Cross-Correlation Effects in NMR Spectra of a Spin 1/2 Scalar Coupled to a Spin S ≥ 1

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Abstract. In the frame of the density matrix formalism the lineshapes and dynamic frequency shifts in the multiplet structure of a spin I = 1/2 scalar coupled to a quadrupolar nucleus with a spin S ≥ 1 undergoing dipolar (D), quadrupolar (Q) and chemical shift anisotropy (CSA) relaxation are studied. Analytic expressions for the cross-correlation spectral densities $J_{Q-CSA}$, $J_{D-Q}$, $J_{D-CSA}$ and also for the real and imaginary Redfield elements of the relaxation matrix were obtained in the general case of noncoincident and nonaxial Q, D, and CSA tensors. On the assumption that CSA and Q interactions are comparable in magnitude the contributions of cross-correlation terms CSA-Q, CSA-D, Q-D in the linewidth and dynamic shifts of the multiplet pattern of a spin $I = 1/2$ were analyzed in a wide interval of correlation times ($10^{-12}$–$10^{-7}$ s) for a spin system $^{13}$C-$^{15}$B and $^{31}$P-$^{59}$Co as an example.

1 Introduction

The study of relaxation processes in the high-resolution nuclear magnetic resonance (NMR) spectroscopy in liquids has become an important tool for the investigation of the structure and dynamics of molecules. The structure and dynamic information can be extracted from nuclear Overhauser effect (NOE), spin-lattice relaxation times and linewidths, which depend on spectral densities of the time-dependent correlation functions of the interactions [1]. If more than one interaction contributes to spin relaxation, the interference (cross-correlation) effects can occur when it is possible to describe the interactions by tensors of the same rank. Although the cross-correlation effects in NMR were widely discussed about 40 years ago [1–8], these effects were routinely observed when the use of high-field NMR spectrometry became common [7–9]. The largest effect induced by the cross-correlation is that on the evolution of transverse magnetization [10]. It results in a different width for each line of multiplet [10–15], because the relaxation rates for each component of a multiplet are different. The existence of
cross terms can be detected by inspecting inversion recovery spectra [11] or by observation of extra cross peaks in COSY experiments [16].

The investigation of relaxation processes in scalar coupled spin systems involving a quadrupole nucleus $S \geq 1$ is of greatest interest. Methods for the analysis and extraction of useful data derived from NMR studies of these nuclei were relatively limited if compared with manifold techniques for studies of one-half-spin nuclei. It is explained by a variety of factors, particularly, the very short relaxation times, small NOE, and wide lineshape to complicate the extraction of the structure information. Such problem can be avoided, particularly when half-spin nuclei would be observed which are scalar coupled to quadrupolar nuclei. According to the theoretical and experimental results [17, 18], the relaxation behavior of the nucleus with one-half spin scalar coupled to a high-spin nucleus and the linewidth depend on the quadrupolar tensor parameters and dynamic properties of the quadrupolar nucleus.

In addition to probing these conventional NMR parameters, the study of such spin systems yields the information about internuclear distances. Internuclear distances of molecules in a solution are commonly determined by NOE measurements that are based on the relaxation, governed by the dipolar interaction. However in the presence of nuclei with higher spin, the transverse and longitudinal relaxation times are dominated by the quadrupolar interaction and NOE cannot be observed in such spin systems. In such situation the internuclear distances between $S$ spins and $I$ can be extracted from the dynamic frequency shift arising from quadrupolar-dipolar cross-correlation if the quadrupolar coupling constant is defined in the preceding experiments. There are several situations where the dynamic frequency shift will exceed the linewidth whenever the extreme narrowing approximation fails. In such situation the dynamic frequency shift becomes more important as one moves to higher field [19–22]. Asymmetric positioning of the central component relative to the outermost components in the $^{13}$C spectra of the $^{13}$C coupled to $^2$H ($S = 1$) was explained by dipole-quadrupole (D-Q) cross-correlation [20].

The structure information can be obtained from the study of D and chemical shift anisotropy (CSA) cross-relaxation effects as these depend on the relative orientation of the tensors describing dipole interaction and chemical tensors. Thus, analysis of spin-lattice and transverse relaxation effects can provide stereo-chemical information. The theoretical study of the cross-correlation and dynamic shift effects on the lineshape variation of half-spin nuclei scalar coupled to quadrupolar nucleus undergoing Q, D and CSA relaxation was examined in the presence of radio-frequency irradiation [23] for spin systems $IS$ with $S = 1$. The CSA-Q cross-correlation effect on the lineshape of the $^{31}$P ($I = 1/2$) nucleus $J$-coupled to $^{59}$Co ($S = 7/2$) in tetrahedral clusters HFeCo$_2$(CO)$_{11}$PPh$_2$H has been investigated in [24, 26, 27] in the general case of noncoincident Q and CSA tensors for a spin in extreme narrowing conditions. In [27] it was assumed that the relaxation of the $^{59}$Co nuclei in the CSA mechanism is weaker than the Q mechanism. However this assumption is invalid for other clusters with $^{59}$Co [26, 28], such as in HFeCo$_3$(CO)$_9$[P(OCH$_3$)$_3$]$_3$. The experimental $^{59}$Co NMR spin-echo spectra of HFeCo$_3$(CO)$_9$[P(OCH$_3$)$_3$]$_3$ at two values of available magnetic field strengths have