JOURNAL OF MAGNETIC RESONANCE **99**, 495–506 (1992)

Sensitivity of Optically Excited and Detected Magnetic Resonance

DIETER SUTER

Institute of Quantum Electronics, Swiss Federal Institute of Technology (ETH) Zürich,
CH-8093 Zurich, Switzerland

Received November 6, 1991; revised January 16, 1992

Compared to other forms of spectroscopy, the sensitivity of magnetic resonance experiments is relatively low, so that large numbers of spins are necessary for an experiment. This contrasts with related fields, most notably optical spectroscopy, where it has become possible, in recent years, to obtain spectroscopic information from individual atomic and molecular systems. This article investigates possible means for transferring some of this sensitivity advantage to the domain of magnetic resonance and gives numerical estimates of the expected signal-to-noise ratios, as well as experimental examples.

Magnetic resonance experiments have become an extremely useful tool in many areas of chemistry, physics, and medicine, mainly because of the great versatility of the method and the large information content of magnetic resonance spectra. One of the few remaining problems is the relatively low sensitivity that can be achieved, making it necessary to use samples with a large number of spins (typically $\geqslant 10^{18}$ spins for NMR). In other fields of spectroscopy, the number of atoms or molecules that are needed for a successful experiments is considerably lower. In optical spectroscopy, e.g., experiments with single atoms (*1, 2*) or molecules (*3, 4*) both in solution (*3*) and in solids (*4*) have been demonstrated.

In the domain of magnetic resonance experiments, various techniques have been developed to enhance the sensitivity, e.g., by using SQUIDS for detection (*5*), using polarized hydrogen to increase the magnetization (*6*), detecting spin polarization via energetic photons (*7*), detecting optical transitions whose wavelength is shifted by magnetic interactions (*8*), and optical pumping (*9*). These techniques basically aim at boosting the sensitivity in two different ways, either by enhancing the amount of polarized spins that is available in a given sample per unit of time (*6, 9*) or by improving the efficiency of the detection of the magnetization present in the sample (*5, 7, 8*).

Optical methods have been used for both purposes, with the first precursor experiments (*10*) dating back even before the first "direct" magnetic resonance experiments using radiofrequency fields. The basis for most of these methods is an exchange of angular momentum between the optical photons and the atoms. On the side of excitation, this transfer from the completely polarized optical field to the essentially unpolarized spins is used to enhance the polarization of the spin system. In the case of optical detection of magnetization, the transfer occurs in the opposite direction: the angular momentum of the polarized atom is carried away by the emitted photons,

0022-2364/92 $5.00

thereby amplifying the signal energy from radiofrequency range to optical frequencies. With this technique, the resulting photon energy becomes much higher than the noise background so that highly efficient techniques, such as single photon counting, can be used for detection.

While these methods have been used for some time, interest in them has been revived recently (*11–13*), largely due to the developments in laser technology. Nevertheless, there is considerable uncertainty about the quantitative impact of such techniques. The goal of this article is therefore an investigation into the possibilities offered by these methods and the sketching of the limits that are given by physical properties of the systems under study. The next section discusses the basic principle and shows in which cases they can be used. The two following sections discuss two particular aspects of the procedure, polarization of spin systems by optical pumping and detection of magnetization by optical means.

PRINCIPLE

In general, the effect of a polarized optical field on a spin system depends strongly on the energy level system involved (*13*). Figure 1 summarizes schematically the effect in a simple atomic system. The ground state and the electronically excited state have an angular momentum (spin plus orbital) of $J = \frac{1}{2}$. The quantization axis has been chosen parallel to the direction of propagation of the optical field so that the angular momentum of the two ground-state sublevels is either parallel or antiparallel to the direction of propagation of the laser beam. Since the photons have angular momentum ±1, only the transitions indicated by the dashed arrows couple to the laser field.

