Contribution ID: **52** Type: **Invited speakers**

Polarised neutron scattering from dynamic polarised nuclei.

Monday, 26 September 2022 10:50 (25 minutes)

It was in September 1972 when Konrad Ibel and myself put a solution of sperm whale myoglobin into the sample chamber of D11. To our great surprise it was after a few seconds of irradiation by thermal neutrons – I think the A-selector was not yet in place – when a beautiful central peak of scattered neutron intensity emerged on the screen, the first picture of neutron small-angle scattering with D11.
The was also the beginning of neutron small-angle scattering from macromolecules in mixtures of heavy water, D2O, and H2O. The large difference in the scattering lengths of the isotopes 1H (=H) and 2H (=D) has been beneficial for studies of composite structures like membranes, nucleoproteins, lipoproteins and viruses. The demand of beam time largely exceeded the time available at D11.
At the same time Hayter, Jenkins and White (Physical Chemistry Laboratory Oxford) came up with a method using the spin dependence of the interaction of polarised neutrons with polarised protons. The variation of the scattering length b with proton polarisation largely exceeds that obtained with isotopic substitution. No echo for a long time.
About a decade later, a growing interest of neutron scattering from dynamic polarised bulk protons in macromolecules developed, mainly triggered by the introduction of glassy hydrogenous substances as polarized target material in high energy physics (reviewed by Niinikoski, 2013). The selective depolarisation of dynamically polarised proton spins or deuteron spins by the method of adiabatic fast passage (AFP) in specifically deuterated ribosomal particles has been extensively used in polarised neutron small-angle scattering in collaboration with CERN (Knop et al. 1986, Willumeit et al. 1996). This method which became known as nuclear spin contrast variation has also found numerous applications in structural studies on polymers (Koghi et al. 1987, Glättli et al. 1989, Kumada et al. 2010). This work was done outside the ILL.
What about the evolution of proton polarisation at the onset of microwave irradiation? The answer could be interesting with radical proteins, like tyrosyl doped catalase. The study of free radicals of different size would help to find an answer. On that substantially enlarged basis a Swiss-French-German collaboration was established. The polarised target facility from PSI was temporarily installed at the instrument D22 of the ILL. In fact, the results from solutions of free radicals were quite clear. The creation of a local proton polarisation in the vicinity of an unpaired electron is followed by its diffusion into the bulk. The barrier confining the domain of local polarisation is identical with the molecular surface of small free radical molecules dissolved in a deuterated solvent. With larger free radical molecules an intramolecular magnetic spin diffusion barrier cannot be ignored.
Now let us turn to catalase. This enzyme converts hydrogen peroxide incredibly fast into water and oxygen. Replacing one of the hydrogens of the H2O2 by CH3CO this derivative is accepted by catalase like H2O2 but treated in a quite different way: first, the response is slow and, second, after some intermediate steps, one of its amino acids, tyrosine, is converted to a tyrosyl radical. The number of tyrosyl radicals created in this way is small, typically less than one among the 500 amino acids of one of the four subunits of catalase molecule. The contribution of a small domain of reasonably strong polarised protons near a tyrosyl radical to the polarisation dependent scattering intensity is expected to be small. The direction of DNP has been changed several thousand times in order to obtain the polarisation dependent scattering intensity of only 1/1000 of the total intensity with a sufficient accuracy. The unpaired electron is probably that of the tyrosines fairly close to the centre of the catalase molecule (Zimmer et al. 2016).
A more sophisticated version of time-resolved neutron scattering using the inversion of the proton polarisation by AFP appears to confirm the existence of the tyr-369 radical in agreement with an earlier analysis of

the EPR of tyrosyl doped catalase (Hautle et al. manuscript in preparation).

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Session Classification: Talks