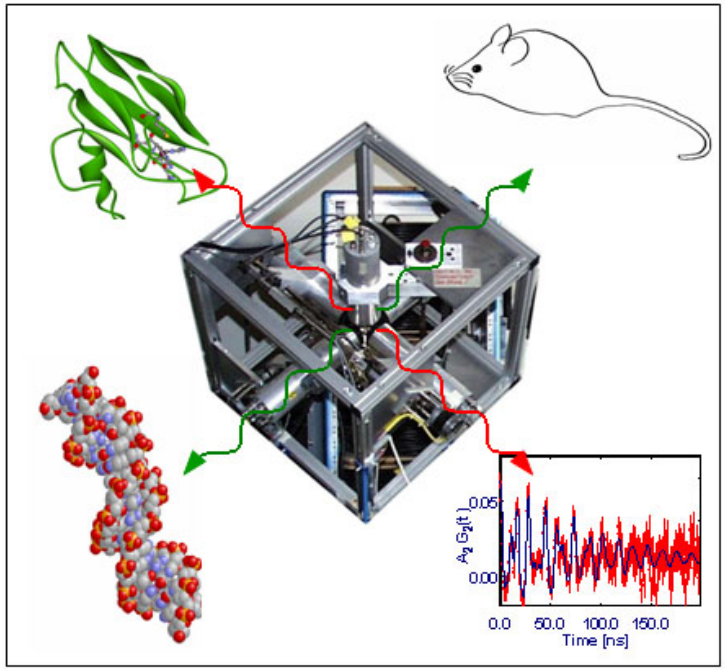
Pb(II) and Hg(II) binding to proteins and model systems studied by ^{204m}Pb and ^{199m}Hg – Perturbed angular Correlation of γ-rays (PAC) spectroscopy

IS448
Spokesperson: Lars Hemmingsen



Our Group:
Uwe Heinz[b], Lars Hemmingsen[b], Marianne Jensen[b], Kristian Jensen[b], Magnus Magnussen[a], Anni Vibenholt[a]. Johan Vibenholt[a]

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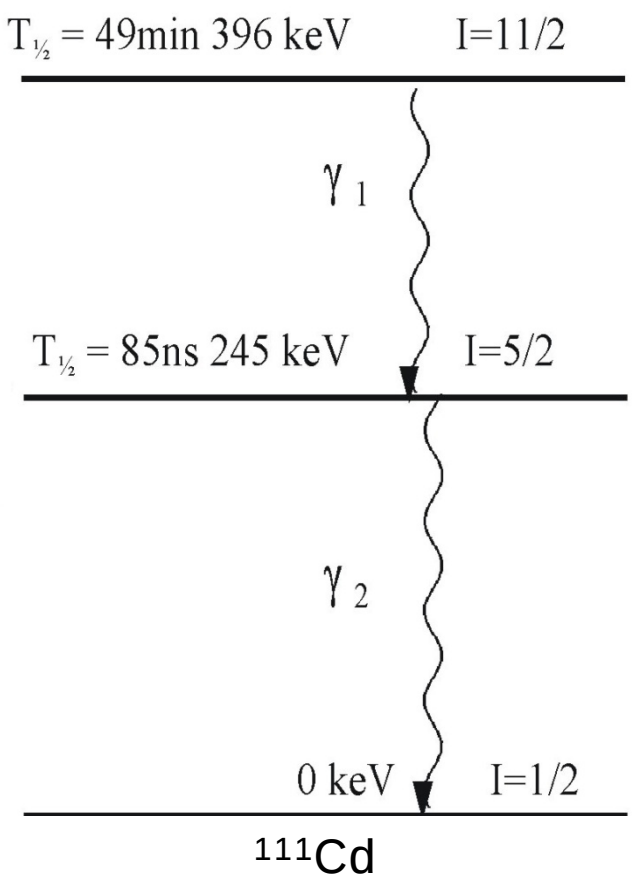
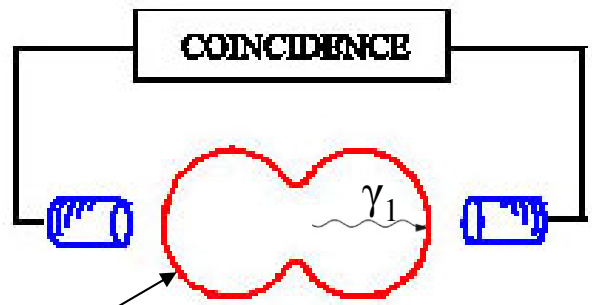
Angular correlation of γ-rays

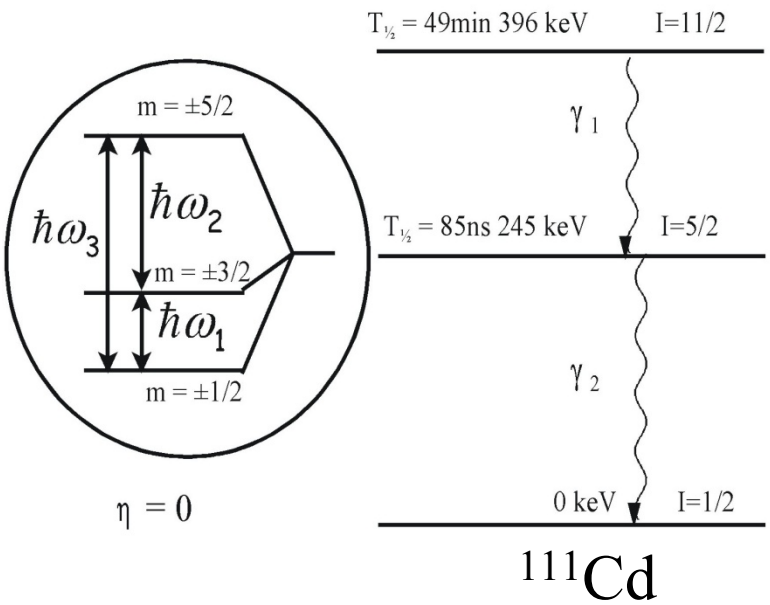


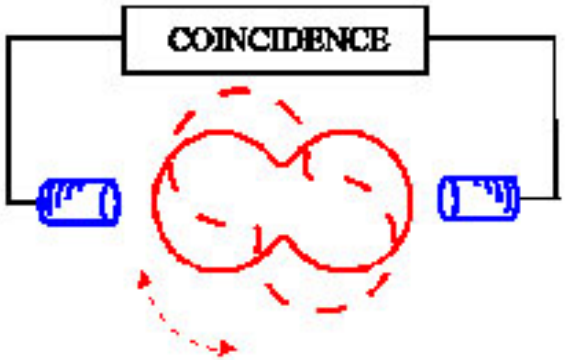
Angular correlation of γ-rays is a property of the nuclear decay:



