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New approaches to ultrasensitive magnetic resonance

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ABSTRACT

Spectroscopic methods tend to exhibit an inverse correlation between sensitivity and the ability to discriminate between similar structures. Were they obtainable with adequate sensitivity, magnetic resonance spectra could resolve structural controversies involving the nature of clusters, ions, semiconductor defects and catalytic intermediates. This talk will describe several novel approaches to magnetic resonance, which have in common that the spins are coupled to other degrees of freedom in order to obtain nonequilibrium polarization and/or greater detection sensitivity. The methods under development include single-ion electron spin resonance (ESR) detected by ion trapping frequencies, catalyst NMR detected by the branching ratio to different spin symmetry species, and semiconductor nuclear magnetic resonance (NMR) detected via the circular polarization of luminescence.

1. INTRODUCTION

Magnetic resonance is among the most widely used and definitive tools for structural studies, providing highly discriminating information on nuclear positions and electronic structure together with dynamic information over a wide range of time scales. With regard to sensitivity, however, it is among the weakest of spectroscopies, with nuclear magnetic resonance (NMR) typically requiring 10^{17} – 10^{20} target spins for practical experiments and electron spin resonance (ESR) several orders of magnitude fewer. This limitation nearly excludes ordinary magnetic resonance, especially NMR, from important areas of molecular and device physics, such as the characterization of single crystal surfaces, dilute semiconductor defects, transient intermediates in catalysis, clusters formed in molecular beams, and gaseous ions.

Our principal goal in this paper is describe our work in technique development along three lines aimed at one or more of these problems. These are:

- ESR of an ion by electrically measuring spin-dependent changes of its orbit in an ion trap;¹
- NMR of an intermediate through detection of the spin symmetry of its product (eg. ortho vs. para dihydrogen)²;
- NMR of GaAs semiconductors by optical detection of photoelectron spin polarization³.

A historical perspective is valuable in order to see what these projects have in common with one another and earlier work. The reasons for the poor sensitivity of the standard method of magnetic resonance (detection of the Larmor frequency field associated with the transverse magnetic polarization of the sample) are well-known⁴. Indeed it is the only form of molecular spectroscopy where one can routinely and *a priori* calculate relative and even absolute sensitivities with accuracy that exceeds that of experiment.

The smallness of standard magnetic resonance signals has several aspects. The first, which is shared by all spectroscopies of internal degrees of freedom, is that only one or a few quanta are exchanged with the radiation field at a given frequency. Anharmonicity, molecular dissociation, or, in the case of spins, the finiteness of the Hilbert space terminate the sequence. The special problem of magnetic resonance is that these quanta are relatively small, lying in the audio to microwave spectral regions for accessible magnetic field strengths. This smallness diminishes the sensitivity in two distinct ways. The radiating magnetic moment of the sample is small, because the spin polarization or fractional difference in population between states of opposite magnetic moment is small ($\approx 10^{-5}$ for high field NMR at room temperature). Secondly, the available signal energy competes with abundant thermal noise at these low frequencies, so that the sensitivity never reaches the quantum limit associated with photon statistics.

There has been diverse recent progress in methods which increase the nuclear spin polarization to large values. Examples are:

- optical nuclear polarization of noble gases directly⁵⁻⁷ or by way of their interactions with optically pumped alkali metal atoms⁸;
- dynamic nuclear polarization^{4 9-11} of solids in which ESR transitions, sometimes optically pumped¹²⁻¹⁴, provide the polarization;
- polarization of surfaces by contact with ³He at millikelvin temperatures¹⁵⁻¹⁷;
- the transformation of symmetrization order, exemplified by a population difference between parahydrogen and orthohydrogen, into magnetization¹⁸⁻²⁵.

In these cases a method might be considered advantageous only if the polarization increase is sufficiently rapid and applies to a large enough ensemble of spins that the signal power is increased relative to the possibly larger sample that might be usable with the ordinary method of waiting for thermal equilibrium in a high magnetic field. On the other hand, a good deal of the information content is associated with the dynamics of the polarization process as distinct from the spectral frequencies themselves, providing an additional motivation for exotic polarization methods.

2. TRIGGER METHODS

It is evident that the most sensitive magnetic resonance experiments require the solution of both of the problems associated with the smallness of the quantum. It is not sufficient to reach polarizations of order unity and, for some of the methods discussed below, spin polarization is not even necessary. For ultrasensitivity it is necessary to measure the resonant changes in polarization by some method more sensitive than detection of the Larmor frequency radiation. Abragam refers to these as trigger methods and reviews early examples⁴. The three topics of this paper are novel trigger methods.

Note that although there is considerably less research activity on the detection end of the problem, the stakes are in fact higher; the improvement in NMR sensitivity per shot due to polarization increases cannot exceed $\approx 10^5$, while something in excess of ten orders of magnitude lie between the best present methods of Larmor frequency detection and the single-molecule limit. The wide diversity of trigger methods can be appreciated from some other recent examples:

- the detection of the electron spin Larmor frequency of a single molecule at a surface as a peak in the spectral density of the current fluctuations of a scanning tunnelling microscope;²⁶
- surface NMR by deposition of optically polarized alkali metal atoms and the detection of their polarization with beam methods after desorption;^{27 28}
- electron-nuclear double resonance of dilute paramagnetic sites in semiconductors by magnetic circular dichroism;²⁹
- ESR and NMR of sites near a semiconductor interface by way of magnetoresistance

measurements on electrons localized to two dimensions;³⁰

— optical polarization and detection of nuclear quadrupole resonance by way of excited state molecular triplets.³¹

It is of at least historical interest that NMR began in a form whose sensitivity is independent of the size of the quantum. In the molecular beam deflection method of Rabi,³²⁻³⁴ the resonant transition occurs in a homogeneous field region between two magnetic field gradients each of which exerts spin–state dependent forces transverse to the beam, as in the Stern–Gerlach experiment. The deflections due to these forces add constructively or cancel depending on whether or not the spin flipped in the interim. It suffices to measure the beam flux in the original direction as a function of field or frequency to map out the spectrum. Since induced transitions in either direction have the same net consequence for the beam focus, the method requires no initial spin polarization. Since beam detection methods, for example those based on ionization, can readily and generally detect single molecules, the method can be ultrasensitive.

This remarkable idea, though duly celebrated and half a century old, has had a surprisingly small impact on modern magnetic resonance activity. In part, this is certainly historical accident. There are, however, several substantive reasons for the relative neglect of molecular beam resonance. Perhaps the most important is that with generally accessible (thermal) velocities, the time of flight through an apparatus of practical size severely limits the resolution, thereby vitiating one possible motivation for studying molecules under collisionless conditions. Also, the background pressure at the detector generally prevents the single–molecule limit from being reached.

