Optically Enhanced Magnetic Resonance

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1 INTRODUCTION

1.1 Motivation

The physical mechanism of nuclear magnetic resonance spectroscopy, the excitation of transitions between nuclear spin states, was explored in the years after World War II, and is by now well characterized. Today's interest in the field is based largely on the immense potential for applications: spins can serve as probes for their environment because they are weakly coupled to other degrees of freedom. In most magnetic resonance experiments, these couplings are used to monitor the environment of the nuclei, like spatial structures or molecular dynamics. While the direct excitation of nuclear spin transitions requires irradiation with a radiofrequency field, many systems offer the alternative possibility of using light for polarizing the spin system or for observing its dynamics. This possibility arises from the coupling between the spins and the electronic degrees of freedom: optical photons excite transitions between states that differ both in electronic excitation energy as well as in their angular momentum states.

The light can serve three different purposes: it can polarize the spin system, thereby creating the 'raw material' for spectroscopic experiments; it can measure the spin polarization, serving as a detector; and it can influence the dynamics of the system. Some motivations for using light in magnetic resonance experiments include the following:

Sensitivity. In many cases, the possible sensitivity gains are the primary reason for using optical methods. Compared to conventional NMR, sensitivity gains of more than 10 orders of magnitude are possible. Thus so far, two groups have demonstrated the magnetic resonance of individual molecules,[1,2] while a typical NMR sample contains of the order of 10^{20} spins.

Selectivity. Using lasers, it is possible to observe selectively signals from certain regions in space, such as surfaces. Alternatively, a laser pulse may define the time of an observation with a resolution of 10^{-14} s or select a particular chemical environment like the chromophore of a molecule or a quantum well in a semiconductor. Crystal imperfections can change the optical properties of an atomic or molecular site in such a way that optical excitation can distinguish those sites against a background that is orders of magnitude larger.

Speed. Conventional magnetic resonance requires the presence of population differences between spin states to excite transitions between them. In most cases, thermal relaxation establishes these population differences. At low temperatures, this coupling process may be too slow for magnetic resonance experiments. In the case of optical excitation, a polarizing laser beam creates the population differences. The time required for polarization of the system then depends only on the laser intensity and can be instantaneous on the timescale of the magnetic resonance experiment, independent of temperature.

Experiments in electronically excited states. If information about an electronically excited state that is not populated in thermal equilibrium is desired, it may be necessary to use light to populate this state. It is then certainly advantageous to populate the different spin states unequally to obtain at the same time the polarization differences that are needed to excite and observe spin transitions.

1.2 Laser Spectroscopy

Apart from magnetic resonance, the interaction of matter with laser light is the second most important ingredient for the experiments that will be discussed below. In laser spectroscopy, light induces transitions between different electronic states. Many of the differences between laser spectroscopy and magnetic resonance arise from the different frequency scales: optical frequencies are more than six orders of magnitude higher than rf frequencies. An important consequence is that laser spectroscopy is much more sensitive as a technique: optical experiments on individual atoms[3,4] and molecules[5,6] have become routine in the last few years. While the first experiments of this type used atomic ions in ultrahigh vacuum, they can now also be performed in condensed matter, like solutions[5] or solid matrices.[6]

Another attractive feature of laser spectroscopy is the high time resolution, which is of course also intimately linked to the high frequencies of optical radiation. Technical limits to the time resolution are now of the order of a few femtoseconds, corresponding to only a few optical cycles. In chemistry, this resolution allows 'real time' monitoring of chemical reactions, e.g. by measuring the intermolecular potential as a function of time during the reaction. Also in solid state physics, laser spectroscopy allows the monitoring of fast processes, such as the excitation and recombination of electrons and holes in semiconductors.

In the field of high-resolution spectroscopy, it is also possible to achieve very high frequency resolution: some systems can now reach resolutions of better than 1 Hz, corresponding to a relative frequency stability of some 10^{15}. This high-frequency resolution is especially attractive for metrology, where many groups are trying to build new, more precise frequency standards based on optical transitions. These properties of laser spectroscopy, high-frequency resolution and high temporal resolution open attractive possibilities for applications in optically enhanced magnetic resonance experiments.

The next section discusses the most important physical phenomena that permit the use of laser radiation in magnetic resonance experiments. Examples of applications to specific systems are discussed in the third section.

2 PHYSICAL BACKGROUND

2.1 Angular Momentum

The possibility of using optical radiation for exciting and detecting spin polarization can be traced to the angular momentum of the photon. Photons as carriers of the electromagnetic interaction carry one unit ($\hbar$) of angular momentum, which is oriented parallel or antiparallel to the direction of light propagation. Since angular momentum is a conserved quantity, the total angular momentum of the system (radiation and matter) remains constant during absorption and emission of radiation. When an atom or molecule absorbs a photon, it must incorporate not only the photon energy but also its angular momentum (see Figure 1). The resulting angular momentum of the atom is the vector sum of its initial angular momentum plus the angular momentum of the absorbed photon.
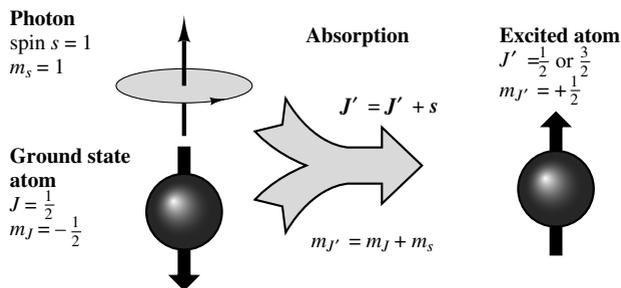
Figure 1   Conservation of angular momentum during absorption of a photon

Magnetic resonance spectroscopy requires a spin polarization inside the medium. In conventional magnetic resonance experiments, thermal contact of the spins with the lattice establishes this polarization. This process is relatively slow, especially at low temperatures where relaxation times can be many hours. The polarizations are limited by the Boltzmann factor, which is typically less than 10^{-5}. Photon angular momentum, in contrast, can be created in arbitrary quantities with a polarization that can be arbitrarily close to unity. If it is possible to transfer this polarization to nuclear or electronic spins, their polarization can reach the same values.

