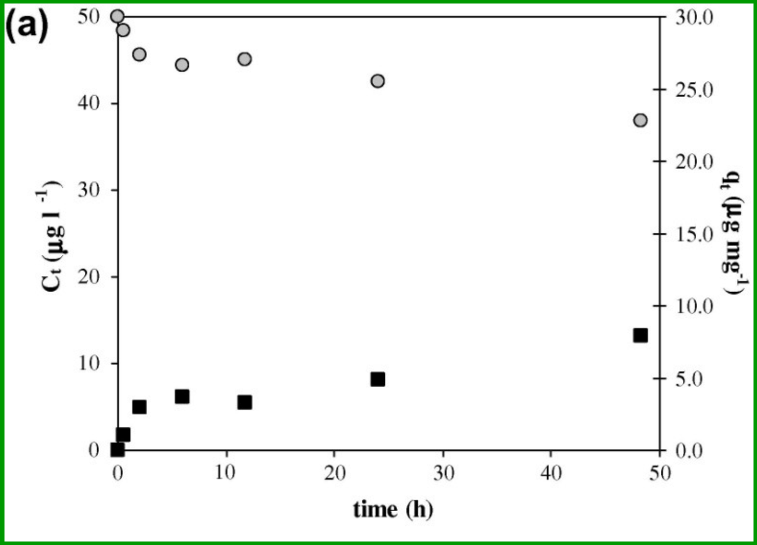




Magnetic separation

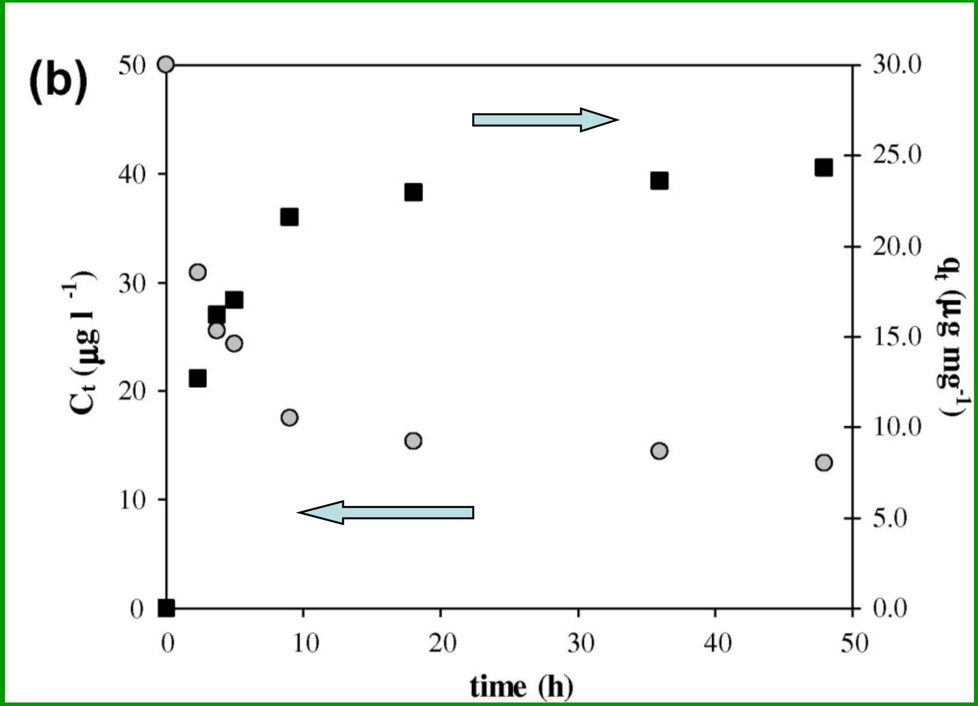
Removal of heavy metals from water

The sorption of Hg2+, Pb2+ and Cd2+ ions from aqueous solutions has been investigated monitoring the bulk solution concentration of the cation using vapour atomic fluorescence spectrometry.



surface modified (silica)

Girginova et al, J. Colloid and Interface Science, 345, 234 (2010)



functionalized of with dithiocarbamate groups

Microscopic questions: coordination

How the nature of the nanoparticles surface influences the overall process?

each metal ion is coordinated by the functional group of the organic ligand located at the nanoparticles surface

ion binds to more than one molecule (if they are dense enough at the surface)
two or more ions are loosely bound to one molecule

can largely change the efficiency and stability of the process

non-passivated regions of the SiO_2 surface can participate in the cations up-take process leading to a distinct behaviour as compared to the chelating sites.

Microscopic questions: coordination

Mercury/Cadmium dithiocarbamate structures and coordinations are complex, and present monomeric and dimeric types

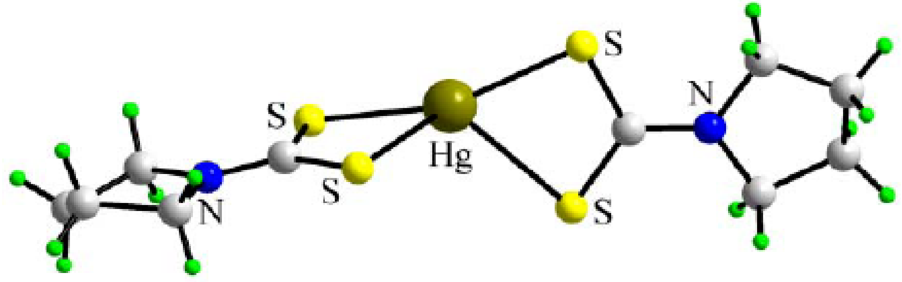
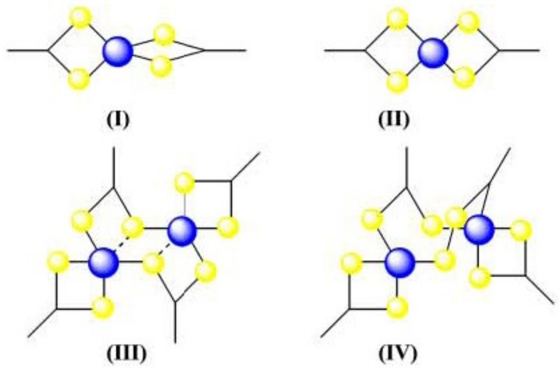


