NMR of protons in gypsum. I. Experimental proof of the existence of four thermodynamic invariants

H. Eisendrath
Vrije Universiteit Brussel, Belgium

W. Stone
Université Catholique Louvain, Belgium

J. Jeener
Université Libre de Bruxelles, Belgium
(Received 18 April 1977)

In this paper we present a detailed experimental verification of the existence of four independent invariants for the nuclear spin system in a single crystal of gypsum oriented in the magnetic field in such a way that all the protons are spectroscopically equivalent and that the rf absorption spectrum gives a single well-separated doublet.

I. INTRODUCTION

Since the very beginning of NMR in solids, gypsum ($CaSO_4 \cdot 2H_2O$) has been used as a pedagogical example because it has the appealing simplicity of containing essentially nuclear spins of a single kind with a spin of $\frac{1}{2}$ (protons), but nevertheless shows an obvious structure in its absorption spectrum. In his classical paper, Pake[1] has shown that this structure reflects the fact that the protons in gypsum are paired in water molecules, and that these proton pairs are trapped between the other atoms of the crystal, only executing small-amplitude vibrations and 180° flips. In agreement with crystallographic data, NMR also shows that there exist two types of proton pairs in gypsum, differing only by their orientation in the crystal.

Holcomb and Pedersen[2] have measured the rate of spin-lattice relaxation of Zeeman energy in gypsum over a wide temperature range. They have shown that this relaxation is dominated by the modulation of the coupling between protons in different water molecules, by the thermally activated 180° flips of the individual water molecules.

Look and Lowe[3] have studied the rate of spin-lattice relaxation "in the rotating frame" in gypsum (with an applied rf field). They could explain their observations with impressive accuracy assuming the same rate of independent and thermally activated 180° flips of the water molecule which is derived from the Zeeman T_1 results.

We have made a detailed investigation of the nuclear magnetism of protons in a single crystal of gypsum oriented in such a way that all proton pairs are spectroscopically equivalent (i.e., make

the same angle with the large external magnetic field) and that the separation between the two components of the Pake doublet is as large as the first condition permits. Under these conditions, the two components of the Pake doublet are well resolved, but do have some overlap at the center of the line.

Two plausible, but opposite, assumptions could be made about the thermodynamic properties of the protons in such a situation.[4,5]

If the two components of the Pake doublet are not appreciably resolved, a natural assumption would be that this assembly of protons with dipolar couplings between them has the same general thermodynamic properties as, for instance, the assembly of fluorines in a crystal of CaF_2. In a large external field, we would then expect to find two independent quasi-invariants of the motion: for instance, the Zeeman energy (or the difference between the numbers of "up" and "down" spins) and the total proton-proton coupling energy. This is indeed what we have observed in gypsum at an orientation of the external magnetic field such that the two components of the Pake doublet are superimposed for all proton pairs (Fig. 7).

On the other hand, if the Pake doublet is widely split, the normal assumption is to regard gypsum as an assembly of equivalent proton pairs, with a weak coupling between the pairs. In a large external field, each proton pair has four unequally spaced energy levels, and we thus anticipate that the population of each of these four levels will be a quasi-invariant of the motion and that the total energy of coupling between pairs will also be a quasi-invariant. Of course, the sum of the four populations is equal to the number of water molecules, so that we predict four independent quasi-

invariants, three of which are associated with the populations of the four unequally spaced levels.

In this paper we present a detailed experimental verification of the existence of these four independent invariants in the case of a single well-separated Pake doublet in gypsum for times limited only by spin-lattice relaxation and extending up to a few seconds.[6] The three invariants corresponding, respectively, to Zeeman energy, intrapair dipolar energy, and interpair dipolar energy, have been selectively prepared out of equilibrium by a pair of phase-shifted pulses[7] applied to the spin system in complete equilibrium with the lattice. A "read pulse" applied some time after these three different preparations causes the appearance of three completely different (although easily predictable) free-precession signals. The rates of spin-lattice relaxation were also markedly different, starting from the three different deviations from complete equilibrium with the lattice. The fourth invariant, which is associated with the population of the nonmagnetic singlet level of each proton pair, is much more difficult to study because there are no allowed magnetic dipolar transitions between the singlet and the components of the triplet, so that this invariant can neither be affected nor observed directly by means of rf fields. Fortunately, the fourth invariant is coupled to the three others by spin-lattice relaxation, and this enabled us to clearly demonstrate its existence.