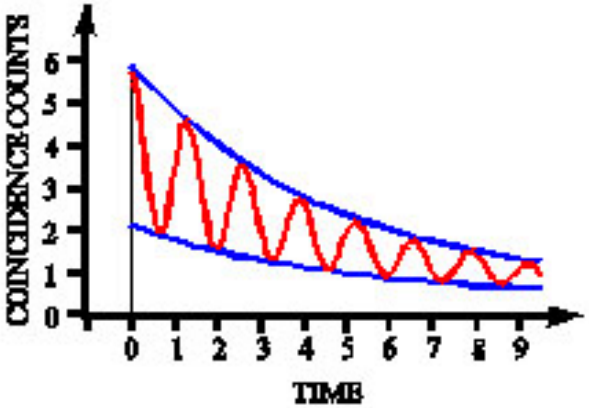
The distance from the centre to the curve gives the probability of emission of γ_2 in that direction

Perturbed angular correlation of γ-rays: The influence of extra-nuclear fields



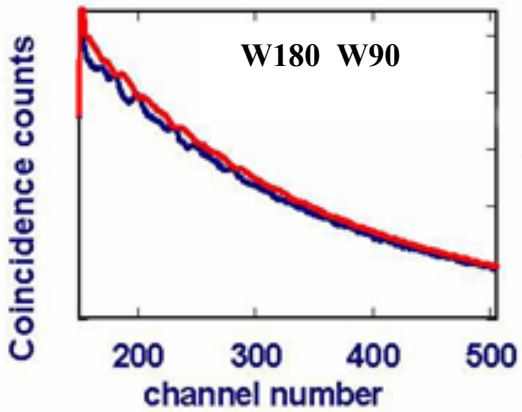


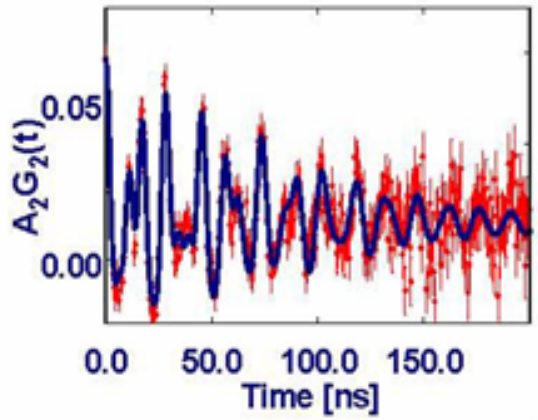
Oscillations in the angular correlation give ω_1, ω_2, and ω_3 – a finger print of the local charge distribution

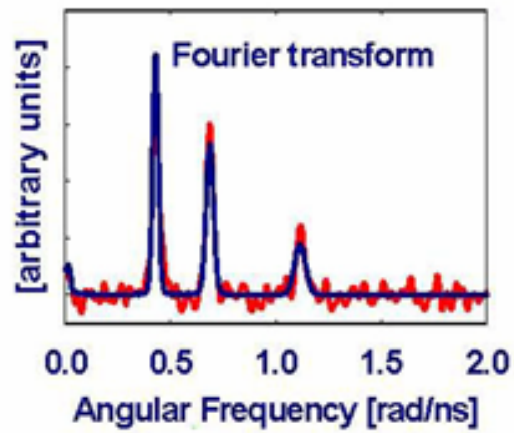


Hamilton *Phys. Rev.*, **1940**, 58:122, Brady and Deutsch *Phys. Rev.* **1947**, 72:870, Goertzel *Phys. Rev.*, **1946**, 70:897, Aeppli et al. *Phys. Rev.*, **1951**, 82, 550, Leipert et al. *Nature*, **1968**, 220:907

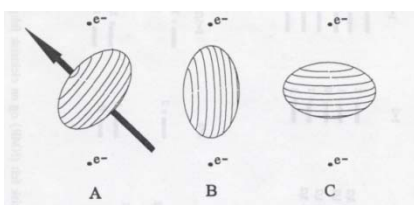
Butz *Z. Naturforsch.* **1996**, 51A:396





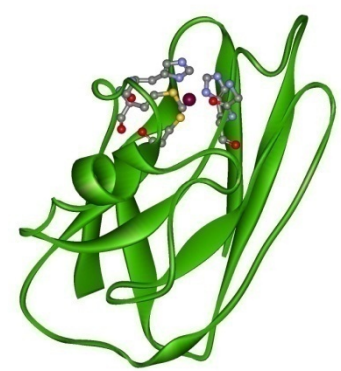


Combining Nuclear Physics with BioChemistry

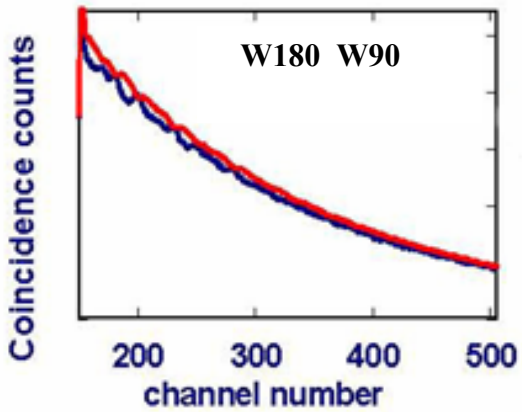


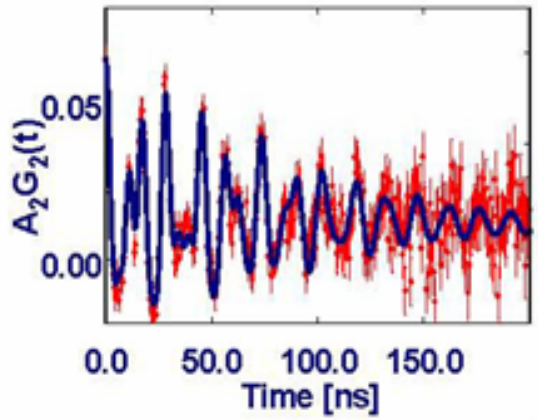
$$\text{NQI} \;\alpha\; \frac{\partial^2 \phi}{\partial x_i \partial x_j}\Big|_{r=0} \text{eQ}$$