Fig. 1 Molecular structure of $Hg(S_2CN(CH_2)_4)_2$, representing tetrahedral motif (I). Click here to access a 3D representation. Colour code



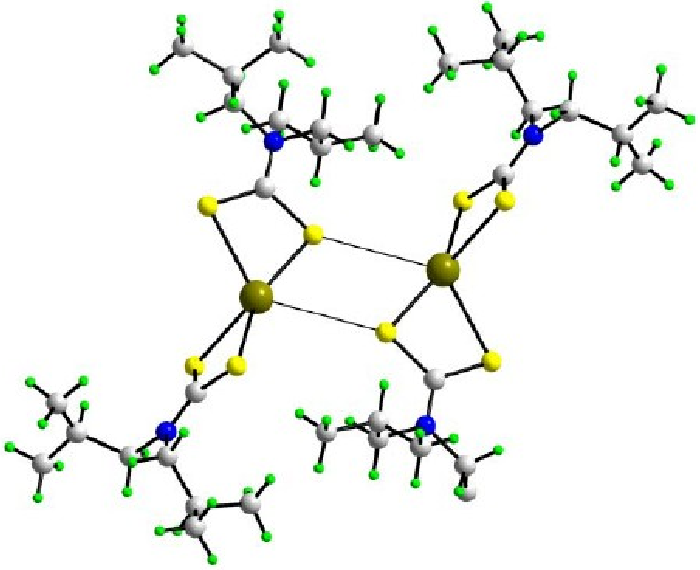


Fig. 2 Molecular aggregation *via* weak intermolecular Hg···S interactions in the crystal structure of $Hg(S_2CN(iBu)_2)_2$ showing the potential of the mononuclear motif (I) to dimerise.

Microscopic questions: coordination

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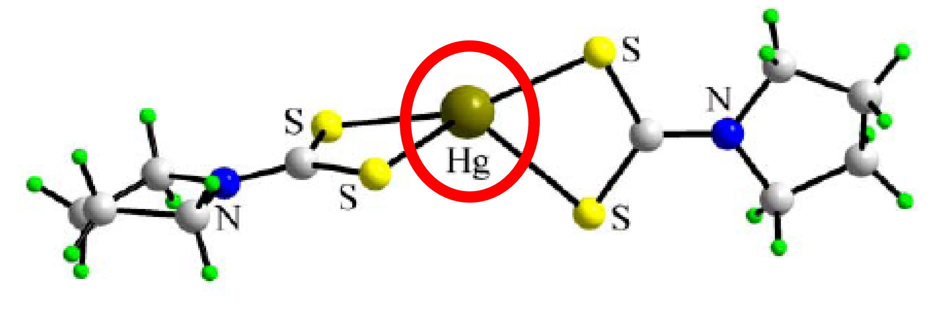

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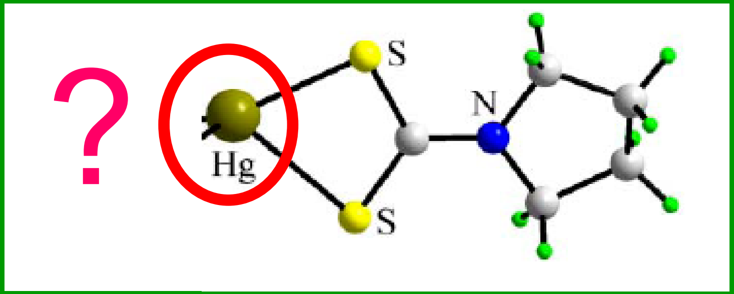


Can we probe the local environment of the ions?

Use radioactive isotopes and hyperfine techniques

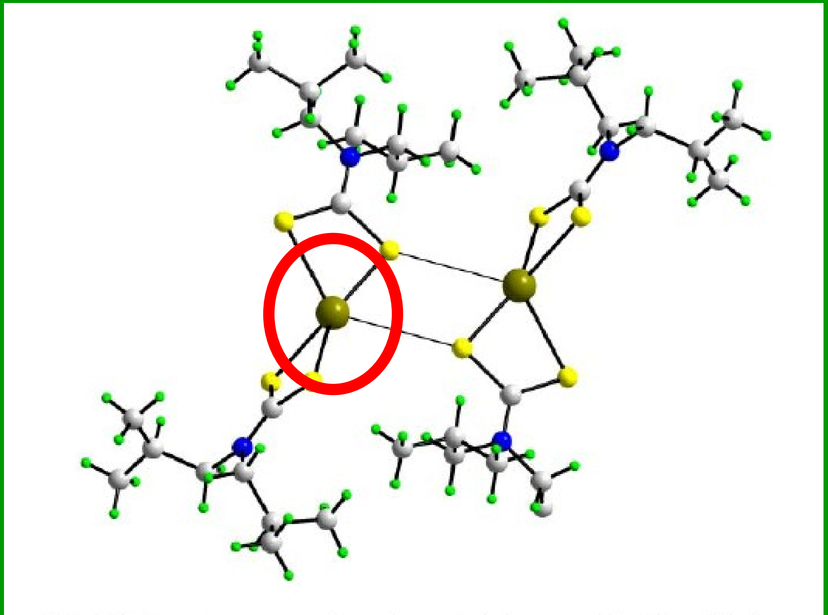


Fig. 2 Molecular aggregation *via* weak intermolecular Hg···S interactions in the crystal structure of $Hg(S_2CN(iBu)_2)_2$ showing the potential of the mononuclear motif (I) to dimerise.