It is intriguing to note that when the singlet-level population has been put out of equilibrium, no rf saturation whatsoever will affect it, but the other invariants will feel its influence after the saturation. In other words, an rf saturation does *not* destroy all spin order as is usually assumed. This is in fact the idea of the "trick" by which we experimentally demonstrated the existence of the fourth invariant.

II. HAMILTONIAN, INVARIANTS, AND QUASIEQUILIBRIUM SITUATIONS

The spin Hamiltonian for the protons in gypsum can be written as

$$\mathcal{H} = \sum_i \mathcal{H}_0^i + \sum_{i<j} \mathcal{H}^{ij}, \tag{1}$$

where i and j label the proton pairs, $\mathcal{H}_0^i$ describes the dipolar coupling between the two spins of the ith pair and the coupling of those two spins with the large external magnetic field, and $\mathcal{H}^{ij}$ is the coupling between the ith pair and the jth pair. We immediately note that $\mathcal{H}_0^i$ is not affected by an interchange of the two protons of the pair, whereas the coupling between two pairs is affected by such

an interchange.

In most of the temperature range in which we are interested here, the rate of thermally activated interchange is much larger than the linewidth due to pair-pair coupling, so that an appropriate "effective" $\mathcal{H}^{ij}$ will be obtained by averaging the pair-pair coupling over the proton interchanges. What will be neglected in this way is essentially spin-lattice relaxation, which we plan to discuss in detail in a forthcoming paper.

We shall now focus our attention on situations in which the large external magnetic field is oriented in such a way as to be at the same angle with respect to all proton pairs (after averaging out lattice vibrations, of course). All single-pair Hamiltonians $\mathcal{H}_0^i$ then have the same spectroscopy: three slightly unequally spaced components of a triplet (denoted +, 0, and −) and a nonmagnetic singlet (denoted by s), as shown in Fig. 1. An external rf magnetic field can cause transitions between the components + → 0 and 0 → − of the triplet, but not between the singlet and the triplet.

For further convenience, we shall write the single-pair Hamiltonian under the form

$$\mathcal{H}_0^i = \mathcal{E}_+\mathcal{N}_+^i + \mathcal{E}_0\mathcal{N}_0^i + \mathcal{E}_-\mathcal{N}_-^i + \mathcal{E}_s\mathcal{N}_s^i, \tag{2}$$

where the $\mathcal{E}$'s denote the eigenvalues of $\mathcal{H}_0^i$ and the $\mathcal{N}^i$'s denote the projectors on the corresponding eigenstates of $\mathcal{H}_0^i$ (these projectors have also been called "occupation number operators"[5]).

In the situation in which we are interested in
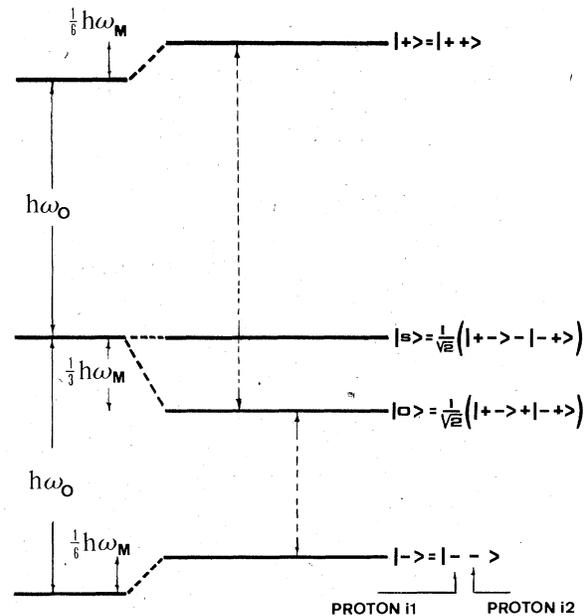
FIG. 1. Energy-level diagram for a system of two spins $\frac{1}{2}$ in a large external magnetic field, with a weak dipolar coupling between the spins.

