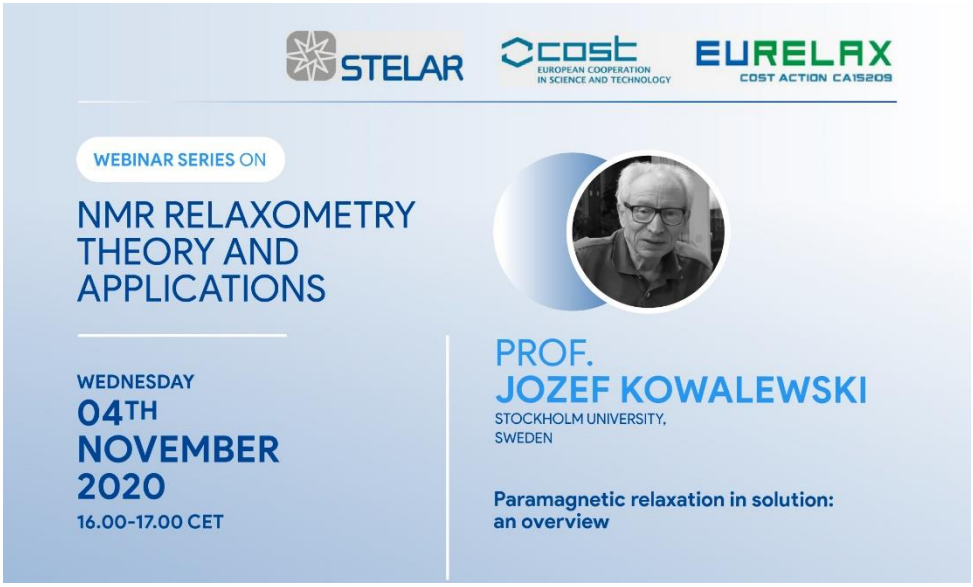

Abstract

Paramagnetic relaxation in solution: an overview

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Presence of paramagnetic species in solution has a profound effect on NMR properties, not least on nuclear spin relaxation which is strongly enhanced. The origin of the effect is the interaction between nuclear spins and the unpaired electron spins – the hyperfine interaction. The hyperfine interaction is commonly divided into a dipolar and scalar part, similar to the dipolar interactions between the nuclear spins and the J-coupling, respectively. The difference is that the hyperfine interaction is much stronger, because of the very large magnitude of the magnetic dipole associated with an unpaired electron, about 650 times larger than that of a proton. The electron spin is also subject to other strong interactions, among which the electron Zeeman and the zero-field splitting (ZFS) are most important. The strong interactions of the electron spin result also in very rapid electron spin relaxation.

The nuclear spin relaxation is usually described by second order perturbation theory, in a formulation known as Redfield theory. This approach can be applied to paramagnetic relaxation. However, the fact that the electron spin interacts so strongly with its surroundings sets limits to the validity and applicability of the Redfield theory. As a consequence, theoretical description of NMR relaxation in paramagnetic solutions becomes rather complicated and a decisive progress has first occurred during the last few decades.

The historical development of our understanding of paramagnetic relaxation effects will be presented. Experimental strategies, mainly nuclear magnetic relaxation dispersion (NMRD) measurements based on the fast field-cycling (FFC), will be described and illustrative examples – from the field of MRI contrast agents as well as from paramagnetic metalloproteins – will be provided.

Author Biography

Jozef Kowalewski received his PhD from Stockholm University in 1975. He began working with nuclear spin relaxation as a postdoctoral fellow at Florida State University and this has ever since been the main area of his research. He became professor of physical chemistry at Stockholm University in 1986 and was chairman of the department of physical, inorganic and structural chemistry between 1993 and 2005. Dr Kowalewski supervised 17 PhD students and authored about 200 scientific papers and a book (together with Lena Mäler). Since 2014, he is professor emeritus at Stockholm University.