hyperfine techniques: PAC

Two-Photon PERTURBED ANGULAR CORRELATION

Hyperfine splitting → Electric field gradient / Magnetic hyperfine field

Probe nucleus:

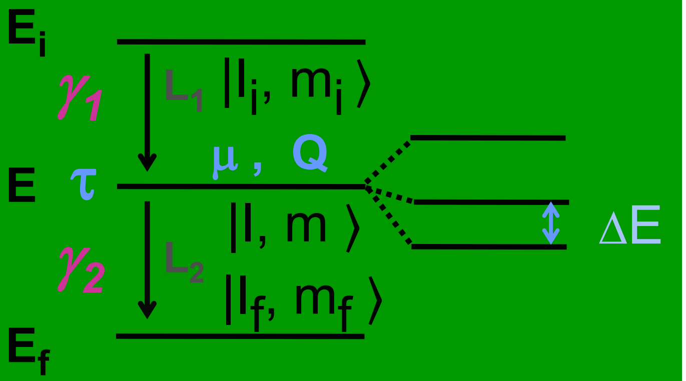
Q – *quadrupolar moment*

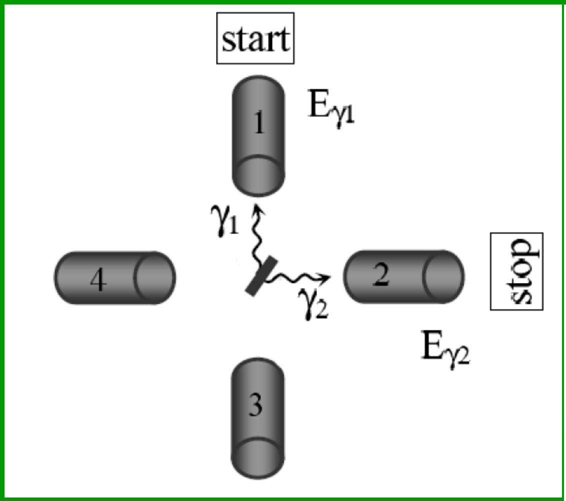
μ - *magnetic moment*

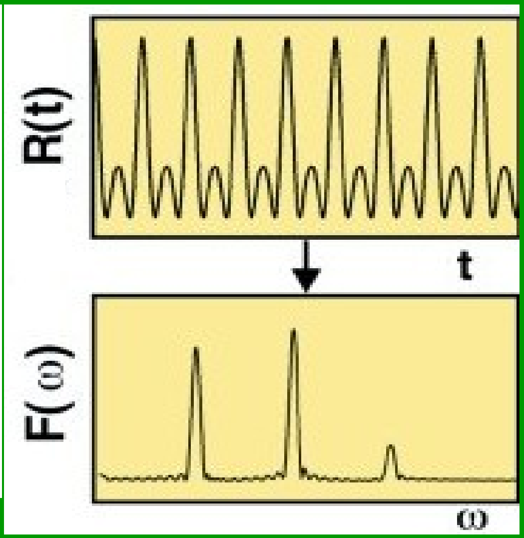
V_{zz} - *EFG principal component*

η - *Asymmetry parameter*

B_{hf} - *Magnetic hyperfine field*

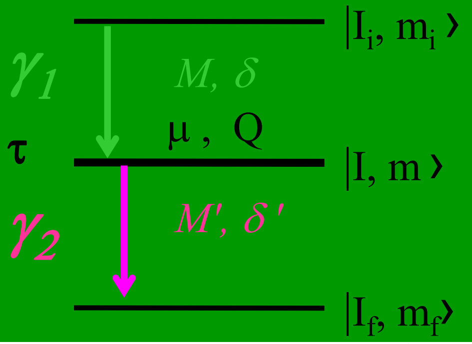




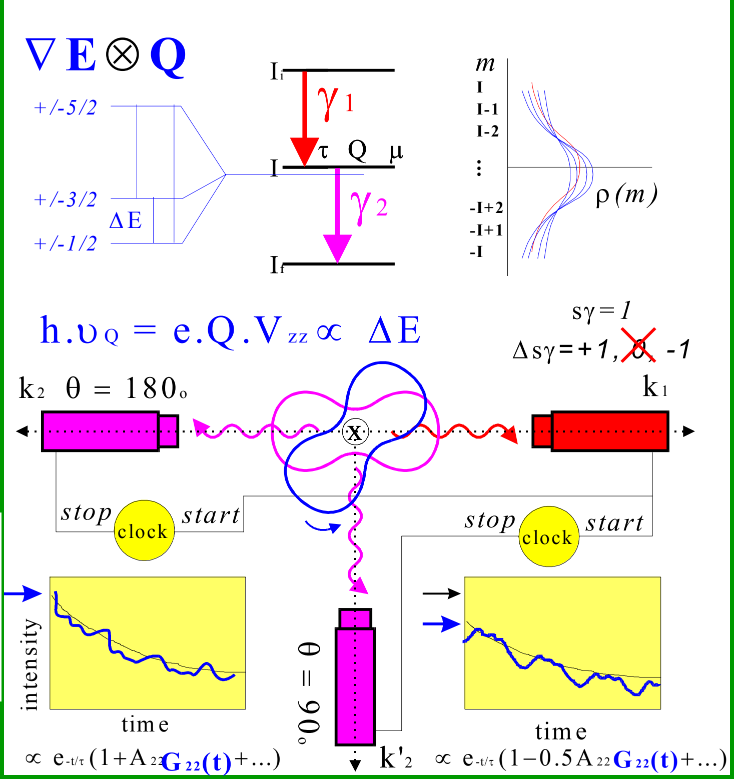


Time dependence gives access to splitting of hyperfine levels

Perturbed Angular Correlations (PAC) How does it work ?



