



Nuclear Techniques for Studying Soft Matter at ISOLDE

M. Stachura, A. Gottberg, M. Kowalska, K. Johnston
and L. Hemmingsen

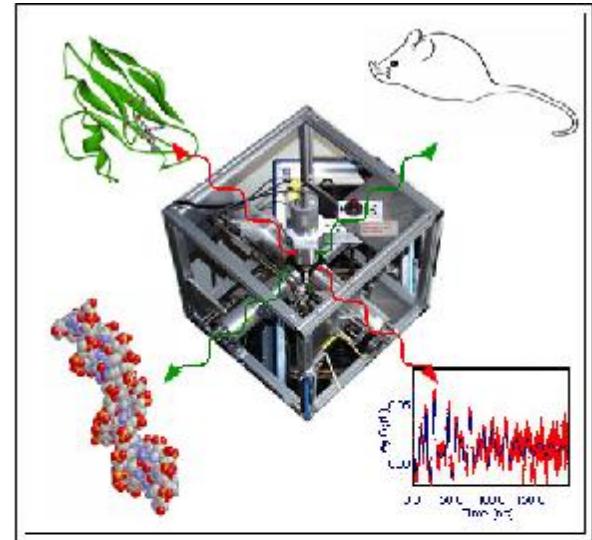


EURORIB12
Abano Terme, Padova, Italy
May 20-25, 2012



Outline

- 1) Motivation
- 2) Techniques and Experiments
- 3) Results
- 4) Outlook



Motivation



Human body:

99%: H, O, C, N

1%: 19 other elements

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Periodic Table of the Elements																		
http://chemistry.about.com ©2010 Todd Helmenstine About Chemistry																		
1A		2A		3A		4A		5A		6A		7A		8A		2		
1 H [1.00794]		2 Be [9.01218]		3 Li [6.941]	4 Be [9.01218]	5 B [10.811]	6 C [12.011]	7 N [14.011]	8 O [16.000]	9 F [18.9984]	10 Ne [20.197]	13 Al [26.981598]	14 Si [28.0855]	15 P [30.97376]	16 S [32.065]	17 Cl [35.453]	18 Ar [39.948]	
11 Na [22.989769]	12 Mg [24.306]	21 Sc [44.95591]	22 Ti [47.946]	23 V [50.944]	24 Cr [51.940}	25 Mn [54.93814]	26 Fe [55.845]	27 Co [58.93135]	28 Ni [58.93135]	29 Cu [63.546]	30 Zn [65.401]	31 Ga [69.724]	32 Ge [71.943]	33 As [74.94414]	34 Se [78.904]	35 Br [79.904]	36 Kr [83.798]	
19 K [39.092]	20 Ca [40.08]	21 Sc [44.95591]	22 Ti [47.946]	23 V [50.944]	24 Cr [51.940}	25 Mn [54.93814]	26 Fe [55.845]	27 Co [58.93135]	28 Ni [58.93135]	29 Cu [63.546]	30 Zn [65.401]	31 Ga [69.724]	32 Ge [71.943]	33 As [74.94414]	34 Se [78.904]	35 Br [79.904]	36 Kr [83.798]	
37 Rb [85.4678]	38 Sr [87.62]	39 Y [88.90585]	40 Zr [91.224]	41 Nb [92.90638]	42 Mo [95.96]	43 Tc [98]	44 Ru [101.07]	45 Rh [102.9555]	46 Pd [106.43]	47 Ag [107.8952]	48 Cd [111.411]	49 In [114.818]	50 Sn [118.710]	51 Sb [121.760]	52 Te [127.60]	53 I [126.90447]	54 Xe [131.293]	
55 Cs [132.905451]	56 Ba [137.327]	57-71 Lanthanides [138.90547]	72 Hf [178.49]	73 Ta [180.93419]	74 W [183.94]	75 Re [186.207]	76 Os [190.23]	77 Ir [192.217]	78 Pt [196.229]	79 Au [197.565]	80 Hg [204.951]	81 Tl [204.951]	82 Pb [208.99448]	83 Bi [210.00]	84 Po [217.00]	85 At [221.00]	86 Rn [222.00]	
87 Fr [223]	88 Ra [226]	89-103 Actinides [267]	104 Rf [268]	105 Db [271]	106 Sg [272]	107 Bh [276]	108 Hs [278]	109 Mt [281]	110 Ds [289]	111 Rg [289]	112 Cn [289]	113 Uut [284]	114 Uuo [289]	115 Uup [298]	116 Uuh [298]	117 Uus [294]	118 Uuo [294]	
Lanthanides																		
57 La [138.90547]	58 Ce [140.116]	59 Pr [140.90705]	60 Nd [144.242]	61 Pm [147]	62 Sm [150.34]	63 Eu [151.964]	64 Gd [154.9251]	65 Tb [162.500]	66 Dy [164.93032]	67 Ho [167.259]	68 Er [169.03421]	69 Tm [173.054]	70 Yb [174.9068]	71 Lu [186.93421]				
89 Ac [227]	90 Th [232.03608]	91 Pa [231.03569]	92 U [238.02891]	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [251]	98 Cf [252]	99 Es [257]	100 Fm [258]	101 Md [258]	102 No [259]	103 Lr [262]				