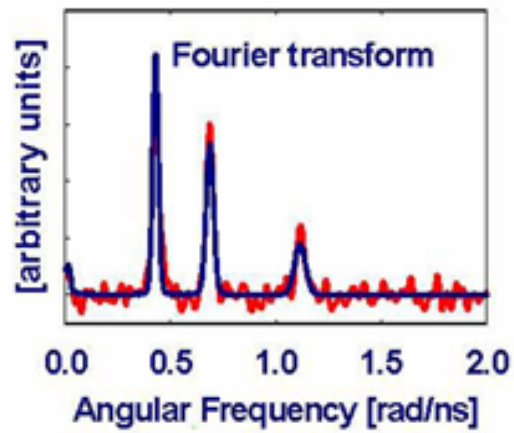
Nuclear Physics



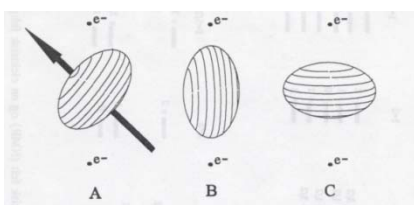
BioChemistry





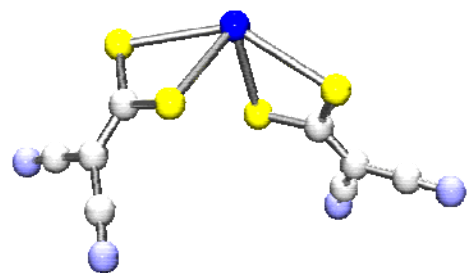


Combining Nuclear Physics with BioChemistry

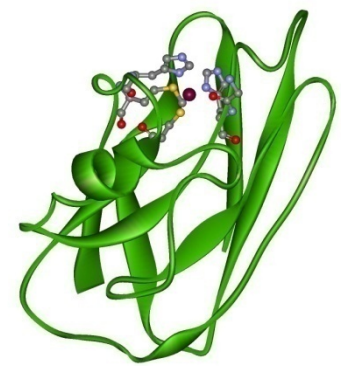


$$\text{NQI} \;\alpha\; \frac{\partial^2 \phi}{\partial x_i \partial x_j}\Big|_{r=0} \text{eQ}$$

Nuclear Physics



Coordination Compounds
as model systems



BioChemistry

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Planning the Experiments

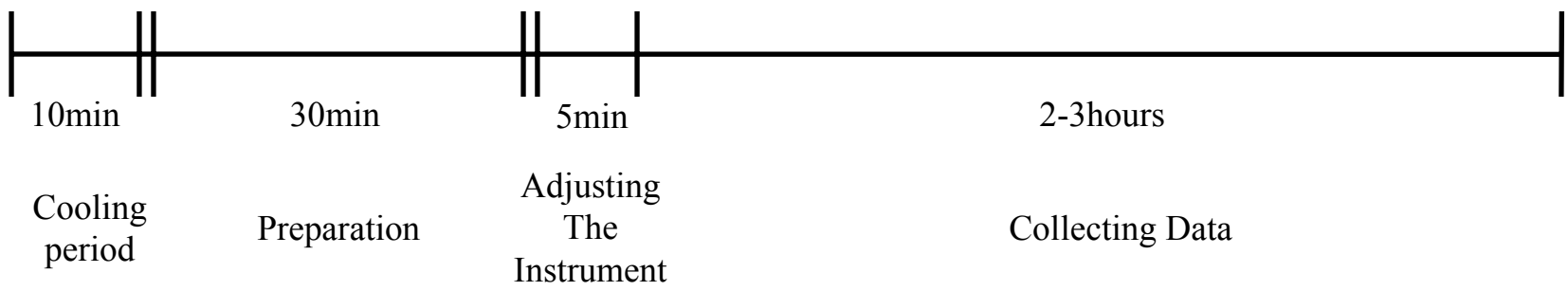
Reduce the time for preparation to max. 1 half-life of the isotope of interest

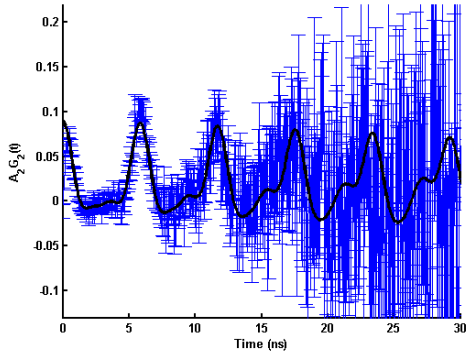
Reproduce and Verify the Compounds (XRPD, microanalysis etc.)

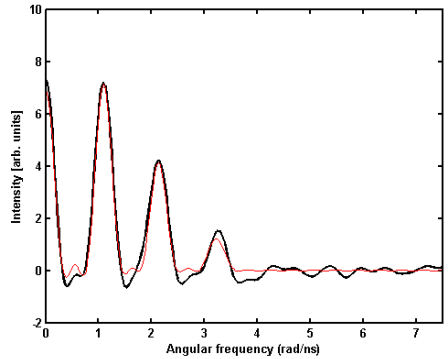
Preparation of our Compounds (½hour):

- Batch precipitation
- Collection on a glass funnel
- Washing
- Drying under dynamic vacuum

