NUCLEAR SPIN RELAXATION STUDIES IN MULTIPLE SPIN SYSTEMS

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ABSTRACT

Nuclear spin relaxation in multiple spin systems in diamagnetic liquids, studied by the techniques of (1) high-resolution nuclear magnetic double resonance and (2) T_1-measurements, is discussed.

The principle of the double resonance method along with features of strong and weak irradiation spectra and inhomogeneity effects are given. The information obtainable on relaxation mechanisms is presented, including a discussion of the isotropic random field model, its applicability and limitations in relation to intermolecular dipolar interactions. Scalar coupling with quadrupolar nuclei and symmetry features of relaxation effects are also considered.

T_1-measurements are discussed with emphasis on cross-relaxation effects, multiple exponential relaxation decays and their analysis. It is pointed out that even for systems dominated by a single exponential decay mode the dipolar relaxation rate is not usually a linear superposition of the intermolecular and intramolecular contributions.

1. INTRODUCTION

It has been generally recognized that the study of nuclear spin relaxation is a simple but powerful tool for probing the microdynamical behaviour in liquids since the relaxation parameters are often direct measures of various types of correlation times for fluctuations in molecular orientation, angular velocity, position and so on[1-6]. In practice, for liquids containing several spins per molecule the determination and analysis of the relaxation parameters are usually complicated, owing to, among other causes, the multiplicity and linewidth variations in the resonance spectra that arise from the chemical environments of the spins[7, 8] and the cross-relaxation effects and internal motions that arise from their geometrical arrangement[9-11]. In the past few years we have been engaged in the study of nuclear spin relaxation in multiple spin systems by high-resolution nuclear magnetic double resonance (NMDR) and the spin-echo methods, in an effort to disentangle some of the foregoing complexities. In this paper the significant results obtained in these studies are presented.

In Section II the principal features of NMDR spectra and the information that is obtained on the relaxation processes are described. T_1-measurements

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on multiple spin systems are considered with particular emphasis on cross-relaxation effects and multiple exponential decays in Section III, followed by a concluding discussion in Section IV.

In what follows the mathematical framework of the density matrix theory[8, 12, 13], which was often required for the full understanding of relaxation effects in double resonance, will not be introduced. The emphasis would be on the principal features and results, which may sometimes have been obscured by the theoretical detail that occurs in the analyses.

2. NMDR

A. Principal features

(i) *The method*: The basis of the NMDR method for relaxation studies is the following. The line positions, intensities and linewidths in the single resonance spectra of spin-1/2 nuclei in diamagnetic liquids do not normally contain any information on the spin relaxation processes. This information can be injected into the spectrum by selectively irradiating some transitions in the spectrum by a strong radiofrequency field which effectively competes with the relaxation processes. The extent of disturbance caused by a given strength of irradiation on a known single resonance spectrum is then an implicit measure of the relaxation parameters of the system[8].

The irradiating field in NMDR is capable of producing, in general, changes in intensities, linewidths as well as line positions of single resonance spectra, in addition to causing new transitions. All the transition frequencies in an NMDR spectrum can be derived by diagonalizing the spin Hamiltonian in a coordinate frame rotating at the angular frequency of the irradiating field, and are thus independent of the relaxation processes[14, 15]. The intensities and linewidths critically depend on the relaxation parameters and irradiation strengths. A comprehensive description of all the features of NMDR requires the use of the density matrix formulation, which we shall not describe. We merely note that in this formalism the NMDR spectrum, $S(\omega)$, is given by [8, 12]:

$$S(\omega) \propto \frac{\mathrm{d}}{\mathrm{d}t} \left[\mathrm{Tr}(\sum_i \gamma_i I_y(i)\sigma) \right] \tag{1}$$

where $I(i)$ and γ_i are the spin and gyromagnetic ratio of the ith nucleus and σ is the spin density matrix with an equation of motion[8, 12]:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = -i[\mathcal{H}(t), \sigma] - \Gamma(\sigma - \sigma_0) \tag{2}$$