 Natural elements

 Toxic elements

 Elements used in drugs



Techniques and Experiments

Goals:

- 1) Understand heavy metal ions toxicity (Hg^{2+} and Pb^{2+})
- 2) Monitor Zn^{2+} and Cu^+ containing proteins

Nuclear and Hyperfine Interaction Techniques used in Biology:

- 1) Mössbauer Spectroscopy
- 2) ESR / EPR Spectroscopy
- 3) NMR Spectroscopy
- 4) NQR Spectroscopy
- 5) PAC Spectroscopy

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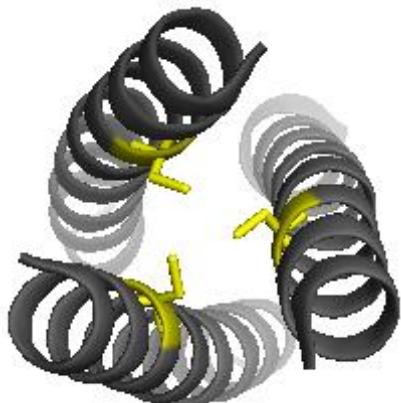
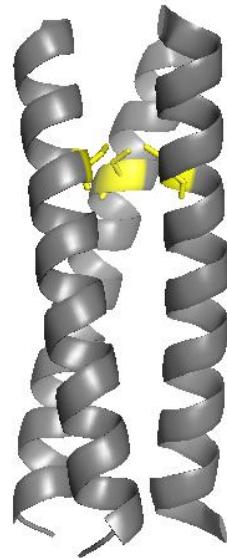
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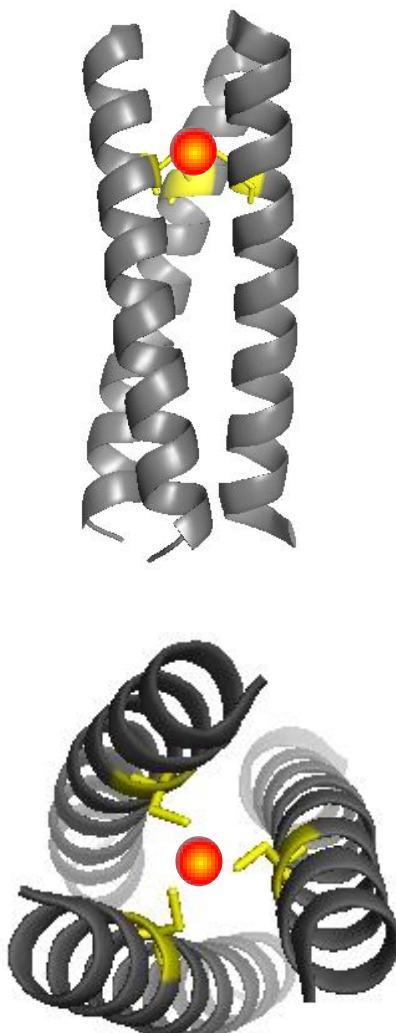


- 6) βNMR Spectroscopy (?)

