Experimental Effects of R.F. Irradiation on N.M.R. Lines in Solids Dynamics of the Equilibrium Establishment

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The rates of dipolar and Zeeman energy creation under detuned irradiation are measured as function of the distance to resonance in isolated spin systems and in systems with known coupling to the lattice.

The experimental results are compared with the Provotorov theory and, with some restrictions for the long correlation time region, the agreement with theory is found to be excellent.

I. Introduction

An important step in the understanding of the behaviour of a rigid spin system under r.f. irradiation was made with the work of PROVOTOROV [1] in 1962. In this description the spin system is characterised by two invariants of the motion namely the Zeeman energy and the secular part of the dipolar energy. To each of these reservoirs is associated a temperature, T_Z and T_D *, respectively, and the absorption of non resonant photons modifies both of them introducing thus changes in the line intensity as well as in the line shape. These results are of course in strong contradiction with the early B.P.P. [2] theory where the role of the dipolar subsystem was not recognized and where the spin assembly was mainly characterised by the populations of its Zeeman levels.

Little work has been done up to now in order to get quantitative checks on the Provotorov results. In a former paper [3] we have studied the steady state of both Zeeman and dipolar energies on a nuclear spin system submitted to r.f. irradiation. The complete equilibrium with respect to the r.f. field and to the lattice was there examined without any attention to the dynamics of the process. In this paper, on the contrary, we describe a few experiments where the way of the equilibrium approach is checked. The results are compared with the Provotorov theory and, in general, excellent agreement is obtained except in the region of long correlation times for the spin-lattice relaxation. In this region the theory follows the experimental behaviour only for H_1 fields much smaller than those considered by Provotorov ($H_1 \ll H_L$), a fact already mentioned in Ref. [3].

In a first experiment the rate of dipolar energy creation under r.f. irradiation is measured as a function of Δ. The field H_1 is large so that an equilibrium with respect to the irradiation is reached in a time short compared to the spin-lattice relaxation times. This experiment is very similar to a recent investigation [4] concerning the rate of saturation establishment in solids.

Secondly, we have measured the amplitude of the dipolar signal as a function of the irradiation time for some definite H_1 and Δ values. H_1 is such that the associated transition probability is of the same order as $1/T_{1Z}$ or $1/T_{1D}$.

Finally, in the region of long correlation times, the rate of approach of the Zeeman energy to its equilibrium is presented as a function of Δ and for several H_1 values.

The various parameters, namely the Zeeman and dipolar relaxation times, the unsaturated line shape, needed for the interpretation of the experiments were also experimentally determined. The spins used for this investigations are those of the proton nuclei in polycrystalline benzene. The experimental technique used throughout the work is essentially the same as that used in the former paper [3], and we will not describe it again.

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* In this work, the symbols used are the same as in Ref. [3] and the reader is referred to that paper for their exact meaning.

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II. Rate of Dipolar Energy Creation by r.f. Irradiation

A. The Lattice is Neglected. Short r.f. Pulses

According to the early B.P.P. theory, the change in Zeeman energy induced by a r.f. irradiation, and in the absence of spin lattice relaxation, is given by:

$$\mathrm{d}E_Z/\mathrm{d}t = -\omega_1^2 \pi f(\omega)\, E_Z \tag{1}$$

the solution of which goes to zero exponentially with a characteristic time

$$\tau_0(\omega) = 1/\omega_1^2 \pi f(\omega)\,. \tag{2}$$

Such a solution in which the Δ dependence is contained in the shape function, $f(\omega)$, and where the behaviour of the dipolar system is omitted, is only valid in the center of the line.

However, absorption of a non resonant photon, $h\nu$, not only changes the Zeeman energy by an amount $h\nu_0$ but also the dipolar energy by a quantity $h\Delta$.