in which $\mathcal{H}(t)$ is the total spin Hamiltonian including the chemical shifts, spin–spin coupling constants and the interactions of the spin system with the observing and irradiating radiofrequency fields, and $\Gamma(\sigma - \sigma_0)$ is the relaxation term the matrix elements of which can be conveniently written in the Redfield notation[13]. σ_0 is the equilibrium density matrix. The first term in equation (2) represents the 'spectrum' inclusive of the coherence effects due to the irradiating and observing fields. The second term encompasses the relaxation effects. The procedure for the analysis, therefore, consists of

obtaining a steady state solution of equation (2) for the irradiation conditions of the experiment with different chosen relaxation mechanisms for the calculation of $\Gamma(\sigma - \sigma_0)$. The theoretical spectrum for each set of relaxation parameters can be obtained from equation (1). A comparison with the experiment then allows a determination of the mechanism and parameters of relaxation.

(ii) *Weak and strong irradiation spectra*:—NMDR spectra obtained with strengths of irradiation, v_2, appreciably less than the linewidths, $(v_2 < (\Delta\omega)_{\alpha\alpha'})$ are referred to as weak irradiation spectra. Those with $v_2 > (\Delta\omega)_{\alpha\alpha'}$ are referred to as strong irradiation spectra. These two categories of NMDR spectra have their special experimental and theoretical features which should be noted[8, 16].

The weak irradiation spectra exhibit intensity changes with respect to single resonance with no observable effects on either transition frequencies or linewidths. The intensity changes can be qualitatively understood in terms of 'population-pumping' effects and can be analysed as a generalized form of 'nuclear Overhauser effect'[17]. The solution of equation (2) can be carried out in the laboratory frame in the single resonance basis. The identification and categorization of the relaxation matrix elements are thus straightforward and this allows some generalizations useful in identifying the relaxation mechanism (see Section 2. B(ii)). Furthermore, the intensity changes depend on the absolute values of the relaxation matrix elements[8, 16].

The strong irradiation spectra, on the other hand, exhibit all the effects mentioned in Section 2. A(i) Equation (2) should be solved in a coordinate frame rotating at the frequency of the irradiating field, in a basis that diagonalizes the corresponding stationary Hamiltonian. The calculation is considerably more complicated than the weak irradiation case and simple generalizations do not easily obtain. The intensities of the transitions depend only on the relative values of the relaxation matrix elements. However, the strong irradiation spectra provide considerably more experimental data than the weak irradiation spectra, which can be used to fit the relaxation parameters[16]. For very large strengths of irradiation 'inverted' transitions are observed in the spectra of strongly coupled spin systems as a result of 'coherence effects' in addition to the usual double resonance transitions[18-20].

There is one further aspect of strong irradiation spectra which should be noted, viz. the fact that the magnetic field inhomogeneity contributes different linewidths to different transitions, a feature that does not occur in single resonance. This arises from the circumstance that the double irradiation introduces an explicit dependence of the linewidth on the inhomogeneously broadened Larmor frequency of the irradiated nuclei through a factor that is different for different transitions. In some situations this can partly or fully cancel the normal inhomogeneity width, which leads to very sharp resonances[8, 16, 21, 22].

B. *Information on Relaxation Processes*

(i) *Isotropic random field model*.—The mechanisms known to mediate relaxation for spin-1/2 nuclei in diamagnetic liquids are[8, 12]:

1. Intermolecular dipolar interactions modulated by translational diffusion.

2. Intramolecular dipolar interactions modulated by molecular reorientation.

3. Spin–rotation interaction modulated by (a) angular velocity fluctuations and (b) molecular reorientation.

4. Anisotropic chemical shift modulated by molecular reorientation.

5. Scalar or dipolar coupling with a quadrupolar nucleus modulated by the rapid relaxation of the latter.

6. Scalar or dipolar coupling modulated by chemical exchange.

7. Interactions with paramagnetic impurities modulated by (a) molecular motion and (b) the rapid relaxation of the impurity.

