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WEAK PERTURBING RADIO-FREQUENCY FIELD EFFECTS IN NUCLEAR MAGNETIC DOUBLE RESONANCE. IV.

Relaxation transition probabilities of a strongly coupled two-spin system

Э. ЛИППМАА, Ю. ПУСКАР. ЭФФЕКТЫ СЛАБОГО ВОЗМУЩАЮЩЕГО РАДИОЧАСТОТНОГО ПОЛЯ В ЯДЕРНОМ МАГНИТНОМ ДВОЙНОМ РЕЗОНАНСЕ. IV. ВЕРОЯТНОСТИ РЕЛАКСАЦИОННЫХ ПЕРЕХОДОВ СИЛЬНО СВЯЗАННОЙ ДВУСПИНОВОЙ СИСТЕМЫ

E. LIPPMAA, J. PUSKAR. NÕRGA RAADIOSAGEDUSLIKU HÄIREVÄLJA EFEKTID TUUMA MAGNETILISES TOPELTRESONANTSIS. IV. TIHEDALT SEOTUD KAHESPINILISE SÜSTEEMI RELAKSATSIOONIVÄLJAKUTE TÕENAOSUSED

Most relaxation studies have been performed by pulse or saturation methods that have only limited applicability for the study of systems with several unequal spins [20]. Since little is known about the relative contributions of various relaxation mechanisms and probabilities of relaxation transitions which, however, can provide much unique information about molecular motion and allow to predict line intensity changes in double resonance experiments, several attempts have been undertaken to determine these. All methods use double resonance for this purpose and measure either dynamic [11] or steady-state Overhauser effects [16, 17, 19], or both [5-10, 12]. To simplify the very complicated problem of interpreting of experimental results, drastic assumptions are usually made; for example, instead of measuring the actual transition probabilities, only the relative contributions are estimated by fitting the observed spectrum with a combination of the mechanisms [11, 16, 19]. It has always been assumed that the condition of extreme narrowing is exactly fulfilled, even at very low temperatures, and that hydrogen nuclei do not relax by spin-rotation [18] or shift anisotropy mechanisms [15]. In addition to this, the theory of Solomon [5, 6] excludes all intermolecular interactions. The interactions between like molecules are not taken into account properly by Noggle [11]. Even the very complete theory of Mackor and MacLean [7-10] has no place for external dipolar interactions of the $AA'BB'$ system, either with halogen nuclei in the same molecule or with the possible external random fields of obscure origin [13], or those caused by impurities. Only Hoffman and Forsen [12] have taken into account practically all relaxation mechanisms. Most methods allow to differentiate between the relaxation by external random fields and by dipole-dipole interaction of the two spins under consideration. The use of difference magnetization [7-10] allows such intramolecular interaction to be separated from the intermolecular one. In many cases the technique is applicable to AX systems only [5-10, 12], and a large spin-spin coupling constant may be necessary as well [7-10]. The measurement of dynamic Overhauser effects is only possible if the overall relaxa-

tion time of the sample is large. The stationary methods are free from this difficulty [16-18], but since split lines were avoided [11, 19] a full analysis was not possible [19]. The methods that depend upon the use of moderately strong [17] or very strong [16] perturbing *rf* fields are difficult to apply and to interpret since the relaxation matrix must be re-evaluated in every particular case and the signal to noise ratio is low.

Since a universal method that would allow the actual transition probabilities to be measured without any *a priori* assumptions is clearly needed, we have investigated the possibilities of measuring all the stationary Overhauser effects, even for the split lines, and using the Kirchhoff laws of Bloch [1] to calculate the transition probabilities. Our method is applicable to all compounds with sufficiently intense spectral lines that allow the tickling condition (2) to be satisfied. The demands for spectrometer performance and experimental technique are very high, but can just be met.