If circularly polarized light is used, as in the case of optical pumping, the optical photons have definite angular momentum so that only a single transition couples to the laser field, as indicated by the solid arrow. In this case only atoms in the $m_J = +\frac{1}{2}$ ground state are excited by the field; via absorption of a photon with angular momentum -1, they are temporarily excited into the $m_{J'} = -\frac{1}{2}$ state. Since the excited atoms decay spontaneously into either of the two ground states, repeated absorption/emission cycles tend to depopulate the level to which the optical field is coupled and

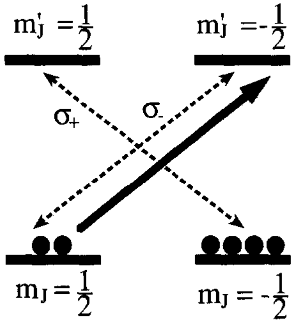

FIG. 1. Schematic representation of the effects of polarized light on a spin system. The two lower levels represent an atomic or molecular ground state with angular momentum $J = \frac{1}{2}$. The solid line represents the effect of optical pumping and the dashed lines indicate the principle of optical detection of magnetization. The quantization axis is parallel to the direction of propagation of the optical field.

populate the other. In many cases, the optical pumping rate, which can in principle approach the spontaneous emission rate of the excited state, significantly exceeds the relaxation rate of the ground-state sublevels and it is therefore possible to achieve almost complete polarization of the system.

The principle of optical detection of magnetization can also be illustrated by the level scheme of Fig. 1. If the system is irradiated by linearly polarized light, both transitions indicated by the dashed arrows are excited. If the populations of the two ground-state sublevels are different, the two circularly polarized components of the optical field experience different atomic densities and therefore different transition strengths. This difference results in circular birefringence, i.e., different index of refraction for the two circular components, and circular dichroism, i.e., different absorption. By measuring these effects it is possible to detect population differences between the angular momentum substates. With this method, one directly measures the magnetization component parallel to the laser beam, in contrast to the usual solenoid (i.e., Faraday law) detectors that measure the time derivative of the same quantity.

While the two methods discussed here can readily be combined in an experiment, this is by no means necessary and in many cases only one of the two methods is used. Since their impact on the experimental sensitivity is independent of each other, they will be discussed separately in the following sections.

OPTICALLY ENHANCED POLARIZATION

The "raw material" for magnetic resonance is basically the excess in the number of spins of a certain orientation over the number of spins with the opposite orientation. Since this raw material is often used up in a resonance experiment, the sensitivity depends strongly on the rate at which it is available, i.e., the amount of polarization that is created in a unit of time. This rate can be factored into the total number of spins available and the rate at which the individual spins are polarized. In the case of "classical" magnetic resonance, the polarization is given by the Boltzmann distribution of the spins in a magnetic field and established by thermal relaxation. As a specific example, the equilibrium polarization of a water sample at room temperature is

$$\Delta N = N_+ - N_- = 2N_{\mathrm{tot}} \frac{\hbar \omega_{\mathrm{L}}}{kT}, \qquad [1]$$

where N_+ and N_- represent the number of spins parallel and antiparallel to the field, N_{tot} represents the total number of spins, and ω_{L} represents the Larmor frequency. Assuming for simplicity a Larmor frequency of $\omega_{\mathrm{L}}/2\pi = 100$ MHz and a sample size of 1 cm^3, the total number of spins becomes $N_{\mathrm{tot}} = 6.6912 \times 10^{22}$ and the difference at room temperature is therefore $\Delta N = 2.15 \times 10^{18}$. This polarization is available at a rate of approximately $\Delta N / T_1$, i.e., approximately 5×10^{18} spins s^{-1}.

An optically pumped system, on the other hand, is polarized at a rate that is determined largely by the rate at which photons are absorbed from the optical field. If the absorbed photons transfer their angular momentum to the spin system, the rate of polarization is therefore

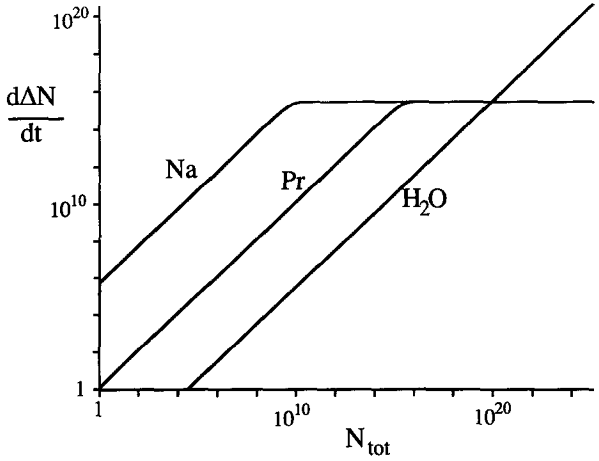

FIG. 2. Number of spins polarized per unit time as a function of the total number of spins. The curve labeled "Na" represents Na atoms polarized by optical pumping via the D_1 transition with an assumed laser power of 1 mW and a sample diameter of 1 mm. The curve labeled "Pr" represents the same data for praseodymium. The third curve represents the ^{1}H spins polarized by thermal relaxation of a 1 cm^3 sample.

