

Optical detection of liquid-state NMR

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Nuclear magnetic resonance (NMR) in liquids and solids is primarily detected by recording the net dipolar magnetic field outside the spin-polarized sample. But the recorded bulk magnetic field itself provides only limited spatial or structural information about the sample. Most NMR applications rely therefore on more elaborate techniques such as magnetic field gradient encoding¹ or spin correlation spectroscopy², which enable spatially resolved imaging and molecular structure analysis, respectively. Here we demonstrate a fundamentally different and intrinsically information-rich modality of detecting NMR, based on the rotation of the polarization of a laser beam by the nuclear spins in a liquid sample. Optical NMR detection has in fact a long history in atomic vapours with narrow resonance lines^{3,4}, but has so far only been applied to highly specialized condensed matter systems such as quantum dots⁵. It has been predicted⁶ that laser illumination can shift NMR frequencies and thus aid detection, but the effect is very small and has never been observed. In contrast, our measurements on water and liquid ¹²⁹Xe show that the complementary effect—the rotation of light polarization by nuclear spins—is readily measurable, and that it is enhanced dramatically in samples containing heavy nuclei. This approach to optical NMR detection should allow correlated optical and NMR spectroscopy on complex molecules, and continuous two-dimensional imaging of nuclear magnetization with spatial resolution limited only by light diffraction.

The connection between light and liquid-state NMR was initially explored when it was suggested that NMR frequencies could be shifted by illumination with a circularly polarized laser far-detuned from optical resonances^{7,8}. However, more detailed experimental⁹ and theoretical^{10–14} work showed that these frequency shifts are extremely small, at most of the order of 10⁻⁵ Hz, and cannot be detected with present techniques. But the complementary magneto-optic effect, the rotation of far-off-resonance light polarization caused by nuclear spins, is readily measurable with a simple experimental apparatus because of the high density of nuclear spins in a liquid.

Both magneto-optic effects discussed can be related to the Faraday effect (the rotation of the plane of polarization of a light beam by a magnetic field). Nuclear magnetization in a liquid induces a magnetic field B_M that leads to optical rotation $\phi = lVB_M$, which is proportional to the Verdet constant V and the length of the sample l . Illumination by circularly polarized light induces electron spin magnetization in the excited state through the inverse Faraday effect¹⁵ that generates a magnetic field, causing NMR frequency shifts. The induced magnetic field B_M can be divided into a local contact field and a distant dipolar field. For example, for a long cylindrical sample with uniform magnetization M parallel to its axis, the classical magnetic field $B_M = 4\pi M$ consists of a contact interaction $B_c = 8\pi M/3$ and a distant dipolar field $B_d = 4\pi M/3$. The distant dipolar field depends on the shape of the sample (for example, it averages to zero for a spherical sample¹⁶), while the contact term can be enhanced or suppressed depending on the overlap of the wavefunction of the

virtual electron excitation created by the laser and the nuclear spin. We find that nuclear-spin optical rotation (NSOR) from ¹H in water is comparable to the size expected from the Faraday effect assuming no enhancement of the contact interaction, while for heavier atoms the contact term enhancement increases with the atomic number Z , making NSOR 135 times larger than Faraday rotation in liquid ¹²⁹Xe.

More formally, magneto-optic effects discussed in this Letter can be expressed in terms of the vector atomic polarizability α (ref. 17). The interaction energy for atoms in an oscillating electric field $\mathbf{E} = (E_0/2)(\boldsymbol{\epsilon}e^{-i\omega t} + \boldsymbol{\epsilon}^*e^{i\omega t})$ is given by $H = -(E_0^2/4)\boldsymbol{\alpha}\cdot\mathbf{s}$, where \mathbf{s} is the average photon spin, $\mathbf{s} = i\boldsymbol{\epsilon} \times \boldsymbol{\epsilon}^*$, whereas rotation of light polarization is determined by the vector susceptibility of the medium, $\chi = N\alpha$, where N is the number density of atoms. For atoms with a nuclear spin \mathbf{I} and a ¹S₀ electronic ground state, the vector polarizability as a function of laser frequency ω can be written as^{18,19}:

$$\boldsymbol{\alpha} \equiv \alpha_v \mathbf{I} = \frac{2\omega r_e c^2}{\hbar} \sum_k \frac{f_k a_k}{(\omega_k^2 - \omega^2)^2} \mathbf{I} \quad (1)$$

where the sum is taken over dipole-transition-allowed excited states ($J = 1, L = 1, S = 0$) with resonance frequencies ω_k , oscillator strengths f_k and hyperfine coupling constants given by $H_k^{\text{hf}} = a_k \mathbf{L}\cdot\mathbf{I}$, and r_e is the classical electron radius. Hence, the NMR frequency shift for right circularly polarized light ($s = -1$) with intensity I_0 is given by:

$$\Delta\nu = \frac{I_0}{\hbar n c} \alpha_v \quad (2)$$

where n is the index of refraction of the liquid. The polarization rotation angle for a linearly polarized beam propagating in the z direction through the medium of length l is given by:

$$\phi = -\frac{2\pi\omega l N}{nc} \alpha_v \langle I_z \rangle \quad (3)$$

Thus, laser-induced NMR shift and NSOR depend on the same vector polarizability and can be easily related to each other. The polarizability is proportional to the strength of the hyperfine interaction and increases for heavier atoms. Our measurements in liquid ¹²⁹Xe and water illustrate the range of possible effects.