here, the coupling between pairs is definitely weaker than the couplings which are responsible for the single-pair Hamiltonians, so that the dominant spectroscopic effects of the coupling between pairs will be adequately described as a first-order perturbation. As a consequence of this, we will have to retain only that part $\mathcal{H}'_I$ of $\sum \mathcal{H}^{ij}$ which is secular with respect to $\sum \mathcal{H}^i_0$. We can now write the relevant part of the proton Hamiltonian as

$$\mathcal{H} = \mathcal{E}_+ \mathfrak{N}_+ + \mathcal{E}_0 \mathfrak{N}_0 + \mathcal{E}_- \mathfrak{N}_- + \mathcal{E}_s \mathfrak{N}_s + \mathcal{H}'_I$$

$$= \hbar \omega_0 (\mathfrak{N}_+ - \mathfrak{N}_-) + \hbar \omega_M (\tfrac{1}{3}\mathfrak{N}_+ + \tfrac{1}{3}\mathfrak{N}_- - \tfrac{2}{3}\mathfrak{N}_0) + \mathcal{H}'_I, \quad (3)$$

where the occupation number operators $\mathfrak{N}$ are the sums over all pairs i of the corresponding single-pair occupation number operators $\mathfrak{N}^i$, the average NMR frequency of the protons is ω_0, and the separation between the two components of the Pake doublet is ω_M (see Fig. 1). The various operators which appear in expression (3) of $\mathcal{H}$ all commute with each other, so that they can be diagonalized simultaneously, and the corresponding eigenstates $|N_+, N_0, N_-, N_s, E_I, n\rangle$ can be labeled by the eigenvalues N of the occupation number operators $\mathfrak{N}$, the eigenvalue E_I of the total pair-pair coupling, and possibly some other quantum numbers n required to completely label the states in case of degeneracy.

If the pair-pair coupling can indeed be treated as a small perturbation, the usual arguments (see, for instance, Ref. 4 of Ref. 5) indicate that the five quantities $\mathfrak{N}_+$, $\mathfrak{N}_0$, $\mathfrak{N}_-$, $\mathfrak{N}_s$, and $\mathcal{H}'_I$ will all behave as quasi-invariants of the motion. We immediately note that the closure relation $\mathfrak{N}^i_+ + \mathfrak{N}^i_0 + \mathfrak{N}^i_- + \mathfrak{N}^i_s = 1$ implies that $\mathfrak{N}_+ + \mathfrak{N}_0 + \mathfrak{N}_- + \mathfrak{N}_s = \mathfrak{N}_T$, where N_T is the number of proton pairs in the crystals, so that only three combinations of the $\mathfrak{N}'_s$ can be *independent* invariants of the motion. We shall choose our four remaining *independent* invariants in the following way which makes them all traceless and orthogonal to each other, gives them simple physical meanings, and relates them directly to specific techniques of preparation and observation.

$\mathfrak{N}_+ - \mathfrak{N}_-$ is proportional to the total coupling energy between the protons and the large external field (the Zeeman energy). $\tfrac{1}{3}\mathfrak{N}_+ + \tfrac{1}{3}\mathfrak{N}_- - \tfrac{2}{3}\mathfrak{N}_0$ is proportional to the total dipolar coupling energy of the protons inside each pair (the molecular energy). $\tfrac{3}{4}\mathfrak{N}_s - \tfrac{1}{4}\mathfrak{N}_+ - \tfrac{1}{4}\mathfrak{N}_0 - \tfrac{1}{4}\mathfrak{N}_-$ is the difference between the population of the singlet level and the average population of the components of the triplet. $\mathcal{H}'_I$ is the total energy of coupling between protons belonging to different pairs.