$$\frac{d\Delta N}{dt} = \frac{1}{2}\frac{P_{\text{abs}}}{h\nu} = 1.5 \times 10^{18}\ \text{s}^{-1}, \qquad [2]$$

where P_{abs} represents the absorbed optical power. For the numerical example, we have assumed an optical power $P_{\text{abs}} = 1$ W and an optical wavelength $\lambda = c/\nu$ of 600 nm.

For a more detailed analysis of the situation, we write the absorbed optical power as

$$P_{\text{abs}} = P_0(1 - e^{-\alpha l}) \qquad [3]$$

where P_0 represents the incident power and α the absorptivity of the sample. We are now especially interested in the connection between the absorbed power and the total number of spins and express the absorptivity by the absorption cross section α_1 of the relevant optical transition and the number of atoms per volume N_{tot}/V as

$$\alpha l = \alpha_1 \frac{N_{\text{tot}}}{V} l = N_{\text{tot}} \frac{\alpha_1}{A}, \qquad [4]$$

where A represents the sample cross section perpendicular to the laser beam. The number of spins that can be polarized per unit time is therefore

$$\frac{d\Delta N}{dt} = \frac{1}{2}\frac{P_{\text{abs}}}{h\nu} = \frac{1}{2}\frac{P_0}{h\nu}\left[1 - \exp\left(-N_{\text{tot}}\frac{\alpha_1}{A}\right)\right]. \qquad [5]$$

Figure 2 shows this function for a range of the total number of spins in the sample. The two curves labeled "Na" and "Pr" represent the data for two optically pumped systems, atomic sodium gas ($\alpha_1 = 2 \times 10^{-16}$ m^2) and the rare-earth atom Pr in an ionic solid ($\alpha_l = 10^{-22}$ m^2). In both cases, an incident laser power of 1 mW and a sample cross section of 1 mm^2 are assumed. These two examples are intended to give an idea of the effect of the transition strength.

These data are compared to the polarization generated by thermal relaxation for the example given above, a 1 g sample of water. The amount of polarization that is available per unit time is clearly higher with optical pumping as long as only a relatively small number of spins is available. Under these conditions, the sample is optically thin and the number of absorbed photons and therefore the amount of polarization grows linearly with the total number of spins.

The situation changes when the sample becomes optically thick. In this case all the radiation incident on the sample is absorbed and the polarization generated is limited by the available laser power. This power is of course not only limited by the laser itself, but also by the limits on the heat dissipation in the sample. For a large enough number of spins, thermal relaxation becomes more efficient as a source of polarization, while optical pumping appears interesting mainly for the case in which the number of available spins is relatively small.

The effect of this rate of generation of polarization is most easily understood by considering the dynamics of a spin system under the influence of optical pumping. For an optically thin system of spins $-\frac{1}{2}$, the polarization process can be described by the equation of motion (*13*)

$$\frac{d\Delta N}{dt} = P_+ N_{\text{tot}} - \gamma_{\text{eff}} \Delta N \qquad [6]$$

with

$$P_+ = \frac{P_0}{h\nu}\frac{\alpha_l}{A}, \qquad \gamma_{\text{eff}} = \gamma_0 + P_+. \qquad [7]$$

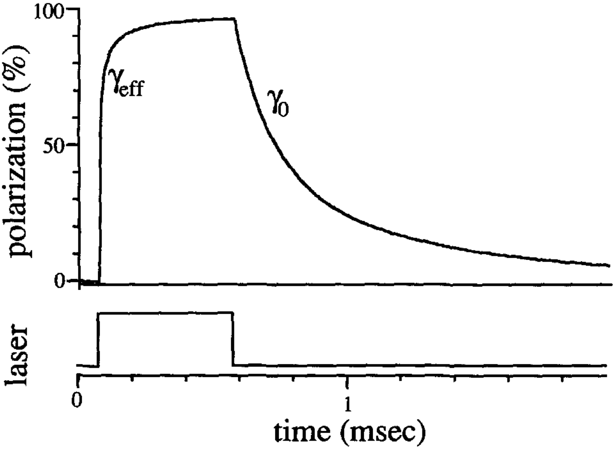

FIG. 3. Experimental measurement of the polarization of Na atoms. The polarization of the sample is measured as a function of time. The lower trace represents the pump laser intensity, and the upper trace the polarization.