Angular correlation (not perturbed)



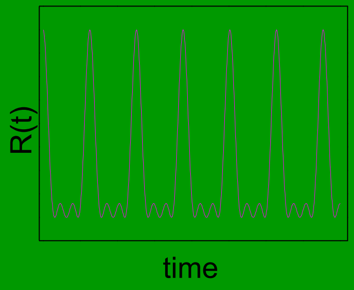
$$h.\upsilon_Q = e.Q.V_{zz} \propto \Delta E$$

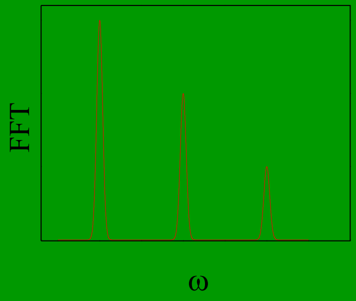
$$N(\theta,t) \propto w(\theta,t) = e^{-t/\tau}\left(1 + \sum_{k=2,4\ldots} A_k(\gamma_1)A_k(\gamma_2)G_{kk}(t)P_k(\cos(\theta))\right)$$

$$\cancel{e^{-t/\tau}}$$

$$R(t) = 2\frac{N(180^o,t) - N(90^o,t)}{N(180^o,t) + 2N(90^o,t)} \approx A_2(\gamma_1)A_2(\gamma_2)G_{22}(t) + \ldots$$

Time dependence



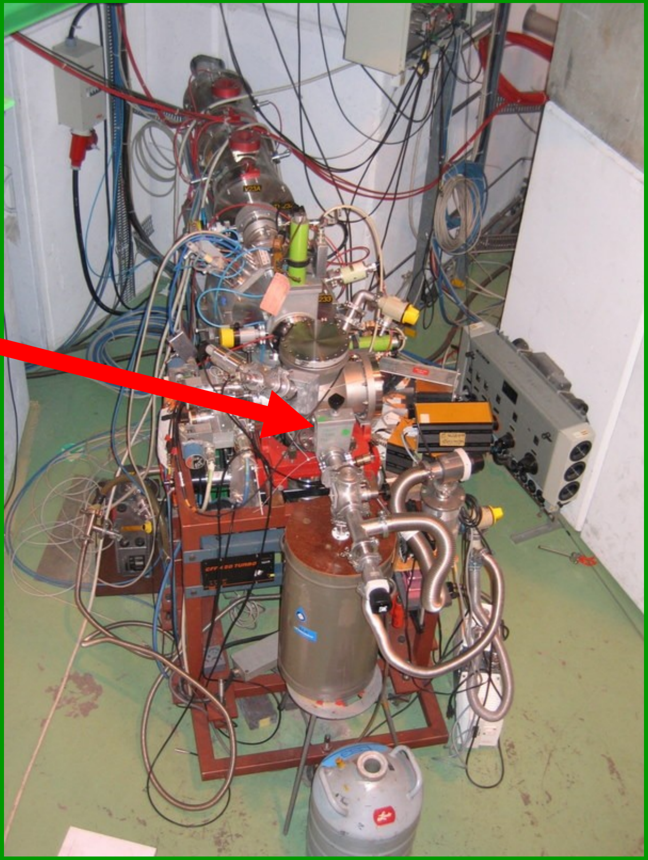


$$G_{22}(t) = e^{(-\lambda t)}\left(S_0 + \sum_n S_n \cos(w_n t)e^{(-\delta w_n t)}\right)$$

hyperfine techniques: PAC

Used ^{199m}Hg (half-life 42 min)

implanted on ice



hyperfine techniques: PAC

Used ^{199m}Hg (half-life 42 min)

implanted on ice

The radioactive solution is added to samples to be studied (in solution)

Concentrations of the order of 10^{13} ions/cm^{3} ⟷ legal limit

hyperfine techniques: PAC

Used ^{199m}Hg (half-life 42 min)

implanted on ice

The radioactive solution is added

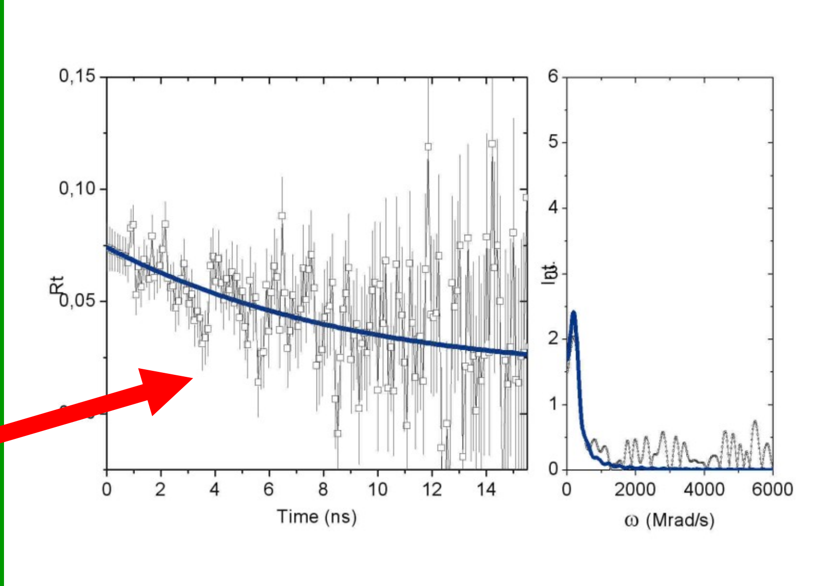
to samples to be studied (in

solution)

The signal from coordinated Hg will provide information on local environment.

