

# MODERN DEVELOPMENT OF MAGNETIC RESONANCE

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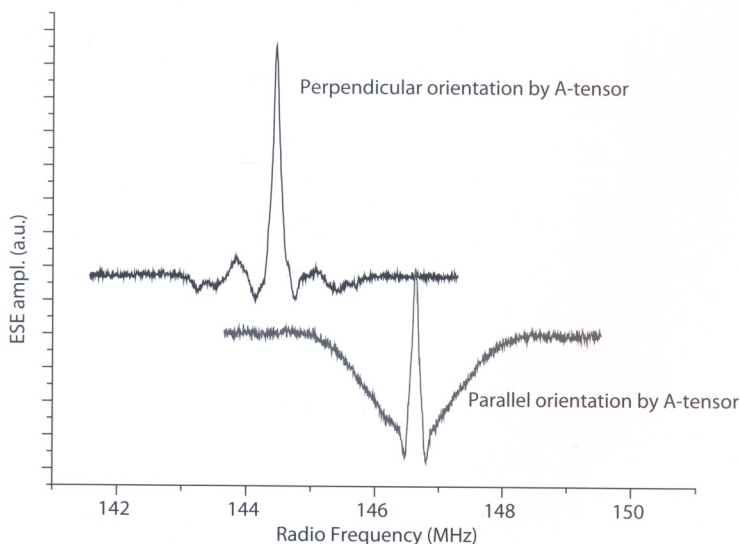
## Stable Self-Organized Paramagnetic Complexes in the Asphaltenes' Structures from the W-band EPR and ENDOR

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Structural characterization of asphaltenes and their aggregates in native hydrocarbons (oil, bitumen, coal, oil-containing cores, etc.) as well as in their fractions are in the focus of scientific and industrial interests since many years. However, after decades of intensive studies, the association and aggregation of asphaltenes are still not well characterized and are subjects of debates [1, 2]. The content of the high-molecular asphaltene components could reach the values of 45 wt% in native oils and up to 73 wt% in natural asphalts and bitumen. Asphaltene impact all aspects of crude oil production and utilization. Undesirable asphaltene precipitation is a serious concern to the petroleum industry because asphaltenes can plug up well bores and stop oil production, in addition to blocking pipelines [3].

Commercial availability of the pulsed high field EPR/ENDOR spectrometers [4–7] open new ways for the hydrocarbon analysis and the asphaltenes' structural investigation using intrinsic paramagnetic centers (PC) as sensitive probes. Asphaltenes can contain up to  $10^{22}$  PC per 1 gram of substance which are essentially due to "free" carbon radicals (FR) mainly localized within the



**Fig. 1.** Difference (for initial asphaltene sample and those deposited and on the surface of  $\text{Al}_2\text{O}_3$ ) ENDOR spectra of protons involved in the network of the self-organized asphaltene complexes.  $T = 20$  K, W-band.

polyaromatic condensed nuclei of the asphaltene molecules and/or vanadyl ( $\text{VO}^{2+}$ ) complexes which also revealed in another constituent of hydrocarbons – resins.

We present pulsed EPR and ENDOR approaches and some preliminary results to study paramagnetic  $\text{VO}^{2+}$  complexes of initial asphaltenes and those deposited on surface of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) [8, 9] in the magnetic field of about 3.4 T (W-band). Application of high magnetic field allows to separate FR and  $\text{VO}^{2+}$  signals due to the difference in their  $g$ -factors, choose “pure” parallel and perpendicular orientations for  $\text{VO}^{2+}$  complexes. The anisotropy of the self-organized asphaltene complexes is demonstrated by ENDOR (Fig. 1).

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