Here, P_+ is the rate at which individual atoms absorb photons, γ_0 the decay rate in the absence of irradiation, and γ_{eff} the total decay rate. Starting from an unpolarized sample, the evolution of the system thus proceeds as

$$\Delta N(t) = \Delta N_\infty (1 - e^{-\gamma_{\text{eff}} t}), \qquad [8]$$

where

$$\Delta N_\infty = N_{\text{tot}} \frac{P_+}{\gamma_{\text{eff}}} \qquad [9]$$

represents the equilibrium polarization.

In many cases of optical pumping, it is possible to reach the limit $P_+ \gg \gamma_0$ so that, according to Eq. [9], the system becomes fully polarized ($\Delta N_\infty \approx N_{\text{tot}}$). An experimental example is shown in Fig. 3, where the polarization of a sample of Na atoms is monitored before, during, and after a pulse of polarized laser light applied to the D_1 transition ($\lambda = 589$ nm). The population difference was determined by an optical detection scheme discussed in the next section. The growth of the magnetization at the beginning of the pulse is determined by the rate γ_{eff}, while the decay after the pulse occurs at the rate γ_0. From the experimental data, the rates can be determined as $\gamma_0 = 3.5 \times 10^3\ \text{s}^{-1}$ and $\gamma_{\text{eff}} = 1.2 \times 10^5\ \text{s}^{-1}$. According to the formula given above, the equilibrium magnetization should therefore be >99%, slightly more than the experimental value of 96%. The difference can be attributed to incomplete overlap of pump and probe beam in the experimental setup, resulting in an inhomogeneous system with regions where the optical pump rate is considerably lower than the average. The same effect is also responsible for the nonexponential behavior of the magnetization: the growth rate of the magnetization decreases during the pulse.

As can be seen from the figure, the buildup of the spin polarization is much faster than that in typical cases of thermal relaxation. According to Eq. [7], this rate is determined primarily by the number of photons passing through the probe volume per unit time, i.e., by the pump laser intensity. Since these data were recorded with a relatively weak cw laser beam ($P_0 = 1.5$ mW), they by no means represent an upper limit. If pulsed lasers are used, the polarization is established virtually instantly (on the time scale of a typical magnetic resonance experiment). Since a single laser pulse can consist of as many as 10^{16} photons, it is in principle possible to polarize completely a spin system within a few picoseconds. It is clear that such an approach has a considerable potential, especially for systems in which the difference between transverse and longitudinal relaxation rates is large, so that the increase in the relaxation rate would be most pronounced and the optical pulses could be applied at a relatively high repetition rate.

The polarization in a given system can be maximized by increasing the laser intensity. Since the total available laser power cannot be increased arbitrarily, the only alternative is the reduction of the diameter of the laser beam. Focusing the laser beam increases the absorption probability for the individual photons, given by the ratio α_1/A, if the system under study can be confined to these dimensions and remains optically thin. Another alternative is the use of optical cavities to enhance the power density of the optical field and thereby the rate of polarization.

OPTICAL DETECTION

Detecting spin polarization by optical means usually relies on changes in the polarization of the light. The light that is detected can originate either from the fluorescence emitted by the system or from light transmitted through the system. Both methods have their advantages and disadvantages: The fluorescence light can be detected free of any background signal in the sense that every photon that is detected has been emitted by one of the atoms being studied and therefore carries information on the system of interest. The disadvantage of this method is that the collection efficiency of the detection system is usually relatively low. The second method uses a coherent laser beam that propagates through the system of interest and is subsequently analyzed in a polarization-sensitive detector. In this case, the collection efficiency can be maximized, but the detector also receives light that has not interacted with the atoms. These "background photons" carry no information but contribute to the detector noise.