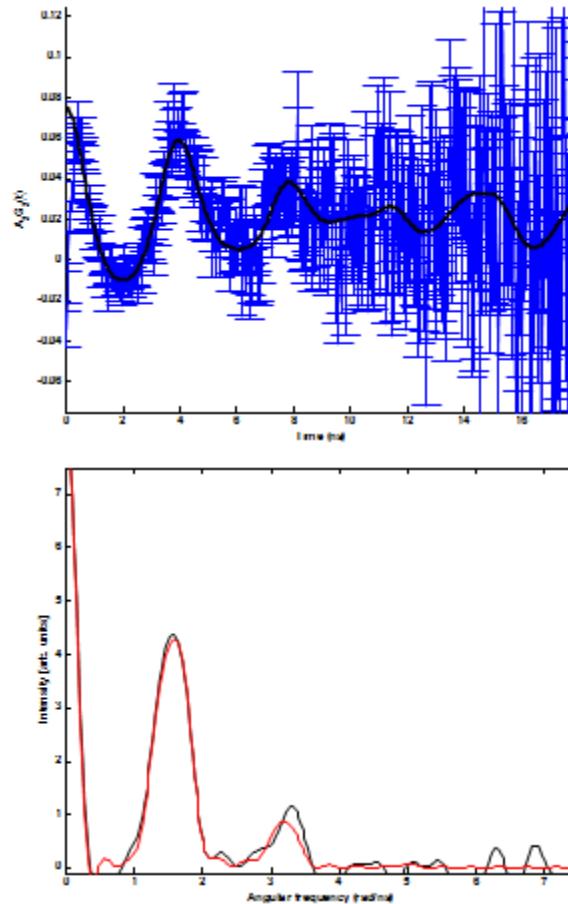
PAC Spectroscopy



PAC Spectroscopy

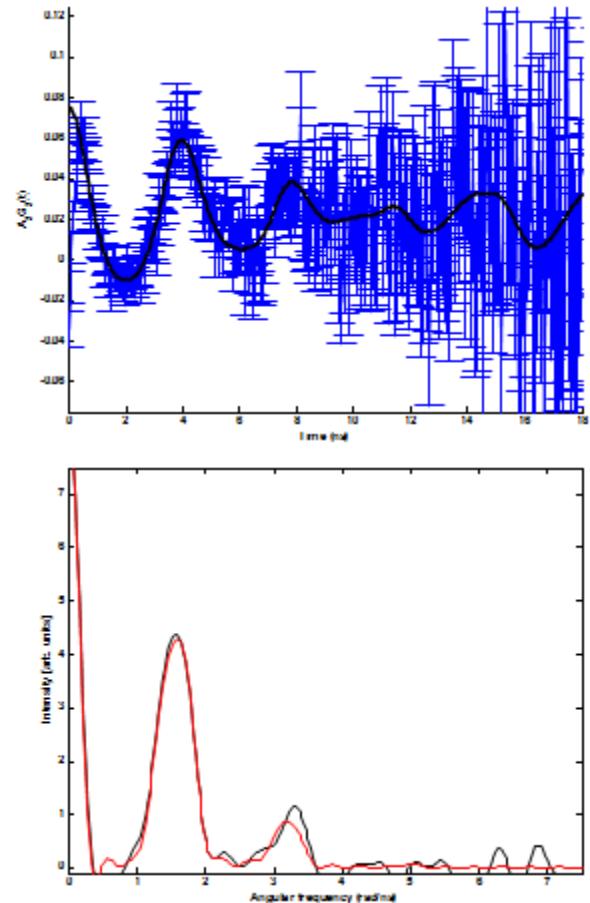
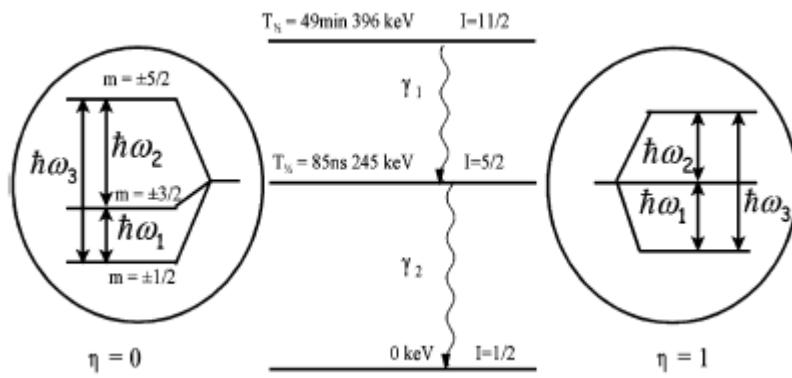