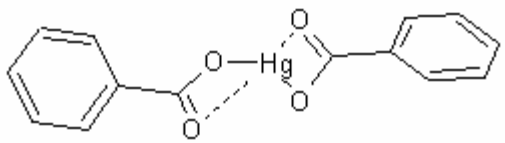
Time-scale for the Experiment

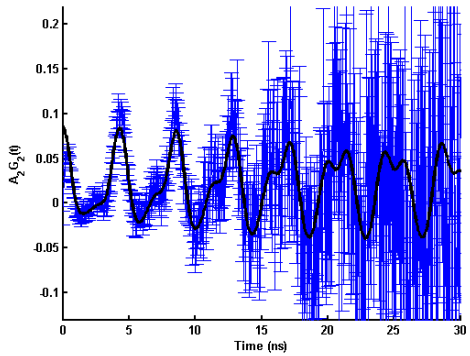


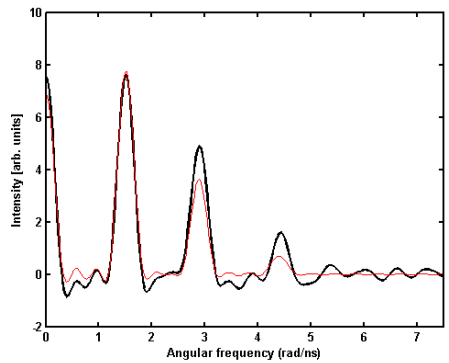




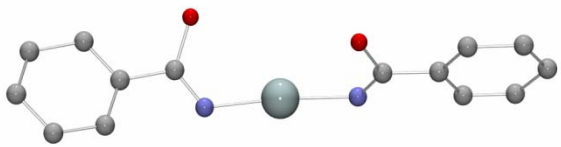
$Hg(benzoato)_2$

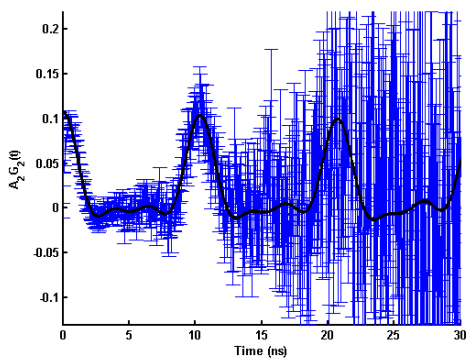


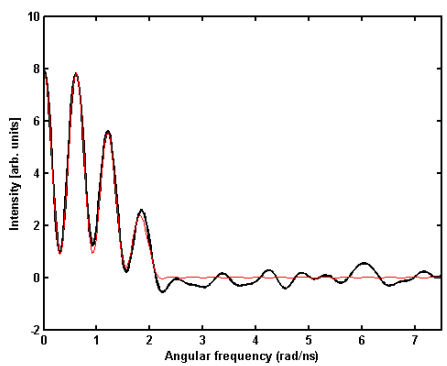




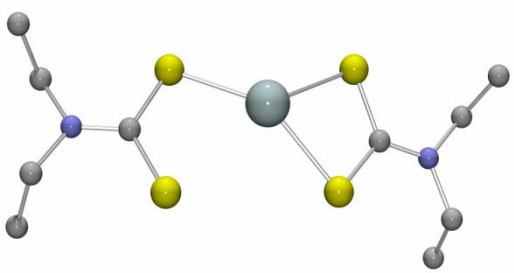
$Hg(benzamido)_2$







$Hg(Et_2NCS_2)_2$



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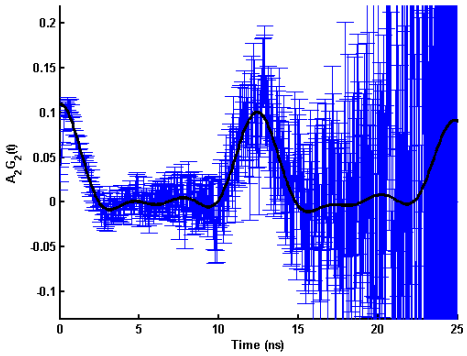
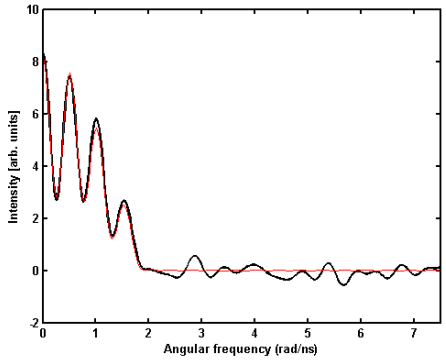
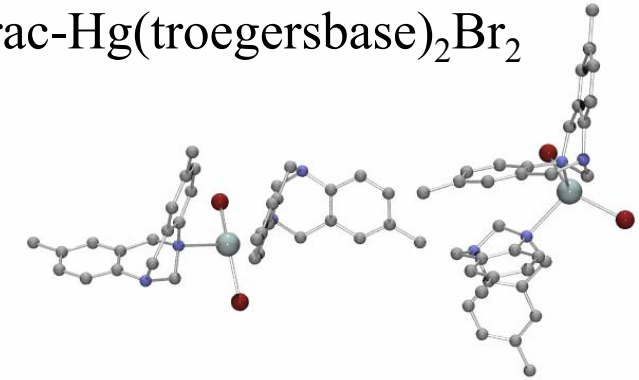
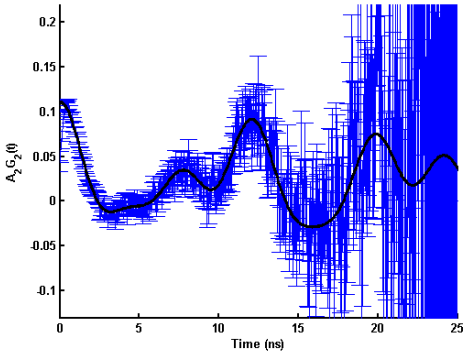
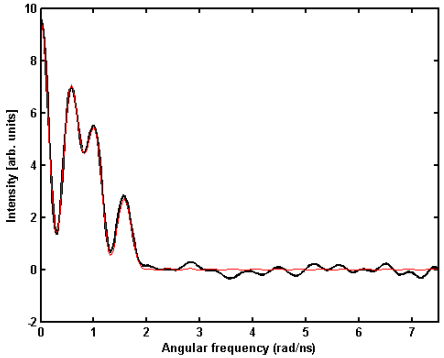