An optical measurement of magnetization via polarization-selective detection of the transmitted light can rely on changes in either the absorption or the dispersion of the sample. The physical process as well as the experimental setup for both types of measurement is very similar. The main difference is the dependence of the sensitivity on the detuning of the laser frequency from the optical resonance. If the laser wavelength is near the optical line center, absorption measurements provide usually the higher sensitivity, but if the laser is tuned far from resonance, dispersion measurements are more sensitive.

A possible experimental setup for an absorption-type measurement is shown in Fig. 4: the transmitted light is passed through a $\lambda/4$ retardation plate which converts circular into linear polarization. The two orthogonal polarizations are then separated by the polarizing beam splitter (*13*). The two photodetectors measure intensities that correspond to the circularly polarized components of the light. If the laser light is at exact resonance with the optical transition and the sample is completely polarized (all atoms are in the same ground-state sublevel), the absorption of (say) right circularly polarized light goes to zero, while the absorption of left circularly polarized light becomes twice

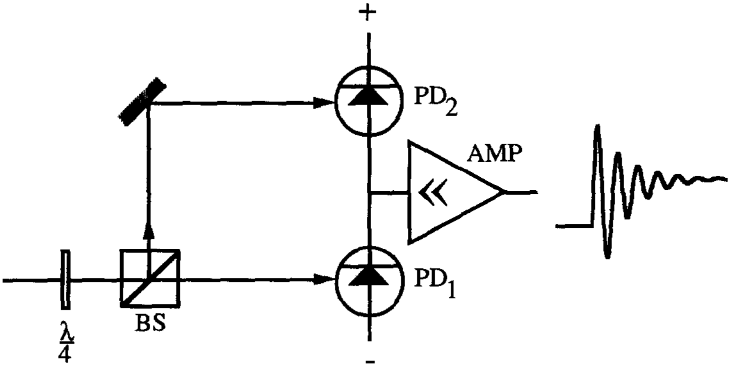

FIG. 4. Schematic representation of the experimental setup used for optical detection of a magnetic dipole moment. BS, polarizing beam splitter; PD, photodiode; AMP, amplifier.

the absorption of the unpolarized sample α_0. For the experimental setup of Fig. 4, the number of photons arriving on the two photodiodes is therefore

$$n_{1,2} = \tfrac{1}{2} n_{\mathrm{laser}} e^{-\alpha_0 l(1 \pm m_z)}, \qquad [10]$$

where n_{laser} represents the total number of photons, the different signs refer to the two photodetectors, and m_z ($-1 \leqslant m_z \leqslant 1$) is the relative population difference between the two ground-state sublevels. Since the quantization axis is parallel to the direction of propagation, Eq. [10] can be derived readily from inspection of Fig. 1. Expressing the signal in terms of photon numbers has the advantage that the analysis is independent of the actual detector used. The numbers can easily be converted into signal energy by multiplying them with the photon energy $h\nu$ and the conversion efficiency of the photodetector. In most cases it is advantageous to measure not directly the intensity of one partial beam, but to make a difference measurement, as shown in Fig. 4. The actual signal then becomes

$$\Delta n = n_1 - n_2 \approx -n_{\mathrm{laser}} e^{-\alpha_0 l} \alpha_0 l m_z \approx -n_{\mathrm{laser}} \alpha_0 l m_z, \qquad [11]$$

where the successive approximations are valid in the case of weak absorption, i.e., $\alpha_0 l \ll 1$. In order to see the dependence on the number of spins more clearly, it is useful to express the absorptivity α_0 again in terms of the transition cross section of the individual atoms α_1,

$$\Delta n = -n_{\mathrm{laser}} N_{\mathrm{tot}} \frac{\alpha_1}{A} m_z, \qquad [12]$$

which is again valid if the sample is optically thin ($\alpha_0 l \ll 1$), i.e., if the number of atoms is small. The signal is therefore directly proportional to the magnetization component parallel to the propagation axis of the light and to the laser intensity. However, while a higher laser intensity can lead to a higher signal, it should not exceed the level at which the spin system is significantly damped by the interaction with the laser field. Under the condition that the number of photons scattered by an individual spin should not exceed $1/T_2$, the total number of photons passing through the sample with lateral dimension A during the measurement time T_{meas} is therefore

$$n_{\mathrm{laser}} = \frac{A}{\alpha_1} \frac{T_{\mathrm{meas}}}{T_2}. \qquad [13]$$