199mHg-PAC Spectroscopy on *de novo* synthesized peptides



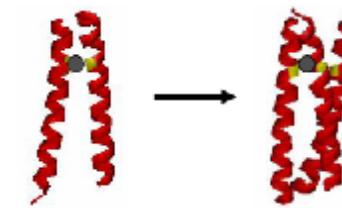
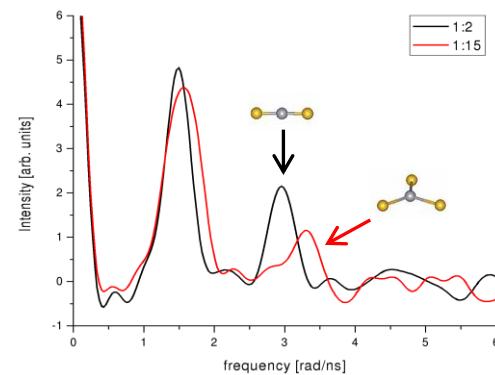
PAC Spectroscopy

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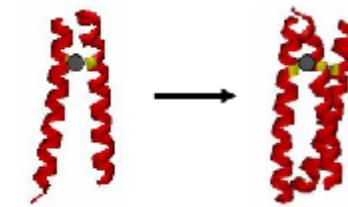
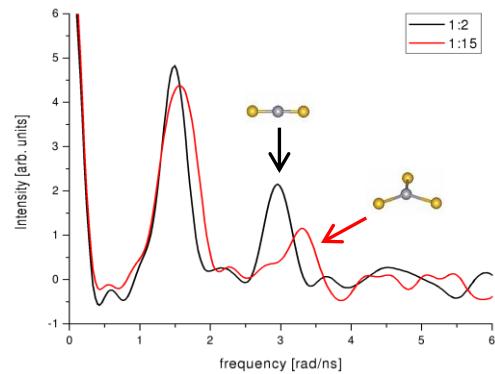
PAC Spectroscopy

Metal : peptide ratio
1:2 → 1:15

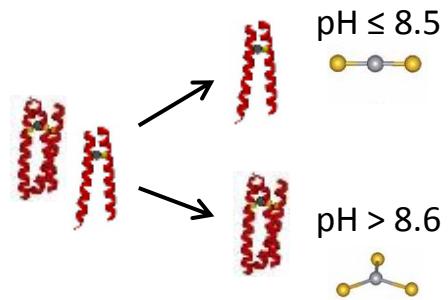
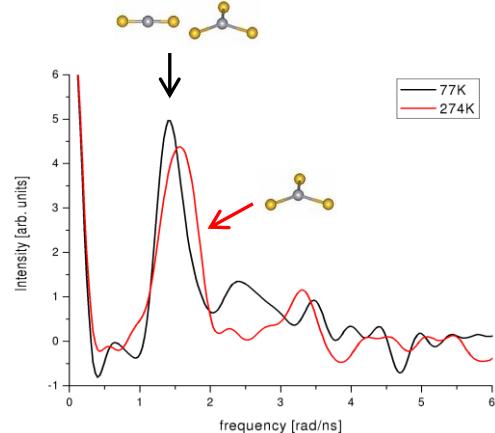