3. ION TRAPS

There is another collisionless environment for molecules, which does not suffer from these problems. This is an ion trap, where electromagnetic fields act to constrain charged molecules to orbit for many seconds within a small volume. The best known application is Fourier transform ion cyclotron resonance (FTICR)³⁵⁻³⁷, a form of mass spectroscopy, in which a coherent ion motion near the cyclotron frequency $\omega_c = qB_0/m$ is used to measure the charge–to–mass ratio q/m . The most precise theoretical analysis can be given for a particular trapping field geometry, known as the Penning trap,³⁸⁻⁴¹ which is illustrated in Fig. 1. The ion momentum transverse to the static magnetic field \vec{B}_0 is trapped by the Lorentz force, while the axial motion is trapped by the additional application of a static electric field ideally of the form $\vec{E} = (V_0/d^2)(x\hat{x}/2 + y\hat{y}/2 - z\hat{z})$, where \hat{z} is the magnetic field direction, V_0 the trapping potential and d a characteristic linear cell dimension. The net result is harmonic axial motion at frequency $\omega_z = (qV_0/md^2)^{1/2}$ and transverse motion which is the vector sum of motions around the cell center at frequencies $\omega_{\pm} = (1/2)[\omega_c \pm (\omega_c^2 - 2\omega_z^2)^{1/2}]$. The higher frequency ω_+ is the one usually detected as an oscillating induced charge on the capacitor formed by the cell walls. Typical FTICR practice is to detect the coherent motion of hundreds of ions, but single–ion detection is within the reach of modern preamplifiers. At 4.2 K the axial frequency of single–ions has been detected^{38 39} and used to monitor ω_+ indirectly.³⁹ Direct FT detection of ω_+ is even more favorable, but has not been reported at the single–ion level of sensitivity.

In seminal work by Dehmelt and coworkers^{38 40 41}, the g –factor of individual trapped electrons was monitored by adding to the trapping fields a magnetic bottle field of the form $\Delta\vec{B} = B_2[(z^2 - \rho^2)/2] \hat{z} - z\rho\hat{\rho}$. This quadratic gradient couples the axial motion to the spin. Spin flips were

detected as shifts in the axial frequency. This trigger method has been called the "continuous Stern–Gerlach effect"⁴¹, because the spin state determination is made by an extended observation without terminating the spatial motion. In addition to this "non–demolition"⁴² character with respect to the spin degree of freedom, such trapping frequency measurements differ qualitatively from internal spectroscopies in the number of quanta exchanged by the mode coupled to the radiation field. Indeed, the axial motion can be adequately treated classically. The experiment, however, required a quantum–mechanical description of the transverse motion. In particular it required that the electron be in a known state of the harmonic

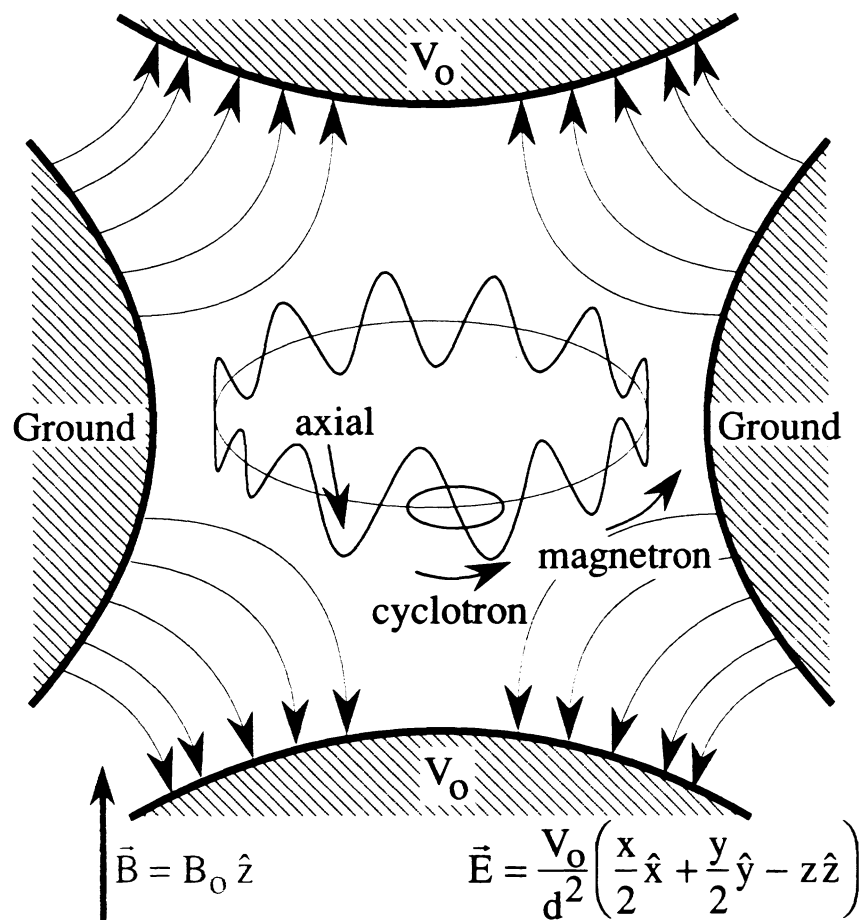


Fig. 1. Illustration of the motion of a charged particle in a Penning trap. The motion is a superposition of three separable motions. The axial motion is harmonic oscillation along the magnetic field direction \hat{z} . The transverse position is the sum of two radial vectors rotating around the origin at the frequencies ω_+ and ω_- (see text). These motions are labelled cyclotron and magnetron, respectively. The amplitudes and frequencies are arbitrary and chosen for clarity.

progression $\hbar\omega_+(n + 1/2)$ and this was achieved by cooling into the ground state ($n = 0$) in high field. Ground state trapping is not practical for ions, for which the quantum $\hbar\omega_+$ is thousands of times smaller due to the proportionally higher mass. The thermal occupation of an effectively continuous distribution of states describing the transverse motion leads to an inhomogeneous broadening of the axial frequency much greater than the spin dependent shifts, which scale as $m^{-1/2}$.