2.2 Optical Pumping

This possibility was first suggested by Kastler.[7,8] Figure 2 illustrates the principle of operation. The model atomic system consists of two electronic states, labelled $|g\rangle$ for ground state and $|e\rangle$ for excited state. We assume that both have an angular momentum $J = \frac{1}{2}$; their angular momentum substates are labeled as $J_Z = +\frac{1}{2}$ and $J_Z = -\frac{1}{2}$ in the figure. If the system is irradiated by circularly polarized light, the photons have a spin quantum number $m_s = +1$. Since the absorption of a photon is possible only if both the energy and the angular momentum of the system are conserved, only those ground state atoms that are initially in the $J_Z = -\frac{1}{2}$ state can absorb photons. If an atom is initially in the state $J_Z = +\frac{1}{2}$, the resulting excited
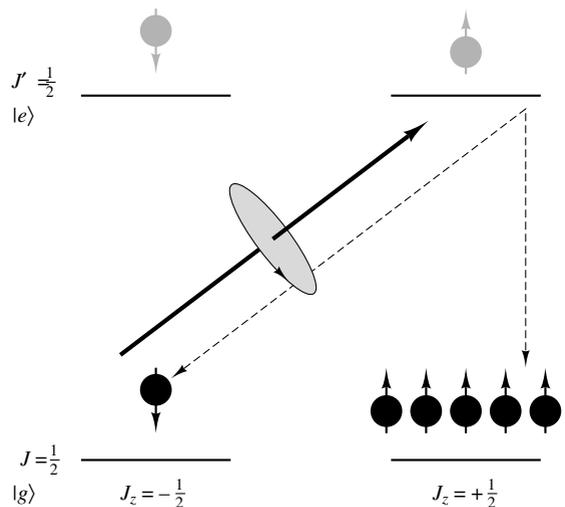
Figure 2   Principle of optical pumping illustrated for a simple atomic system

state would have to be a $J_Z = +\frac{3}{2}$ state, which does not exist in the atom of our model system.

An atom that has absorbed a photon will re-emit one after the excited state lifetime. Spontaneous emission can occur in an arbitrary direction in space and is therefore not subject to the same selection rules as the excitation process with a laser beam of definite direction of propagation. The spontaneously emitted photons carry away angular momentum with different orientations and the atom can therefore end up in either of the two ground states. If it ends up in the original state, it can absorb another photon and repeat the cycle; if it ends up in the other state, it no longer couples to the laser field and remains in this state indefinitely. The net effect of the absorption and emission processes is therefore a transfer of population from one spin state to the other and thereby a polarization of the atomic system.

2.3 Dynamics

As in conventional magnetic resonance, the spin polarization undergoes Larmor precession in an external magnetic field. If we use light to drive the spin system, it also affects the spin dynamics: if the laser couples to a particular transition, it appears to shift the energy of the levels to which it couples.[9,10] Shifts of energy levels always affect the dynamics of the corresponding system. In this case, the energy level shift has exactly the same effect as a magnetic field parallel to the direction of the laser beam. The light shift effects are therefore often analyzed in terms of virtual magnetic fields. The strength of this virtual magnetic field depends on the detuning of the laser from the electronic transition frequency. Besides these level shifts, the laser light also causes a damping of the spin polarization. In contrast to the light shift effect, which has a dispersive dependence on the laser detuning, the damping effect has an absorptive behavior, i.e. its maximum occurs when the laser frequency is exactly resonant with the optical transition frequency. Light shift and damping are the main contributors to laser-induced dynamics in atomic spin systems.[11]
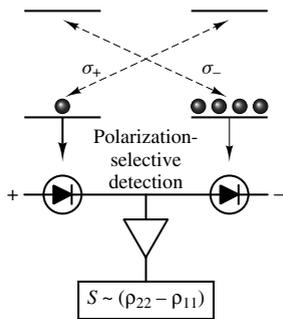
Figure 3 Principle of observation of spin polarization by optical radiation

2.4 Observation

The last requirement for optically enhanced magnetic resonance is a method for observing the spin polarization. An early suggestion that magnetic resonance transitions should be observable in optical experiments is due to Bitter.[12] The physical process used in such experiments is the complement of optical pumping: it transfers spin angular momentum to the photons and polarization-selective detection measures the photon angular momentum. Figure 3 illustrates this for the same model system that we considered for optical pumping. Light with a given circular polarization interacts only with one of the ground state sublevels. Since the absorption of the medium is directly proportional to the number of atoms that interact with the light, a comparison of the absorption of the medium for the two opposite circular polarizations yields the population difference between the two spin states directly. This population difference is directly proportional to the component of the magnetization parallel to the laser beam. This analysis of the transmitted light allows the observation of spin polarization in the electronic ground state. Another possibility is the analysis of the fluorescence light: angular momentum conservation imposes correlations between the direction and polarization of the spontaneously emitted photons, which depend on the angular momentum state of the excited atom.