As a consequence of this fact the Zeeman susceptibility in general does not approach zero under irradiation and Eq. (1) has to be replaced by the couple of relations:

$$\frac{\mathrm{d}E_Z}{\mathrm{d}t} = -\frac{1}{\tau_0(\omega)}\left(E_Z + \frac{\Delta \nu_0}{\nu_L^2} E_D\right) \tag{3 a}$$

and

$$\frac{\mathrm{d}E_D}{\mathrm{d}t} = -\frac{1}{\tau_0(\omega)}\left(\frac{\Delta}{\nu_0} E_Z + \frac{\Delta^2}{\nu_L^2} E_D\right) \tag{3 b}$$

showing that both energies reach their equilibrium values with a characteristic time:

$$\frac{1}{\tau(\omega)} = \frac{1}{\tau_0(\omega)}\left(1 + \frac{\Delta^2}{\nu_L^2}\right). \tag{4}$$

Figure 1 represents an experimental plot of the quantity $\tau(\omega)/\tau_0(\omega_0)$ against Δ^2 as measured from the rate of creation of dipolar signal under irradiation. The solid line is the theoretical prediction given by Equation (4). The shape function $f(\omega)$ was assumed to be gaussian, as confirmed by the free decay, with a second moment

$$\langle \Delta\nu^2 \rangle^{1/2} = 4.58\ \mathrm{kc/s}\,.$$

The quantity $\tau_0(\omega_0)$ was directly calculated from Eq. (2) with a careful calibration of the H_1 field [3]. Furthermore this field was chosen large enough so that al the measured rates were at least twenty times faster than both spin lattice relaxation times:

$$\tau(\omega_0) = 7\ \mathrm{ms},\quad T_{1D} = 240\ \mathrm{ms},\quad T_{1Z} = 745\ \mathrm{ms}.$$

Agreement with theory is excellent and the poor sensitivity for $\Delta > 10$ kc easily justifies the small deviation observed.

B. Effect of the Lattice. Long r.f. Pulses

In order to describe the combined effect of irradiation and spin-lattice relaxation the Zeeman and dipolar relaxing terms are simply added in Eq. (3). A new set of relations is obtained:

$$\frac{\mathrm{d}E_Z}{\mathrm{d}t} = -\frac{1}{\tau_0(\omega)}\left(E_Z + \frac{\Delta\nu_0}{\nu_L^2} E_D\right) - \frac{1}{T_{1Z}}\,(E_Z - E_0)\,, \tag{5 a}$$

$$\frac{\mathrm{d}E_D}{\mathrm{d}t} = \frac{-1}{\tau_0(\omega)}\left(\frac{\Delta}{\nu_0} E_Z + \frac{\Delta^2}{\nu_L^2} E_D\right) - \frac{1}{T_{1D}} E_D \tag{5 b}$$

where the dipolar energy in complete equilibrium has been omitted.

Such a linear superposition is, however, only valid when relaxation of the Zeeman and dipolar energies takes place independently from one another and from all other energies. It is also assumed that the H_1 field is small, $\omega_1 \tau_c \ll 1$ so that higher order terms containing the mixed effects of relaxation and irradiation can be neglected. Solving Eq. (5) for E_D we obtain:

$$E_D = \left[\alpha_2 E_D^\infty - \frac{\Delta}{\nu_0 \tau_0(\omega)} E_0\right] \exp\{\alpha_1 t\}/[\alpha_1 - \alpha_2] + \left[\frac{\Delta}{\nu_0 \tau_0(\omega)} E_0 - \alpha_1 E_D^\infty\right] \exp\{\alpha_2 t\}/[\alpha_1 - \alpha_2] + E_D^\infty \tag{6}$$

where E_D^∞ for infinite irradiation time is given by:

$$E_D^\infty = -E_0 \frac{\Delta}{\nu_0} \Big/ \left(\frac{T_{1Z}}{T_{1D}} + \frac{\Delta^2}{\nu_L^2} + \frac{\tau_0(\omega)}{T_{1D}}\right)$$

and α_1, α_2 are the roots of the characteristic equation:

$$2\,\alpha_{1,2} = -\frac{1}{\tau(\omega)} - \left(\frac{1}{T_{1Z}} + \frac{1}{T_{1D}}\right) \pm \left[\left(\frac{1}{\tau(\omega)}\right)^2 + \left(\frac{1}{T_{1Z}} - \frac{1}{T_{1D}}\right)^2 + \frac{2}{\tau_0(\omega)}\left(\frac{1}{T_{1Z}} - \frac{1}{T_{1D}}\right)\left(1 - \frac{\Delta^2}{\nu_L^2}\right)\right]^{1/2}. \tag{7}$$

In Figs. 2 and 3 we have plotted our experimental results for the quantity E_D as a function of the irradiation time t for several values of Δ and H_1. For short times, the fast increase of E_D is mainly due to the effect of the irradiation and the following slow decrease to the action of spin lattice interactions.

