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RADIATIVE DETECTION OF NUCLEAR MAGNETIC RESONANCE

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INTRODUCTION

An exciting development taking place in chemistry today is the widespread evolution of techniques for studying matter on a truly atomic scale. Chemists are naturally motivated to explore new, high-sensitivity techniques because chemical thought and discussion is most often directed toward matter at the atomic level, while classical measurements usually deal with macroscopic properties. While statistical mechanics helps to resolve this problem, it seems clear that the acquisition of much information about the behavior of matter on an atomic scale awaits the development of experimental methods that are sensitive to small numbers of atoms.

Nuclear magnetic resonance (NMR) is an area for which these comments are especially appropriate. Its very high precision and wide applicability make NMR a powerful method. Unfortunately conventional NMR has relatively low sensitivity, and a sample of macroscopic dimensions is required to obtain an observable signal. This is true only because resonance is detected through a change in the macroscopic magnetization of nuclei in the sample. Nuclear magnetic moments are small; therefore many nuclei are required in order to produce a sizable magnetization. The resulting low sensitivity is a major weakness of conventional NMR.

This article describes a small, new area of very unconventional NMR in which the sensitivity problem is avoided by utilizing a microscopic detection scheme. The area is termed "radiative detection of nuclear magnetic resonance", or NMR/RD.(1) Applicable to metastable nuclear states, NMR/RD employs nuclear decay products—beta or gamma radiation—to detect resonances. Because nuclear counters are sensitive enough to record individual nuclear events, a resonance can be confirmed whenever it causes a statistically significant change in the counting rate. Only about 10^6 nuclei are usually required to achieve this result, making NMR/RD the most sensitive type of NMR by many orders of magnitude. Unfortunately the range of application of NMR/RD is apparently very limited.

In the next section the distribution of radiation from oriented nuclei is discussed, and three methods for orienting nuclei are briefly discussed. The third section deals with the power requirements for producing observable resonances in oriented nuclear spin systems. Finally in the fourth section the results to date are summarized and the outlook for NMR/RD is surveyed.

RADIATION FROM ORIENTED NUCLEI

The only way in which NMR can appreciably affect the radiations from oriented nuclei is to alter their angular distributions. In an ordinary assembly of radioactive nuclei, however, the distribution of radiation is spherically symmetrical, and an impressed radiofrequency field can have no effect. For an NMR/RD experiment to be feasible a very special kind of sample is required: a sample whose nuclei are oriented. By this we mean that the nuclear spins must be "pointed" along a certain direction in space. The

nuclei may be polarized, with their spins parallel, as in a ferromagnet, or they may be only aligned, with spins oriented in direction but not in sense, as in an antiferromagnet.

Each nucleus by itself has a radiation probability pattern which is spatially anisotropic, analogous to that of an antenna. For an assembly of unoriented nuclei the individual patterns add incoherently, but when the nuclei become oriented the intensities of these individual probability patterns add coherently, and the entire assembly exhibits an anisotropic radiation pattern. An illustrative example is shown in Figure 1. We consider a nucleus with a spin-zero ground state and a metastable state of spin 1. Application of a magnetic field H resolves the degeneracy of the metastable state, giving three magnetic substates with magnetic quantum numbers M=1, 0, and -1. A nucleus in the metastable state can emit a dipole γ ray and decay to the ground state, and the probability for this process is unaffected by H. The substates have different γ-ray angular distributions, however. Suppose that a counter placed near the sample registered A counts/sec before H was applied. With H present the total counting rate is still A, but the contribution from each substate depends on θ, the angle between the γ-ray direction and H. The M=0 substate contributes $(A/2)\sin^2\theta$, and, while each of the M= $\pm$1 states contributes $(A/4)(1+\cos^2\theta)$. Note that the total counting rate is still isotropic, as $\sin^2\theta + \cos^2\theta = 1$.

Now suppose that the nuclei are aligned along H. The quantum-mechanical description of this situation is simple: more nuclei are in each of the two states M = $\pm$1 than are in the M=0 state. A $\cos^2\theta$ term appears in the radiation intensity, which is thereby enhanced along the H direction relative to perpendicular directions. If radiofrequency radiation is subsequently used to equalize

the substate populations, the radiation ansiotropy will decrease or disappear: this is the essence of NMR/RD. Most real cases are more complicated, but the principles are still the same: oriented nuclei radiate anisotropically, and NMR decreases this anisotropy. Let us now consider the three common methods for orienting nuclei.