The identification and separation of the contributions of these mechanisms in a given system is an important aspect of relaxation studies. In the double resonance method the explicit inclusion of these mechanisms in the theoretical calculation and a meaningful analysis of the spectra on that basis would be highly cumbersome if not virtually impossible. It was shown, however, that all the mechanisms except (2) and (4) can be well approximated by an isotropic randomly fluctuating magnetic field $\mathbf{H}_i(t)$ at the sites of the nuclei i[23, 24]. The interaction is written as

$$\mathscr{H}''(t) = -\sum_i \gamma_i I(i).\mathbf{H}_i(t) \tag{3}$$

with the isotropy given by

$$\langle | H_{xi}(t) |^2 \rangle_{av} = \langle | H_{yi}(t) |^2 \rangle_{av} = \langle | H_{zi}(t) |^2 \rangle_{av} = \frac{f_i}{3\gamma_i^2} \tag{4}$$

This model is basically 'phenomenological' and does not precisely correspond to any particular interaction. It is particularly convenient for computational purposes, as it is linear in the spin variables and possesses isotropy. The analysis of double resonance spectra is capable of yielding f_i and possible correlations C_{ij} of these random fields at different sites i and j defined by[16, 24]

$$C_{ij} = \frac{\langle H_{zi}(t) H_{zj}(t) \rangle_{av}}{[\langle | H_{zi}(t) |^2 \rangle_{av} \langle | H_{zj}(t) |^2 \rangle_{av}]^{\frac{1}{2}}} \tag{5}$$

These parameters f_i, C_{ij} can then be interpreted in terms of the mechanisms above.

The spin–rotation and anisotropic chemical shift mechanisms do not contribute significantly to proton relaxation at room temperature. Unless the experiments are explicitly aimed at studying the effect of paramagnetic impurities, the liquids used in relaxation studies by double resonance should be carefully degassed to reduce dissolved oxygen to levels insignificant for the purpose of relaxation. The sources of the isotropic random fields would then be confined to mechanisms (1), (5) and (6). Since mechanisms (5) and (6) are often identifiable by other features in the spectrum[20], mechanism (1) is usually the chief source for the random fields.

(*ii*) *Intermolecular and intramolecular dipolar interactions.*—Theoretical analyses of double resonance spectra are often performed in terms of intramolecular dipolar interactions and isotropic random fields where the primary

source of the latter is intermolecular dipolar interactions[16, 18, 20, 25]. It can be shown that in simple spin systems these two mechanisms can be clearly distinguished in terms of the intensity variations produced by the irradiation, e.g. in a strongly coupled two-spin system of the type AB with the transitions labelled $1 \to 3$, $2 \to 4$, $1 \to 2$, $3 \to 4$ (where $| 1 > = | 1/2, 1/2 \rangle$, $|2\rangle = | 1/2, -1/2 \rangle \cos \theta + | -1/2, 1/2 \rangle \sin \theta$, $|3\rangle = | -1/2, 1/2 \rangle \cos \theta - 1/2, -1/2 \rangle \sin \theta$, $|4\rangle = | -1/2, -1/2 \rangle$), and S_{ij}^0 and S_{ij}^d defined as the single and double resonance intensities of transition $i \to j$, when the line $2 \to 4$ is irradiated weakly the following relations obtain [25, 26]:

(a) if the relaxation mechanism is internal dipolar interaction,

$$3\frac{S_{13}^d}{S_{13}^0} + \frac{S_{34}^d}{S_{34}^0} = 4.0$$

(b) if the relaxation is by isotropic random fields with $f_A = f_B$ and $C_{AB} = 0$,

$$\frac{S_{13}^d}{S_{13}^0} + \frac{S_{12}^d}{S_{12}^0} = 2.0$$

(c) if the relaxation is by isotropic random fields with $f_A = f_B$ and $C_{AB} = 1.0$,

$$\frac{S_{13}^d}{S_{34}^d} = 1.0$$

Similar relations can be obtained for other transitions in the same spectrum, and it is, in general, possible to choose simple functions of this type for most simple spin systems[25, 26].

While the foregoing illustrates the point that the double resonance spectra may, in some cases, readily distinguish between the two mechanisms, there is one limitation of the description of intermolecular dipolar interactions by an isotropic random field which should be noted. It will be shown in Section 3. A that if the spin system contains several groups of spins all of which do not experience the same strength of intramolecular dipolar interactions, the relaxation decays have multiple exponential character[9, 10]. This arises from the very nature of dipolar interactions[12]. The isotropic random field model does not exhibit this feature owing to the circumstance that in approximating the mechanism by an interaction linear in the spin variables the cross-relaxation effects leading to multiple exponentials are implicitly ignored[27].