We can now write the usual expression for the quasiequilibrium density operator as

$$\rho_{qe} = (1/Z) \exp[-\alpha_Z (\mathfrak{N}_+ - \mathfrak{N}_-) - \alpha_M (\mathfrak{N}_+ + \mathfrak{N}_- - 2\mathfrak{N}_0)$$

$$- \alpha_s (3\mathfrak{N}_s - \mathfrak{N}_+ - \mathfrak{N}_0 - \mathfrak{N}_-) - \beta \mathcal{H}'_I], \quad (4)$$

where the number Z is fixed by the normalization condition $\mathrm{Tr}(\rho_{qe}) = 1$ and the quantities α and β are analogous to chemical potentials or inverse temperatures. As almost all NMR experiments, our measurements were performed in a situation of "very high temperature" or "very weak order," in which it is an excellent approximation to expand ρ as a power series in the α's and β limited to first-order terms

$$\rho_{qe} = [1 - \alpha_Z (\mathfrak{N}_+ - \mathfrak{N}_-) - \alpha_M (\mathfrak{N}_+ + \mathfrak{N}_- - 2\mathfrak{N}_0)$$

$$- \alpha_s (3\mathfrak{N}_s - \mathfrak{N}_+ - \mathfrak{N}_0 - \mathfrak{N}_-) - \beta \mathcal{H}'_I]/\mathrm{Tr}(1). \quad (5)$$

In this weak-order approximation, quantities such as energy, rf susceptibility, free-precession signals ... can be expressed as linear combinations of the α's and β. The Zeeman energy is proportional to α_Z, the molecular energy is proportional to α_M, and the pair-pair coupling energy is proportional to β. When the spin system is in complete equilibrium with the lattice, the only significant deviation of ρ_{qe} from complete disorder corresponds to $\alpha_Z \neq 0$ and $\alpha_M = \alpha_s = \beta = 0$.

III. SELECTIVE PREPARATION AND OBSERVATION OF THE VARIOUS INVARIANTS

The intense transitions caused by rf irradiation of our assembly of weakly coupled proton pairs obey the same selection rules as the corresponding transitions for one isolated pair: transitions only occur between eigenstates of the occupation number operators $\mathfrak{N}$ which can be related by a jump of one proton pair between two components of the triplet (separated by approximately $\hbar \omega_0$). A typical allowed transition would be from $|(N_+ + 1), N_0, N_-, N_s, E_I, n\rangle$ to $|N_+, (N_0 + 1), N_-, N_s, (E_I + \epsilon), n'\rangle$. Furthermore, it is very improbable that a transition will take place if it involves a rearrangement of the relative states of many proton pairs, so that the important transitions are those which correspond to a change ϵ in pair-pair coupling energy not much larger than the rms coupling of one pair with its neighbors.

The contribution of any transition to the absorption spectrum is given by a product of two terms of different origins: a spectroscopic term proportional to the square of the matrix element of the rf perturbation between the two relevant states (as discussed above), and a thermodynamic term proportional to the difference in population (or occupation probability) between the upper and the lower state. The qualitative discussion of the influence of the thermodynamic state on the absorp-

tion spectrum will be simplified if we use a graphical representation of the (average) populations of the relevant states versus total energy, as shown in Fig. 2. The relation between total energy E and population P is read directly from expression (5) for the density operator by noting that the occupation probabilities are the diagonal matrix elements of ρ_{qe} for instance,

$$P[(N_{+}+1), N_{0}, N_{-}, N_{S}, (E_{I}+\epsilon), \ldots] - P[N_{+}, (N_{0}+1), N_{-}, N_{S}, E_{I}, \ldots] = (-\alpha_{z} - \alpha_{M} - \beta\epsilon)/\mathrm{Tr}(1),$$

and

$$E[(N_{+}+1), N_{0}, N_{-}, N_{S}, (E_{I}+\epsilon), \ldots] = [\hbar\omega_{0}(N_{+}-N_{-}) + \hbar\omega_{M}(\tfrac{1}{3}N_{+}+\tfrac{1}{3}N_{-}-\tfrac{2}{3}N_{0}) + E_{I}] + \hbar(\omega_{0}+\tfrac{1}{3}\omega_{M}) + \epsilon$$

(6)

When the α's and β have the values used to draw Fig. 2, the NMR line will be emissive, for instance, at the frequency $2\pi(\omega_{0}+\omega_{M})$ of the center of the high-frequency component of the doublet because for such a transition the upper-state population is higher than the lower-state population, as shown in Fig. 2.