4. ESR OF TRAPPED IONS¹

What is needed for ions is a continuous version of the Rabi molecular beam resonance experiment. We have recently devised several such schemes¹ and are currently working on their experimental implementation. As in the Rabi scheme, the ions are exposed to a magnetic field gradient before and after the magnetic resonance period in a homogeneous field. All three steps take place in an ion trap with a switchable magnetic bottle field serving as the gradient. The analog of beam deflection is a shift in a trapping frequency. This may be the axial frequency, as in the electron g experiment,⁴⁰ or the higher frequency transverse signal ω_+ , which has the potential advantage of higher sensitivity (due to typically higher frequency), better mass discrimination, and spin-dependent shifts only weakly dependent on mass. Another way in which the various schemes differ is that the spin-dependent shift may be either that associated with a change in spin state alone, as in the electron g experiment, or others resulting from spin-dependent changes in the action or energy of the ion orbit under the influence of spin-dependent forces controlled by spin resonance.

The key to single ion ESR in a trap is to overcome the inhomogeneous distribution of the trapping frequency, which inevitably accompanies the gradient needed to make the frequency spin-dependent. We can look to the the Rabi beam experiment for one solution. The analog of the orbit-independent trapping frequencies in the absence of the magnetic bottle is the narrow distribution of transverse positions in a collimated neutral beam. The analog of the inhomogeneous distribution of frequencies in the presence of the magnetic bottle field is the distribution of Stern-Gerlach deflections in the first field gradient; both reflect the distribution of particle velocities. In the Rabi "flop out" experiment³²⁻³⁴ this distribution is refocused by arranging that the second field gradient is equal, but opposite, to the first. Thus, in the absence of any change in magnetic moment between the gradients, the deflection is refocused onto the detector for all velocities that pass through the collimating slit. A spin flip prevents this refocussing and is detectable as a reduction in beam intensity.

What is the ion trap analog? If the second application of the magnetic bottle is reversed in sign, then so are the bottle-dependent frequency shifts. The net result is a refocussing or echoing of the orbital phase accumulation due to the first bottle field. A spin flip will make this echo imperfect, since the spin-dependent part of the frequency shift due to the magnetic bottle will then not be reversed. If the ion ensemble had been prepared with appropriate spatial localization, then the corresponding coherent signal (induced charge near ω_z , ω_\pm , or ω_c) would detect this echo and its diminution.

The notion of bypassing inhomogeneous distributions with refocussing or with echo phenomena is, of course, a recurring theme of the "optics" of various sorts of beams and also of magnetic resonance. In both cases it is intimately associated with coherence, here broadly viewed as some restriction in the phase space of the system to a nonstationary state as a result of a

preparatory step. In this view a collimated beam, a coherent superposition of spin states, and an ion ensemble with a time-dependent average position are all analogous quantities. The use of such coherent ion ensembles is central to FTICR practice, but is in fact not an indispensable aspect of the detection of trapped ion motion, once the detector noise is reduced to a value comparable to the signal from a single ion. At this level of sensitivity, the "continuous" nature of the measurement allows one to follow the frequency history of a single ion. Inhomogeneity can even be viewed as an advantage under such conditions, since it becomes unlikely that two simultaneously trapped ions will have overlapping frequencies and thus interfere destructively.

Signals from such incoherent ensembles of ions are, in a sense, noise. The expectation value of the induced charge on the detecting electrodes is at all times zero. The only information available is in the fluctuations about this mean. The advantage of such signals is that no coherent preparation of the detected mode is needed. We would like to keep the favorable aspects of beam magnetic resonance, stimulated (and possibly coherent) spectroscopy in a homogeneous field on an unpolarized spin ensemble, but combine it with the convenience of noise analysis on the detected degree of freedom, the ion motion.

This requires a broader notion of noise spectroscopy than the usual idea that the power spectrum is the Fourier transform of the autocorrelation function formed from the fluctuating time domain data. The needed generalization is to find a similar Fourier pair which incorporates in a broadband manner the intuitive idea of comparing the trapping frequencies of a given ion before and after the ESR period, in order to determine if and by how much it has shifted due to a spin flip. If the second application of the bottle field were identical to the first, the desired operation would be the convolution of the frequency domain spectra taken before and after spin resonance. This is equivalent to multiplication in the time domain followed by Fourier transformation. If the second application of the bottle is opposite in sign to the first, then the second record needs to be reversed in time prior to the multiplication and Fourier transformation.¹ The net result is a spectrum in which all ions whose spin did not flip contribute in phase to a line at twice the observed trapping frequency. Those whose spin did flip similarly contribute in phase to two satellite lines just above and below this value at a separation equal to the spin-dependent part of the frequency shift. The intensity modulation of these lines as a function of an ESR frequency (or time) variable, which is varied between successive repetitions, is the ESR spectrum (or time-domain interferogram). In other words, an ion which undergoes a spin transition "flops out" of the center line into one of the two satellites. In summary, this approach replaces the inhomogeneous and incoherent trapping spectrum, which would result from Fourier transformation of a single time record, by a homogeneous spectrum of frequency differences obtained as the transform of a novel second order correlation function. This reveals the effect of refocusing of each ion with respect to its own history, even though there is no ensemble coherence.

5. SYMMETRIZATION ORDER AND ULTRASENSITIVE NUCLEAR MAGNETIC RESONANCE

Several years ago we described a new handle on NMR sensitivity¹⁸, which can be viewed as a coupling of the spin orientation to molecular rotation in a manner that has no analog in classical mechanics. As a consequence of the symmetrization postulate of quantum mechanics, only certain nuclear spin states are associated with a given rotational state of a symmetrical molecule. In comparison to the profound consequences of exchange symmetry for electronic structure and the statistical mechanics of fluids, this restriction on the states seems a mere curiosity. However, in combination with chemical reactions which interconvert symmetric with asymmetric molecules, it provides a route to large nuclear polarizations¹⁸⁻²⁵ and to a potentially ultrasensitive trigger method for NMR detection² in situations where this would not otherwise be possible.

For the prototypical molecule H_2 , the well-known⁴³ consequence of the symmetrization postulate is that molecules with any even number of rotational quanta (parahydrogen) all have a unique nuclear spin wavefunction, which is the antisymmetric combination of the possible states of the two protons. The odd rotational states (ortho-hydrogen) only occur with the symmetric nuclear spin states. The interconversion of these species is normally very slow; gas samples that are highly enriched in parahydrogen relative to the equilibrium proportions may even be dissolved in room temperature solvents.

Parahydrogen itself exhibits no NMR signal, but, because of its well-defined nuclear spin state, turns out to be an interesting reagent. We predicted¹⁸ and then showed experimentally¹⁹ that chemical reactions that deposit the two hydrogen nuclei into nearby, but magnetically inequivalent environments result in product molecules with NMR spectra up to four orders of magnitude more intense than is observed ordinarily. These intense spectral features are the result of the fact that only a subset of the nuclear spin states of the product molecule correlate with the parahydrogen spin state. Thus, parahydrogen addition creates large nonequilibrium population differences across transitions that are spectroscopically allowed as a result of the broken symmetry.