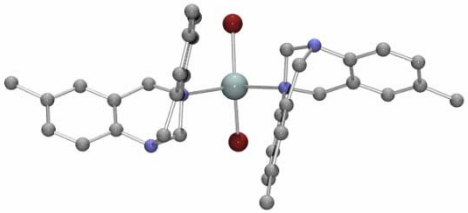
rac-Hg(troegersbase)$_2$Br$_2$

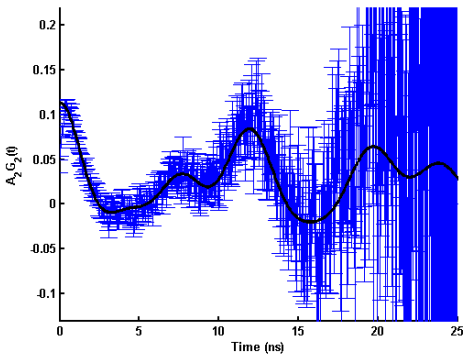


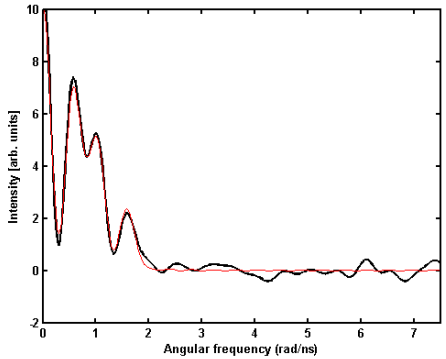




(+)Hg(troegersbase)$_2$Br$_2$







(-)Hg(troegersbase)$_2$Br$_2$

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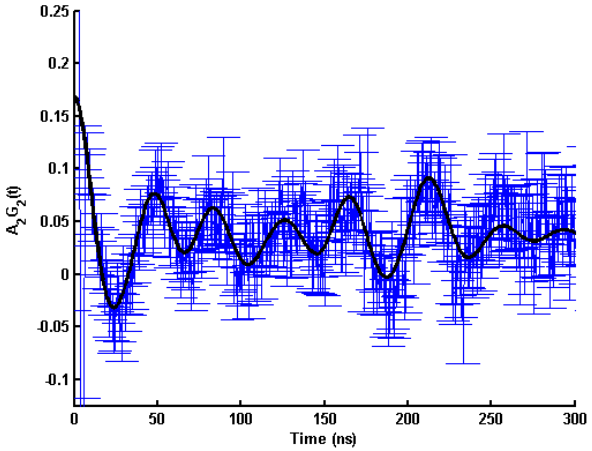
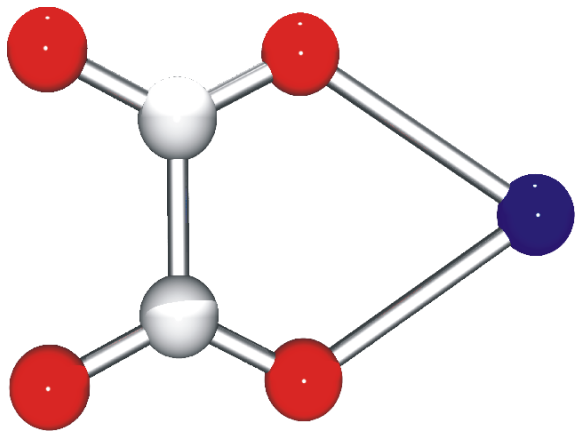
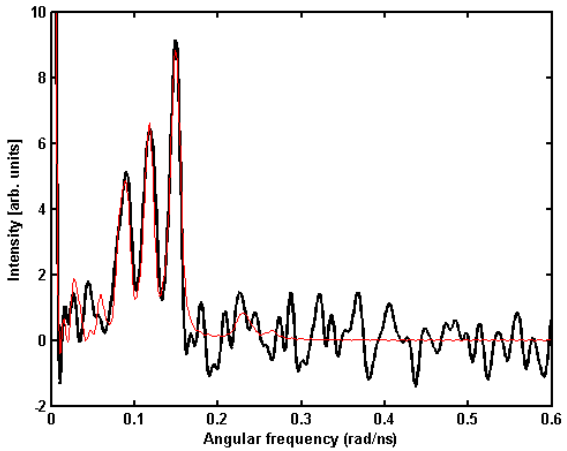
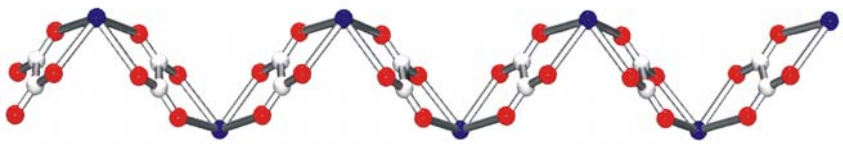
Aquaoxalatolead(II) – $[Pb(C_2O_4)(H_2O)]$

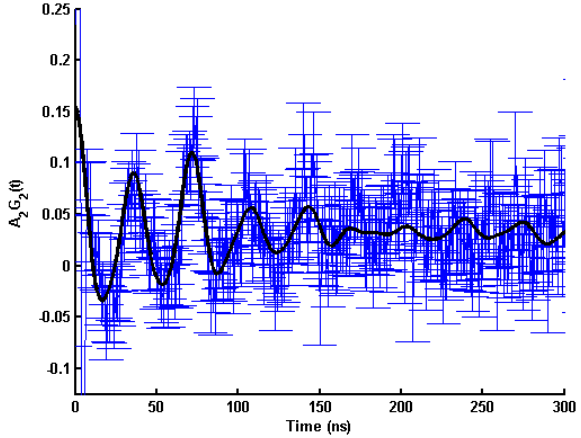


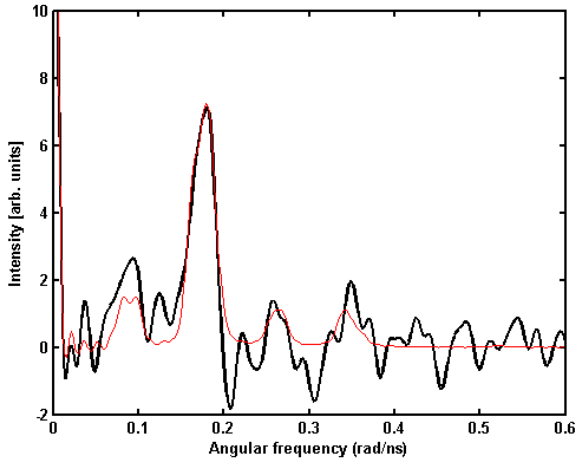


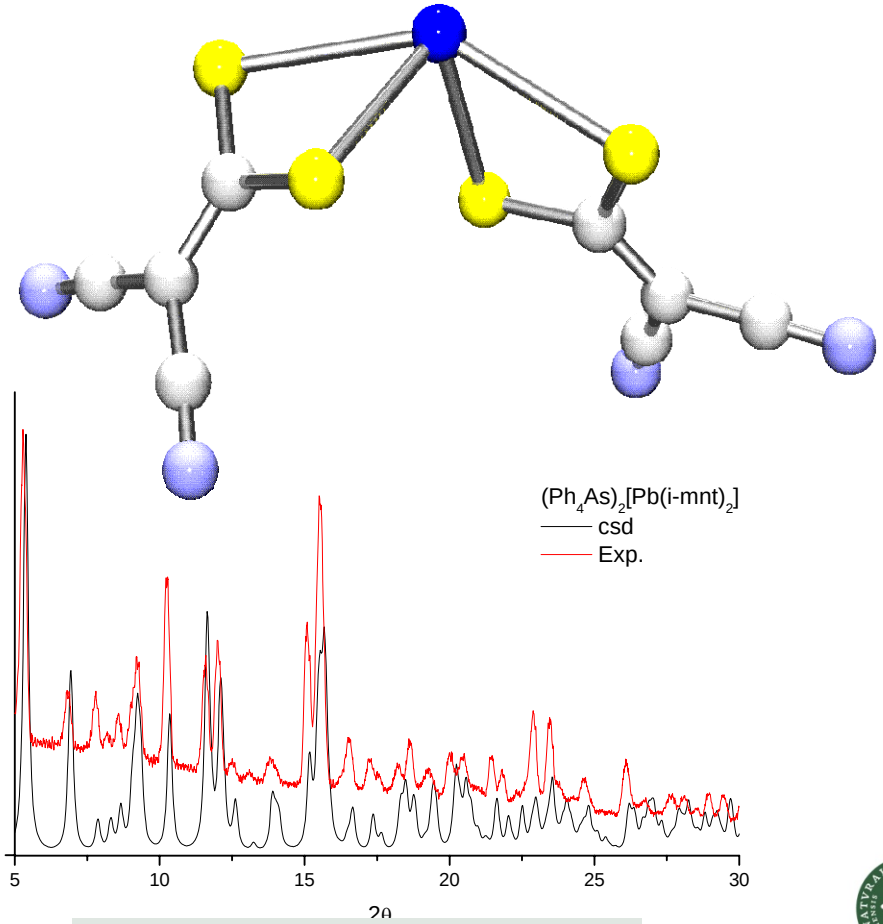




Tetraphenylarsonium[bis(iso-maleonitriledithiolato)lead(II)] $(Ph_4As)_2[Pb(S_2C_2(CN)_2)_2]$