Hg in solution gives only a decaying signal.

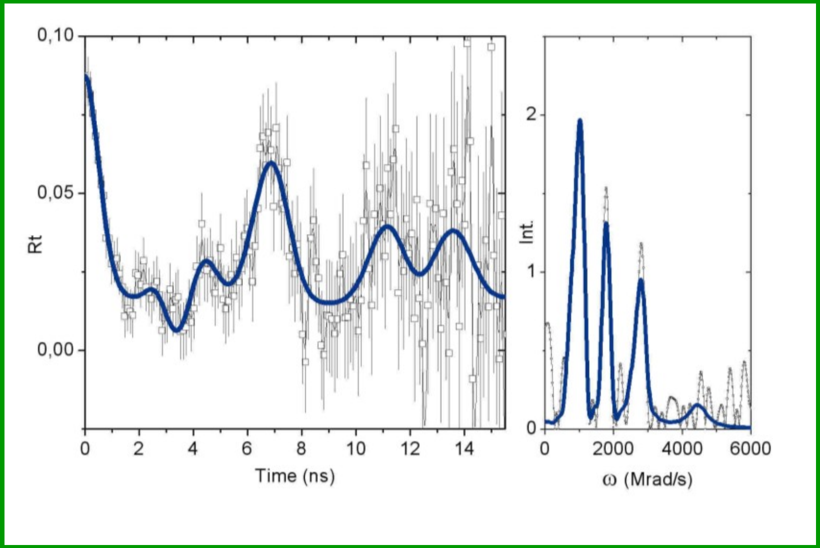
without particular features



Measurement of the radioactive solution in a tube pre-washed with Hg nitrate

Results : local environment

Measurement on Hg dithiocarbamates: fresh HgDTC



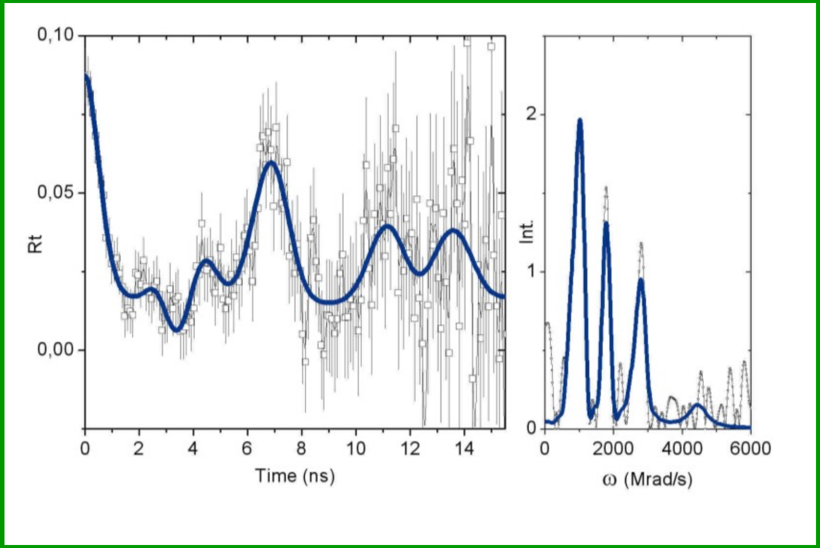
NaDTC+^{199}Hg

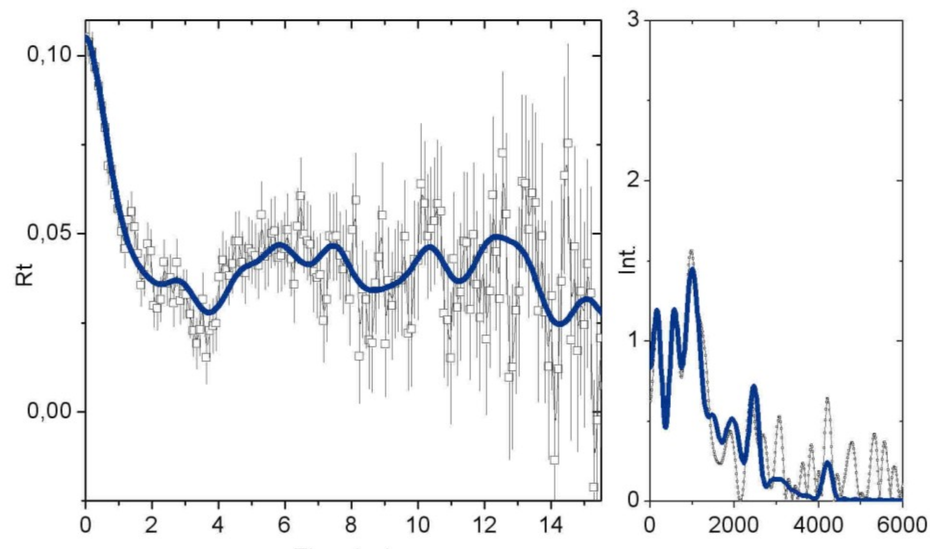
ω_0(Mrad/s	η	%	Δ
917	0.4	33	0
471	0.9	18	8
2297	0.4	49	8

Formation of unsoluble Hg dithiocarbamate by adding Hg ions to solution of Na dithiocarbamate