As shown schematically in Figure 4, the difference between the atomic angular momentum of the excited and ground states determines the angular momentum J_ν of the spontaneously emitted photon. This condition determines the polarization of the emitted radiation for a given direction. In the first experiments on optical pumping, observation of the fluorescence allowed not only the measurement of the excited state polarization, but also the ground state polarization to be inferred.[13]
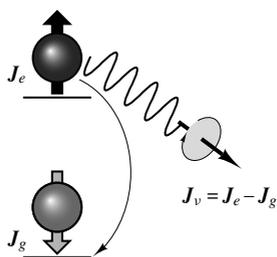
Figure 4 Polarization of the fluorescence depends on the spin state of the excited atoms
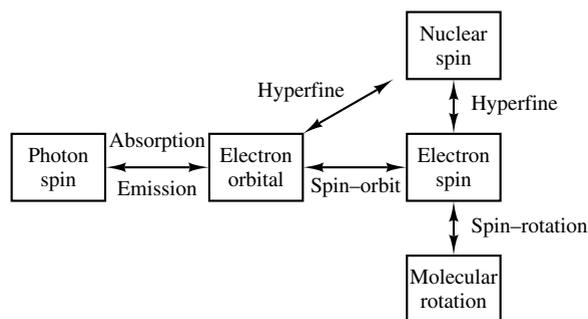
Figure 5 Summary of the most important reservoirs of angular momentum

2.5 Angular Momentum Reservoirs

Atoms and molecules may contain different types of angular momentum. The most important reservoirs include the rotational motion of molecules, the orbital angular momentum of electrons, and the spin angular momentum of electrons and nuclei. Not all these types of angular momentum couple directly to the radiation field: in free atoms, only the orbital angular momentum of the electrons is directly coupled to the optical transitions. However, various interactions couple the different types of angular momentum to each other and allow the polarization to flow from the photon spin reservoir through the electron orbital to all the other reservoirs, as shown schematically in Figure 5. This is, of course, of spatial interest for nuclear magnetic resonance, since there is no direct transfer to nuclear spins. However, the coupling between electronic and nuclear angular momentum is usually strong enough to provide an efficient transfer mechanism. This even allows the polarization of nuclear spin systems in diamagnetic ground states.

In the example of Figure 6, the electronic ground state is diamagnetic and has a nuclear spin $I = \frac{1}{2}$. Since the nuclear spin does not affect the absorption of light, both spin states interact with a circularly polarized laser beam. Angular momentum conservation requires that optical excitation populates only the states with an electronic angular momentum of $m_J = 1$. If electronic and nuclear spin are parallel in the excited state ($m_J = 1$, $m_I = \frac{1}{2}$, dashed line in Figure 6), the resulting state does not evolve until it reemits a photon and decays into the state from which it was excited. If, however, the nuclear spin is oriented antiparallel to the electronic angular momentum ($m_J = 1$, $m_I = -\frac{1}{2}$), the hyperfine interaction can induce simultaneous spin flips that conserve the total angular momentum and transfer the atom into the ($m_J = 0$, $m_I = \frac{1}{2}$) state. Spontaneous decay from this state again leaves the nuclear spin unchanged and thus brings the
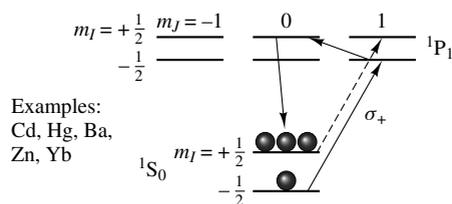
Figure 6 Polarization of nuclear spin reservoirs in diamagnetic ground states

atom into the $m_I = +\frac{1}{2}$ ground state. The net effect of the absorption−hyperfine−emission cycle is therefore the transfer of an atom from the $-\frac{1}{2}$ to the $+\frac{1}{2}$ nuclear spin state. A sequence of such cycles polarizes the nuclear spin system in complete analogy to the case of electronic spin polarization.

Spin polarization can be transferred between different reservoirs, not only within one atomic species but also between different particles. This was first demonstrated by Dehmelt who used transfer to free electrons to polarize them.[14] Another frequently used transfer process includes optical pumping of alkali atoms, in particular Rb and Cs, and the transfer of their spin polarization to noble gas atoms like Xe. This method was pioneered by Happer et al.[15] and applied to the study of surfaces in systems with high surface to volume ratios like graphitized carbon[16] or to the construction of NMR gyroscopes.[17,18] The transfer from alkali to noble gas atoms is relatively efficient because they form van der Waals complexes. During the lifetime of this quasi-molecule, the dipole−dipole interaction between the two spins induces simultaneous flips of the two spin species, which transfer polarization from the Rb atoms to the Xe nuclear spin. Typical cross-polarization times are on the order of minutes, but the long lifetime of the Xe polarization permits reaching polarizations close to unity. The spin polarization survives freezing[19] and can be transferred to other spins by thermal mixing.[20]