In general, Eq. (6) gives the influence of α_{z}, α_{M}, α_{s}, and β on the energy dependence of the populations, from which one can infer the frequency dependence of the absorption spectrum, or, more exactly, some symmetry properties of this frequency dependence. Using the Kramer–Kronig relations, one can deduce the corresponding symmetry properties of the dispersion part of the rf susceptibility. In the limit of small exciting pulses, the "complex" free-precession signal (the real and imaginary parts of which are the "in-phase" and the "out-of-phase" components of the free-precession signal) can be evaluated as the Fourier transform of the complex susceptibility. This provides a usable scheme for predicting the influence of the thermodynamic parameters α_{z}, α_{M}, α_{s}, and β on the properties of the free-precession signal.

Let us now examine the four simple situations in which only one of the four thermodynamic parameters α_{z}, α_{M}, α_{T}, and β is different from zero, as shown in Fig. 3.

1. *Zeeman order*   If only α_{z} is different from zero, one has, as expected, the "traditional" ab-
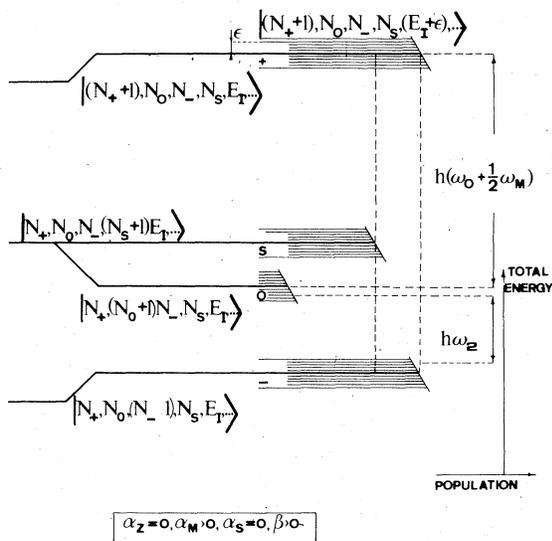
FIG. 2. Population vs total energy for a subset of states relevant to the discussion of the NMR absorption spectrum. rf energy is absorbed by the spins at frequency $\omega_{2}/2\pi$ and emitted at frequency $\tfrac{1}{2}(\omega_{0}+\tfrac{1}{2}\omega_{M})/\pi$.
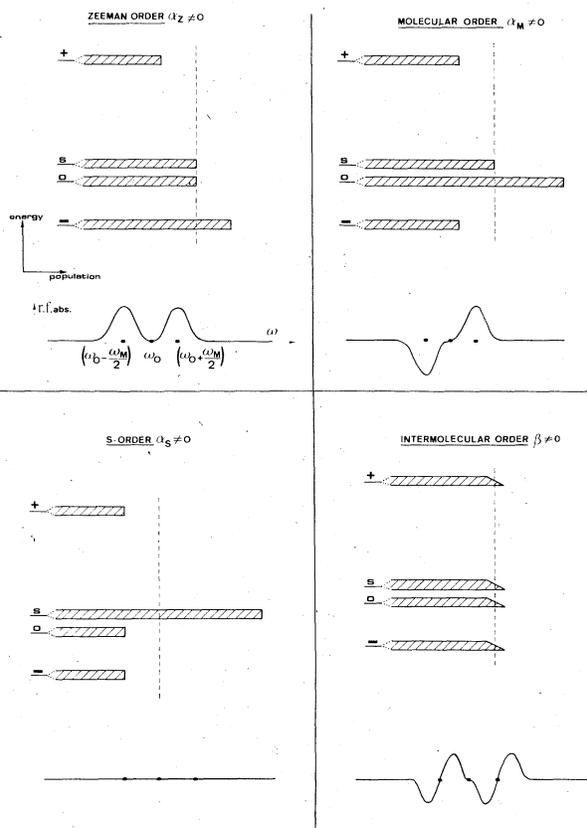
FIG. 3. Average population of the various energy levels as a function of energy, absorption spectrum, and free-precession signals for the four typical situations of Zeeman order, molecular order, singlet order, and intermolecular order.

sorption spectrum of gypsum, with both compon-
ents of the Pake doublet in absorption. The cor-
responding free-precession signal is completely
out of phase with the exciting pulse and it is easy
to show that its amplitude is proportional to
$\alpha_z \sin\theta$, where θ is the angle by which the exciting
pulse rotates the magnetization of each proton.
The time dependence of the Zeeman free-preces-
sion signal is shown in Fig. 4.