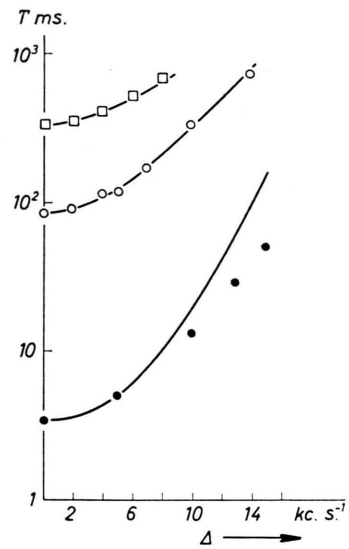

Fig. 1.

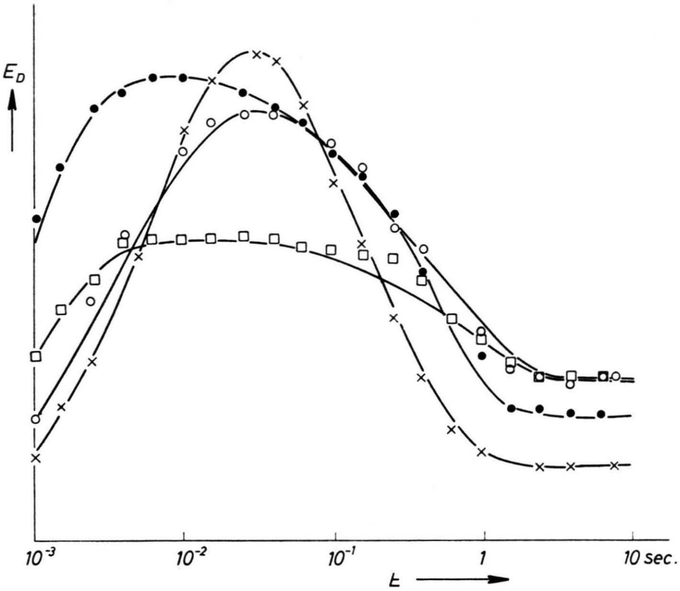

Fig. 3.

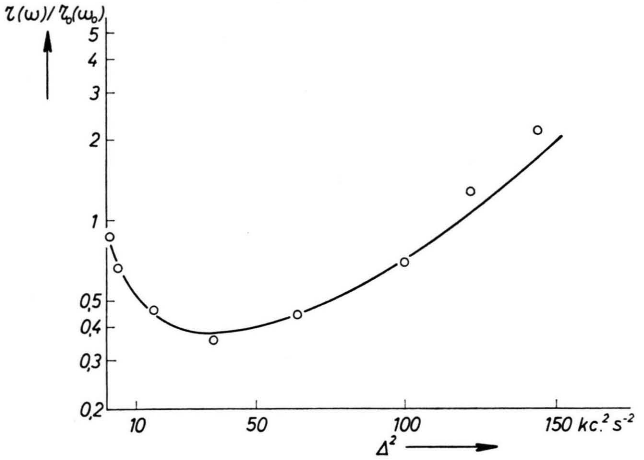

Fig. 2.

Fig. 1. Characteristic time for dipolar energy creation, $\tau(\omega)/\tau_0(\omega)$, under short detuned irradiations as function of Δ^2: ($T=223$ °K, $\langle\Delta\nu^2\rangle^{\frac{1}{2}}=4.58$ kc/s).

Fig. 2. Dipolar energy as function of the irradiation time for several H_1 and Δ values (relative units) ($T=248$ °K, $T_{1Z}=1425$ ms, $T_{1D}=144$ ms, $\langle\Delta\nu^2\rangle^{\frac{1}{2}}=4.58$ kc/s).
×: $H_1=0.1$ G, $\Delta=2$ kc/s;
○: $H_1=0.1$ G, $\Delta=6$ kc/s;
●: $H_1=0.2$ G, $\Delta=4$ kc/s;
□: $H_1=0.2$ G, $\Delta=8$ kc/s.