Experimental

The changes of line intensities in double resonance spectra (steady-state nuclear Overhauser effects O_{pr}^{st}) [2, 3, 19] are given by

$$(I_{pr}^0 - I_{pr}^{st}) / I_{pr}^0 = T_{pr1} / T_{st1} = O_{pr}^{st}, \quad (1)$$

where I_{pr}^0 is the intensity of a spectral line *pr* in a monoresonance spectrum as measured with a very weak *rf* field that causes no saturation and I_{pr}^{st} is the intensity of the same line, measured with some other line *st* saturated, but otherwise under identical conditions. The quantities $T_{pr1} = T_p - T_r$ have the dimension of time but are not relaxation times [1]. It has been shown in earlier communications [2] that the relation (1) holds both for split and unsplit lines as long as individual spectral lines can be saturated so that the intensity changes achieve their asymptotic values without violating the condition for a weak perturbing *rf* field

$$1/T_2^* \ll \gamma H_2 \ll |(p-r) - (s-t)|. \quad (2)$$

The line intensities are proportional to the diagonal elements of the deviation matrix χ [1] and both χ and T as well as the Overhauser effects can be calculated from corresponding systems of equations if all relaxation transition probabilities W are known. The systems of equations are similar to Kirchhoff laws and if some line *st* is saturated we have for quantities T [2, 3]:

$$\begin{aligned} \sum_r W_{sr} T_{rs1} &= 1; & \sum_r W_{tr} T_{rt1} &= -1; \\ \sum_r W_{pr} T_{rp1} &= 0 \text{ if } p \neq s, t; & \sum_r T_r &= 0. \end{aligned} \quad (3)$$

Let us consider a strongly coupled two-spin system *AB* with four energy levels $a < b < c < d$ with eigenfunctions:

$$\begin{aligned} |a\rangle &= \alpha\alpha; & |b\rangle &= \beta\alpha \sin \Theta + \alpha\beta \cos \Theta; \\ |c\rangle &= \beta\alpha \cos \Theta - \alpha\beta \sin \Theta; & |d\rangle &= \beta\beta, \end{aligned} \quad (4)$$

where $\sin 2\Theta = J_{AB}(\delta_{AB}^2 + J_{AB}^2)^{-1/2}$. If one uses the spin Hamiltonian as given in [3], then the resonance frequencies are in the order $dc < ba < db < ca$ and *dc*, *ca* correspond to the external, and *ba*, *db* to the internal lines

with intensities proportional to $1 - \sin 2\theta$ and $1 + \sin 2\theta$. The relation of any spectral line to the saturated line in the energy level diagram can be denoted as is usual in double resonance, that is, progressive, regressive [14] and non-connected transitions are marked with subscripts 2; 0 and 1. It follows then from the "Kirchhoff equations" (3) that the Overhauser effects are not independent, and one has for each of the four possible experiments [3]

$$O_1^{st} + O_0^{st} - O_2^{st} = 1, \quad (5)$$

and also

$$O_{ca}^{dc} O_{ba}^{ca} O_{dc}^{ba} = O_{ba}^{dc} O_{ca}^{ba} O_{dc}^{ca};$$

$$O_{ca}^{dc} O_{db}^{ca} O_{dc}^{db} = O_{db}^{dc} O_{ca}^{db} O_{dc}^{ca}; \quad O_{db}^{dc} O_{ba}^{db} O_{dc}^{ba} = O_{ba}^{dc} O_{db}^{ba} O_{dc}^{db}. \quad (6)$$

If W_{cb} is set equal to 1, we have

$$W_{dc} = (O_{ca}^{ba} O_{ba}^{db} - O_{ca}^{db}) (O_{dc}^{ba} O_{ca}^{db} - O_{ca}^{ba} O_{dc}^{db})^{-1}, \quad (7)$$

and similar expressions for all the other transition probabilities. The system of equations (3) is overdetermined, since altogether 12 Overhauser effects can be measured, but there are only 5 independent relative transition probabilities. For example, W_{dc} could be calculated from other Overhauser effects as well, and since the denominator of (7) is in all cases a small difference of large quantities, the inevitable measurement errors lead to very large errors in W and to very different results. It is much more practical to solve the system of equations (3) for W on a computer as a whole, using a program that gives equal importance to all Overhauser effects.