The signal Δn for a completely polarized spin system ($m_z = \pm 1$) then becomes

$$n_{\mathrm{signal}} = n_{\mathrm{laser}} \alpha l = \frac{A}{\alpha_1} \frac{T_{\mathrm{meas}}}{T_2} N_{\mathrm{tot}} \frac{\alpha_1}{A} = N_{\mathrm{tot}} \frac{T_{\mathrm{meas}}}{T_2}. \qquad [14]$$

The maximum signal is therefore independent of the transition cross section α_1 and determined simply by the fact that each atom scatters one photon during the lifetime of the spin state. Figure 5 shows the expected number of signal photons as a function of the total number of spins for the two examples used before, atomic sodium and Pr in an ionic solid. The function was calculated for a laser beam diameter $A = 0.5\ \mathrm{mm}^2$ and $T_{\mathrm{meas}} = \mathrm{T}_2$. The graph does not use the approximation [11] so that the signal

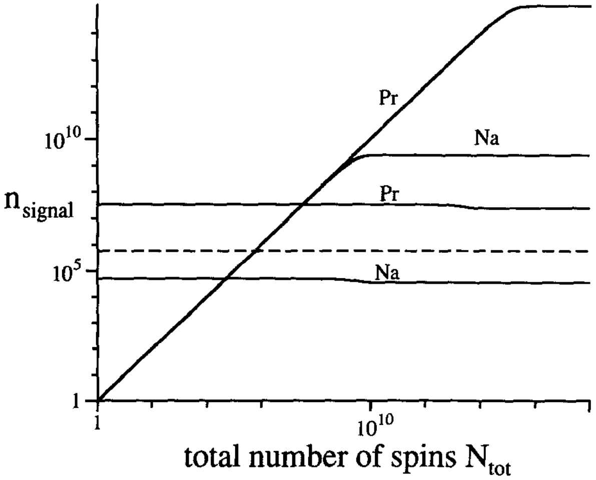

FIG. 5. Signal and noise in optically detected magnetic resonance experiments: The number of photons collected during an experimental period $T_{\text{meas}} = T_2$ is plotted as a function of the total number of spins. The curves labeled "Na" refer to atomic sodium gas and those labeled "Pr" to praseodymium. The full horizontal lines indicate the corresponding shot-noise level, the dashed line indicates the experimentally determined noise level for Na, and the other curves indicate the theoretical signal.

saturates when the sample becomes optically thick for one polarization component, while the other is transmitted without attenuation.

In order to determine the sensitivity of the detection scheme, the signal must be compared to the noise recorded by the detector. With the experimental setup described above, the signal is in first order independent of the fluctuations in the laser intensity, but in higher order they can also affect the signal. In addition, thermal noise is of course always present as well as electronic noise. However, while these sources of noise can, at least in principle, be reduced or eliminated, there is always shot noise from the optical field itself which is anticorrelated between the two detectors and therefore adds in the signal. If the optical field can be described as a coherent state, the shot noise should be equal to the square root of the total number of photons arriving at the detector. As a function of the number of spins, it is therefore

$$n_{\text{noise}} = \sqrt{\frac{n_1 + n_2}{2}} = \sqrt{\frac{A}{\alpha_1}\,\frac{T_{\text{meas}}}{T_2}\,\frac{1 + \exp\left(-N_{\text{tot}}\,\frac{\alpha_1}{A}\right)}{4}}, \qquad [15]$$

where $n_{1,2}$ represent the number of photons arriving at the two photodetectors. This function is represented graphically in Fig. 5, again for the two examples Na and Pr. It is almost independent of the number of spins; only a small drop indicates where the sample becomes optically thick for one polarization so that half of the photons are absorbed. The dashed line represents the experimentally determined noise level of our detector, expressed in terms of the equivalent photon flux. It is approximately an order of magnitude above the shot-noise level. The difference is due to thermal noise, electronic noise from the amplifier, residual laser intensity fluctuations, and the quantum efficiency of the photodiodes (~50%).

