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 propagation direction. Since angular momentum is a conserved quantity, the total angular momentum of the system (radiation and matter) remains constant during absorption and emission processes. When an atom or molecule absorbs a photon, it must incorporate not only the photon energy but also its angular momentum (see Figure 2.1). The resulting angular momentum of the atom is the vector sum of its initial angular momentum plus the angular momentum of the absorbed photon.

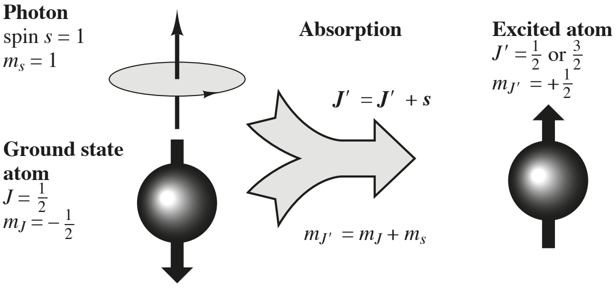

Figure 2.1: Conservation of angular momentum during absorption of a photon.

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 polarization is 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

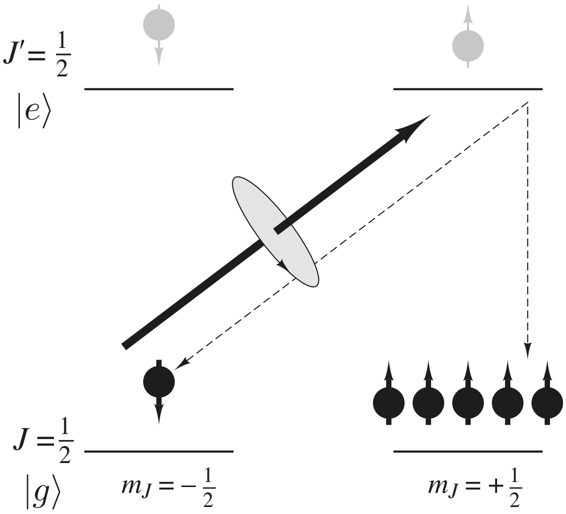

Figure 2.2: Principle of optical pumping illustrated for a simple atomic system.

This possibility was first suggested by Kastler. [1, 2] Figure 2.2 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 $J = 1/2$. Their angular momentum substates are labeled as $m_J = +1/2$ and $m_J = -1/2$ 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 $J_z = -1/2$ state can absorb photons. If an atom is initially in the state $m_J = +1/2$, the resulting excited state would have to be a state $m_J = +3/2$, which does not exist in our model atom.

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. [3, 4] These level shifts have 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. [5]

2.4 Observation in Transmission

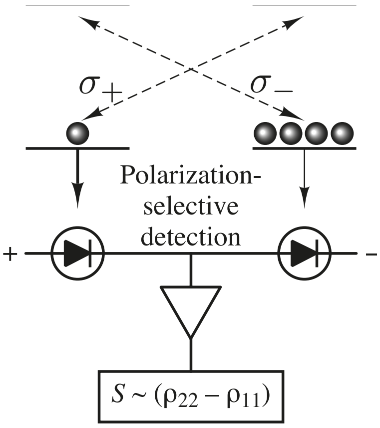

Figure 2.3: Principle of observation of spin polarization by transmission of optical radiation.

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.[6] 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 2.3 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.

2.5 Observation in Emission

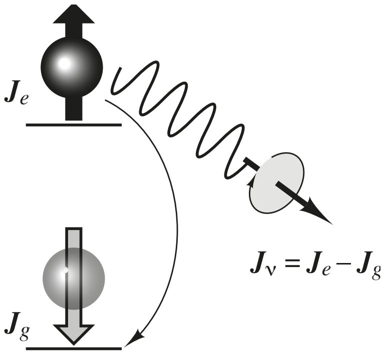

Figure 2.4: The polarization of the fluorescence depends on the spin state of the excited atoms.

An alternative detection scheme that provides even higher sensitivity is to detect the photons emitted by the medium, i.e. the photoluminescence. As shown schematically in Figure 2.4, 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. [7]

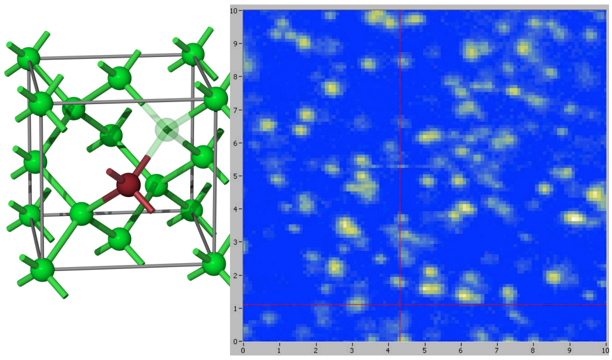

Figure 2.5: The left-hand part shows the structure of the nitrogen-vacancy center in diamond: the red ball represents a N atom substituting for a carbon, the empty ball an adjacent missing carbon. The right-hand part shows a confocal scan of a diamond crystal; each bright spot is a single N/V center.