This phenomenon, which has been given the acronym PASADENA (parahydrogen and synthesis allow dramatically enhanced nuclear alignment¹⁹⁻²¹), involves no unpaired electrons and does not require for its existence that the nuclear spin states affect reaction rates. Applications of PASADENA have been made to the study of hydrogen addition to form metal dihydrides in room-temperature solution and the homogeneous catalytic transfer of the hydrogen to unsaturated organic precursors.¹⁹⁻²⁵ Recently we have extended the effect to sites at a solid surface.⁴⁴⁻⁴⁵ Despite considerable destructive interference over the powder pattern of transitions that appear in emission and absorption, large enhancements were predicted to occur⁴⁴ if the two protons from a single dihydrogen molecule remain as neighbors for a time at least comparable to the inverse of their spin coupling, which is dominated by the direct dipolar interaction. Such enhanced proton NMR signals have been observed on the surface of ZnO ⁴⁵ immediately following parahydrogen binding. This correlates with reversible dihydrogen binding sites which were known from temperature programmed desorption and infrared studies⁴⁶⁻⁵⁰, but were previously inaccessible to NMR.

Analogous reactions with other symmetric molecules may be possible, but the reduced rotational splittings of heavier molecules make production and maintenance of a reagent with an excess of one nuclear-spin symmetry species more difficult than for H_2 or D_2 . Symmetry-selective photodissociation⁵¹ is one possibility.

The PASADENA effect shows that nuclear spin order can be created from rotational population differences. An intriguing possibility is the inverse effect², whereby the nuclear spin order of an ensemble of precursor molecules would be probed by monitoring the proportions of the different symmetry species formed in a subsequent reaction. Such a scheme could provide NMR spectra of the precursors without the sensitivity disadvantages of the usual methods of detecting spin states through radiofrequency photons. At least with dihydrogen, one has the great advantage that once desorbed, the spin symmetry will be retained through most any procedure that might be desirable to concentrate the desorbed material for analysis. Ultrasensitive optical methods for measuring the rotational state of dihydrogen are well-established⁵²⁻⁵³. Another detection possibility would be single ion ESR¹; since the hyperfine line intensities report on the nuclear spin state, this would become a trigger method for surface NMR. Unlike optical methods, which depend on rotational resolution and symmetry restricted selection rules, ion trap methods would have the advantage of being generally applicable to nuclear spin state analysis of other reaction products, such as alkanes, that are known⁵⁰ to incorporate the hydrogen by catalytic molecular

addition.

Elsewhere we have given a detailed density operator description and lineshape calculation for NMR detection through the parahydrogen mole fraction². It is shown that this quantity reports directly on the zero-quantum coherence of the precursor, which is a dipole forbidden transition. Other transitions, including the dipole-allowed ones, can be obtained by two-dimensional experiments, in much the same way that dipole forbidden transitions are obtained by way of allowed ones in ordinary NMR.⁵⁴

6. OPTICAL POLARIZATION AND DETECTION

There are numerous examples of systems in which electron spin has detectable optical consequences either as Zeeman or hyperfine structure or spin-state dependence of absorption or emission probabilities. No attempt will be made here to review this large literature, but a few general features are worth noting in order to have a context for discussing our work on GaAs.³ The first point is that optically detected magnetic resonance is a very specific probe. It does not work in most systems because a change in electron multiplicity or spin projection in an optical transition is the exception rather than the rule, becoming appreciably allowed predominantly through spin-orbit coupling. When the selection rules are favorable, the result is a highly local probe, since its range is normally just that of the wave function of the unpaired electron spins. This is an advantage in that the optical signature provides information on the identity of the signal and discriminates against other potential magnetic resonance signals. On the other hand it is a disadvantage that one cannot apply the sensitivity enhancement of optical methods to any site in a given material. Quantification is also frequently difficult, because signals typically depend on poorly known matrix elements involving the optically excited state and on hyperfine couplings that are not necessarily separately measurable. In addition, these quantities vary from site to site.

The near-infrared optical transitions near the bandgap of GaAs provide a particularly intriguing opportunity for the coupling of NMR to light, both because of favorable intrinsic properties of this coupling and because of the potential for developing an analytical tool with unique capabilities for an important material. The essential elements for ultrasensitivity are present; the nuclei can be rapidly optically polarized, perhaps to values of order unity, and this polarization can be optically detected. The pioneering work in this area, both experimental⁵⁵⁻⁵⁷ and theoretical⁵⁸⁻⁶⁰, was done in Leningrad and several excellent reviews have appeared⁶¹⁻⁶³. An important feature of the coupling mechanism is the degree of localization of the polarized electron (≈ 10 nm) with which it has been shown to operate^{59 60 64 65}. While this is, by some measures, still a molecular scale, it is an order of magnitude larger than that usually associated with hyperfine couplings, corresponding to many tens of bond lengths. In bulk GaAs this scale arises as the radius of some (generally unidentified) donor state wavefunction into which the optically polarized electron has localized^{59 60 64}. The same order of magnitude of localization is obtainable by epitaxial growth methods in which photocarriers are confined in one or more directions by a barrier of another material. Steady state optical NMR of GaAs has recently been observed in such quantum well structures^{13 14}.

7. TIME-SEQUENCED OPTICAL NUCLEAR MAGNETIC RESONANCE

We recently described and demonstrated a new method of optical nuclear magnetic resonance in GaAs which dramatically improves both the sensitivity and the resolution. It relies upon mechanisms of optical nuclear polarization and optical detection elucidated in earlier work^{56 57 64 65 68}, but combines them in way that optimizes their analytical value.