The transition probabilities themselves give no very clear picture about the relative importance of various possible relaxation mechanisms. If one wants to interpret the results in those terms, then it is logical to divide the probabilities into three parts:

$$W = W' + W'' + W'''. \quad (8)$$

The first part corresponds to intra- and intermolecular dipole-dipole interactions between the two spins A and B , the second includes such interactions between spins A and A or B and B as well as spin-rotation interaction and the third group includes dipolar interactions with external random fields and other magnetic nuclei, especially halogen atoms, in the same molecule. The random fields may be spatially correlated ($C = 1$) or uncorrelated ($C = 0$) [11, 13, 16]. In this particular case there is no need to consider relaxation effects caused by chemical shift anisotropy and chemical exchange processes.

$$W'_0 = W'_{cb} = 0.667 K_1 \cos^2 2\theta; \quad W'_2 = W'_{da} = 4K_1;$$

$$W'_1 = W'_{dc} = W'_{ca} = K_1(1 - \sin 2\theta); \quad W'_1 = W'_{db} = W'_{ba} = K_1(1 + \sin 2\theta);$$

$$W''_0 = 0; \quad W''_2 = 0; \quad W''_1 = W''_{dc} = W''_{ca} = K_2(1 - \sin 2\theta);$$

$$W''_1 = W''_{db} = W''_{ba} = K_2(1 + \sin 2\theta);$$

$$W'''_0 = W'''_{cb} = K_3(1 - C) \sin^2 2\theta; \quad W'''_2 = 0;$$

$$W'''_1 = W'''_{dc} = W'''_{ca} = K_3(1 - C \sin 2\theta); \quad W'''_1 = W'''_{db} = W'''_{ba} = K_3(1 + C \sin 2\theta).$$

The Overhauser effects were measured with a very weak measuring rf field that caused no saturation and with various values for the perturbing rf field up to saturation of the perturbed line. Peak values were measured for the unsplit lines, but split lines were integrated, using a multichannel analyser with digital printout [4] and special linear circuits (especially phase detectors) in the spectrometer [21]. The asymptotic values for line intensities were found by a least-squares fit, using the linear dependence of $(I_{pr}^{st})^{-1}$ on $(\gamma H_2)^{-2}$ for this purpose. The first sample was a nearly saturated 60 per cent solution of transchloroacrylic acid (TCAA) in hexadeuteroacetone, the second an 18 per cent solution of specially purified TCAA in a 4:1 by weight mixture of carbon disulphide and hexadeuteroacetone. Samples were degassed by bubbling pure argon gas through them. To avoid sample contamination with proton-rich compounds, no internal TMS standard was used and the spin stabilizer worked with a separate probe. All measurements were made at 40 Mc and room temperature $27 \pm 2^\circ \text{C}$. The internal chemical shift between the olefinic protons was 49.0 cps and the spin-spin coupling constant $J_{AB} = +13.8$ cps, $\sin 2\theta = 0.273$. The total relaxation time $T_T = 2W_{da} + W_{ca} + W_{ba}$ [1], as measured for all four lines under conditions of low resolution with adiabatic fast passage, was $T_T = 4.3 \pm 0.5$ sec for the first and $T_T = 30 \pm 1$ sec for the second sample.

Results and discussion

All possible Overhauser effects were measured for the first sample.

When the external lines of the spectrum were saturated, the following asymptotic values for the Overhauser effects were measured:

$$\begin{aligned} O_{db}^{dc} &= +0.266 (+0.285); & O_{ba}^{ca} &= +0.256 (+0.278) \\ O_{ba}^{dc} &= +0.259 (+0.262); & O_{db}^{ca} &= +0.254 (+0.255) \\ O_{ca}^{dc} &= -0.457 (-0.453); & O_{dc}^{ca} &= -0.450 (-0.467). \end{aligned}$$

The irradiation of the internal lines gave the following results:

$$\begin{aligned} O_{ca}^{ba} &= +0.329 (+0.365); & O_{dc}^{db} &= +0.359 (+0.385) \\ O_{dc}^{ba} &= +0.333 (+0.354); & O_{ca}^{db} &= +0.327 (+0.334) \\ O_{db}^{ba} &= -0.251 (-0.281); & O_{ba}^{db} &= -0.284 (-0.280). \end{aligned}$$

The sum and multiplication rules are reasonably well fulfilled, even though the sample was a concentrated solution.