The above inadequacy of the model has been examined further in one case. A double resonance study of the AB system in 2-chloroacrylonitrile showed that the relaxation is dominated by the random field mechanism representing the intermolecular dipolar interactions[25, 26]. To verify this conclusion the spectra were reanalysed by explicitly considering the intermolecular dipolar interactions[27]. In order to do this it is necessary to enlarge the dimension of the problem, since these interactions require at least two molecules at a time. In fact this is the aspect that forbids a general treatment of this relaxation mechanism[28]. For 2-chloroacrylonitrile binary collision complexes with 16 spin-energy levels were considered. By making a few reasonable approximations that make the problem tractable the double resonance spectra were computed for different fractional contributions of the intermolecular dipolar

interactions. The results show that this mechanism accounts for over 70% of the total relaxation in this molecule, in agreement with the results obtained on the basis of the random field model[27].

The above discussion indicates that the isotropic random field model provides an adequate description of the intermolecular dipolar interactions for the two spin system. It should, however, be used with caution for larger spin systems in which the factors leading to multiple relaxation decays quite easily obtain.

(*iii*) *Scalar coupling with quadrupolar nuclei.*— The resonances of spin–1/2 nuclei scalar coupled to a quadrupolar nucleus in the molecule often exhibit a broadening, since the multiplet structure due to this scalar coupling is 'washed out' by the rapid quadrupolar relaxation. Under the conditions that normally obtain in single resonance a study of this broadening might lead to a determination of the scalar coupling constants with the quadrupolar nucleus. A double resonance study on such spin systems is, however, capable of yielding magnitudes as well as relative signs of the coupling constants with the quadrupolar nucleus[20, 24, 26]. This is due to the fact that double resonance spectra depend, in general, on a variety of relaxation matrix elements besides those that are involved in linewidths[20]. The relative signs are unlikely to be available in other methods.

(*iv*) *Symmetry features.*—The symmetry characteristics of frequencies in strong irradiation double resonance spectra of weakly coupled spin systems were studied earlier[29]. These spectra also exhibit symmetry features in the relaxation effects with respect to frequency offset of irradiation and with respect to intensity and linewidth changes produced on either side of the centre of a spectrum. Some significant generalizations regarding the properties of the relaxation mechanisms can be derived for such systems by exploiting the fact that the spin states involved in these weakly coupled systems can be related by spin-inversion symmetry[30]. For example, the following theorems obtain when all the relaxation matrix elements possess spin-inversion symmetry in a weakly coupled spin system $A \cdot\cdot M \cdot\cdot X$ in which irradiation is done on the X-spins with frequency offset Δ: (For an accurate description of these symmetry effects see reference 30.)

(1) The double resonance spectra of A(or M) spins corresponding to frequency offsets $(+\Delta)$ and $(-\Delta)$ are mirror images of each other with respect to the centre $(\Delta = 0)$.

(2) The intensity changes produced by double irradiation on two transitions symmetric with respect to the centre of the A(or M) spectrum are equal in magnitude and opposite in sign.

Generalizations of this type are of considerable value in deducing the nature of the relaxation processes operative in the spin system.

3. T_1-MEASUREMENTS

A. *Cross-relaxation effects*

We now turn to the discussion of cross-relaxation effects in the T_1-measure-

ments on multi-spin systems which were mentioned in Section II. B (ii). These arise from the basic fact that the equations of motion for the z-components of magnetization of two spins due to their mutual dipolar interaction are coupled[12, 31]. For a liquid system containing two groups of spins A and X the equations of motion for the z-components of the magnetization of the A- and X-spins are given by[9, 10]