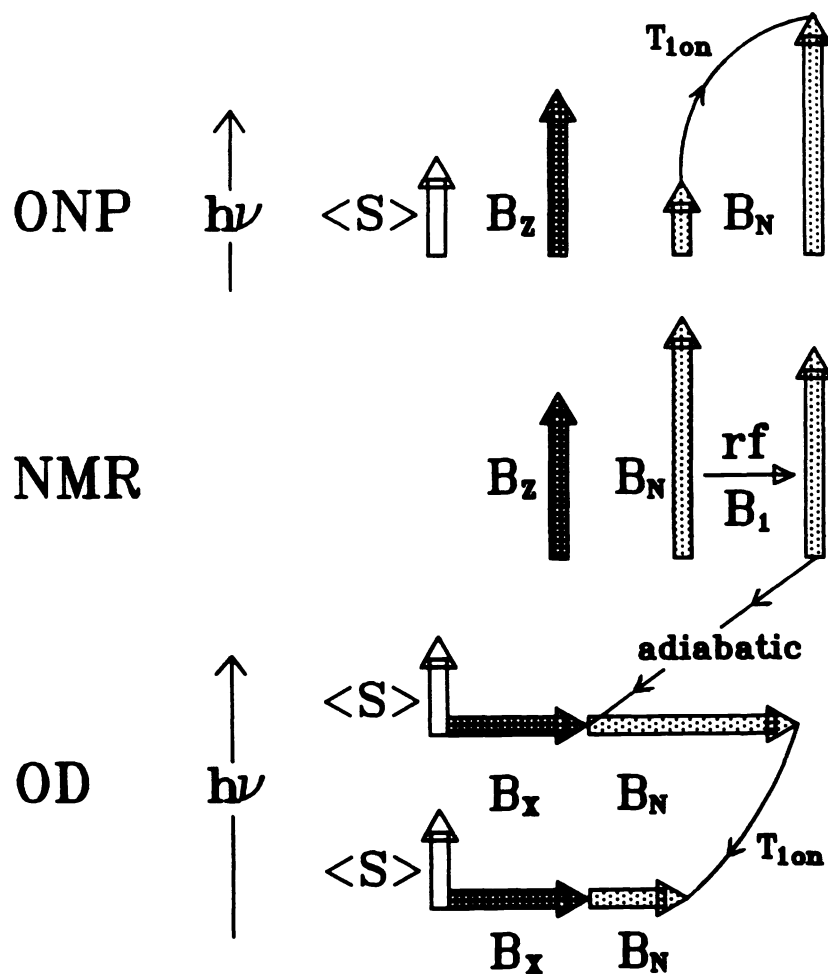


Fig. 2. Vector picture of time-sequenced optical nuclear magnetic resonance. The three processes of optical nuclear polarization (ONP), nuclear magnetic resonance (NMR) and optical detection (OD) occur in separate intervals and thus sensitivity and resolution can be simultaneously optimized. The applied magnetic field \vec{B} is reoriented from parallel to the optical axis during polarization to perpendicular during detection so that the precession of the optically pumped electron spin polarization $\langle S \rangle$, as detected as the circular polarization of luminescence, is maximally sensitive to the magnitude of the nuclear field B_N . Turning the light off during the NMR period to eliminate paramagnetic excited states is essential to high resolution.

This is accomplished with an experimental sequence, illustrated in Fig. 2., consisting of three distinct periods, one for each of the physical processes of optical nuclear polarization, NMR, and optical detection. In the first period, with the magnetic field along the optical z axis, irradiation with circularly polarized light at the bandgap creates excited state electrons with spin-polarization of order unity. The hyperfine coupling to all nuclei in the region of the electron localization contributes substantially to the nuclear spin-lattice relaxation, thereby leading to an enhanced nuclear ordering, in analogy to the Overhauser effect. In the second period the light is blocked and some NMR irradiation sequence is performed in the dark. At this point the direction of the magnetic field is rotated by $\pi/2$ slowly enough that the nuclear polarization follows adiabatically. The light is then restored. This initiates the detection period in which the circular polarization of the luminescence is recorded. These steps are repeated for successive increments of time, field or frequency in the NMR sequence.

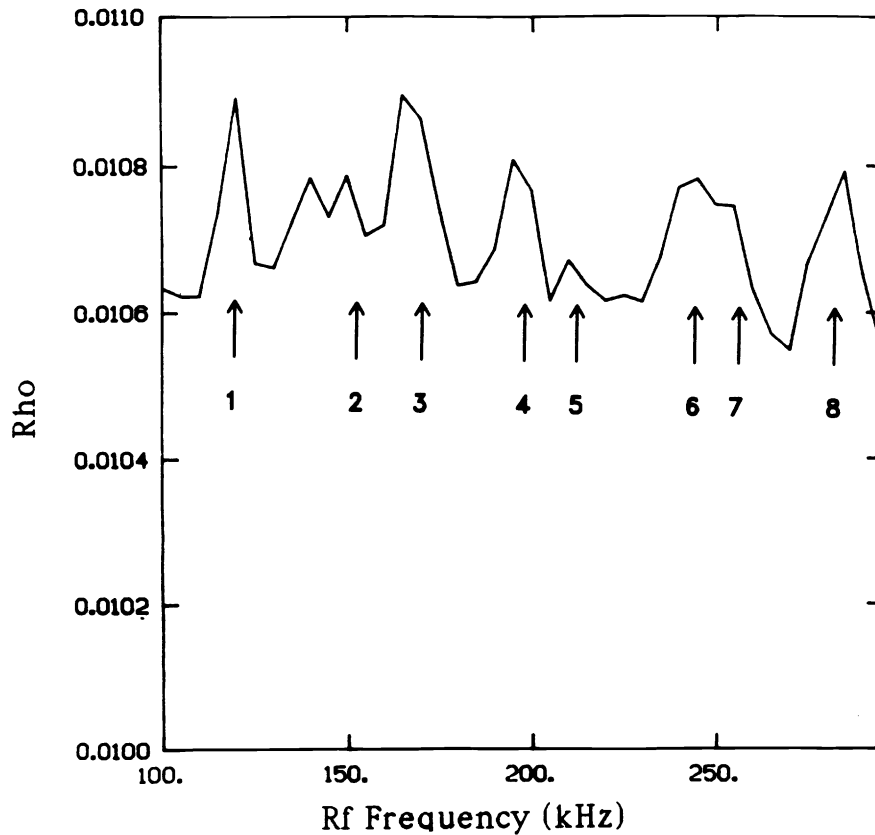
An example is the spectrum of Fig. 3, in which the rf irradiation frequency was varied between 100 kHz and 300 kHz in a field of 16 mT. The spectral line assignments include overtone transitions⁶⁹, in which two or three nuclear spins change state. These are seen because of the relatively high rf field (≈ 1 mT for 100 ms) used and the low static field.

The mechanism of detection is a form of the Hanle effect⁵⁷⁻⁶⁴, the optical detection by luminescence polarization of the precession of the excited state electron spin around the magnetic field. This field consists of the applied field and the "nuclear field" from the hyperfine coupling. The observed luminescence polarization during the detection period is proportional to the quasi-steady-state electron spin polarization obtained by finding the steady-state solution to the Bloch equation for electron spin precession with rapid ($\approx 10^{-9}$ s) optical and spin-lattice relaxation in a total field, which includes the slowly (≈ 1 s) changing nuclear field contribution. In contrast to earlier methods, in which the transverse magnetization at resonance provided the nuclear field contribution to the Hanle field⁵⁶⁻⁶⁵⁻⁶⁷, our time-sequenced method uses magnetization longitudinal to the magnetic field. The sensitivity advantage of this approach is due to the absence of an orthogonal applied field component, which, if comparable or greater than the nuclear field, rotates the precession axis away from the optimal orientation for detection.