At low magnetic fields, the coupling between the reservoirs can exceed the Zeeman interaction between the individual spins and the magnetic field. This implies that the spins do not evolve independently, but as a collective entity that may include electronic as well as nuclear spins. Under these conditions, the traditional distinction between ESR and NMR loses its meaning: electronic and nuclear spins undergo simultaneous transitions. Nevertheless, it may be possible to extract the different physical parameters for the various interactions. Figure 7 shows an example: in Na atoms, the hyperfine interaction couples the electron ($S = \frac{1}{2}$) and nuclear spins ($I = \frac{3}{2}$) with a coupling constant of 1.8 GHz. In fields less than 0.1 T, the hyperfine interaction is therefore significantly stronger than the Zeeman interaction. For the spectrum shown here, the atoms were placed in a field of 0.7 mT. At these field strengths the two spins remain strongly coupled but, as shown in the spectrum, the electron Zeeman interaction can be determined as 5 MHz and the nuclear Zeeman interaction as 19 kHz.
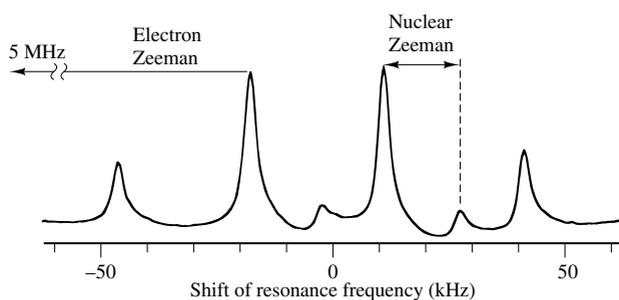
Figure 7 Example of an optically detected magnetic resonance spectrum in a strongly coupled system
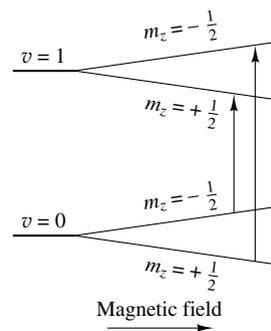
Figure 8 Principle of laser magnetic resonance

2.6 Laser Magnetic Resonance

A method for the optical detection of magnetic resonance transitions that does not directly rely on the conservation of angular momentum is laser magnetic resonance. It uses transitions between states that differ both in their electronic or vibrational and angular momentum quantum numbers. Transitions between such states depend on magnetic interactions but fall into the optical frequency range. The population difference between the two states is thus close to unity and the detection of the radiation is highly efficient.

Figure 8 illustrates the principle of the method: a magnetic field lifts the degeneracy of both the ground and excited states. For the figure, only a single spin $I = \frac{1}{2}$ was assumed. If the laser induces transitions that change both the vibrational and the spin quantum number, such as the transitions indicated by arrows in Figure 8, the resonance frequency depends clearly on the magnetic field strength. The resulting spectra contain the information about the magnetic interactions in both the excited and the ground state. Experiments of this type were performed in molecular gases[21] as well as in semiconductor materials, where the process is known as spin-flip Raman scattering.[22,23]

While this method allows high sensitivity, its resolution is lower than with direct detection. In most experimental settings, the laser linewidth limits the resolution. Optical rf double resonance methods[24] or a modification of the basic Raman experiment that is known as coherent Raman scattering can overcome this limitation.

2.7 Coherent Raman Processes

Raman processes can be considered as an interaction between two optical photons and a material excitation, as shown schematically in Figure 9. The arrows labeled ω_1, ω_2 represent two optical fields that couple to two allowed optical transitions that share the energy level $|3\rangle$. If two laser fields with these frequencies are incident on the three-level system, they excite coherences in all three transitions of the three-level system, in particular also the coherence labeled ω_{12} in the transition that is not directly coupled to the laser fields. If, conversely, the coherence in transition $|1\rangle \leftrightarrow |2\rangle$ is already present in the material, and a single laser field at frequency ω_1 is incident on the system, it excites a Raman field at frequency $\omega_2 = \omega_1 + \omega_{12}$. This Raman field propagates with the incident laser field and the frequency ω_{12} can be measured as the difference between the two optical frequencies. If the laser frequency drifts, the frequency of the incident field as well
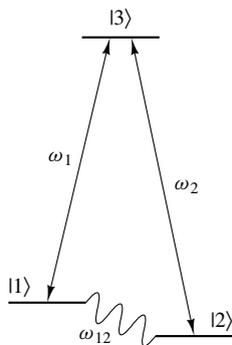
Figure 9 Raman processes couple two electromagnetic fields (ω_1, ω_2) with a material excitation

Figure 10 Principle of the measurement of nuclear quadrupole interaction by laser spectroscopy

as that of the Raman field changes by the same amount. As a result, the difference frequency is unchanged and the resolution of the measurement is not affected by laser frequency jitter or broad optical resonance lines.[25] Coherent Raman processes therefore provide a combination of high resolution with high sensitivity.