2. *Molecular order*. If only α_M is different from
zero, the population difference shown in Fig. 3
imply that one component of the Pake doublet is
in absorption, whereas the other component is in
emission. The major difference in symmetry of
this absorption spectrum from the Zeeman case
is directly reflected in a major difference in the
symmetry properties of the free-precession sig-
nal: when $\alpha_M \neq 0$, the free-precession signal is
in phase with the exciting pulse, and its time de-
pendence is shown in Fig. 4. It is easy to show[7]
that the amplitude of this free-precession signal
is proportional to $\alpha_M \sin 2\theta$.

3. *s order*. If only α_s is different from zero,
Fig. 3 shows that the absorption spectrum is ab-
sent; consequently, s order also does not cause
any free-precession signal.

4. *Intermolecular order*. If only β is different
from zero, Fig. 3 shows the rather unusual frequency
dependence of the rf absorption. This reflects into a
free-precession signal which is in phase with the
exciting pulse, just as for intermolecular order, but
has a markedly different time dependence, as
shown in Fig. 4. The molecular free-precession
signal has an amplitude proportional to $\beta \sin 2\theta$.

When the various types of order are present
simultaneously, the free-precession signal is the
sum of the contributions from Zeeman, molecular,
and intermolecular order. However, it is always
very easy to selectively measure the quantities
α_z, α_M, and β. For instance, α_z is proportional
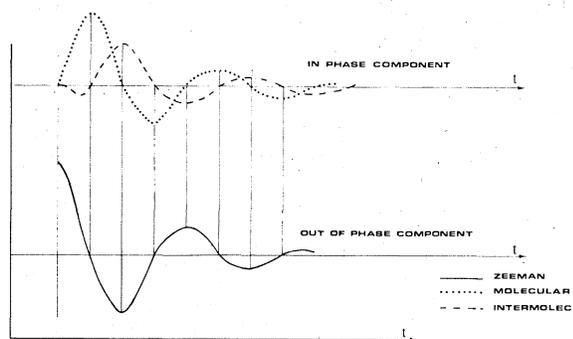
FIG. 4. Time dependence of the in-phase and out-of-
phase components of the free-precession signal corres-
ponding to pure Zeeman, pure molecular, and pure in-
termolecular order.

to the amplitude of the out-of-phase component
of the free-precession signal, α_M is proportional
to the magnitude of the in-phase component mea-
sured at a zero of the intermolecular signal, and β
is proportional to the magnitude of the in-phase
component measured at the time of a zero of the
molecular signal.

In complete thermal equilibrium with the lat-
tice, only α_z differs enough from zero to cause
observable signals. It is, of course, very easy
to create a situation in which α_z deviates from its
thermal-equilibrium value in an observable way:
a 90° pulse will lead to $\alpha_z = 0$, whereas a 180° pulse
will change the sign of α_z. Starting from such a
situation, one can, for instance, study the spin-
lattice relaxation of Zeeman energy by measuring
α_z as a function of the delay between a 90° "pre-
paration pulse" and the " read pulse."

