^{1}H and ^{14}N ENDOR on low spin Fe- and Co-Hemoglobin Derivatives

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As is well known, the hemoglobin (Hb) molecule undergoes a structural change of its protein shell upon oxygenation on the prosthetic group. Structural changes in the heme crevice and the closer neighbourhood of the heme center in particular are still not known in full details, and different models and hypotheses are in the discussion concerning the role of the proximal histidine and movement of the central ion relative to the prophyrin plane in relation to such a structure change.

We have used frozen solutions of a liganded ferric form ($Hb^{+}N_3^{-}$) and a ferrous form (HbNO), to study spectral changes in the coupling strength of weak protons and the proximal histidine to the iron-heme-center. Also we have studied the Cobalt-OxyHb as it is a good model analog of the native Hb_AO_2 and is, in contrast to the latter, accessible to ESR spectroscopy.

Observed changes among those different substances involve the ^{1}H-coupling from the heme environment and ^{14}N-couplings from the proximal histidine, obtained from ENDOR spectra which could, in general, be observed on different g-sites of the ESR-spectra. For g_{zz}, both the number and coupling strength of the protons varies with ligand, the latter from 1.8 G ($Hb^{+}N_3^{-}$) to 2.8 G (HbNO) for the largest coupling observed. The ^{14}N-Histidin couplings are nearly equal in the two Fe-containing samples (6.1 G) whereas they drop to 4 G for the Cobalt-OxyHb. These and related findings obtained from monomeric samples (work in progress) will be discussed in terms of understanding the role of the close neighbourhood of the heme during structure change.