

Dynamical and conformational changes in dissolved iron-porphyrin complexes

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The object of presented project is study of the dynamics of iron porphyrins containing iron these are derivatives of PPIX (*protoporphyrin IX*) and TPP (*tetraphenyl*) porphyrins, including μ -oxo dimerised forms. PPIX is the core of the heme molecule, while mostly TPP and its iron derivatives is treated like a heme model compound, being not as chemically reactive as PPIX. The local electronic state of iron and the dynamical and structural features of the whole molecule might be investigated complementary, using XAFS and Mössbauer spectroscopies. Mössbauer spectroscopy is very sensitive on the nuclei-probe, here ^{57}Fe , movements, but also may provide information on the molecular motion of the Brownian origin. The results supply rather unique information on the properties on Fe-porphyrins in a liquid medium, not disturbed by intermolecular interactions and solid state effects. That approach would provide information much closer to the natural environment of the porphyrins involved in the life processes. Listed complexes have been examined in the dissolved states, compared to the results of the previous powder studies [1,2].

The main technical goal was construction and application of adequate cells for liquid samples, what has been successfully achieved. The structural information of the secondary interactions, analyzed also from the time domain point of view, might gain knowledge of the relevance of such interactions in solutions. The role and scale of the conformational changes of the whole molecule and its influence to the absorbing Fe-atom, sensitive both to the concentration and temperature conditions is investigated (10-300K). Model independent thermal vibrations in the dissolved compounds are analyzed. Unfortunately, the XAFS spectra, due to the low concentration of the absorbing iron and the solvent evaporation under, are not the highest quality. Additionally, a technical problem was temperature instability during measurements. Still some additional analysis are being performed. However, supporting method - Mössbauer spectroscopy, has already provided some primer results.

It has been found that for the powder samples the replacing of the outer hydrocarbonate chains in Fe-PPIX-Cl by the phenyl rings in Fe-TPP-Cl increases the Debye temperature from $\Theta_D = 150$ K up to 164 K, respectively. In the frozen solution the isolated porphyrin molecules coexisted with molecular aggregates. This made possible the estimation of the influence of the inter-molecular interaction on the total $\langle x^2 \rangle$. The mean square displacement of the resonance nucleus $\langle x^2 \rangle$ may be approximated by a sum of two components: $\langle x^2 \rangle_i$ arising from internal vibrations of the Mössbauer probe and $\langle x^2 \rangle_m$ from the motion of the entire molecule. The $\langle x^2 \rangle_i$ factor is related to the strength of the chemical bounding while $\langle x^2 \rangle_m$ carries the information of the inert-molecular interactions. It turned out that with increasing temperature the intensity of the fraction assigned to the isolated molecules decreases very fast which leads to the $\Theta_D = 84$ K. The value of the standard deviation, σ^2 , of the distances between the central ion (in our case Fe) and the neighbouring atoms (here N atoms) analyzed from the EXAFS spectra provides direct information on the dynamics of the absorbing atom. In case of the Fe-PPIX-Cl powder compound σ^2 is much less than $\langle x^2 \rangle$ which points out the collective vibration of Fe and its N ligands [1]. From the first analysis it seems to be the case also for Fe-TPP-Cl compound.

References

- [1] K. Dzedzic-Kocurek, J. Stanek, K. Burda, *Hyperfine Interactions*, 185, 97(2008).
- [2] K. Dzedzic-Kocurek, J. Stanek, K. Burda, P. Fornal, *HASYLAB Annual Report* (2007).