The simplest method is to apply a strong magnetic field H, splitting the M substates by γH (where γ is the nuclear gyromagnetic ratio), and to lower the temperature. Populations of adjacent substates are related by the Boltzmann factor $e^{-\gamma H/kT}$. For $kT \cong \gamma H$ appreciable population differences, and nuclear orientation, can occur. Very low temperatures ($\sim 10^{-2}$°K) are required to orient nuclei in this way, but the method can be applied to nearly every element in the periodic table. Since it takes time to reach such low temperatures, only metastable states with lifetimes of 10^3 sec or more can usually be studied in this way. If magnetic resonance is performed, the method is termed "NMR in oriented nuclei" or NMR/ON.

The second technique for obtaining oriented nuclei is more subtle. It is based on the angular correlation that exists between two radiations emitted successively from the same nucleus. If the two radiations (γ_1 and γ_2 in Figure 2) are detected in two separate counters, and recorded only when they are in coincidence, then this coincidence counting rate $W_{12}(\theta)$ will vary with the angle θ between the propagation directions of the two γ quanta. This result may be understood by analogy to the thermal nuclear orientation method described above. After a nucleus has emitted a γ_1 quantum in a certain direction it is oriented with respect to that direction. Radiations emitted subsequently will be distributed anisotropically about that direction; i.e., the distribution will

depend on θ. Coincidence counting is employed only to select nuclei oriented in the γ_1 direction. When a magnetic field H is applied and NMR is performed on the intermediate state, the method is termed "NMR detected by perturbed angular correlations", or NMR/PAC. It is applicable to metastable states with lifetimes in the 10^{-8}-10^{-6} sec range, and these states must be preceded by radiative transitions.

The third way to orient nuclei is by producing them in an oriented configuration, through nuclear reactions at an accelerator. When a particle in the beam collides with a target nucleus in a nuclear reaction, there is most often a sizable orbital angular momentum between the two particles. The angular-momentum vector is perpendicular to the beam direction, so the reaction-product nuclei are oriented with their spins perpendicular to the beam, and they radiate anisotropically. Nuclei thus produced in nuclear reactions are candidates for NMR if their lifetimes lie in the range 10^{-6}-10^{3} sec. This method is abbreviated NMR/NR.

POWER REQUIREMENTS FOR NMR/RD

Turning now to the other side of the NMR/RD methods, we need a description of the magnetic resonance phenomenon that will allow us to determine the requirements for a successful NMR/RD experiment. Conventional NMR is often discussed using perturbation theory, but that approach is not suitable for NMR/RD because these experiments require that nearly every metastable nucleus undergo a transition in a very short time. The approach sketched below is ideal for NMR/RD experiments, and it is actually simpler than the perturbation-theory method.

A particle with magnetic moment $\vec{\mu}$ in a magnetic field H will precess about H according to the equation

$$\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu} \times \vec{H}.$$

The precession frequency ν is given by $h\nu = \nu H$, where h is Planck's constant. Resonance is brought about at frequency ν by applying a radiofrequency field $H_1(t) = 2H_1 \cos 2\pi\nu t$ perpendicular to H. The problem is greatly simplified by transforming into a coordinate frame that rotates about H with frequency ν. In this "rotating frame" the influence of H is removed and μ is fixed in space. From $H_1(t)$ only a component H_1 survives the transformation. This component is time-independent and is perpendicular to the original H axis. Now we can write another equation

$$\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu} \times \vec{H}_1$$

for the motion of μ in the rotating frame. Thus μ precesses about H_1 in this frame with frequency ν_1 given by $h\nu_1 = \gamma H_1$. When this precession has carried μ through a sizable angle—about 90° or $\pi/2$ radians—the probability is high that magnetic resonance absorption will have taken place, because the orientation of μ in the laboratory frame would now be given by a different magnetic quantum number M.

