

Isolation of the Mutual Transverse Dipolar Relaxation of a Pair of Coupled Spins

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The potential of relaxation measurements to provide dynamic information about a molecule often goes unrealized due to the complexity of the processes which occur and the difficulty in separating them. Generalized expressions for several elements of the dipolar relaxation matrix are derived. It is shown that by taking the appropriate linear combination of these relaxation rates it is possible to isolate the mutual dipolar relaxation of a pair of coupled spins, even when both also relax with an arbitrary number of others. The technique is demonstrated experimentally using 5,7-dimethoxy coumarin. © 1995 Academic Press, Inc.

INTRODUCTION

The relaxation properties of NMR (1–6) are potentially an invaluable source of information on molecular dynamics. Unfortunately, this potential usually goes unrealized due to the sheer complexity of the relaxation processes that occur and the difficulty in unraveling them. Where relaxation has been used to obtain dynamic information, it is usually the case that circumstances permit the mutual relaxation of a few spins to be considered in isolation from all others, thus greatly simplifying the problem of analysis. One of the most widely exploited examples of this approach is the analysis of the relaxation of ^{15}N in the backbone of ^{15}N -labeled proteins (7–10). In this case the ^{15}N nucleus can be considered to relax solely due to its dipolar interaction with its bonded proton and its own chemical-shift anisotropy. However, while informative, this approach has the disadvantage that it is only a special case, and consequently the extraction of dynamic information from the relaxation properties of most nuclear spins is precluded.

In this paper we explore an approach for obtaining dynamic information from the relaxation properties of nuclei that is in principle more generally applicable. We show that in a system undergoing purely dipolar relaxation, by taking a linear combination of certain transverse relaxation rates it is possible to isolate the mutual relaxation of a pair of coupled spins, even when both spins also relax with an arbitrary

number of others. Experimental procedures for making the required measurements are also considered.

TRANSVERSE DIPOLAR RELAXATION

The time dependence of the density operator can be described by (1–3)

$$d\{\sigma(t)\}/dt = -i[\mathcal{H}, \sigma(t)] - \Gamma\{\sigma(t) - \sigma_0\} \quad [1]$$

where \mathcal{H} is the time-independent nuclear spin Hamiltonian, Γ is the relaxation superoperator, $\sigma(t)$ is the density operator at a time t , and σ_0 is the density operator at equilibrium. For practical purposes this equation is usually recast in matrix form,

$$d\{\sigma(t)\}/dt = -\{i\bar{\mathcal{H}} + \Gamma\}\{\sigma(t) - \sigma_0\}, \quad [2]$$

where $\bar{\mathcal{H}}$ is now a superoperator. The density operator $\sigma(t)$ is usually expanded as products of shift operators to calculate its time dependence and then converted into single transition operators by using a unitary transformation to enable theory to be compared with experiment (11). However, here we find it more convenient to leave $\sigma(t)$ in the product-operator basis. Diagonal elements of the relaxation matrix give the rates of decay of the components of coherence, and off-diagonal elements give the rates of relaxation-induced evolution between them.

The dipolar interaction Hamiltonian, which is responsible for dipolar relaxation, can be written as the product of two second-rank tensors (1, 3, 12),

$$\mathcal{H}_1(t) = \sum_q F^{(q)}(t)A^{(q)}, \quad [3]$$

where $F^{(q)}(t)$ are random functions of time and $A^{(q)}$ are operators acting on the variables of the system (1, 3). If the operators $A^{(q)}$ are expanded into eigenoperators $A_p^{(q)}$ of the unperturbed Hamiltonian, it can be shown (1, 12) that evo-