The implementation of coherent Raman scattering must somehow create the coherent excitation of the material. This can be achieved either with optical fields[26–28] or with radiofrequency irradiation.[29]

2.8 Sensitivity

Several mechanisms contribute to the increase in sensitivity by optical methods. The first is the spin polarization that can be achieved. If thermal relaxation establishes the spin polarization, it cannot exceed the Boltzmann factor which is at most on the order of 10^{-5}. Optically, it is possible to polarize the spins completely and thereby gain some five orders of magnitude.[30] In addition, the optical detection process occurs at much higher energies: optical photons have energies some seven orders of magnitude higher than that of rf photons. Detecting a small number of optical photons is therefore significantly easier than detection of rf photons. At the same time, thermal noise is almost negligible at optical frequencies. A third reason for the increased sensitivity is that laser irradiation can polarize the spins much faster: depending primarily on the laser intensity, complete polarization of the spin system may require less than 1 μs.[31]

Since optical detection directly measures the magnetization, in contrast to pick-up coils that measure its time-derivative, the detection sensitivity is independent of the resonance frequency. It is therefore possible to perform experiments at low or vanishing fields with the same detection efficiency as at high fields. This is of particular interest in cases where one wants to measure small effects like rotational velocities, which cannot be seen in high fields.[32]

2.9 Information Content

Apart from the advantage of sensitivity, optically enhanced magnetic resonance is sometimes capable of providing information which conventional methods cannot provide. We illustrate this with the measurement of the sign of the nuclear
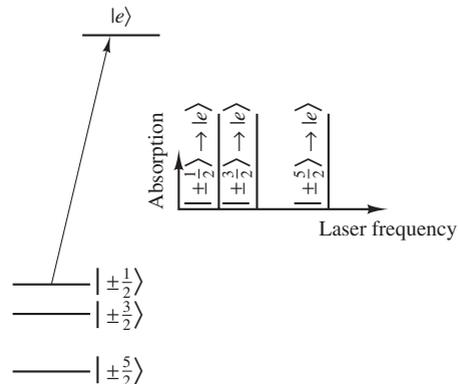
quadrupole interaction. The nonspherical part of the charge distribution of atomic nuclei with spin $I > \frac{1}{2}$ is a sensitive probe of the electric field at the site of the nucleus. Measurements of the interaction between the nuclear quadrupole moment and the electric field gradient (EFG) tensor can provide information about the electronic and structural environment of the nuclei, as well as about motional processes. Many experiments in magnetic resonance are therefore performed to measure quadrupole couplings.[33] However, conventional magnetic resonance experiments cannot provide the sign of the coupling.[34]

In the simplest case of axial symmetry, the Hamiltonian $\hat{\mathcal{H}}_Q$ of the nuclear quadrupole interaction is given by a coupling constant D multiplied by the square of the nuclear spin operator $\hat{I}_Z$, $\hat{\mathcal{H}}_Q = D\hat{I}_Z^2$. The coupling constant D is determined by the size of the nuclear quadrupole moment and the electric field gradient. It can be measured either without a magnetic field, which corresponds to the case of pure quadrupole coupling, or in a high magnetic field, which corresponds to the case of high-field NMR. In both cases, the spectra are identical for positive and negative sign of the coupling constant D.

Figure 10 schematically shows how laser spectroscopy can be used to measure the nuclear quadrupole interaction with the sign information. In the model system considered here, the spin is $\frac{5}{2}$ and a measurement is performed in zero magnetic field. In the electronic ground state, the system then has three sets of doubly degenerate states. If we can neglect the quadrupole splitting in the excited state, as assumed in Figure 10, the absorption spectrum directly provides the splittings between the levels. Reversal of the sign of the quadrupole splitting leads to a reversal of the line positions in the spectrum (Figure 11). In actual systems, the inhomogeneous broadening of the optical resonance lines complicates the procedure. Closely analogous measurements are nevertheless possible and have allowed the measurement of the quadrupole coupling constant of Pr^{3+} in the host material $YAlO_3$ as shown in Figure 11.[35]

3 APPLICATIONS

It is of course impossible to give a complete summary of the large number of applications that have used optically enhanced magnetic resonance techniques in various systems. The present selection tries to demonstrate the wide range of systems for
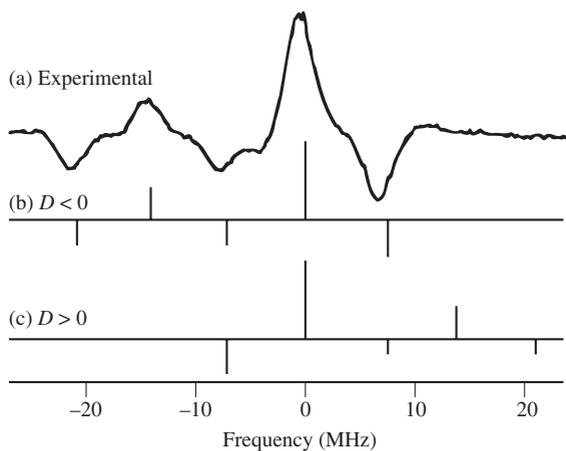
Figure 11 Comparison of the experimental spectrum (top) with theoretical stick spectra for negative and positive quadrupole coupling

Figure 12 Example of NQR spectra obtained by purely optical excitation and detection of nuclear spin coherence. Both spectra were combined from three partial spectra which were recorded with different modulation frequencies in order to reduce distortion due to finite excitation range

which optical methods can be used, but also in addition the various ways in which optical radiation can enhance magnetic resonance spectroscopy.

