WHAT DO WE KNOW ABOUT ^{14}N QUADRUPOLE RELAXATION ENHANCEMENT?

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The possibility of performing spin relaxation experiments versus magnetic field has lead to revealing several relaxation effects originating from a quantum-mechanical interplay between different types of spin interactions. One of them is Quadrupole Relaxation Enhancement (QRE).

A very "superficial" description of the QRE effect is as follows. Tis effect involves at least one nucleus of spin-quantum number $I=1/2$ (typically ^{1}H) and one nucleus of spin quantum number $S \geq 1$; let us think about ^{14}N ($S = 1$) as Nitrogen is one of the fundamental components of organic matter, from simple molecules, via proteins to tissues. The two nuclei (^{1}H and ^{14}N) have to be mutually coupled by ^{1}H-^{14}N dipole-dipole interactions. The energy level structure of ^{1}H is fully determined by its Zeeman interaction and, hence, its magnetic spin quantum number, $m_I = \pm 1/2$. ^{14}N nucleus experiences two kinds of interactions: Zeeman interaction and quadrupole coupling – *i.e.* a coupling with the electric field gradient tensor at its position. When the orientation of the electric field gradient tensor is fixed with respect to the direction of the external magnetic field (*i.e.* the molecular dynamics is slow), the energy level structure of ^{14}N is determined by a superposition of the two interactions. This implies that at some magnetic fields the ^{1}H resonance frequency (the transition frequency between the ^{1}H energy levels) matches one of the ^{14}N transition frequencies between its energy levels, the ^{1}H polarization can be "taken over" by ^{14}N leading to a frequency specific enhancement of the ^{1}H spin-lattice relaxation rate, often referred to as "quadrupole peaks". As the positions of the quadrupole peaks depend on the quadrupole parameters which are determined by the electric field gradient tensor at the ^{14}N site, the positions shift in response to even subtle changes in the electric field gradient. Moreover, the presence of the quadrupole peaks can serve as a proof of slow dynamical processes in the system. In consequence, QRE is a very sensitive fingerprint of molecular arrangement exploited in material science, biology and medicine. In the last case the position and the shape of the quadrupole peaks can potentially reflect pathological changes in tissues (*e.g.* early stage tumors).

The mechanism outlined above is, however, very confusing. It does not provide answers to numerous pertinent questions, like:

- Why QRE effects are observed for molecular motion occuring on an intermediate time scale (not only for slow dynamics)?
- Is is possible to precisely formulate the conditions under which they become visible?
- Why in some cases the quadrupole peaks are of Lorentzian shape and in some others not?
- Is their amplitude indeed a measure of an immobilized fraction of protons in the system?
- May one reveal the QRE effects by a simple "extracting" of the relaxation background from the overall relaxation dispersion profiles?
- Why the relative amplitudes of the quadrupolar peaks are different for different systems?

The presentation will answer to these questions and several other.