Optical detection of spin states does not always rely on the polarization of the light - it can also use the intensity. Possibly the best example is the nitrogen-vacancy (N/V)-center of diamond. As shown in Fig. 2.5, the N/V center consists of a nitrogen atom substituting for a carbon and an adjacent vacancy. If this defect is negatively charged, it has a spin $S = 1$, which can be initialized as well as observed by unpolarized laser light: A pulse of green laser light of ≈ 500 ns initializes the defect into the $m_S = 0$ state (the quantization axis is the C_3 symmetry axis connecting the nitrogen with the vacancy). This state is also the “bright state”; at room temperature, it scatters ≈ 2 times as many photons as the $m_S = \pm 1$ states, and at low temperature and narrowband excitation, the difference can be more than an order of magnitude.

This center is very stable, which makes it ideal for optical experiments on single spins at room temperature 8. Since a single defect center can emit only a single photon at a time, it is relatively easy to verify if a single center is being probed: Measuring the correlation of photons arriving at a detector shows a clear “antibunching” signature, as shown in the left-hand part of Fig. 2.6. Immediately after emitting a photon, the center cannot emit another photon until it has absorbed one from the laser beam. The right-hand part shows an ESR spectrum, in which the transition frequency of the electron spin is split by the hyperfine interaction with the nitrogen atom ($I = 1$) and with three ^{13}C nuclear spins ($I = 1/2$). Nuclear spin transitions can also be induced by radio-frequency irradiation and ob-

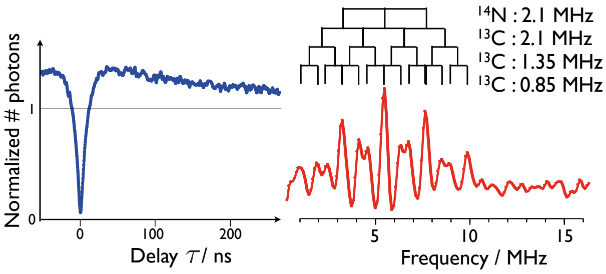

Figure 2.6: Left: The strong anticorrelation for delay $\tau = 0$ proofs that a single N/V center is being probed. The right-hand part shows the ESR spectrum of a single N/V center, with resolved hyperfine splittings due to the nitrogen and three ^{13}C nuclear spins.

served optically [9], in a similar way as the electron spin transitions.

2.6 Angular Momentum Reservoirs

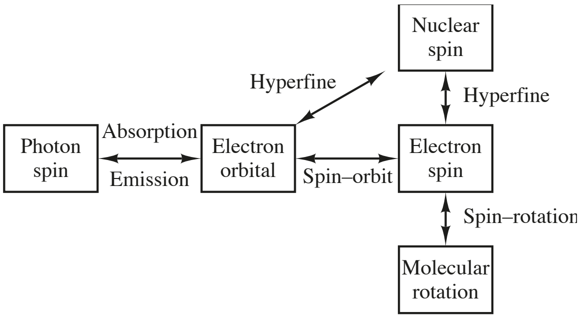

Figure 2.7: Summary of the most important reservoirs of angular momentum.

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 2.7. This is, of course, of special 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.

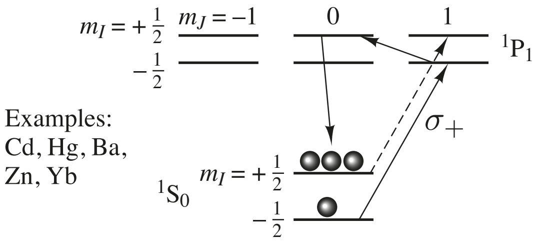

Figure 2.8: Polarization of nuclear spin reservoirs in diamagnetic ground states .

In the example of Figure 2.8, 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 2.8, the resulting state does not evolve until it re-emits 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 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.[10] 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.[11, 12] and applied to the study of surfaces in systems with high surface to volume ratios like graphitized carbon[13], to the construction of NMR gyroscopes[14, 15] or to gas-phase imaging of the lung [16]. The transfer from alkali to noble gas atoms is relatively efficient because they form van der Waals complexes[17]. 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[18] and can be transferred to other spins by thermal mixing.[19]

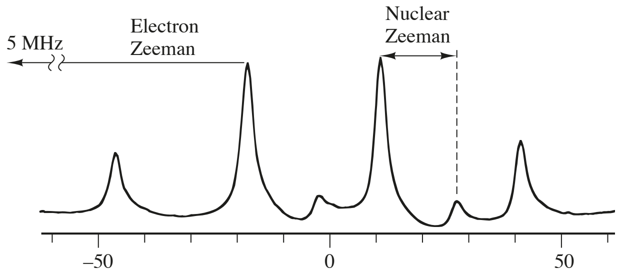

Figure 2.9: Example of an optically detected magnetic resonance spectrum in a strongly coupled system.

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 2.9 shows an example: in Na atoms, the hyperfine interaction couples the electron ($S = \frac{1}{2}$) and nuclear spins ($I = 3/2$) 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.