We have derived an explicit expression for the sensitivity of our experiment and the optimum choice of the detection field³. With the nuclear field values of several tesla, which have been estimated for both bulk⁶⁴ and quantum well samples⁶⁶, and the luminescence fluxes possible with epitaxial samples, a signal-to-noise ratio of unity in a single repetition (≈ 1 minute) should be possible for a ten part-per-million (ppm) change in the nuclear polarization. Since the depolarization due to resonance with a dilute site can be amplified by several orders of magnitude using double resonance⁷⁰⁻⁷² and level-crossing⁷³ methods, detection of defects at below the ppm level appears possible.

In other experiments³ we have shown that, in the limit of low rf power, the linewidth obtained is just that of the bulk spins, which has long been known from high field studies to be due to spin couplings to surrounding spins⁷⁴. This is in sharp contrast to previous optical NMR experiments⁵⁵⁻⁵⁷⁻⁶⁵⁻⁶⁷ on GaAs and its alloys in which the linewidth was at least 20 times greater. Although made on a principal isotope, this observation of high resolution is of great significance for analytical use of the method on dilute sites. It shows that the spatial range of the method extends far enough from the optically relevant defect that NMR spectra undisturbed by its presence are optically observable. Thus a randomly distributed target should be observable and its spectrum interpretable as a point defect without necessary reference to the nearby site or interface responsible for the excited state electron localization. The simple reason for this is that in the time-sequenced experiment³, the diffuse paramagnetic state is absent during the NMR part of the experiment. This option is not available when the transverse magnetization which occurs at spin

resonance provides the Hanle field^{56 65-67}. The time-sequenced method also works with the light left on during the NMR, but the resonances are broadened and shifted³ by the Knight shift of the excited state electrons^{64 65}.



	1	2	3	4	5	6	7	8
⁷⁵ As	+1	+1	0	0	+2	-1	+1	-1
⁶⁹ Ga	0	-1	+1	0	0	+2	+1	0
⁷¹ Ga	0	+1	0	+1	0	0	0	+2

Fig. 3. Overtone transitions in GaAs detected by time-sequenced optical NMR. When the rf power during the irradiation period is increased beyond the linear response region, transitions in which several nuclei change spin state become visible. This effect is pronounced at the relatively low field of 16 mT used here. The assignment of the labelled transitions is given in the table, which indicates the number of nuclei of the three principal isotopes involved and the relative signs of the spin flips.

8. ACKNOWLEDGEMENTS

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9. REFERENCES

1. P.J. Pizarro and D.P. Weitekamp, "Spectroscopy of Trapped Ions by Ion Cyclotron Resonance," submitted for publication; "Spectroscopy of Trapped Ions by Axial Detection," in preparation.
2. C.R. Bowers and D.P. Weitekamp, "Nuclear Magnetic Resonance by Measuring Reaction Yield of Spin-Symmetry Species," *Phys. Rev. Lett.* in press, 1991.
3. S.K. Buratto, D.N. Shykind and D.P. Weitekamp, "Time-Sequenced Optical Nuclear Magnetic Resonance of Gallium Arsenide," submitted for publication.
4. A. Abragam, *Principles of Nuclear Magnetism*, Clarendon Press, Oxford, 1961.
5. F.D. Colegrove, L.D. Scheerer, and G.K. Walters, "Polarization of He³ Gas by Optical Pumping," *Phys. Rev.* **132**, pp. 2561-2572, 1963.
6. M. Leduc and D.S. Betts, "L'hélium polarisé: méthodes et applications," *Ann. Phys. Fr.* **11**, pp. 267-296, 1986.
7. G. Tastevin, P.J. Nacher, L. Wiesenfeld, M. Leduc, and F. Laloe, "Obtaining polarized liquid helium 3 from optically oriented gas," *J. Phys.* **49**, pp. 1-6, 1988.
8. X. Zeng, Z. Wu, T. Call, E. Miron, D. Schreiber, and W. Happer, "Experimental Determination of the Rate Constants for Spin Exchange Between Optically Pumped K, Rb, and Cs atoms and ¹²⁹Xe Nuclei in Alkali-Metal-Noble-Gas van der Waals Molecules," *Phys. Rev. A* **31**(1), pp. 260-278, 1985.
9. A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder*, Clarendon Press, Oxford, 1982.
10. A. Henstra, P. Dirksen and W.Th. Wenckebach, "Enhanced Dynamic Nuclear Polarization by the Integrated Solid Effect," *Phys. Lett. A* **134**, pp. 134-136, 1988.
11. R.A. Wind and H. Lock, "Electron-Nuclear Polarization Transfer in the Rotating Frame," *Advan. Magn. Reson.* **15**, pp. 51-79, 1991.
12. D. Stehlik in: *Excited States*, Vol. 3 ed. E.C. Lim, Academic Press, New York, pp. 204-300, 1977.
13. P.H. Henrich, H. Brunner, R.H. Fritsch and K.H. Hausser, "Time-Resolved Microwave-Induced Optical Nuclear Polarization," *Chem. Phys.* **138**, pp. 203-213, 1989.
14. A. Henstra, T.-S. Lin, J.Schmidt and W.Th. Wenckebach, "High Dynamic Nuclear Polarization at Room Temperature," *Chem. Phys. Lett.* **165**, pp. 6-10, 1990.
15. L. Friedman, P. Millet, R.C. Richardson, "Surface Relaxation of ³He on Small Fluorocarbon Particles," *Phys. Rev. Lett.* **47**, pp. 1078-1081, 1981.
16. J.S. Waugh, O. Gonen, and P. Kuhns, "Fourier-Transform NMR at Low Temperatures," *J. Chem. Phys.* **86**(7) pp. 3816-3818, 1987.
17. P. Kuhns, O. Gonen, and J. Waugh, "NMR Lineshape Thermometry at Low Temperatures," *J. Magn. Reson.* **72**(3), pp. 548-550, 1987.
18. C. R. Bowers and D. P. Weitekamp, "The transformation of symmetrization order to nuclear spin magnetization by chemical reaction and nuclear magnetic resonance," *Phys. Rev. Lett.* **57**, pp. 2645-2648, 1986.
19. C. R. Bowers and D. P. Weitekamp, "Parahydrogen and synthesis allow dramatically enhanced nuclear alignment," *J. Am. Chem. Soc.* **109**, pp. 5541-5542, 1987.