Fig. 3. Characteristic time of the Zeeman equilibrium approach for long detuned irradiation as function of Δ for three H_1 values ($T=126°$, $T_{1Z}=1.1$ s, $T_{1D}=0.2$ ms, $\langle\Delta\nu^2\rangle^{\frac{1}{2}}=5.7$ kc/s). □: $H_1=8$ mG. ○: $H_1=20$ mG. ●: $H_1=104$ mG.

The solid curves are the theoretical interpretations with Eq. (6). Again here, the line shape was taken as gaussian with a second moment

$$\langle\Delta\nu^2\rangle^{1/2}=4.58 \text{ kc/s}.$$

The temperature is 248 °K corresponding to

$$T_{1Z}=1425 \text{ ms} \quad \text{and} \quad T_{1D}=144 \text{ ms}.$$

Agreement with theory is excellent.

III. Rate of Approach of the Zeeman Energy to its Equilibrium Under Weak Irradiation

These experiments were performed in the region of long correlation times. The temperature is 126 °K and the ratio of relaxation times T_{1Z}/T_{1D} is of the order of 5000.

Because of the large T_{1Z}/T_{1D} ratio, it is easy to show that the solution of Eqs. (5) for E_Z is very well approximated by only one exponential i. e. a single characteristic time.

In Fig. 3 this characteristic time T is plotted as a function of Δ for three values of the H_1 field, $H_1 = 8$, 20, and 104 mG. The solid curves are the interpretation with Eqs. (5). Agreement with theory is thus excellent for the two small H_1 values. However, rather large deviations from the Provotorov prediction are already observed for the $H_1 = 104$ mG curve, a surprising result since the second moment of the line at the temperature of the experiment is still much larger compared to H_1 ($\langle \Delta H^2 \rangle^{1/2} = 1.35$ G).

We think that the reason of these deviations can be qualitatively interpreted as follows: It is assumed in the Provotorov work that during the relaxation process the magnetization is kept in z direction rather than along the effective field. In the case of large H_1 values (but still small compared to H_L) the solution of Eqs. (5) shows first a very fast evolution followed by a slower approach to equilibrium given by the characteristic time T:

$$\frac{1}{T} = \frac{1}{T_{1Z}} \left[\Delta^2 + \nu_L^2 \frac{T_{1Z}}{T_{1D}} \right] \Big/ \left[\Delta^2 + \nu_L^2 \right]. \tag{8}$$

This has to be compared with the time obtained by REDFIELD [5, 6] under the assumption of an unique spin temperature in the rotating frame and with the magnetization aligned along the effective field, which is given by

$$\frac{1}{T} = \frac{1}{T_{1Z}} \left[\Delta^2 + \nu_L^2 \frac{T_{1Z}}{T_{1D}} + \nu_1^2 \frac{T_{1Z}}{T_{1X}} \right] \Big/ \left[\Delta^2 + \nu_L^2 + \nu_1^2 \right]. \tag{9}$$

Equation (9) shows that any deviation of the magnetization from the z direction introduces an extra term, $\nu_1^2 \, T_{1Z}/T_{1X}$, shortening the relaxation time as observed experimentally. The effect of this extra term will of course grow with the T_{1Z}/T_{1X} ratio, i. e. in the region of long correlation times. It is also clear that by tilting the magnetization from the z-direction, the r.f. field couples the relaxation along the x and z direction making thus Eqs. (5) invalid.

IV. Conclusion

This series of experiments, together with those of Ref. [3] give a quantitative overall experimental confirmation of Provotorov's theory. However, they show also that some caution has to be applied when considering the spin lattice relaxation in the region of long correlation times. In this region our experiments indicate that in certain cases the H_1 field has to be limited to extremely small values in order to ensure the validity of the theory.

Finally, the author wants to thank Prof. W. MÜLLER-WARMUTH for the constant interest he had for this work.

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