The "power" requirement for NMR/RD is easily obtained from this picture of NMR. We may simply regard NMR as one of two competing processes. The other process is either radioactive decay, with time constant τ (the nuclear lifetime) or relaxation, with time constant T_1 (the spin-lattice relaxation time). For NMR to compete favorably with decay, for example, we require $2\pi\nu_1\tau \geq \pi/2$,

or $\nu_1 \geq 1/4\tau$. This requirement is met for $H_1 \geq h/4\gamma\tau$. Unusually large radio-frequency field strengths are required to satisfy this condition— for $\tau = 10^{-6}$ sec, an H_1 of 100 gauss is needed—but these fields can be attained with some effort.

RESULTS TO DATE

The NMR/RD field started in the early 1950's. It isn't practical to give a complete review of the early work here with a discussion of the value of each contribution, but we can mention a few important papers. A more complete set of references is available in a recent review article (1).

In 1952 Deutsch and Brown reported the radiative detection of magnetic resonance in positronium (2): this work was the precursor of the NMR/RD field. Later, in 1953, Bloembergen and Temmer pointed out the possibility of NMR/ON (3) and Abragam and Pound suggested NMR/PAC the same year (4). During the next twelve years several experiments were reported that were individually very elegant. Among these were an NMR/ON study of dynamically oriented As^{76}, by Pipkin and Culvahouse (5) and an NMR/NR experiment on Li^8 in LiF, by Connor (6). Unfortunately none of the experiments done in this period showed promise of being applicable to any but a few nuclear states. As recently as 1965 no NMR/PAC experiment had been reported, nor had an NMR/ON experiment been successfully carried out on <u>thermally</u> oriented nuclei. This latter fact was particularly important because thermal nuclear orientation has a very wide range of application. The earlier theoretical papers (3,4) had discussed the necessary conditions for these NMR/RD experiments, but had not suggested practical ways to achieve these conditions. There was widespread opinion that the experiments were not feasible.

Early in 1966 a group at our laboratory in Berkeley tried an NMR/PAC experiment based on "hyperfine enhancement" of the applied field in ferromagnetic nickel. This effect, discovered in 1959 by Gossard and Portis (7), has the effect of amplifying the H_1 field by a factor of about 10^3, thereby making the crucial condition $\nu_1 \geq 1/4\tau$ attainable for even very short-lived nuclear states. The first NMR/PAC result, on Rh^{100} ($\tau = 3\times10^{-7}$sec) in nickel, was reported by Matthias et al (8), and later that year another NMR/PAC resonance, on Rh^{100} in iron, was observed with the same apparatus.

After the NMR/PAC experiments had been carried out with the aid of hyperfine enhancement, extension to NMR/ON was a natural next step. NMR/ON experiments in ferromagnetic lattices were especially appropriate because the "universal" method of thermal nuclear orientation employs ferromagnets (9). In fact the NMR/ON experiments appear somewhat less difficult, and far more widely applicable, than the NMR/PAC method. Matthias and Holliday at Berkeley reported the first such NMR/ON result, on Co^{60} in iron, later in 1966 (10). Subsequent work in several laboratories, notably in Oxford and Leiden, has confirmed the generality of the NMR/ON method and has extended it considerably.

With these two methods it was thus possible to perform NMR/RD studies on a wide variety of long-lived ($\tau > 10^3$sec) and short-lived ($\tau < 10^{-6}$sec) nuclear states, but the large intermediate range with $10^{-6} < \tau < 10^3$sec was still not generally accessible. It was clear that only the NMR/NR methods would be applicable here.

Nuclear states with lifetimes in the upper half of this range (i.e., for $10^{-2} < \tau < 10^2$sec) had been studied by Connor and Tsang, by Sugimoto and coworkers, and by others (1), using NMR/RD and employing the asymmetry of β

particles for detection. In 1967 Sugimoto and co-workers extended their work to metallic hosts (11), thereby substantially generalizing the NMR/RD method for these longer-lived cases. There still remained a lifetime range $10^{-6} < \tau < 10^{-3}$ sec in which no NMR work had been done, however, and many interesting γ-emitting nuclear isomers lay in this range.