PAC Spectroscopy

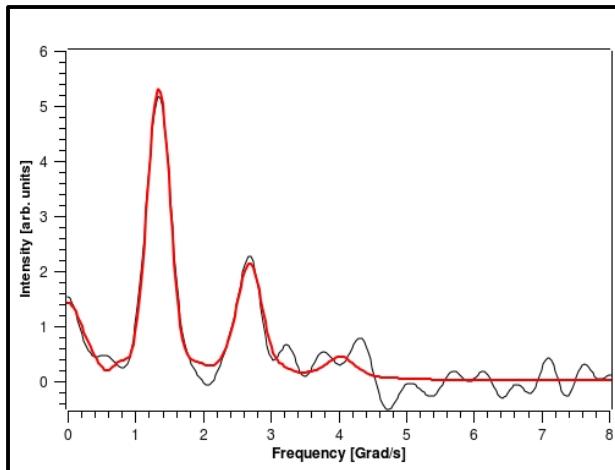
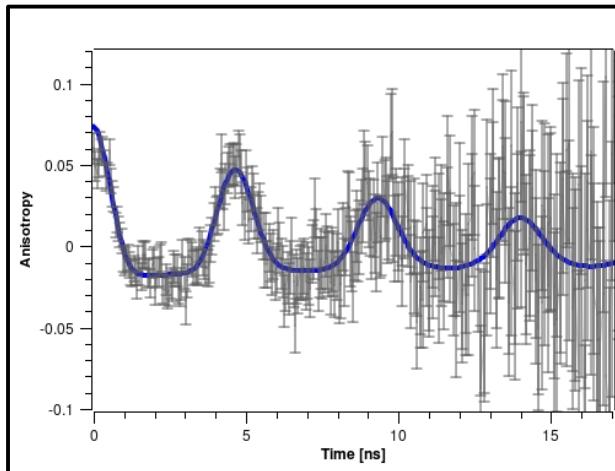
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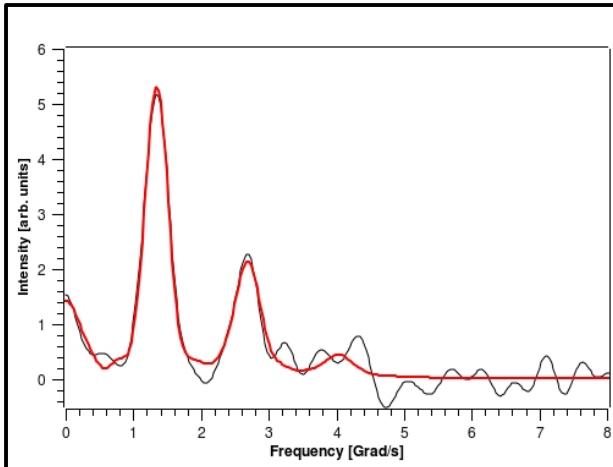
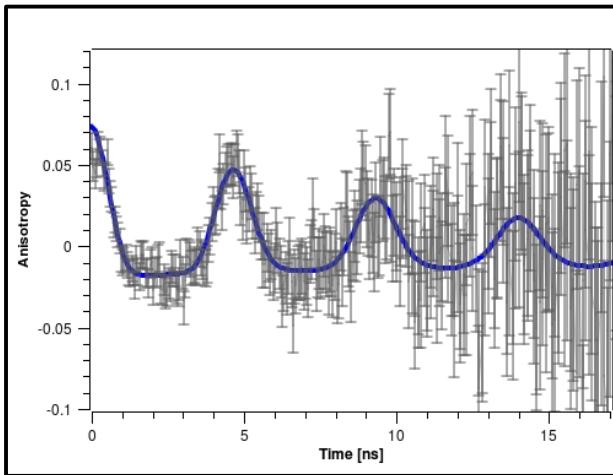
Temperature and pH
77K → 274K
8.5 → 9.4