Results : local environment

Measurement on Hg dithiocarbamates





NaDTC+^{199}Hg

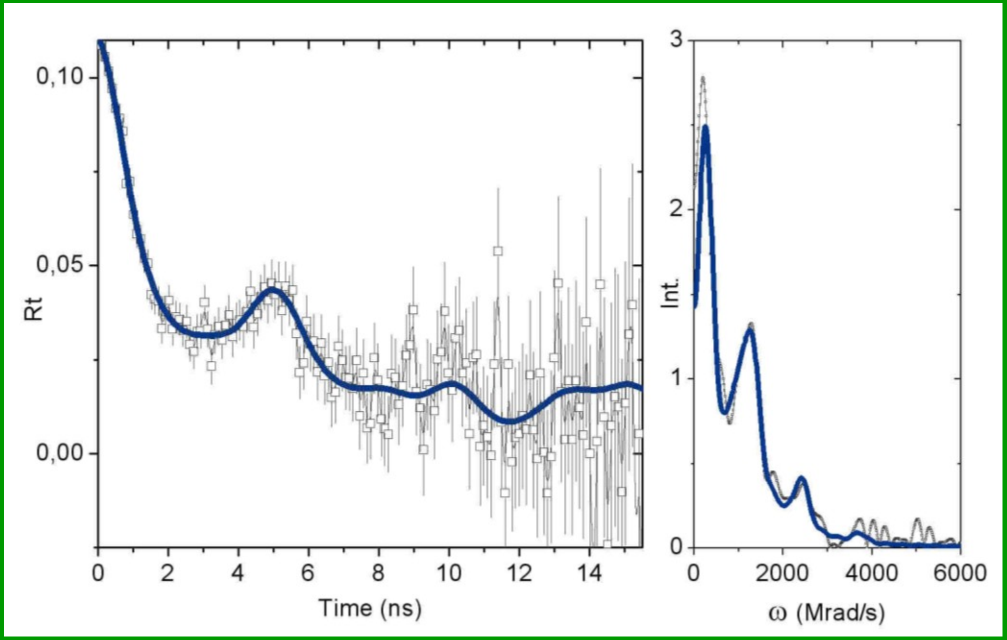
ω_0(Mrad/s	η	%	Δ
917	0.4	33	0
471	0.9	18	8
2297	0.4	49	8

HgDTC + ^{199}Hg (ion exchange)