We have selectively prepared observable amounts
of molecular order and of intermolecular order,
starting from the observable amount of Zeeman
order available in complete thermal equilibrium,
by the phase-shifted pulse-pair method,[5,7] in which
one applies a 90° pulse followed after a delay τ by
a θ pulse phase shifted by 90° from the first 90°
pulse. The τ and θ dependences of the efficiency
of transfer of Zeeman order into X order (X could
be molecular or intermolecular) are exactly the
same as the dependences of the free-precession
signal due to X order on the angle θ of the excita-
tion pulse and the time τ after the pulse (this prop-
erty is shown in Refs. 5 and 7). As a consequence
of this, molecular order can be selectively pre-
pared by applying the phase-shifted θ pulse at a
zero of the intermolecular (or Zeeman) free-pre-
cession signal, and the optimal value of θ is 45°.
Similarly, intermolecular order can be selectively
prepared by applying a phase-shifted 45° pulse at
a zero of the molecular free-precession signal.
We have carefully checked that the selective prep-
aration techniques described above indeed prepare
the spin system in states in which a read pulse
applied somewhat later is followed by the expected
free-precession signal. Figure 5 shows a block
diagram of the pulse spectrometer which was used.
As a further check of the existence and indepen-
dence of the invariant Zeeman energy, molecular
energy, and intermolecular energy, we have mea-
sured the rates at which these invariants initially
relax towards their thermal-equilibrium values
after the above described preparations. Figure 6
clearly shows that these three rates are different
and that they have different temperature depen-
dences. In a forthcoming paper, we shall give a
detailed quantitative interpretation of the various
features of these rates of relaxation.

The proof of the existence of S order as an in-
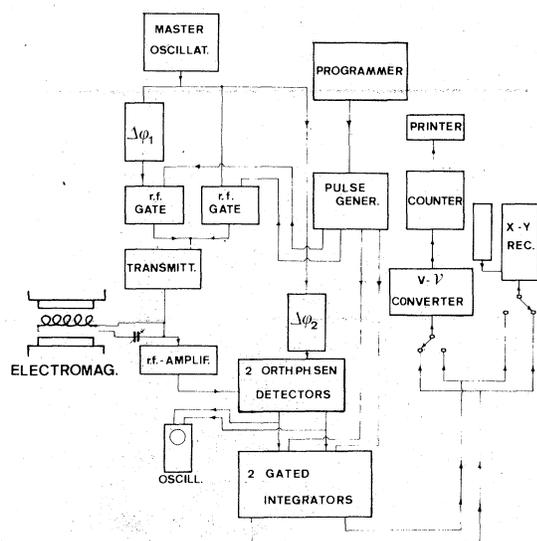
FIG. 5. Block diagram of the pulse spectrometer.