$$\begin{aligned} O_{db}^{dc} + O_{ba}^{dc} - O_{ca}^{dc} &= 0.982; & O_{ba}^{ca} + O_{db}^{ca} - O_{dc}^{ca} &= 0.960 \\ O_{ca}^{ba} + O_{dc}^{ba} - O_{db}^{ba} &= 0.913; & O_{dc}^{db} + O_{ca}^{db} - O_{ba}^{db} &= 0.970 \\ O_{ca}^{dc} O_{ba}^{ca} O_{dc}^{ba} (O_{ba}^{dc} O_{ca}^{ba} O_{dc}^{ca})^{-1} &= 1.02 \\ O_{db}^{dc} O_{ba}^{db} O_{dc}^{ba} (O_{ba}^{dc} O_{db}^{ba} O_{dc}^{db})^{-1} &= 1.08 \\ O_{ca}^{dc} O_{db}^{ca} O_{dc}^{db} (O_{db}^{dc} O_{ca}^{db} O_{dc}^{ca})^{-1} &= 1.06. \end{aligned}$$

Symmetrical experiments give fairly equal results, for example $O_{ca}^{dc} \cong O_{dc}^{ca}$ and it is immediately clear [1] that the transition probabilities

for progressive transition pairs [14] dc , ca and db , ba are nearly equal, but since $O_{db}^{dc} \neq O_{dc}^{db}$ the regressive transition pairs have unequal transition probabilities. The large positive values of O_{ba}^{dc} ; O_{dc}^{ba} ; O_{db}^{ca} and O_{ca}^{db} show that dipole-dipole interaction between the A and B spins, either intra- or intermolecular, cannot be a dominant relaxation mechanism.

The transition probabilities were calculated by solving the system of equations (3) on an electronic computer. Best fit with experiment was achieved with the following values for the relative transition probabilities: $W_{cb} = 1$; $W_{da} = 2.4$; $W_{dc} = 19.8$; $W_{ca} = 20.9$; $W_{db} = 31.1$; $W_{ba} = 31.1$. These numbers were used to calculate the values of Overhauser effects that are given alongside with the experimental values for comparison. The mean differences are only ± 0.01 (3 per cent relative) for unsplit lines and ± 0.017 (5 per cent relative) for split lines.

To give some idea about the active relaxation mechanisms, the optimum values for partition coefficients were also calculated. The results are $K_1 = 0.02$; $K_2 = 0.10$; $K_3 = 0.88$ and $C = 0.8$. The total relative transition probabilities in this case are $W_0 = 1$; $W_2 = 2.1$; $W_{1A} = 19.8$; $W_{1B} = 31.1$. The closeness of both sets of values shows that the division was done sensibly. The large value for K_3 indicates that relaxation by external spatially strongly correlated magnetic fields predominates. This type of relaxation can partly be caused by paramagnetic impurities. But even after a total removal of such possible impurities from a dilute water solution of TCAA with ion exchangers (Amberlite IRC-50 in acid form, regenerated with hydrochloric acid that had itself been freed from $FeCl_4$ and similar ions with Zerolit FF anion exchanger), and using a dilute solution in a much less magnetic solvent, the interaction with external random fields remained the prevalent mechanism as is apparent from the Overhauser effect $O_{ba}^{dc} \cong +0.20$ and a not very long overall relaxation time for the second sample. Whether the coefficient $K_2 = 0.10$ is caused by intermolecular interactions between similar spins $A-A$ and $B-B$ and chlorine nuclei or by spin-rotation interaction [18], is not clear and the question could be solved only by the study of temperature effects. The contribution of intramolecular dipole-dipole interaction between dissimilar spins A and B is quite unimportant in both cases. These results are in accordance with previous results on thiophene derivatives, where the relaxation by external random fields was also very important or prevalent at room temperature [11, 16, 17]. The near equality of $W_{dc} \cong W_{ca}$ and $W_{db} \cong W_{ba}$ shows that relaxation by the anisotropy of chemical shifts is practically absent. This and the high value of the correlation constant C make significant cross terms improbable. There is also no possibility for a scalar relaxation mechanism for the olefinic protons that do not take part in exchange reactions and have zero spin-spin coupling to the carboxyl protons that do exchange between themselves and also, although slowly, with the deuterioacetone deuterons.

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