3.1 Dielectric Solids

Optical pumping and optical detection of magnetic resonance transitions were first demonstrated in atomic vapors[8,13] but soon afterwards also in ionic solids.[36,37] Ruby (Cr^{3+}:Al_2O_3) proved an ideal test material, as it has relatively narrow optical absorption lines and allows different methods of optical pumping. Most experiments reported to date have been performed with inorganic ionic solids, in particular rare earth and transition metal compounds. The experimental techniques used for these studies include purely optical methods such as photon echo modulation[38,39] and coherent Raman beats,[40] as well as double resonance methods such as Raman heterodyne spectroscopy.[41]

We start the discussion with an example for a purely optical method that combines several attractive features: while its sensitivity is that of an optical method, its resolution is not limited by laser jitter or optical dephasing, but only by the natural linewidth. Furthermore, it yields magnetic resonance spectra from an electronically excited as well as from the ground state. The material system that we consider here consists of the rare earth ion $^{141}Pr^{3+}$ with a nuclear spin $I = \frac{5}{2}$. The ions are substituted into the host material of $YAlO_3$, where they occupy the Y sites with a doping concentration of 0.1%. In zero magnetic field, the interaction between the nuclear quadrupole moment and the electric field gradient (EFG) tensor lifts the degeneracy of the nuclear spin states of ^{141}Pr; the interaction with the quenched electronic spin enhances the quadrupole coupling as well as the nuclear Zeeman interaction.

The experimental scheme uses Raman processes for exciting the nuclear spin transitions as well as for observing the spin precession. A laser pulse that couples to two optical transitions sharing a common energy level excites a coherence in the third transition of the three-level system, as explained above. The excitation pulse should not be longer than the spontaneous lifetime of the electronic state. For the $^1D_2$ state of Pr^{3+}, this limits the duration of the laser pulses to $\tau_P < 100\,\mu s$. After the pulse, the coherence is allowed to precess freely and a second,
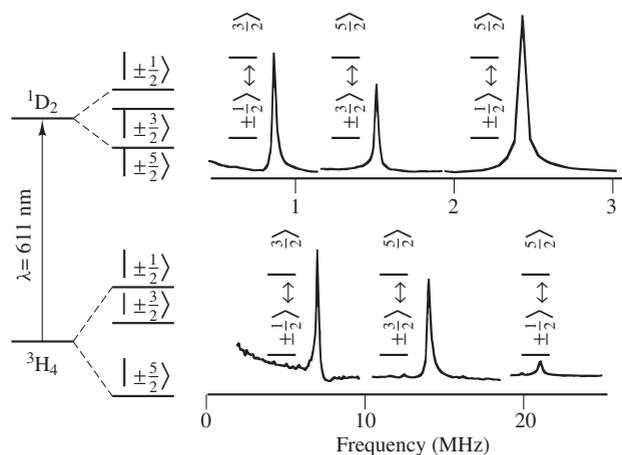
weaker laser beam is used to observe the precession, again using a Raman process. The condition for efficient excitation of the sublevel coherence is that the difference between the two frequency components of the exciting laser pulse is close to the sublevel transition frequency.[28] For the observation process, the laser frequency must be close to one of the two optical transition frequencies. The signal that is observed after the optical pulse can be Fourier-transformed to recover the usual NMR/NQR spectrum.

Figure 12 shows two examples of spectra that were measured with this method. They represent nuclear spin transitions of the electronic ground state and an electronically excited state of Pr^{3+}:$YAlO_3$. For both states, not only the magnetic dipole allowed transitions ($\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}, \pm\frac{3}{2} \leftrightarrow \pm\frac{5}{2}$) are visible, but also the double quantum transition ($\pm\frac{1}{2} \leftrightarrow \pm\frac{5}{2}$), indicating that the selection rules of conventional magnetic resonance do not apply to Raman-detected magnetic resonance. The quadrupole interaction strength differs significantly for excited and ground state (0.9 MHz versus 7 MHz). As with magnetically excited spectra, the bandwidth of the excitation process is limited. In this case, the transition strength is quite low. With a laser power of 20 mW, it was possible to excite subspectra with a width of approximately 1 MHz. To reduce the distortions associated with the excitation of considerably wider spectra, we therefore combined three subspectra containing one resonance line each. The width of the resonance lines is determined by spin-diffusion of the dipole–dipole interaction with the neighboring Al nuclei.

Excitation of magnetic resonance transitions with radiofrequency irradiation relies on the conversion of longitudinal into transverse magnetization; an experiment can therefore start only after thermal relaxation has established population differences by coupling to the lattice. At low temperatures, this process can be very slow in rigid solids. Optical excitation, in contrast, converts population differences between different electronic states into transverse magnetization. Spontaneous emission establishes these population differences on a very short timescale (nanoseconds to femtoseconds), independent of temperature. As a result, purely optical experiments do not require long relaxation delays and allow fast repetition rates.
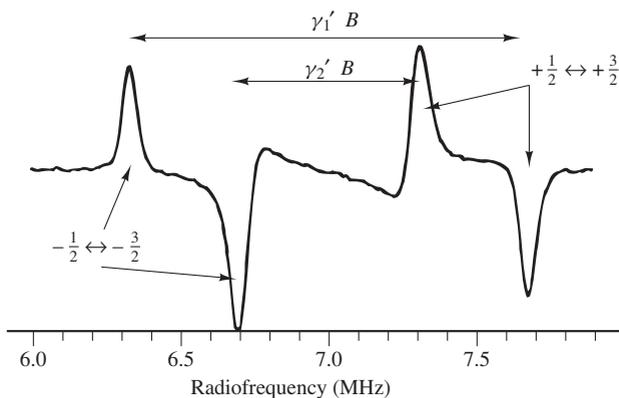
Figure 13 Raman heterodyne spectrum of Pr^{3+}:$YAlO_3$ in a weak magnetic field

Figure 14 Optical pumping in semiconductors: level scheme for a III–V compound with tetrahedral symmetry

