



Field cycling methods as a tool for dynamics investigations in solid state systems: Recent theoretical progress

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ARTICLE INFO

Article history:

Received 12 October 2008

Received in revised form

4 December 2008

Available online 20 January 2009

Keywords:

Polarization transfer

Field-dependent relaxation

Quadrupolar interactions

Relaxation theory

LuF₃

Molecular motion

Solid state systems

NMR

ABSTRACT

In this paper physical mechanisms and theoretical treatments of polarization transfer and field-dependent relaxation in solid state systems, containing mutually coupled spins of spin quantum numbers $I = \frac{1}{2}$ (spins $\frac{1}{2}$) and $S \geq 1$ (quadrupolar spins), are presented. First, theoretical descriptions of these effects are given in detail for an illustrative, simple system. Next, it is shown how to generalize the theories to much more complex spin systems. The polarization transfer and relaxation effects are illustrated by several examples. Typical misunderstandings regarding their physical origins are clarified.

This paper reviews recent theoretical descriptions of the polarization transfer and relaxation phenomena. Its goal is to popularize the proper theoretical treatments with the intention to establish them as standard tools for analyzing field cycling data.

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1. Introduction

The field cycling technique has become a standard method for dynamics and structure investigations of a variety of molecular systems. Among others, field cycling relaxation studies of transition metal ion complexes in solution provide very valuable information on the factors determining the efficiency of paramagnetic contrast agents. This technique turns out to be very profitable for polymer and molecular glasses studies. Field cycling experiments at low temperatures give direct evidence of tunneling effects, while field-dependent relaxation studies of solid state systems give information on the molecular and ion dynamics. The great advantage of this technique is that it is sensitive to motional processes on different time scales.

However, a proper analysis of relaxation experiments is very demanding from a theoretical point of view. The theoretical difficulties are connected with the complexity of investigated systems in which a quantum mechanical component interacts with a complex environment. As long as one deals with an ensemble of spins $\frac{1}{2}$ (typically protons) one can use the well known standard relaxation theories [1–7]. Then the task is, in principle, easier, because one can directly focus attention on

developing motional models that lead to a form of spectral densities which reproduce reasonably well the experimental relaxation profiles. Actually, the problem of developing the appropriate motional model, which could explain the relaxation data in a broad frequency range, is often very complicated (for example polymer and molecular glasses investigations).

When we wish to apply the field cycling technique to investigate dynamics of molecular systems containing different kinds of nuclei (some of them possessing a quadrupole moment) or unpaired electrons, we have to face the problem of the quantum description of the system in addition to that of the motional complexity. The commonly used relaxation formulas [1–7], have been developed under the assumption that the energy level structure of the spin system is determined by Zeeman interactions and there are no other relaxation pathways for the participating spins except the mutual dipole–dipole couplings. In case of quadrupolar nuclei (nuclei of the spin quantum number $S \geq 1$ possessing a quadrupole moment) coupled to spin $\frac{1}{2}$ nuclei ($I = \frac{1}{2}$) the averaged quadrupolar interaction (referred to in the literature as static or permanent) contributes to the energy level structure and even dominates it at low field. In addition, local fluctuations of the electric field gradient tensor provide a relaxation mechanism for the quadrupolar nuclei. The same concerns systems with unpaired electron spins (with total electron spin quantum number $S \geq 1$), but in this case the interactions with the ligand field (the zero field splitting) replace

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the quadrupolar interactions. For such systems the high field theories break down at lower magnetic fields. It is impossible to adapt or extend them, in a straightforward way, beyond the high field regime.

A complete description of nuclear spin relaxation caused by dipole–dipole coupling to an unpaired electron spin (paramagnetic relaxation enhancement), valid for an arbitrary magnetic field and an arbitrary electron spin quantum number, has been formulated in the last years in a series of papers [8–17]. The theory is involved and does not lead, except for a few limiting cases, to closed analytical expressions. Nevertheless, there is no simple alternative. The complexity of this description is due to inevitable quantum properties of the spin system: it exhibits a complex, orientation dependent energy level structure resulting from a superposition of zero field splitting and Zeeman interactions; fluctuations of the ligand field cause transitions between these energy levels (the rates of which also depend on the magnetic field and the molecular orientation); and eventually this complex electron spin dynamics determines the nuclear spin relaxation. Despite the complexity this treatment has become quite popular. There are two main reasons for that. The first reason is the application context of the paramagnetic contrast agent research. It has been experimentally proven that the symmetry of the paramagnetic complex influences the water proton relaxation via the permanent (not fluctuating in a molecular frame) part of the zero field splitting. Since the ‘high field’ relaxation theories do not account for the effects of the permanent zero field splitting they are useless (besides their obvious theoretical inadequacy) for practical purposes. The second reason is that the software based on the proper theoretical description is available for public use (for example via the web page of CERM Magnetic Resonance Center in Florence: <http://www.cerm.unifi.it/home/research/relaxationrelaxometry.html>). A very important factor for popularizing this treatment is its generality. The paramagnetic relaxation enhancement is determined by a set of parameters which is common for all paramagnetic systems in solution.