ω_0(Mrad/s	η	%	Δ
992	0.3	37	9
471	0.5	23	3
2160	0.4	18	0
38	.99	23	60

Results : local environment

Measurement on nanoparticles

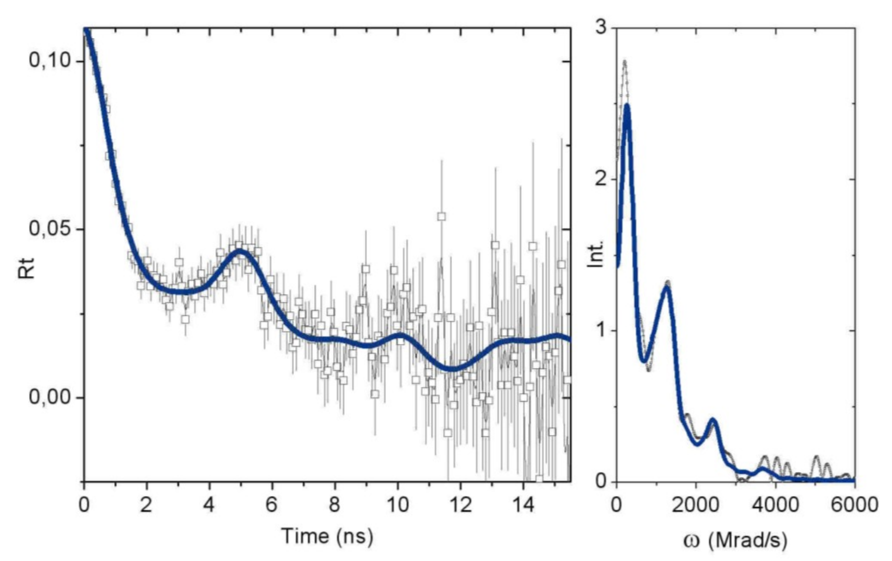


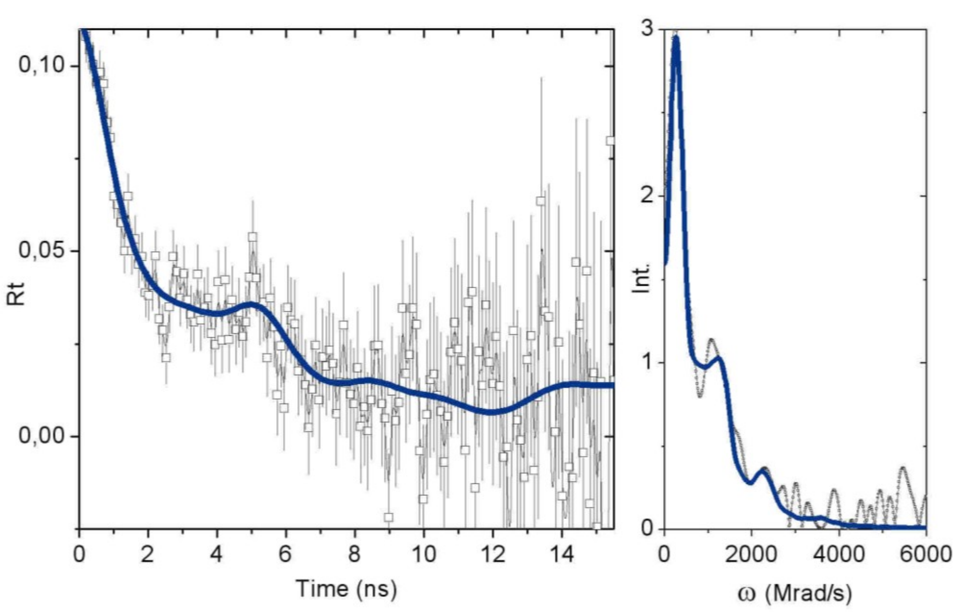
100 nm **nanoparticles**

ω_0(Mrad/s	η	%	Δ
698	0.61	55	10
146	.883	30	1
1226	0.24	15	2

Results : local environment

Measurement on nanoparticles





100 nm **nanoparticles**

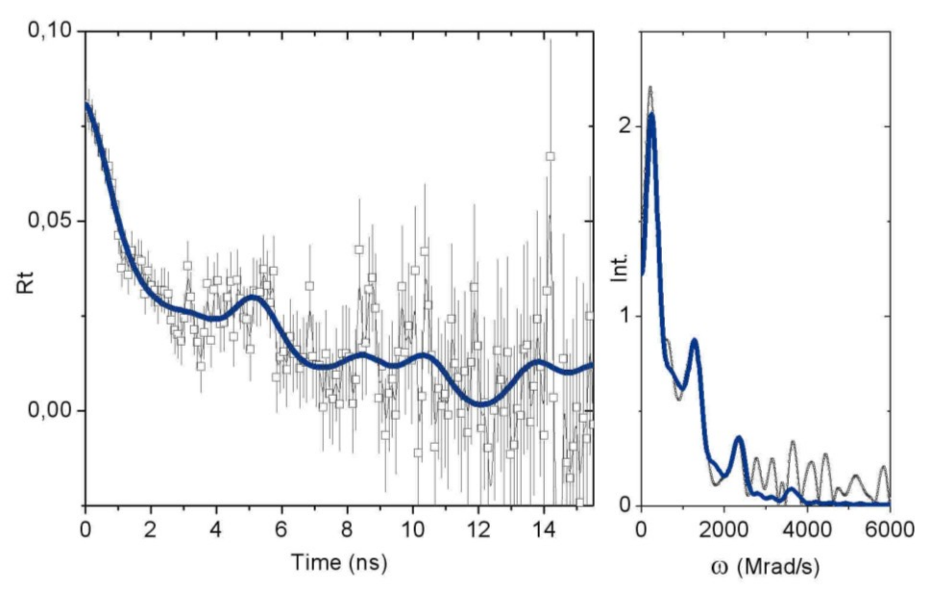
ω_0(Mrad/s	η	%	Δ
698	0.61	55	10
146	.883	30	1
1226	0.24	15	2

30 nm **nanoparticles**

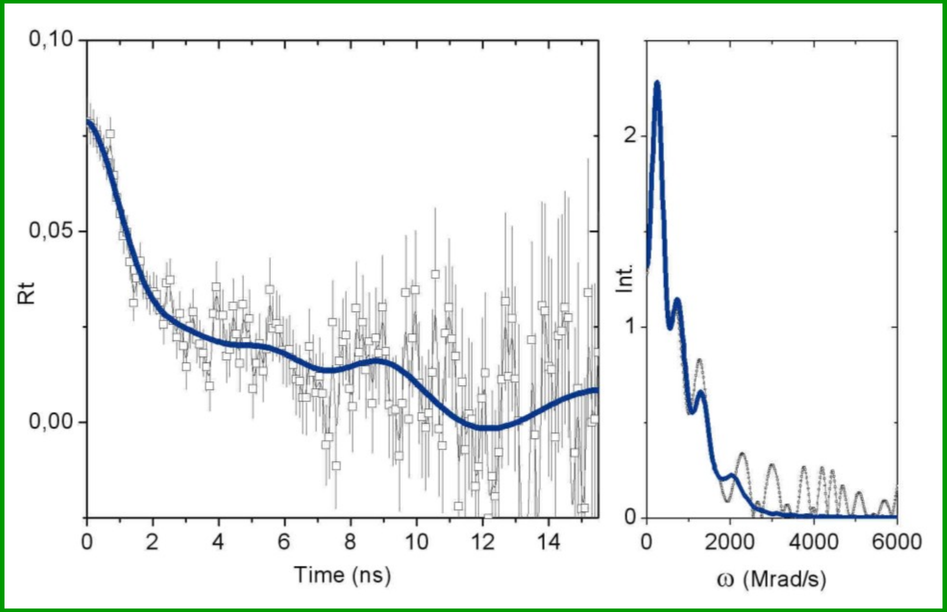
ω_0(Mrad/s	η	%	Δ
681	0.53	49	23!
153	0.9	37	0
1170	0.33	14	6