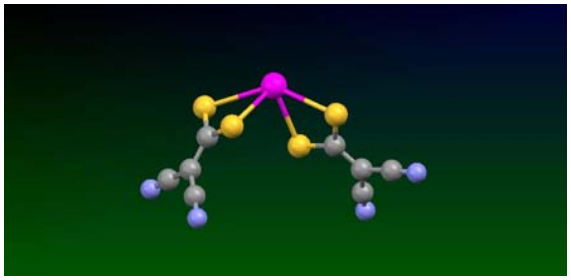




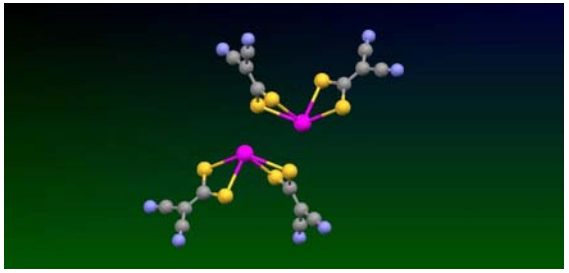


J.Vibenholt, M. Magnussen, M.Stachura and L.Hemmingsen, *To be submitted*

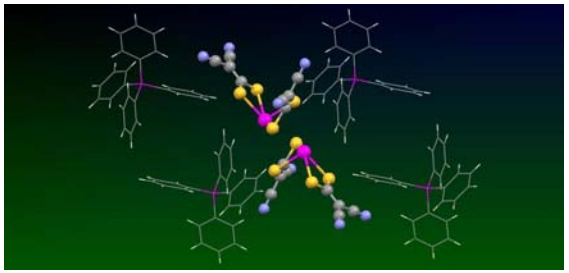
DFT calculations utilizing the ADF-package



Pw91	V_{zz}	V_{yy}	V_{xx}	η
SZ	-1.48E+00	1.47E+00	1.47E+00	9.92E-01
DZ	-1.55E+00	1.53E+00	1.53E+00	9.76E-01
TZP	-1.61E+00	1.35E+00	1.35E+00	6.73E-01
TZ2P	-1.74E+00	1.38E+00	1.38E+00	5.88E-01
QZ4P	-2.48E+00	1.99E+00	1.99E+00	6.03E-01



Pw91	V_{zz}	V_{yy}	V_{xx}	η
SZ	1.20E+00	-1.02E+00	-1.81E-01	6.99E-01
DZ	1.20E+00	-1.02E+00	-1.81E-01	6.99E-01
TZP	9.98E-01	-8.47E-01	-1.51E-01	6.97E-01
TZ2P	1.02E+00	-9.46E-01	-7.58E-02	8.52E-01
QZ4P	-1.50E+00	1.44E+00	6.33E-02	9.16E-01



pw91/TZ2P	V_{zz}	V_{yy}	V_{xx}	η
As(Ph)4	-1.06133	0.94528	0.116055	7.81E-01

	V_{zz}	V_{yy}	V_{xx}	η
Experimental	1.56	-	-	9.65E-01

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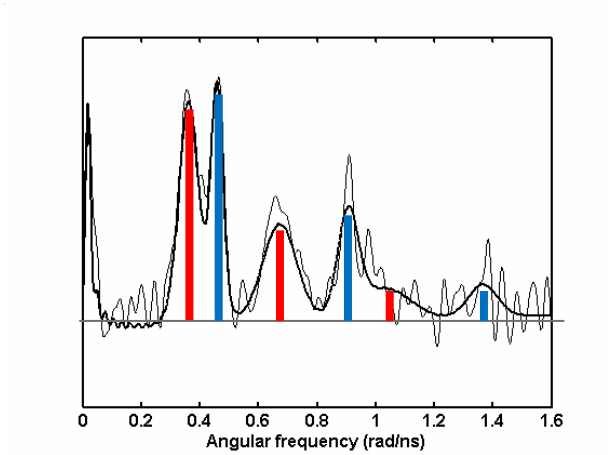
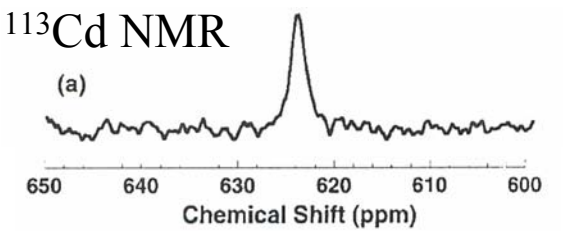
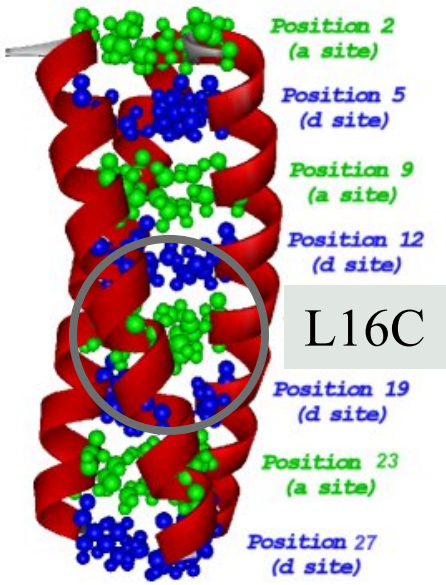
Combination of PAC, NMR, and QM: Exchanging water molecule on ns timescale