In the optically thin region ($N_{\text{tot}} < A/\alpha_1$), the signal-to-noise ratio can now be calculated as

$$n_{\text{signal}}/n_{\text{noise}} = N_{\text{tot}}\sqrt{2\,\frac{\alpha_1}{A}\,\frac{T_{\text{meas}}}{T_2}} = \sqrt{N_{\text{tot}}\alpha_0 l\,\frac{T_{\text{meas}}}{2T_2}}\,. \qquad [16]$$

An experimental example is shown in Fig. 6: the spectrum was obtained as the Fourier transform of an average of 22,000 FIDs recorded at the D_1 transition of atomic sodium at a temperature of 64°C with a probe beam power of 10 μW and a beam diameter of 0.5 mm^2. The average number of atoms in the laser beam can be calculated from the absorption signal and is of the order of 22,000. The repetition rate was 500 Hz and the strength of the magnetic field, which was applied perpendicular to the direction of the laser beam, was $|B| = 8.6\ \mu$T. For details of the experimental procedure, see Ref. (*13*).

For a given system, the experimenter can enhance the detection sensitivity by maximizing the ratio α_1/A, i.e., by tuning the laser on resonance with the optical transition (maximizing α_1) and focusing the laser beam (minimizing A). In the limit of a strong optical resonance line, the absorption cross section is of the order of the square of the optical wavelength. Since an optical beam can in principle be focused into a spot of the size of the wavelength, this ratio can reach values near unity. Experiments with single atoms or molecules may well be possible if the spins can be located at the focus of a laser beam.

Instead of measuring magnetization via changes in the polarization of the transmitted light, it is also possible to use polarization-selective detection of the fluorescence light as the signal. This scheme has the advantage that, in an ideal experiment, photons that have not interacted with the atoms do not reach the detector, so that the shot noise due to the noninteracting photons can be reduced. If the laser intensity is again set so that the atoms scatter on average less than one photon during the lifetime of

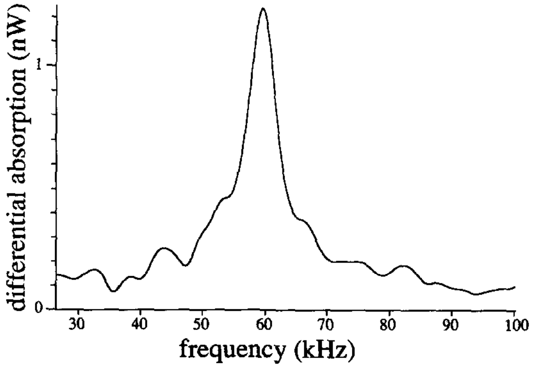

FIG. 6. Experimental spectrum obtained from Na vapor at a temperature of 64°C with a probe beam power of 10 μW and a beam diameter of 0.5 mm^2. The average number of atoms in the laser beam was about 22,000. Number of accumulations = 22,000, repetition rate = 1 kHz, magnetic field $|B| = 8.6\ \mu$T.

the spin state, photons may then be collected at a rate of

$$S = N_{\text{tot}}\eta\delta, \qquad [17]$$

where η represents the collection efficiency of the detection system and δ the magnetic resonance linewidth. If the noise present in this system is determined by shot noise, it is proportional to $\sqrt{S}$ and the sensitivity is largely determined by the collection efficiency η which is of the order of 10^{-4} in typical systems. The signal-to-noise ratio can therefore exceed unity even for a relatively small number of atoms.

CONCLUSION

Both schemes for the enhancement of the sensitivity of magnetic resonance experiments that were discussed here have already been applied to a wide variety of systems (*13*). The main purpose of the discussion presented here is to summarize the possibilities and requirements on the system and to show in what systems optical methods show the greatest promise. For polarization enhancement by optical pumping, the limits are determined by the optical properties of the sample as well as the available laser power which limits the amount of angular momentum that can be transferred to the spin system. In a continuous experiment, the laser power will usually be limited to values of less than approximately 1 W: brighter cw lasers are not only hard to obtain, they would also lead to an unacceptable heating of the sample. Under these conditions, optical pumping will usually not be an interesting alternative to conventional methods if the number of available spins is larger than approximately 10^{18}, as long as the main criterion is the rate of polarization available in a unit time. Other considerations, like the degree of polarization that can be achieved, may modify this range.

The situation is different in the case of pulsed experiments. Not only are the available laser powers larger in this case, but also the sample heating problem is greatly reduced. In the continuous as well as in the pulsed case, if the total number of spins available is too small for conventional magnetic resonance experiments, such as in gases, dilute solids, or quasi-two-dimensional systems, optical pumping can increase the number of polarized spins to levels near 100%, much higher than the level that can be achieved by thermal population relaxation, and thereby make experiments feasible (*12, 14*).