Raman experiments do not have to use only optical techniques. Double resonance techniques that include optical as well as rf irradiation have been used successfully. The rf field establishes a coherence in a magnetic resonance transition, and the same Raman process that we discussed above detects it. In such an experiment, the laser beam serves a threefold purpose: it establishes a population difference, which the rf field converts into transverse magnetization. The same[41] or a second[35] laser beam partially converts the precessing magnetization into optical polarization by a coherent Raman process, and as a third function, the laser beam serves as the local oscillator for the detection of the Raman field. This technique was first used to observe NMR transitions in rare earth compounds[29,41] and later also to ESR[42] and ENDOR.[43,44]

Figure 13 shows the Raman heterodyne signal, again from Pr^{3+}:$YAlO_3$, as a function of the frequency of the rf field. For this spectrum we applied a small magnetic field of a few gauss, so that the transitions between the $+\frac{1}{2}$ and $+\frac{3}{2}$ states were no longer degenerate with the transition from the $-\frac{1}{2}$ to the $-\frac{3}{2}$ state. In addition, the crystal has two nonequivalent sites, resulting in a total of four lines which are assigned in the figure. Again, the width of these resonance lines is independent of the laser linewidth and only due to the properties of the crystal.

In these experiments, the laser beam interacts directly with the atom whose nuclear spin transitions are the subject of interest. In other cases, spin–spin couplings exchange polarizations with neighboring spins. It is then possible to polarize optically those spins and detect their NMR transitions optically.[45,46] In other cases, the interaction between two neighboring atoms manifests itself more strongly in the optical transition. The position of the optical resonance within the inhomogeneously broadened resonance line allowed the assignment of the magnetic resonance spectrum to a pair of neighboring spins.[47] While most experiments of this type were performed in ionic materials, color centers in diamond have also been studied.[43]

3.2 Semiconductors

Semiconductors have become a very active area for applications of optically enhanced magnetic resonance. The first demonstrations of the technique were performed in GaAs.[48] For the optical excitation, one usually chooses a photon energy at the exciton resonance or just above the band gap, thereby creating holes at the top of the valence band and electrons at the bottom of the conduction band. Under these conditions, the system behaves to some degree like free atoms. Figure 14 shows the relevant band structure for the technically important case of a III–V semiconductor with tetrahedral symmetry.
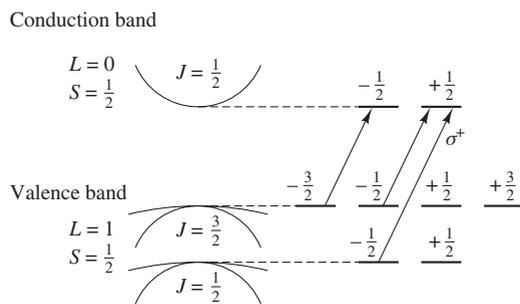
In these compounds, the valence band consists of p type orbitals ($L = 1$). Spin–orbit coupling splits the band into a $J = \frac{1}{2}$ and a $J = \frac{3}{2}$ subband. The conduction band consists of s type orbitals and the total electronic angular momentum of the excited electrons is therefore $J = \frac{1}{2}$. Absorption of a circularly polarized photon by an electron in the $J = \frac{1}{2}$ valence band then creates a hole and a conduction band electron, both with $J_Z = +\frac{1}{2}$. In the valence band as well as in the conduction band the electron spin system becomes polarized to some degree that depends on the thermalization times of the hole and the electron. As in the case of free atoms, the spin polarization reflects itself in the polarization of the luminescence.

The hyperfine interaction between electrons and nuclear spins can transfer spin polarization from the electrons to nuclei. If resonant rf irradiation perturbs the nuclear spin reservoir, it also affects the electron spin polarization and the polarization of the luminescence. By observing the luminescence and scanning the radiofrequency in a constant magnetic field, it is thus possible to record magnetic resonance spectra.[48,49] Figure 15 shows an example of such a spectrum from GaAs, reproduced from Krapf et al.[49] Two different isotopes of Ga are clearly visible, as well as the As resonance. The positions of the resonance lines depend on the polarization of the electron spins, as shown in the lower left part of the spectrum. Such experiments may well become an interesting addition to the analytical tools of the semiconductor industry. Most experiments performed up to now have used GaAs, but Si, Ge,[50] and InSb[51] have also been investigated.

Apart from the polarization and intensity of the light, NMR transitions can also be observed indirectly through changes in the ESR resonance position:[52] the coupling between the electronic and nuclear spins shifts the ESR transition frequency. By applying pulsed or CW radiofrequency fields to the nuclear spins, it is possible to change their polarization and thereby the ESR frequency. If the number of spins is large enough, it is even possible to observe the NMR spectrum directly in a conventional spectrometer modified for optical pumping.[53]
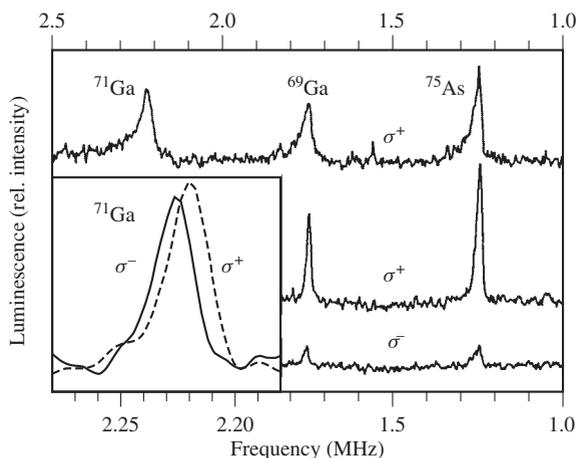
Figure 15 Example of optically detected NMR spectrum of GaAs. The signal was recorded by scanning the radiofrequency and observing the luminescence in a constant magnetic field of 0.17 T