Next, employing the line of analogy between the quadrupolar and zero field splitting interactions, a theory of field-dependent spin $\frac{1}{2}$ relaxation in the presence of neighboring quadrupolar spins has been formulated [15,16,18–20] and applied to fluorine relaxation profiles in LaF₃ [18–20]. This application turned out to be very successful. For example, using the correct theory a long standing belief concerning a distribution of correlation times of ionic motion in crystal systems has been critically reviewed and finally rejected (at least for the analyzed compounds).

In our opinion, this advanced treatment can be very useful for numerous field cycling investigations of dynamic processes in various molecular systems (for example: ionic crystals, powder, large organic cations). However, the variety of molecular systems and motional processes renders it impossible to formulate a description (and provide software) which might be directly used for interpreting relaxation profiles for an arbitrary system containing spin $\frac{1}{2}$ and quadrupolar nuclei. Therefore, the first goal of this paper is to present simple examples illustrating not only the ideas but also explaining in detail practical aspects of the theoretical approach. This should help the reader to perform analogous calculations for other systems under study and make use of the elements of the theory and the software which solve general problems common for most systems. The second objective is to give an overview of recent achievements in the theoretical interpretation of field cycling experiments for systems containing different kind of nuclei. In [18,19], the theory has been presented in a rather compact form typical for regular papers. This way of describing problems might be somewhat discouraging for readers who wish to follow details in order to apply this approach to other

spin systems. The present paper has an educational character and clarifies the theory starting from the basis. We believe that the educational examples complemented by the general overview will help to popularize the proper theoretical treatment of field-dependent relaxation processes.

Performing field cycling experiments for solid state systems containing spin $\frac{1}{2}$ and quadrupolar nuclei one observes not only relaxation but also polarization transfer. The physical mechanisms of both are essentially different. Relaxation is caused by stochastically fluctuating interactions with zero average, while polarization transfer between spin $\frac{1}{2}$ and quadrupolar nuclei requires an efficient mutual coupling with non-zero average between the participating spins. A detailed theory of polarization transfer has recently been published [16,19,21] and applied to some experimental data for systems containing protons and ¹⁴N nuclei ($S = 1$) [21]. Discussing polarization transfer phenomena one should also mention some earlier papers [22–25]. In this paper we present details of the theoretical description of polarization transfer in a simple way, for the same purpose as in the case of the relaxation theory. Besides that we illustrate the polarization transfer processes for higher quadrupolar spin quantum numbers by some examples, while the theoretical analysis published so far [21] concerns only systems of $S = 1$. Experimentally observed polarization transfer dips prove that there is a pair of $I-S$ spins coupled by an interaction with non-zero average. This implies that one should deal carefully with relaxation processes in such systems, since such an interaction may not be treated as a relaxation mechanism [16,19,20].

Analysis of the polarization transfer pattern (i.e. the $I = \frac{1}{2}$ spin magnetization measured versus magnetic field) gives information on the quadrupolar parameters, the orientation of the electric field gradient tensor at the position of the quadrupolar nucleus and the internal molecular geometry. This knowledge is necessary for a proper analysis of relaxation profiles collected for the investigated system. Thus, polarization transfer and relaxation experiments provide complementary and unique information if properly analyzed. One should interpret both phenomena in a consistent way being aware of the complex quantum mechanical properties of such spin systems. This is the general message of the present work.

The paper is organized as follows. First, we introduce the reader to the polarization transfer theory by considering simple, illustrative examples (Section 2.1). Next, a general overview of the polarization transfer theory is given (Section 2.2). In the next step we discuss the essential aspects of relaxation theory showing how to profit from polarization transfer data when analyzing relaxation experiments (Section 3.1). In analogy to the presentation of the polarization transfer theory, a general overview of the relaxation treatment is given (Section 3.2), while some examples are shown in Section 3.3. Advantages of a consistent treatment of polarization transfer and relaxation experiments are pointed out. The paper ends up with concluding remarks (Section 4).

The software used in this paper can be provided upon request.

2. Polarization transfer phenomena

In solid state systems containing coupled quadrupolar and spin $\frac{1}{2}$ nuclei one can observe polarization transfer processes. If the external magnetic field is set to a value which leads to a Zeeman splitting of the spin $\frac{1}{2}$ matching the energy splitting of the quadrupolar spin (determined by its quadrupolar and Zeeman interactions), the spin $\frac{1}{2}$ magnetization can be transferred to the quadrupolar spin. The mutual, usually dipole–dipole, coupling between $\frac{1}{2}$ and quadrupolar spins provides the polarization transfer pathway. Thus, the fundamental condition necessary for

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