20. M. G. Pravica and D. P. Weitekamp, "Net NMR alignment by adiabatic transport of parahydrogen addition products to high magnetic field," *Chem. Phys. Lett.* **145**, pp. 255–258, 1988.
21. C. R. Bowers, D. H. Jones, N. D. Kurur, J. A. Labinger, M. G. Pravica, and D. P. Weitekamp, "The symmetrization postulate and NMR of reacting systems," *Adv. Magn. Reson.* **14**, pp. 269–291, 1990.
22. T. C. Eisenschmid, R.U. Kirss, P.P. Deutsch, S.I. Hommeltoft, R.E. Eisenberg, J. Bargon, R.G. Lawler and A.L. Balch, "Para Hydrogen Induced Polarization in Hydrogenation Reactions," *J. Am. Chem. Soc.* **109**, pp. 8089–8091, 1987.
23. R. U. Kirss, T. C. Eisenschmid and R. E. Eisenberg, "Para Hydrogen Induced Polarization in Hydrogenation Reactions Catalyzed by Ruthenium–Phosphine Complexes," *J. Am. Chem. Soc.* **110**, pp. 8564–8566, 1988.
24. J. Bargon, J. Kandels, K. Woelk, "NMR Study of Nuclear Spin Polarization during Chemical Reactions with Ortho Hydrogen," *Angew. Chem. Int. Ed. Engl.* **29**, pp. 58–59, 1990.
25. C.R. Bowers, "Parahydrogen and Synthesis Allow Dramatically Enhanced Nuclear Alignment," Ph.D. Thesis, California Institute of Technology, 1990.
26. Y. Manassen, R.J. Hamers, J.E. Demuth, and A.J. Castellano, Jr., "Direct Observation of the Precession of Individual Paramagnetic Spins on Oxidized Silicon Surfaces," *Phys. Rev. Lett.* **62**(21) pp. 2531–2534, 1989.
27. D. Fick, "Surface Physics with Nuclear Probes," *Appl. Phys. A* **49**, pp. 343–350, 1989.
28. R.F. Haglund, Jr., "Studies of Surface Chemical Physics Using Nuclear–Spin–Polarized Atomic Beams," *Chem. Rev.* **88**, pp. 697–717, 1988.
29. D.M. Hoffman, B.K. Meyer, F. Lohse and J.–M. Spaeth, "Optically Detected Electron–Nuclear Double Resonance of As–Antisite Defects in GaAs," *Phys. Rev. Lett.* **53**(12), pp. 1187–1190, 1984.
30. A. Berg, M. Dobers, R.R. Gerhardtts and R. v. Klitzing, "Magnetoquantum Oscillations of the Nuclear–Spin Lattice Relaxation Near a Two–Dimensional Electron Gas," *Phys. Rev. Lett.* **64**(21) pp. 2563–2566, 1990.
32. I.I. Rabi, J.R. Zacharias, S. Millman, and P. Kusch, "A New Method of Measuring Nuclear Magnetic Moments," *Phys. Rev.* **53**, p. 318, 1938.
33. I.I. Rabi, S. Millman, and P. Kusch, J.R. Zacharias, "The Molecular Beam Method for Measuring Nuclear Magnetic Moments," *Phys. Rev.* **55**, pp. 526–535, 1939.
34. N.F. Ramsey, *Molecular Beams*, Clarendon Press, Oxford, 1956.
35. M.B. Comisarow, "Signal modeling for ion cyclotron resonance," *J. Chem. Phys.* **69**, pp. 4097–4104, 1978.
36. R.L. Hunter and R.T. McIver, Jr., "Theory for Pulsed and Rapid Scan Ion Cyclotron Resonance Signals," *Lect. Notes in Chem.* **31**, pp. 464–483, 1982.
37. A.G. Marshall, "Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy," *Acc. Chem. Res.* **18**, pp. 316–322, 1985.
38. L.S. Brown and G. Gabrielse, "Geonium Theory: Physics of a single electron or ion in a Penning trap," *Rev. Mod. Phys.* **58**, pp. 233–311, 1986.
39. E.A. Cornell, R.M. Weiskoff, K.R. Boyce, R.W. Flanagan, Jr., G.P. Lafyatis, and D.E. Pritchard, "Single–Ion Cyclotron Resonance Measurement of $M(\text{CO}^+)/M(\text{N}_2)$," *Phys. Rev. Lett.* **63**, pp. 1674–1677, 1989.
40. R. S. Van Dyck, Jr., P.B. Schwinberg, and H.G. Dehmelt in: *New Frontiers in High Energy Physics* ed. B. Kursunoglu, A. Perlmutter, and L. Scott, Plenum Press, New York, 1978; in: *Atomic Physics 9* ed. R.S. Van Dyck, Jr. and E.N. Fortson, World Scientific, Singapore, 1984.
41. H. Dehmelt, "New Continuous Stern–Gerlach Effect and a Hint of 'the' Elementary Particle," *Z. Phys. D. Atoms, Molecules and Clusters* **10**, pp. 127–134, 1988.
42. C.M. Caves in: *Quantum Optics, Experimental Gravitation, and Measurement Theory* ed. P. Meystre and M. Scully, Plenum Press, New York, p. 594, 1983.
43. A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, Cambridge University

Press, London, 1935.