PAC Spectroscopy



PAC Spectroscopy



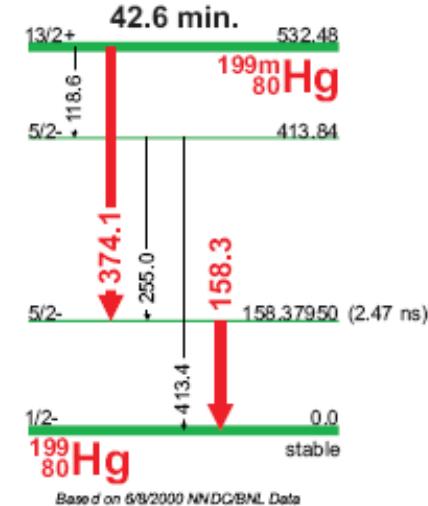
PAC Spectroscopy

Advantages:

- Characterisation of structure and dynamics at the PAC probe site
- High sensitivity to structural changes
- Small amount of PAC probe needed (in principle about 1 pmol)
- Different physical states: crystals, surfaces, solutions, *in vivo*...

Limitations:

- Suitable PAC isotopes do not exist for all elements
- PAC isotope must bind strongly to the molecule
- After effects can cause problems
- Production of PAC-isotopes



Hemmingsen et al. *Chem. Rev.*, 2004, 104: 4027

Hemmingsen and Butz, in "Application of Physical Methods to Inorganic and Bioinorganic Chemistry" 2007

β NMR Spectroscopy

- Measurement: beta decay anisotropy
 - chemical shifts
 - quadrupole interactions (also time dependent)
- Advantage: physics and data analysis basically the same as for “standard” NMR
- Disadvantage: localization

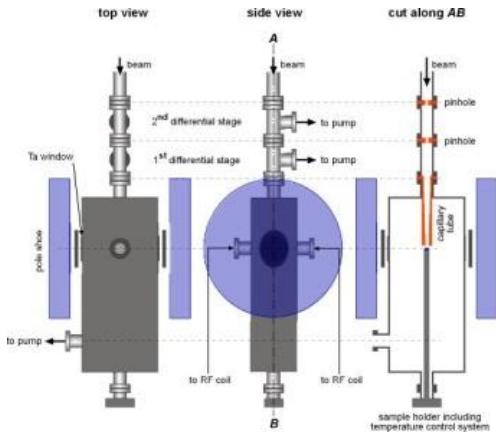
β NMR vs “standard” NMR



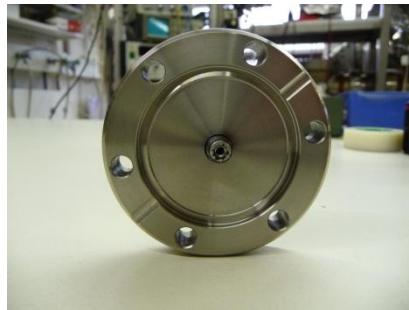
Property	NMR	β NMR
polarization	mag. field	polarized beam
isotopes	stable	radioactive
number of nuclei	10^{18}	10^8
nuclear polarization	small	10 – 100%
magnetic field	yes	yes / no
type of experiment	offline	online