Other systems of interest are those with extremely long relaxation times or low Larmor frequencies: in these cases, the rate at which polarization is generated becomes too small for a classical magnetic resonance experiment. Optical pumping, on the other hand, can often still produce polarization at a rate that makes the experiment feasible. The rate of production of magnetization is then determined essentially by the rate at which photons pass through the system, i.e., by the optical power. If a pulsed laser system is used, the optical peak power can considerably exceed the level of the examples shown here. It is then possible to completely polarize spin systems within the duration of the optical pulse, which may be of the order of picoseconds. In any case, not only the available laser power limits the production of polarization but also the heat dissipation capability of the sample. However, as long as the transfer of polarization from the photons to the spin system has a high enough sensitivity, this limitation should not be a serious one: 1 W of visible laser radiation carries enough angular momentum to polarize more than 10^{18} spins per second.

The experiments described here all rely on the availability of an optical transition coupled to the magnetic resonance transitions under investigation. Nevertheless, optical methods can also be applied to some systems in which this condition is not fulfilled. As an example, it is also possible to optically pump a different spin system and subsequently transfer the polarization to the system under study (*2, 11, 12, 15*). If high-power pulsed laser systems are used, the requirements on matching the resonance frequency and on the strength of the optical transition are further reduced.

In the case of optical detection, the advantage that is gained over direct detection of the precessing magnetic moment depends strongly on the type of the system, especially on the availability of an allowed optical transition. Under favorable conditions, systems with as few as 10^5 spins can be investigated and in the future it may well be possible to perform experiments on individual atomic or molecular systems.

Of course, the methods presented here are by no means the only alternatives to "classical" magnetic resonance. They should always be evaluated not only against the conventional experiments but also against other alternatives, such as using SQUIDs for detection (*5*). Nevertheless, optical methods not only have a long history but have become even more popular recently, especially thanks to the rapid progress in the field of laser technology, such as the availability of relatively cheap and efficient semiconductor lasers.

ACKNOWLEDGMENTS

I thank Professor Richard R. Ernst for asking the question that this paper is trying to answer, and for carefully reading the manuscript. Furthermore, I received experimental assistance from Harald Klepel and financial support from the Schweizerischer Nationalfonds.

REFERENCES

1. G. S. Hurst, M. G. Payne, S. D. Kramer, and J. P. Young, *Rev. Mod. Phys.* **51,** 767 (1979).
2. H. Dehmelt, *Rev. Mod. Phys.* **62,** 525 (1990).
3. D. C. Nguyen, R. A. Keller, and M. Trkula, *J. Opt. Soc. Am. B* **4,** 138 (1987).
4. W. E. Moerner and L. Kador, *Phys. Rev. Lett.* **62,** (1989).
5. C. Connor, J. Chang, and A. Pines, *Rev. Sci. Instrum.* **61,** 1059 (1990).
6. C. R. Bowers and D. Weitekamp, *Phys. Rev. Lett.* **57,** 2645 (1986).
7. W. D. Brewer, *Hyperfine Interact.* **12,** 173 (1982).
8. P. B. Davies, *J. Phys. Chem.* **85,** 2599 (1981).
9. L. C. Balling, *in* "Advances in Quantum Electronics" (D. W. Goodwin, Ed.), Vol. 3, Academic Press, London, 1975.
10. E. Fermi and F. Rasetti, *Nature* **115,** 764 (1925).
11. G. D. Cates, D. R. Benton, M. Gatzke, W. Happer, K. C. Hasson, and N. R. Newbury, *Phys. Rev. Lett.* **65,** 2591 (1990).
12. D. Raftery, H. Long, T. Meersmann, P. J. Grandinetti, L. Reven, and A. Pines, *Phys. Rev. Lett.* **66,** 584 (1991).
13. D. Suter and J. Mlynek, *Adv. Magn. Opt. Reson.* **16,** 1 (1991).
14. Dieter Suter, Jérôme Äbersold, and Jürgen Mlynek, *Opt. Commun.* **84,** 269 (1991).
15. H. G. Dehmelt, *Phys. Rev.* **109,** 381 (1958).