dependent invariant of the motion cannot be provided directly by the rf pulse methods described above, because this invariant is not affected by rf fields: there is no allowed dipolar transition between the singlet and the triplet of a pair of protons. Our proof takes advantage of the fact that this selection rule does not hold for the spin transitions which are caused by the 180° flips of the proton pairs in their crystal cage. In the temperature range where the average rate of flips of the proton pairs is larger than ω_M, but smaller than ω_0, one of the fastest spin-lattice relaxation processes is an exchange of order between molecular order and s order. We have thus been able to prepare appreciable amounts of s order by transforming Zeeman order into molecular order by a phase-shifted pulse pair and then waiting for a time of the order of the inverse of the rate of exchange between molecular order and s order. In order to be sure that further effects would be
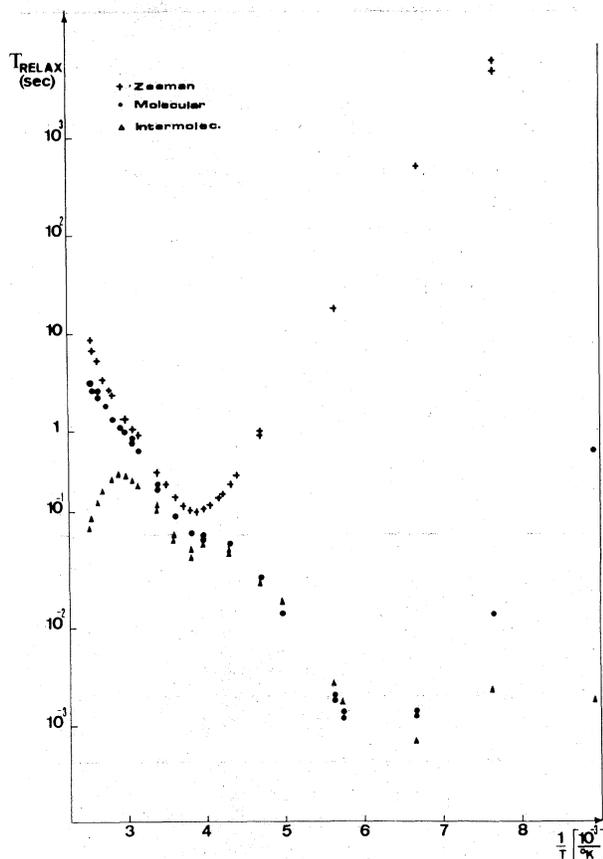
FIG. 6. Initial rate of relaxation of the three invariants, Zeeman energy, molecular energy, and intermolecular energy, as a function of temperature in a single crystal of gypsum at a proton NMR frequency of 28.7 MHz. N.B. The external magnetic field was oriented in such a way as to cause a single Pake doublet of maximum separation.
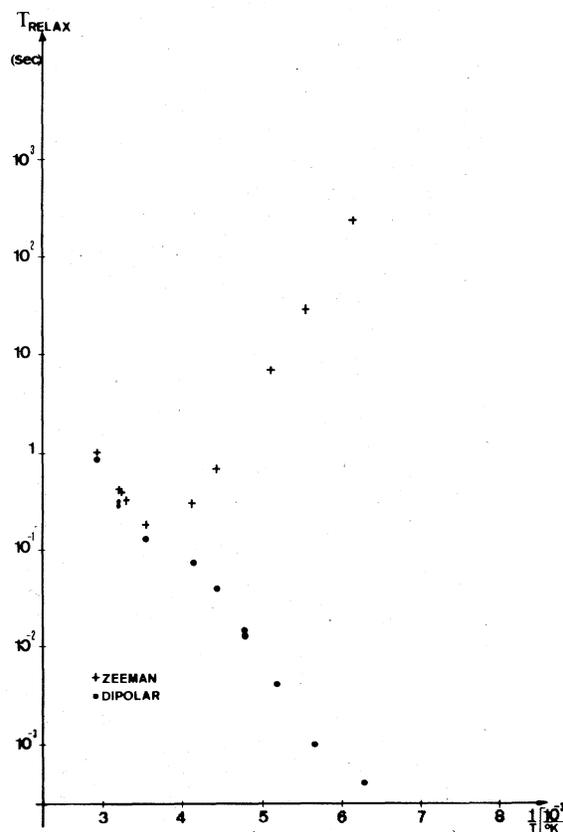
FIG. 7. Initial rate of relaxation of the two invariants, Zeeman energy and dipolar energy, as a function of temperature in a single crystal of gypsum at a proton NMR frequency of 28.7 MHz. N.B. The external magnetic field was oriented in such a way as to cause a single line for the rf absorption spectrum.

due to s order only, we have then destroyed any amount of Zeeman, molecular, or intramolecular order present by a series of rf pulses (making sure that no free-precession signal can be observed any more). After this saturation, molecular order builds up at the expense of the s order, and this molecular order can be observed by our standard rf pulse technique. When we have performed this experiment, we observed the expected "molecular" signal due to the existance of s order. These molecular signals were never larger than about 1% of the maximum molecular signals which can be prepared directly from Zeeman order, but they had all the expected features: the right dependences upon the various delays, a sign which changed when we changed the sign of the amount of molecular order used in the preparation part of the experiment, ...

[1]G. E. Pake, J. Chem. Phys. 16, 327 (1948).
[2]D. F. Holcomb and B. Pedersen, J. Chem. Phys. 36, 3270 (1962).
[3]D. C. Look and I. J. Lowe, J. Chem. Phys. 44, 2995 (1966).
[4]M. Goldman, *Spin Temperature and NMR in Solids* (Clarendon, Oxford, 1970).
[5]J. Jeener, Adv. Magn. Reson. 3, 205 (1968).
[6]H. Eisendrath, W. Stone, J. Jeener, International Conference on Magnetic Resonance and Relaxation, XIVth Colloque Ampère, paper No. 187 (1966) (unpublished).
[7]J. Jeener and P. Broakaert, Phys. Rev. 157, 9 (1967).