2.7 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 2.10 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

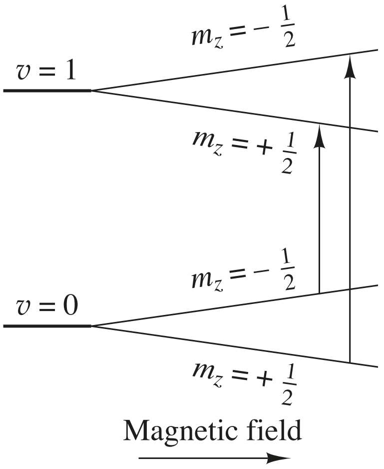

Figure 2.10: Principle of laser magnetic resonance.

as the transitions indicated by arrows in Figure 2.10, 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[20] as well as in semiconductor materials, where the process is known as spin-flip Raman scattering.[21, 22]

While this method allows high sensitivity, its resolution is lower than with direct detection. In most experimental settings, the width of the optical transitions limits the resolution. Optical rf double resonance methods [23] or a modification of the basic Raman experiment that is known as coherent Raman scattering can overcome this limitation.

2.8 Coherent Raman Processes

Raman processes can be considered as an interaction between two optical photons and a material excitation, as shown schematically in Figure 2.11. 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 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.[24]Coherent Raman processes therefore provide a combination of high resolution with high sensitivity.

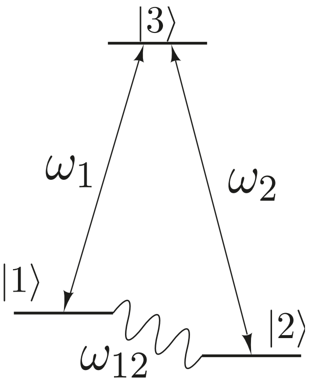

Figure 2.11: Raman processes couple two electromagnetic fields (ω_1, ω_2) with a material excitation.

The implementation of coherent Raman scattering must somehow create the coherent excitation of the material. This can be achieved either with optical fields [25, 26, 27] or with radiofrequency irradiation.[28]

2.9 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 of the order of 10^{-5}. Optically, it is possible to polarize the spins completely and thereby increase the sensitivity by some five orders of magnitude.[29] In addition, the optical detection process occurs at much higher energies: optical photons have energies some six 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, since the photon energy is much higher than the thermal energy, $\hbar\omega \gg k_B T$. 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.[30]

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.[31]

2.10 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[32], as well as about motional processes [33]. Many experiments in magnetic resonance are therefore performed to measure quadrupole couplings.[34] However, conventional magnetic resonance experiments can only provide the absolute value, not the sign of the coupling constant[35].

In the simplest case of axial symmetry, the Hamiltonian $\mathcal{H}_Q$ of the nuclear quadrupole interaction is given by a coupling constant D multiplied by the square of the nuclear spin operator I_z, $\mathcal{H}_Q = D I_z^2$. 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.

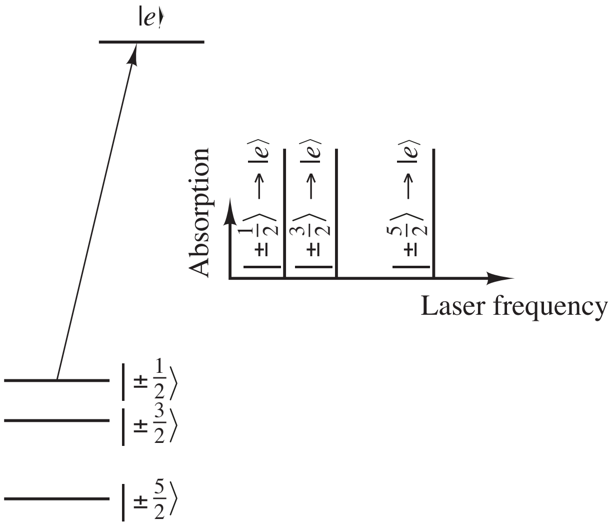

Figure 2.12: Principle of the measurement of nuclear quadrupole interaction by laser spectroscopy.

Figure 2.12 shows schematically 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 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 2.12, 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 2.13). 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 magnitude and sign of the quadrupole coupling constant of Pr^{3+} in the host material $YAlO_3$, as shown in Figure 2.12. [36]

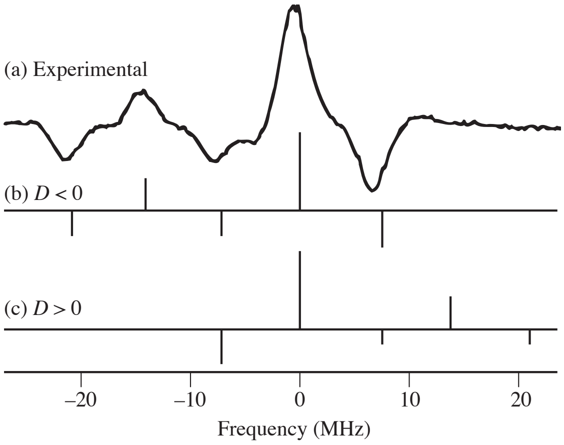

Figure 2.13: Comparison of the experimental spectrum (top) with theoretical stick spectra for negative and positive quadrupole coupling.

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