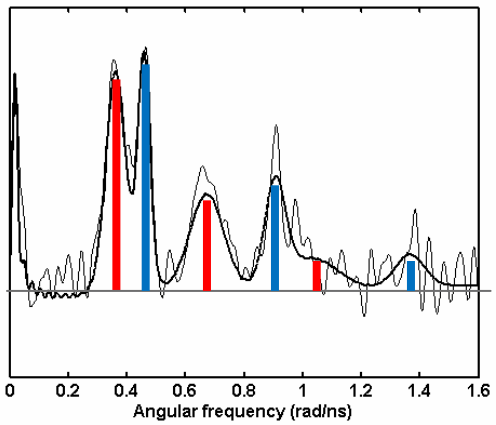


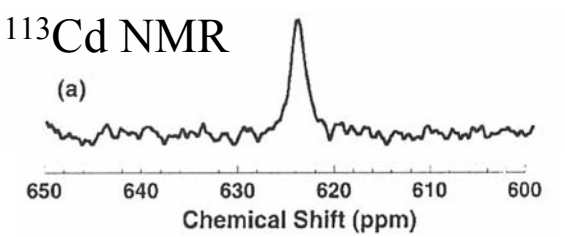


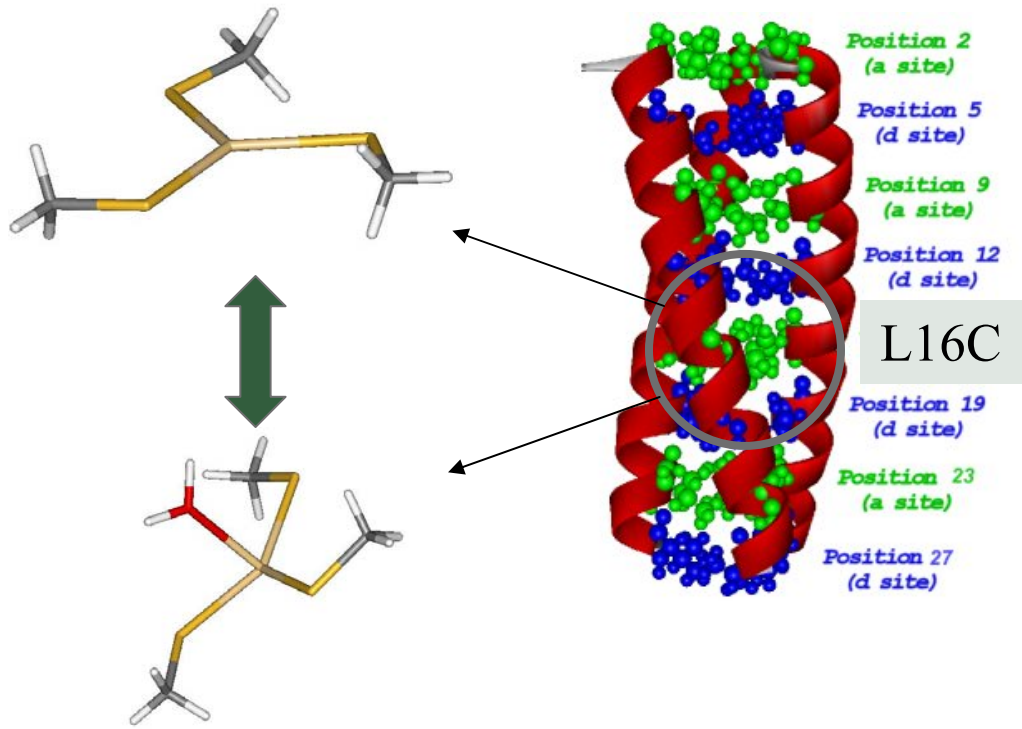


Matzapetakis et al. *J. Am. Chem. Soc.*, **2002**, 124:8024
Lee et al., *Angew. Chemie Int. Ed.*, **2006**, 45:2864

Combination of PAC, NMR, and QM: Exchanging water molecule on ns timescale

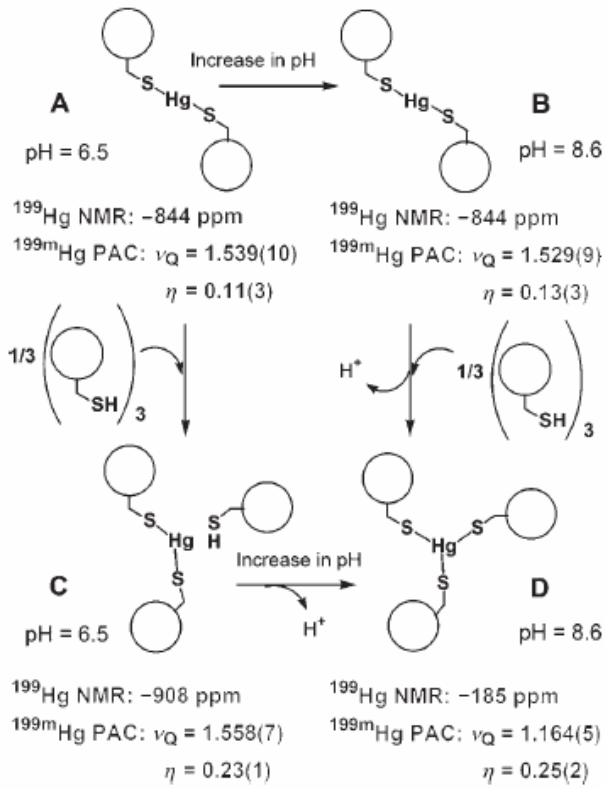






Matzapetakis et al. *J. Am. Chem. Soc.*, **2002**, 124:8024
Lee et al., *Angew. Chemie Int. Ed.*, **2006**, 45:2864

A Case Study:
Designed Two- and Three-Stranded Coiled Coils



Scheme 2. Species present at different peptide/Hg^{II} ratios and pH values.