In 1968 Christiansen and co-workers oriented nuclear isomers in liquid gallium (12), and early this year Quitmann and Jaklevic used a liquid gallium host to observe NMR in a 6-microsecond isomer of As^{73} (13).

With the success of the nuclear reactions-NMR work, NMR/RD can be applied to a great many nuclear states. Resonances have already been observed in about 20 states, and a fair diversity of information has been derived from NMR/RD studies. Several nuclear magnetic moments have been measured accurately. Other nuclear information, particularly about "hyperfine anomalies" (the distribution of magnetism within nuclei) has also emerged from this work.

Applications to solid-state phenomena seem promising. A number of hyperfind magnetic fields, Knight shifts, and relaxation times have already been obtained by NMR/RD. It seems to be uniquely appropriate for very dilute systems or very small samples, where conventional NMR isn't sensitive enough. It also holds promise for studies of ion-implantation and other dynamic processes.

Like many physical techniques NMR/RD has quickly proved its value in physics, while its potential (if any) in chemistry is as yet unexplored. This is understandable, because several barriers must be overcome if NMR/RD is to enjoy widespread use in any area of chemistry. First of all its feasibility in gaseous molecules, or liquids has not yet been demonstrated. Then too, serious restrictions are intrinsic in all three NMR/RD methods. NMR/ON requires very

low temperatures, NMR/PAC usually involves nuclear transmutation, and in NMR/NR the nuclei recoil immediately before the resonance is observed. Overcoming these restrictions will require breakthroughs as substantial as anything described above. The incentive for attacking these problems is provided by the extremely high sensitivity available with NMR/RD—a sensitivity that makes NMR a truly microscopic method.

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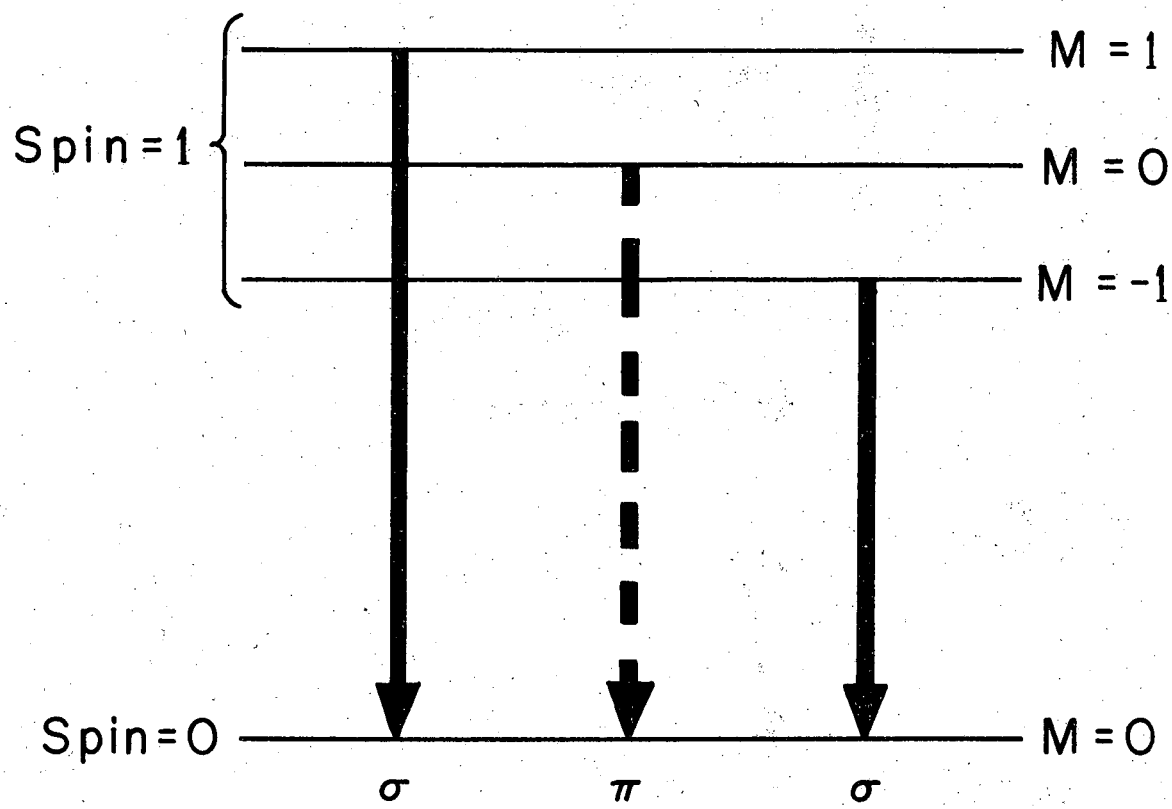
FIGURE CAPTIONS