$$-\frac{d}{dt} M_z(A) = k_A(M_z(A) - M_0(A))$$

$$+ k_c[2f_X(M_z(A) - M_0(A)) + f_A(M_z(X) - M_0(X))] \qquad (6)$$

$$-\frac{d}{dt} M_z(X) = k_X(M_z(X) - M_0(X))$$

$$+ k_c[2f_A(M_z(X) - M_0(X)) + f_X(M_z(A) - M_0(A))]$$

where k_A, k_X and k_c are, respectively, the relaxation rates due to interactions within group A, within group X and between groups A and X; and f_i and $M_0(i)$ are the fractional numbers of spins and equilibrium magnetizations, respectively, of the group $i(= A, X)$. The solutions for $(M_z(A) - M_0(A))$, $(M_z(X) - M_0(X))$ or $(M_z - M_0) = (M_z(A) + M_z(X)) - (M_0(A) + M_0(X))$ are all of the type[9, 10]

$$a_+ e^{-k_+ t} + a_- e^{-k_- t} \qquad (7)$$

where $k_\pm = (1/2)(k_A + k_X + k_c \pm R)$
and $R = + \{[(k_A - k_X) + 2k_c(f_A - f_X)]^2 + 2f_A f_X k_c^2\}^{\frac{1}{2}}$
The coefficients $a_\pm$ depend on the initial conditions of the experiment. Note that k_A, k_X and k_c all involve both intermolecular and intramolecular interactions.

Equations (6) and (7) are straightforward consequences of the nature of dipolar interaction. These imply that in a molecule containing various groups of spins, except in the circumstance that the spins in every group experience intramolecular dipolar interactions of the same strength, relaxation decays of individual groups or the total magnetization contain, in general, multiple exponentials[32].

B. *Analysis of the observed time constants*

Depending on the particular spin system, the relaxation parameters involved in equation (7) and the experimental precision, it is possible to observe only a single time constant in the relaxation decays of either individual groups or the total spin system. It should, however, be pointed out that it is still appropriate to analyse the dipolar contribution to relaxation rate through equations of the type of equation (7)[32–35]. The two examples given below would illustrate this point:

(1) In the three-proton (AX_2) system of 1,1,2-trichloroethane adiabatic rapid passage experiments on the individual A and X resonance resulted in single exponentials with time constants 16.8 s and 7.2 s, respectively[10]. It would be erroneous to interpret these as the relaxation times of the individual

groups A and X—this would be correct if $k_c = 0$, i.e. if there is no cross-relaxation—but these two time constants represent k_+ in equation (7). This interpretation is confirmed by performing two other experiments that measure (a) the over-all relaxation decay by the spin-echo method and (b) the cross-relaxation rate by performing an adiabatic rapid passage on X while observing A[10].

(2) The four protons in the thiophene molecule fall into two equivalent groups, one of which experiences intramolecular dipolar interactions nearly twice as strong as the other. However, relaxation decays of the total magnetization show one time constant rather than two[32, 33]. The analysis of the dipolar contribution on the basis of equation (7) shows that a_- is too small to be observable above the experimental error. Nevertheless it must be noted that the dipolar part of k_+, which is the observed relaxation rate, is not a linear superposition of the intermolecular and intramolecular relaxation rates[32, 33] (see equation 7).

Thus cross-relaxation between different groups in multi-spin systems not only gives rise to multiple exponentials but also causes a non-linear super-position of intermolecular and intramolecular dipolar relaxation rates even when the decays are observed to be single exponentials[32–35].

4. CONCLUSION

The foregoing is an attempt to summarize some of the important aspects of spin relaxation in multi-spin systems in diamagnetic liquids. The information that can be obtained through these studies is useful and significant, although the analysis required is somewhat intricate. One merit of the double resonance method is the possibility of determining the relaxation parameters by working on a single set of external parameters such as temperature, concentration, etc. This is a clear advantage for cases, such as the biologically important systems, which allow limited flexibility in the choice of the external conditions[36, 37]. It may also be noted that in conventional systems considerably more detailed relaxation information can be obtained by studying double resonance at different temperatures, magnetic fields, concentrations, and so on. Furthermore, the rapidly developing technology of n.m.r. instrumentation in recent years through the introduction of Fourier transform methods[38, 39] provides possibilities for the preparation and observation of spin systems under a variety of steady states and dynamical conditions which should enhance the range and depth of relaxation studies in liquids.

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