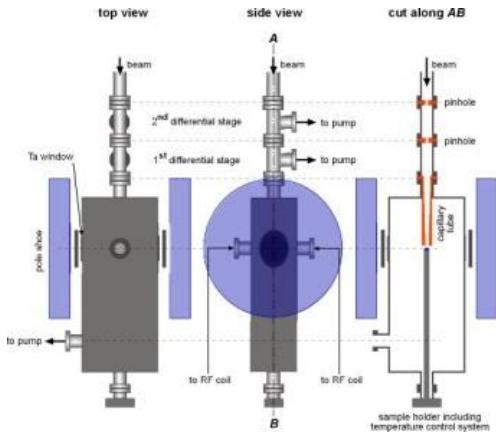
β NMR Spectroscopy: Setup



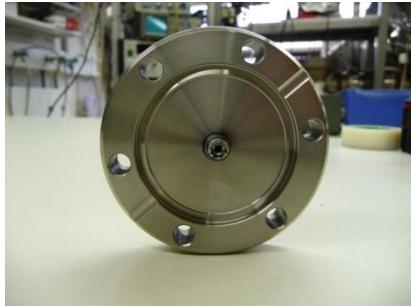
Pinholes



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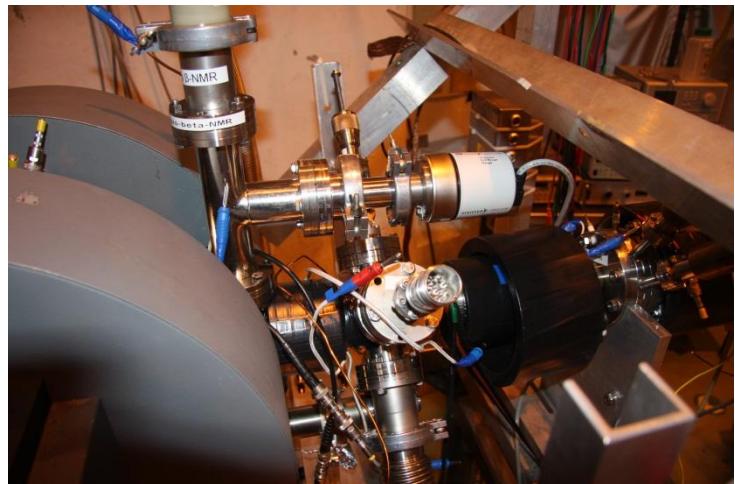
Pinholes



Chamber

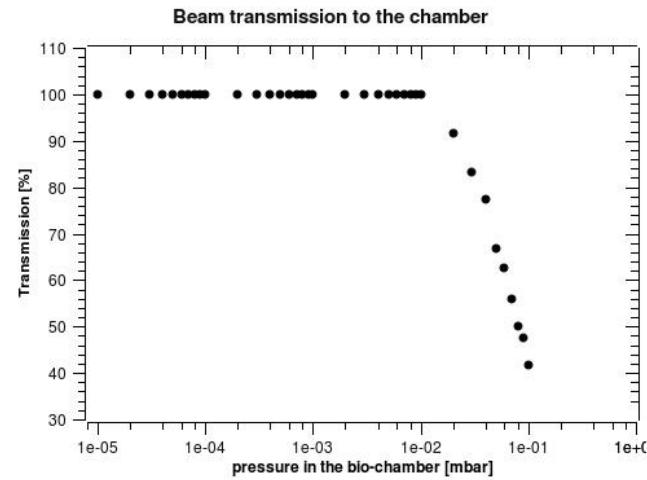
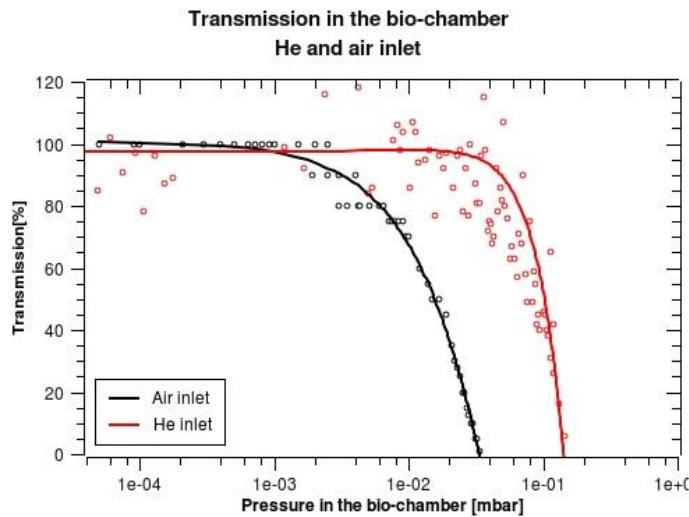