Fig. 1. Level scheme for a nucleus with two levels, of spins 1 and 0, connected by a dipole transition. The σ, π notation is taken from atomic spectroscopy.

Fig. 2. Correlation angle (left) and level diagram for an angular correlation experiment. For $\theta = 180°$ only σ-σ coincidences appear. An NMR transition (heavy arrow) in intermediate state can alter substate populations and affect correlations.



$$W(\sigma) \propto 1 + \cos^2 \theta$$

$$W(\pi) \propto \sin^2 \theta$$

XBL694-2324

Fig. 1

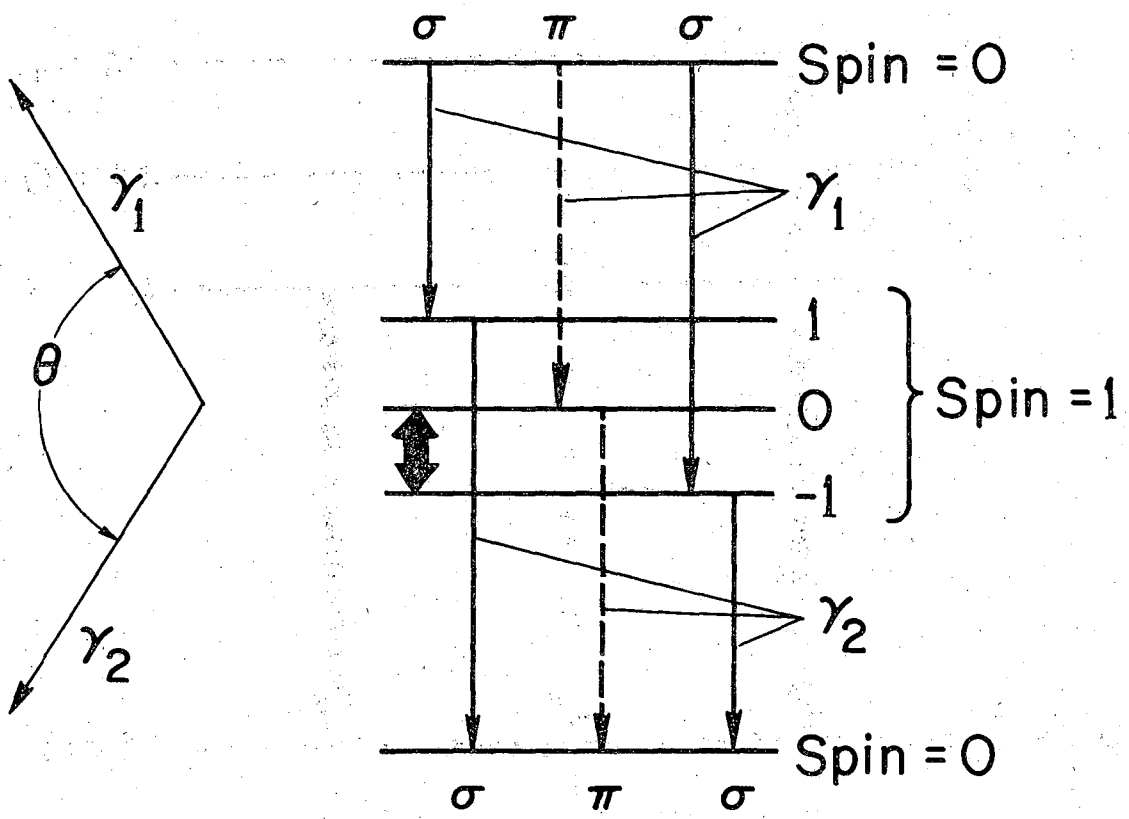


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Fig. 2

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