Results : local environment

Measurement on 100 nm nanoparticles: temperature



T=20ºC



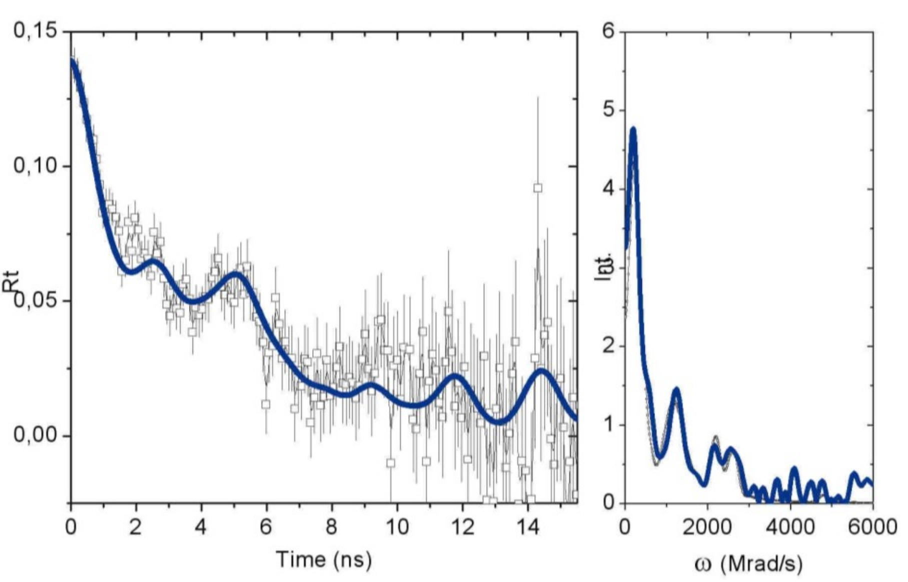
T=1ºC

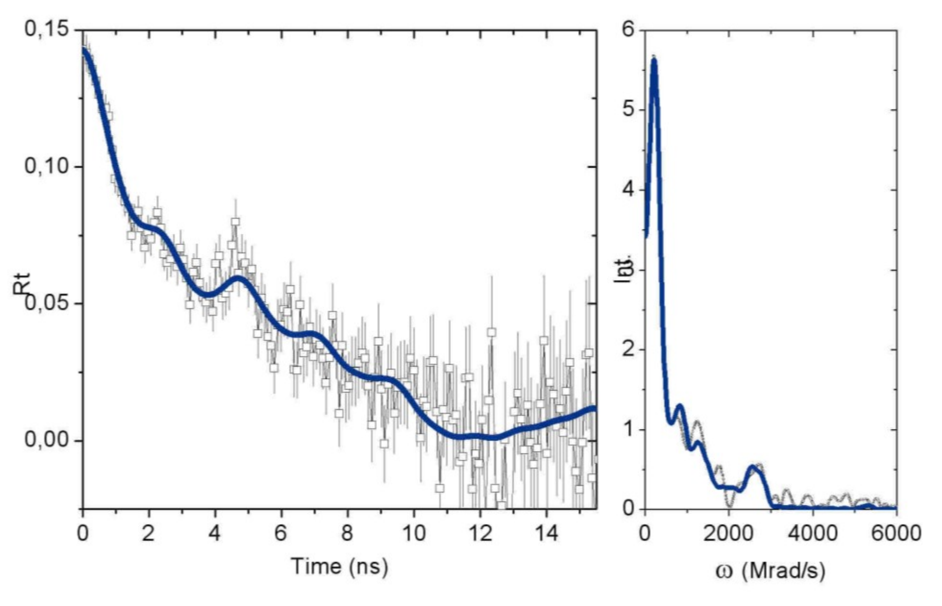
ω_0(Mrad/s	η	%	Δ
636	0.5	51	31
133	0.99	32	0
1191	0.3	16	0.1

ω_0(Mrad/s	η	%	Δ
663	0.4	60	12
134	0.99	40	0

Results : local environment

Measurement on nanoparticles without DTC





100 nm nanoparticles only silica

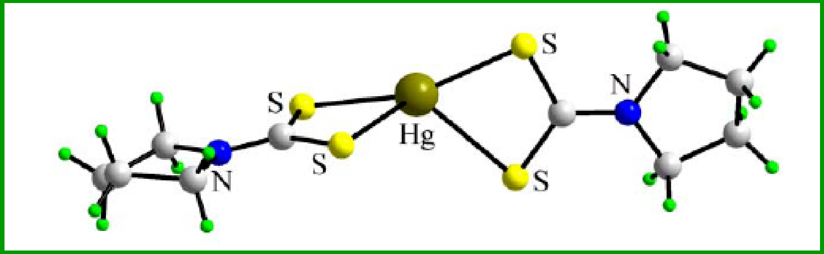
ω_0(Mrad/s	η	%	Δ
731	0.76	40	14
155	0.6	41	0
1434	0.8	19	1.5

30 nm nanoparticles only silica

ω_0(Mrad/s	η	%	Δ
671	0.43	40.2	15
121	0.9	48.5	0
1540	0.9	11.3	0.1

Local environments: main features

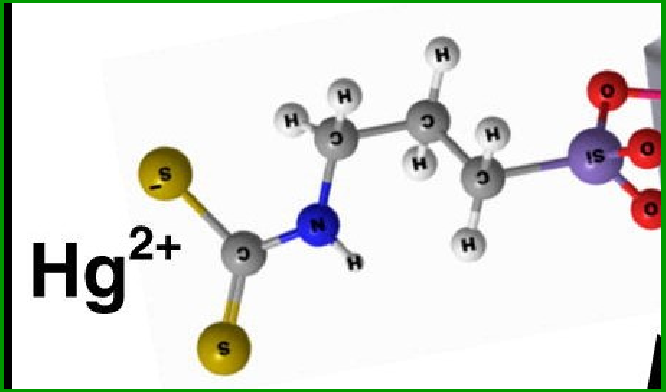
Pure compound:



ω_0(Mrad /s	η	%	Δ
917	0.4	33	0
471	0.9	18	8
2297	0.4	49	8

Coordinated on nanoparticles with DTC:

?



ω_0(Mrad/s	η	%	Δ
698	0.61	55	10
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1226	0.24	15	2

Coordinated on nanoparticles with only Silica:

ω_0(Mrad/s	η	%	Δ
731	0.76	40	14
155	0.6	41	0
1434	0.8	19	1.5

Conclusions, so far

- Successful incorporation of radioactive species, in the pure compound and on the nanoparticles, at relevant concentrations
- Distinct local environments found
- Differences between DTC coordination and Silica are subtle, and require careful data analysis, including EFG theoretical estimates.
- Future: Use of ^{111m}Cd, already studied macroscopically

Motivation:

understanding local coordination mechanisms to help to improve methods of magnetically assisted separation of contaminants from water

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