At the COLLAPS magnet



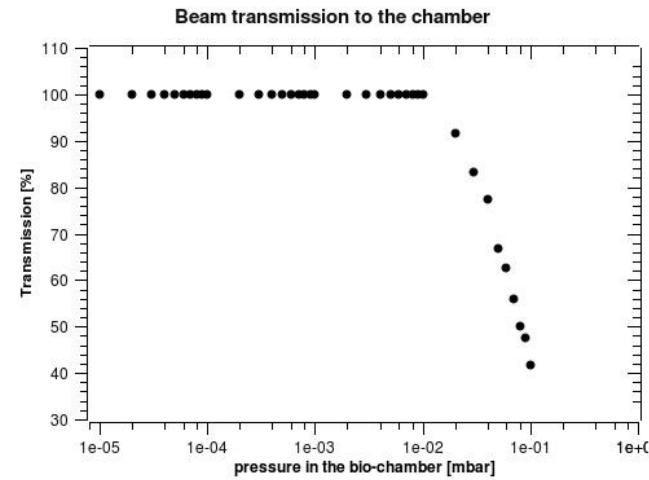
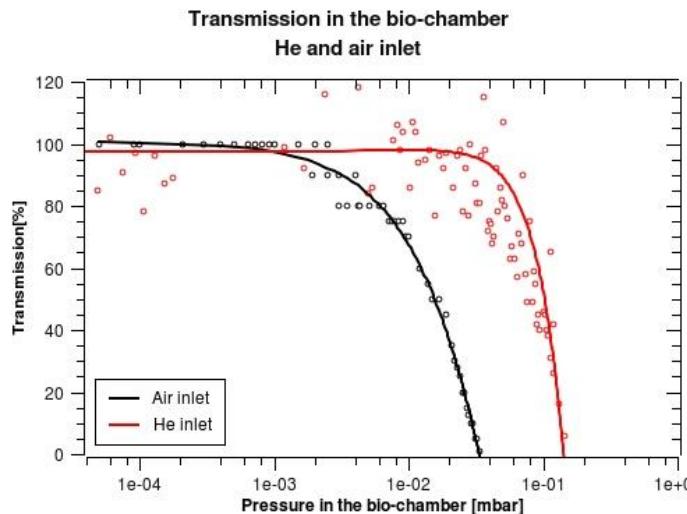
β NMR Spectroscopy

Beam Transmission to the chamber:



β NMR Spectroscopy

Beam Transmission to the chamber:



- Guiding through pinholes (~10%)
- Magnetic field at nominal value (100%)
- Guiding field on (100%)
- He inlet, 2·10⁻² mbar (100%)
- Liquid droplet maintained in the chamber (100%)

Setup ready for radioactive beam



Outlook

PAC Spectroscopy:

- Studies of heavy metal ion binding to proteins and nucleic acids (RNA/DNA)
- Water purification by bacteria
- Heavy metal ion binding by plants and bacteria (in vivo experiments)
- Record the first clearcut ^{204m}Pb PAC for proteins

β NMR Spectroscopy:

- First experiments on ^{31}Mg in Aug 2012
 - different liquid
 - small molecules
 - proteins or RNA
- Setup optimization

Fundings



Bundesministerium
für Bildung
und Forschung



Danish Agency for Science
Technology and Innovation
Ministry of Science
Technology and Innovation



Danish Center for Scientific Computing

VILLUM KANN RASMUSSEN FONDEN
& VELUX FONDEN



Thank you!