44. C.R. Bowers, P.J. Carson, D.J. Norris, and D.P. Weitekamp, "Dihydrogen Addition Studies by the PASADENA Effect" in: *25th Congress AMPERE on Magnetic Resonance and Related Phenomena* eds. M. Mehring, J.U. von Schutz and H.C. Wolf, Springer, Berlin, pp. 148–149, 1990
45. P.J. Carson, C.R. Bowers and D.P. Weitekamp, unpublished results, 1991.
46. G.L. Griffin and J.T. Yates, Jr., "Adsorption Studies of H₂ Isotopes on ZnO: Coverage Induced IR Frequency Shifts and Adsorbate Geometry," *J. Chem. Phys.* **77**, pp. 3744–3750, 1982.
47. G.L. Griffin and J.T. Yates, Jr., "Combined Temperature–Programmed Desorption and Infrared Study of H₂ Chemisorption on ZnO" *J. Catal.* **73**, 396–405, 1982.
48. D.L. Roberts and G.L. Griffin, "On the Role of Specific Hydrogen Adsorption Sites in Methanol Decomposition on Zinc Oxide," *J. Catal.* **101**, 201–211, 1986.
49. G.L. Griffin and J.T. Yates, Jr., "Coadsorption Studies of CO and H₂ on ZnO," *J. Chem. Phys.* **77**, 3751–3758, 1982.
50. K.–I. Tanaka, "Catalysis Controlled by the Constitution of Active Sites," *Adv. in Catalysis*, **33**, pp. 99–158, 1985.
51. B. Schramm, D.J. Bamford, and C.B. Moore, "Nuclear Spin State Conservation in Photodissociation of Formaldehyde," *Chem. Phys. Lett.* **98**, pp. 305–309, 1983.
52. E.E. Marinero, C.T. Rettner, R.N. Zare, and A.H. Kung, "Excitation of H₂ Using Continuously Tunable Coherent XUV Radiation (97.3–102.3 nm)," *Chem. Phys. Lett.* **95**, pp. 486–491, 1983.
53. S.T. Pratt, P.M. Dehmer, and J.L. Dehmer, "Photoionization Dynamics of Excited Molecular States. Photoelectron Angular Distributions and Rotational and Vibrational Branching Ratios for H₂ C ¹Π_u, v=0–4," *J. Chem. Phys.* **85**, pp. 3379–3385, 1986.
54. R.R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Oxford University Press, Oxford, 1987.
55. A.I. Ekimov and V.I. Safarov, "Optical Electron–Nuclear Resonance in Semiconductors," *ZhETF Pis. Red.* **15**(8), pp. 453–455, 1972 [*JETP Lett.* **15**, pp. 319–321, 1972].
56. V.L. Berkovits, A.I. Ekimov, and V.I. Safarov, "Optical Orientation in a System of Electrons and Lattice Nuclei in Semiconductors. Experiment," *Zh. Eksp. Teor. Fiz.* **65**, pp. 346–361, 1973 [*Sov. Phys.–JETP* **38**(1), pp. 169–176, 1974].
57. M.I. D'yakonov, V.I. Perel', V.L. Berkovits, and V.I. Safarov, "Optical Effects due to Polarization of Nuclei in Semiconductors," *Zh. Eksp. Teor. Fiz.* **67**, pp. 1912–1924, 1974 [*Sov. Phys.–JETP* **40**(5) pp. 950–955, 1975].
58. M.I. D'yakonov and V.I. Perel', "Spin Orientation of Electrons Associated with the Interband Absorption of Light in Semiconductors," *Zh. Eksp. Teor. Fiz.* **60**, pp. 1954–1965, 1971 [*Sov. Phys.–JETP* **33**(5), pp. 1053–1059, 1971].
59. M.I. D'yakonov and V.I. Perel', "Hyperfine Interaction in Optical Orientation of Electrons in Semiconductors," *Zh. Eksp. Teor. Fiz.* **63**, pp. 1883–1893, 1972 [*Sov. Phys.–JETP* **36**(5), pp. 995–1000, 1973].
60. M.I. D'yakonov and V.I. Perel', "Optical Orientation in a System of Electrons and Lattice Nuclei in Semiconductors. Theory," *Zh. Eksp. Teor. Fiz.* **65**, pp. 362–375, 1973 [*Sov. Phys.–JETP* **38**(1), pp. 177–183, 1974].
61. M.I. D'yakonov and V. I. Perel' in: *Optical Orientation* ed. F. Meier and B.P. Zakharchenya, North Holland, Amsterdam, pp. 11–71, 1984.
62. D. Paget, and V.L. Berkovits in: *Optical Orientation* ed. F. Meier and B.P. Zakharchenya, North Holland, Amsterdam, pp. 381–421, 1984.
63. V.G. Fleisher and I.A. Merkulov in: *Optical Orientation* ed. F. Meier and B.P. Zakharchenya, North Holland, Amsterdam, pp. 173–257, 1984.
64. D. Paget, G. Lampel, B. Sapoval, and V.I. Safarov, "Low Field Electron–Nuclear Spin Coupling in Gallium Arsenide Under Optical Pumping Conditions," *Phys. Rev. B* **15**(12), pp. 5780–5796, 1977.

65. D. Paget, "Optical Detection of NMR in High-Purity GaAs Under Optical Pumping: Efficient Spin-Exchange Averaging Between Electronic States," *Phys. Rev. B* **24**(7), pp. 3776-3793, 1981.
66. G.P. Flinn, R.T. Harley, M.J. Snelling, A.C. Tropper, and T.M. Kerr, "Optically Detected Nuclear Magnetic Resonance in Semiconductor Quantum Wells," *J. of Lumines.* **45**, pp. 218-220, 1990.
67. G.P. Flinn, R.T. Harley, M.J. Snelling, A.C. Tropper, and T.M. Kerr, "Optically Detected Nuclear Magnetic Resonance of Nuclei Within a Quantum Well," *Semicond. Sci. Technol.* **5**, pp. 533-537, 1990.
68. V.K. Kalevich, V.D. Kul'kov, and V.G. Fleisher, "Onset of a Nuclear Polarization Front due to Optical Spin Orientation in a Semiconductor," *Pis'ma Zh. Eksp. Teor. Fiz.* **35**(1), pp. 17-20, 1982 [*JETP Lett.* **35**(1), pp. 20-23, 1982].
69. V.K. Kalevich, V.D. Kul'kov, I.A. Merkulov, and V.G. Fleisher, "Two-Spin Resonance Transitions of Optically Oriented Nuclei in a Semiconductor Lattice," *Fiz. Tverd. Tela* **24**, pp. 2098-2104, 1982 [*Sov. Phys. Solid State* **24**(7), pp. 1195-1199, 1972].
70. S.R. Hartman and E.L. Hahn, "Nuclear Double Resonance in the Rotating Frame," *Phys. Rev.* **128**(5), pp. 2042-2053, 1962.
71. F.M. Lurie and C.P. Slichter, "Spin Temperature in Nuclear Double Resonance," *Phys. Rev.* **133**(4A), pp. A1109-A1122, 1964.
72. R.E. Slusher and E.L. Hahn, "Sensitive Detection of Nuclear Quadrupole Interactions in Solids," *Phys. Rev.* **166**(2), pp. 332-347, 1968.
73. D.T. Edmonds, "Nuclear Quadrupole Double Resonance," *Phys. Reports* **29**(4), pp. 233-290, 1977.
74. R.G. Shulman, B.J. Wyluda, and H.J. Hrotowski, "Nuclear Magnetic Resonance in Semiconductors. III. Exchange Broadening in GaAs and InAs," *Phys. Rev.* **109**(3), pp. 808-809, 1958.