O. Iranzi et al., *Chem. Eur. J.* **2007**, 13:9178

Collaborations

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- **Harvard Medical School, USA**
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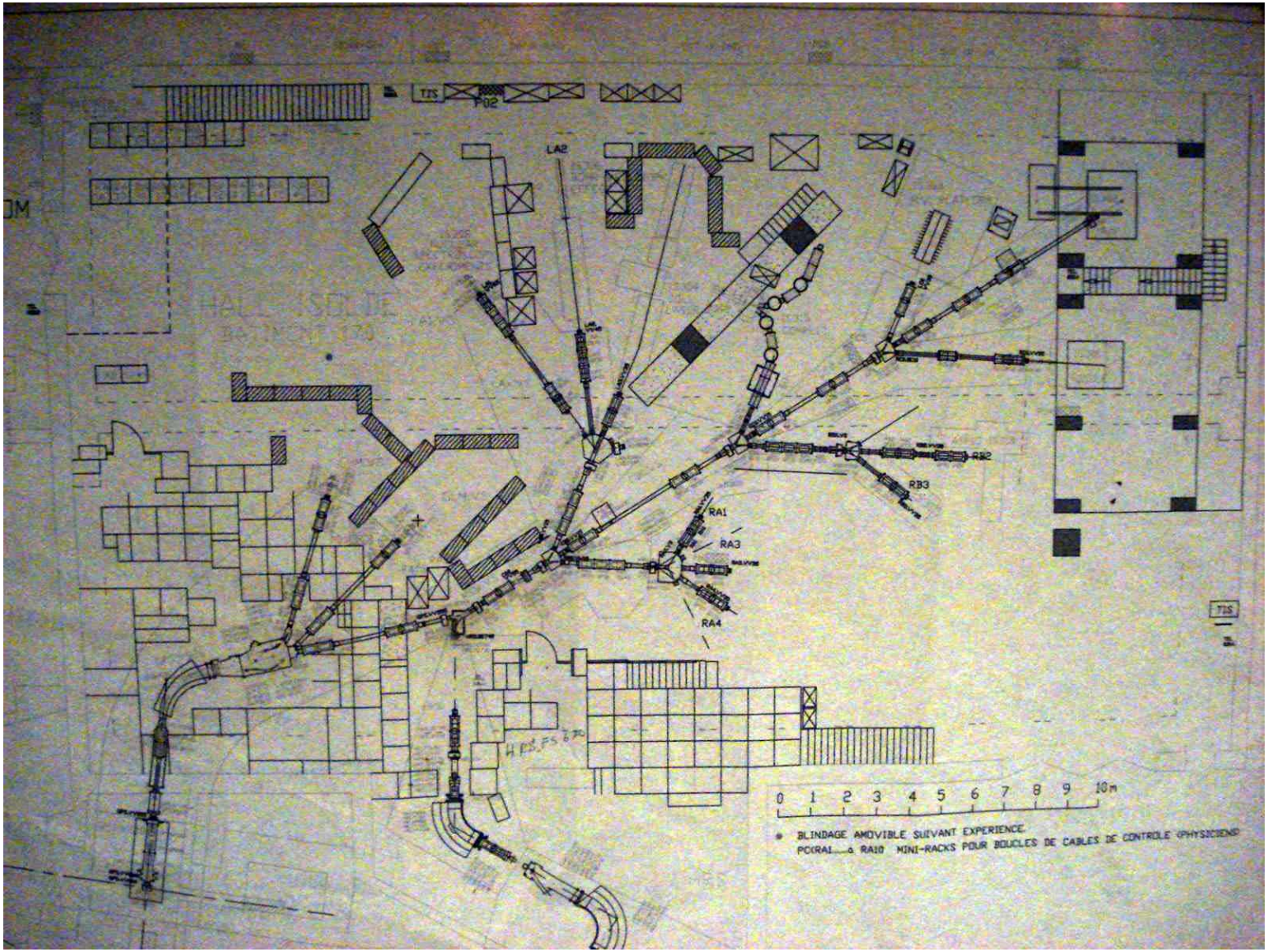
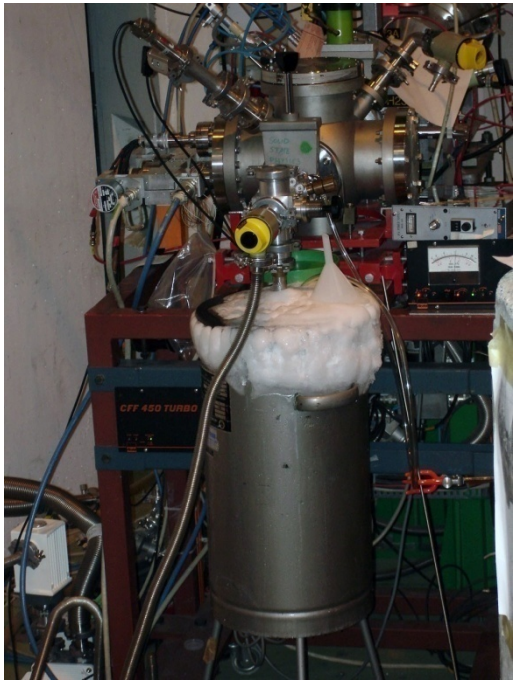
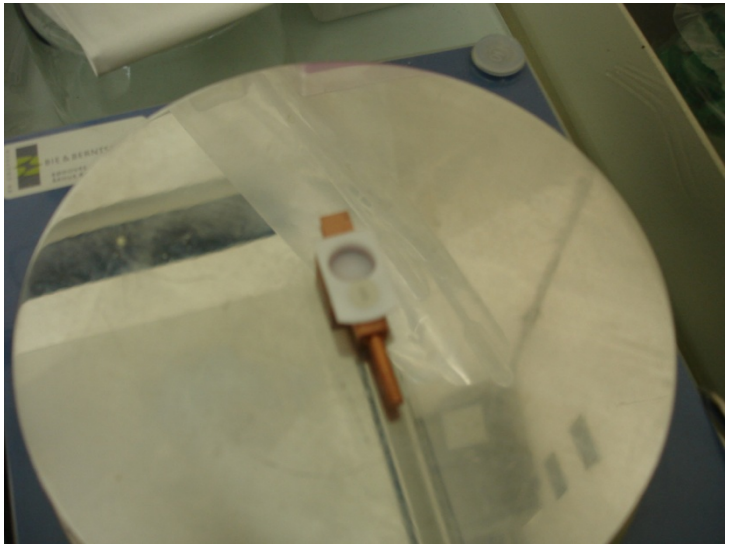
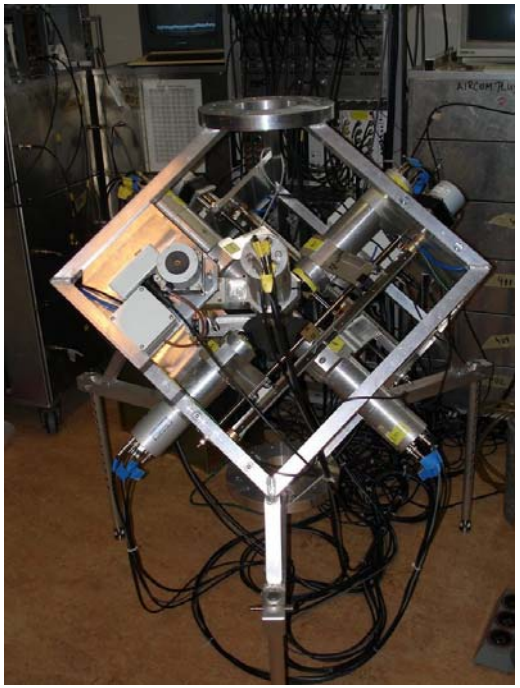
& VELUX FONDEN


LA2
RA1
RA3
RA4
RB2
RB3
0 1 2 3 4 5 6 7 8 9 10m
* BLINDAGE AMOVIBLE SUIVANT EXPERIENCE
PCORAL ... A RA10 MINI-RACKS POUR BOUCLES DE CABLES DE CONTROLE (PHYSICIENS)


CFF 450 TURBO





Future Work

- Additionel Coordination Compound
- ^{199}Hg-NMR studies
- Extract parameters and expand the Angular Overlap Model for PAC