The high sensitivity of optical techniques is a very attractive feature for studying the thin films used in integrated circuits. The optical techniques could become even more attractive for studying quantum confined structures.[54] Confinement of the conduction electrons to small regions, like quantum wells, quantum wires, or quantum dots, modifies the optical absorption spectra considerably. It is then possible to selectively excite only those areas where the electrons are confined and to measure magnetic resonance spectra specifically from those areas. Such experiments therefore require not only high sensitivity for measuring signals from small parts of the sample, but also good selectivity to extract this signal from the large background of the entire sample.

3.3 Surfaces

Quasi two-dimensional systems have always proved difficult to investigate by conventional NMR, since the number of spins in these systems is quite small.[55,56] Increasing the spin polarization by optical pumping has significantly improved the sensitivity of this type of experiment. In particular, the transfer of spin polarization from optically pumped alkali atoms to Xe nuclear spins[15] has allowed the study of the effect of surfaces on the magnetic resonance spectrum.[57,58] In the fast exchange regime, the distribution of spins between the surface adsorbate and vapor phase determines the averaged magnetic resonance spectrum. For oriented surfaces, where most spins are in the vapor phase, the splittings and shifts are then in the mHz range, requiring highly sensitive detection methods. Other work has therefore concentrated on systems with a large surface-to-volume ratio like zeolites[59] where most of the atoms are close to the interface.

For experiments with oriented surfaces, apart from the sensitivity advantages, the use of light for optical pumping as well as for detection also brings the possibility of selecting signal contributions that originate from atoms which are close to the surface. For this purpose, changes in the penetration depth of light with wavelength[60] have been used, but more frequently the selection is achieved by reflecting a laser beam from the interface being investigated. The reflection coefficient for the laser beam depends on the refractive indexes on both
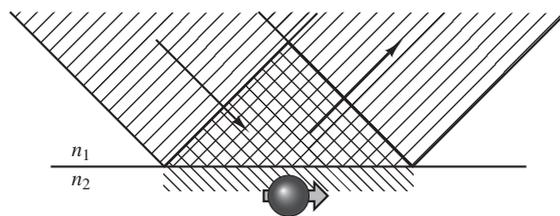
Figure 16 Principle of optical detection of magnetic resonance close to a surface. The refractive indices on both sides of the interface are denoted as n_1 and n_2

sides of the interface and is therefore affected by atoms close to the interface that are resonant with the laser light (see Figure 16). The changes in the reflection coefficient, which can be measured through changes of the amplitude and polarization of the reflected beam, therefore contain information on the atoms close to the interface. The combination of optical pumping with this type of optical detection provides sufficient sensitivity such that it is no longer necessary to use samples with high surface-to-volume ratios and permits the study of oriented surfaces.

One method that relies on such a technique allowed the study of the nuclear quadrupole resonances of Pr^{3+} in LaF_3.[61] In this case, the beam was reflected from an optically dense material. The reverse is also possible: if the laser beam undergoes total internal reflection at an interface to an optically less dense medium, an evanescent wave penetrates into the thinner medium by a distance of the order of the optical wavelength. Atoms in this evanescent wave can thus modify the reflected laser beam by absorbing light from it and by their effect on the reflection coefficient.[62]

3.4 Molecules

Conventional magnetic resonance has been applied most successfully to molecular systems. These systems can also be investigated with optical methods. Aromatic organic molecules are particularly suitable because their chromophores make optical spectroscopy particularly attractive. Experiments with these systems typically use optical excitation from the ground state to an excited singlet state with a pulsed UV laser. From the excited singlet state, intersystem crossing (ISC) can populate a nearby triplet state (see Figure 17). The intersystem crossing populates the different levels of the triplet state unequally. In addition, the triplet substates have in general different lifetimes. The polarization and intensity of the
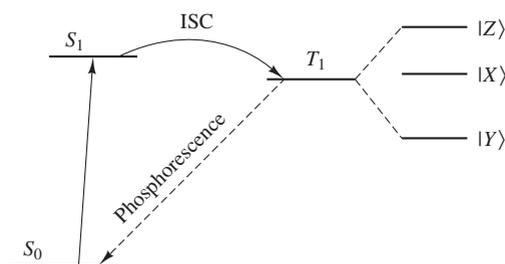
Figure 17 Principle of optically detected magnetic resonance in excited triplet states

phosphorescence depend on the population of the individual states and allow an assessment of the population differences. By applying rf fields to the system, it is possible to induce transitions between the different triplet states; these transitions can be observed in the phosphorescence. Similar experiments have been performed on many other systems. Two groups demonstrated the high sensitivity of the method very strikingly by measuring the magnetic resonance of individual pentacene molecules in *p*-terphenyl hosts.[1,2] Work is now in progress to extend these experiments to NMR transitions.

4   RELATED ARTICLES

Polarization of Noble Gas Nuclei with Optically Pumped Alkali Metal Vapors; Quantum Optics: Concepts of NMR; Ruby NMR Laser.

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