Spin-polarized ¹²⁹Xe was produced by spin-exchange with optically pumped Rb vapour²⁰, and collected as liquid in a 1 cm × 1 cm × 0.8 cm glass cell (Fig. 1a). Optical rotation was measured with a photoelastic modulation technique²¹ using lasers at three wavelengths (532 nm, 770 nm and 1,064 nm), with laser power ranging from 2 mW to 10 mW and beam size of the order of 1 mm. The laser beam was directed perpendicular to a static magnetic field $B_0 = 125$ mG and NSOR was detected at 147 Hz while ¹²⁹Xe spins were locked to an oscillating transverse magnetic field $B_1 = 7$ mG. The optical measurements were alternated with traditional NMR detection using a SQUID (superconducting quantum interference device) magnetometer for ¹²⁹Xe polarization calibration¹⁶. For optical measurements, the frequency of the oscillating transverse field was slowly swept to the NMR resonance at 147 Hz, left on resonance for 40 s, and swept back

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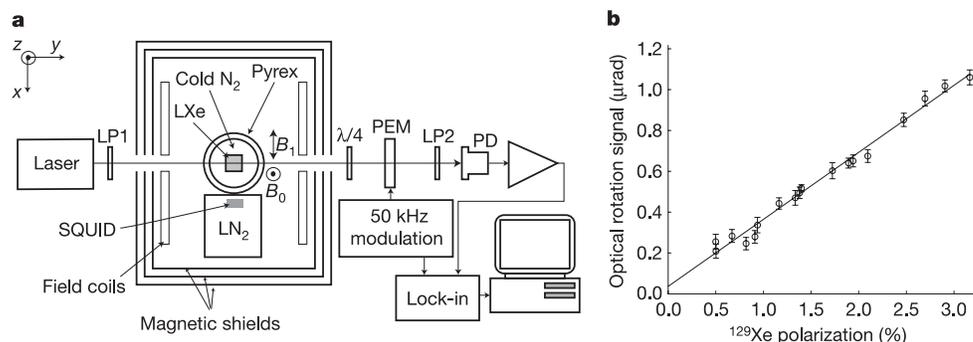


Figure 1 | Detection of nuclear-spin-induced optical rotation in liquid Xe.

a, Diagram showing the experimental set-up for the detection of nuclear-spin-induced optical rotation in liquid Xe (LXe). ^{129}Xe in natural abundance is polarized in a separate apparatus, introduced into a rectangular glass cell inside magnetic shields and maintained at -90°C by flowing cold N_2 gas through a double-wall Pyrex tube. Laser light is polarized by a linear polarizer (LP1) and the polarization rotation caused by liquid ^{129}Xe is converted to a change in intensity with a quarter-waveplate ($\lambda/4$), a photoelastic modulator (PEM) operating at 50 kHz and another linear polarizer (LP2). The light intensity is detected by a photodiode (PD) and

demodulated with a lock-in amplifier. Magnetic fields B_0 and B_1 are applied with field coils inside magnetic shields. A SQUID magnetometer operating in liquid nitrogen (LN_2) is used to independently measure Xe polarization. **b**, Data obtained with this set-up at 770 nm, and shown as the amplitude of the optical rotation signal as a function of ^{129}Xe polarization. The error bars correspond to ± 1 s.d. statistical uncertainty after averaging for 40 s with polarization rotation noise of 1×10^{-7} rad Hz $^{-1/2}$ due to acoustical vibrations near the 147 Hz ^{129}Xe NMR frequency. The solid line is a linear fit with an intercept that is consistent with zero within errors.

off resonance. For calibration, a free induction decay signal was recorded following a 7° tip with a resonant radio-frequency pulse. Figure 1b shows the optical rotation angle as a function of ^{129}Xe polarization recorded during slow decay of nuclear polarization.

NSOR in water was detected using a different apparatus, shown in Fig. 2a. Water continuously flowed through a container placed inside a 9 T superconducting magnet to polarize ^1H spins, and then through a 50-cm-long glass tube held in a field $B_0 = 5$ G. A transverse magnetic field $B_1 = 0.17$ G oscillating at 21 kHz was also continuously applied so that proton spins were adiabatically locked to the rotating field as they flowed into the apparatus. The degree of nuclear spin polarization along the path of the laser beam was independently measured using a non-resonant solenoidal NMR coil wound around the glass tube and connected to a high-input-impedance lock-in amplifier. Polarization loss during flow, inefficiency of adiabatic fast passage and broadening by magnetic field gradients resulted in a rotating nuclear spin polarization corresponding to a 1.5 T field. To avoid spurious cross-talk signals, the B_0 magnetic field was modulated on and off the proton NMR resonance at 8 Hz. The optical

rotation signal was measured using a balanced polarimeter with sensitivity limited by photon shot noise. Optical rotation and pick-up coil signals were recorded with a lock-in amplifier for several thousand seconds. Figure 2b shows the spectrum of the optical rotation signal with a peak at the 8 Hz modulation frequency. The water flow in the tube was in the turbulent regime (Reynolds number, 8,000); several measurements were made with different paths of the laser beam through the tube to verify that water had a uniform transverse distribution of polarization within 10% measurement error. No optical signal was detected when using circularly polarized light, thereby verifying absence of electronic cross-talk.

The optical rotation signals, normalized to 1 mol l^{-1} (1 M) concentration of fully polarized spins, are shown in Fig. 3 for ^{129}Xe in liquid xenon and ^1H in water, together with theoretical estimates. The size of the NSOR can be estimated from equation (1) if the oscillator strengths and hyperfine interaction constants are known. The L - S coupling scheme, used to derive equation (1), is not very accurate for ^{129}Xe owing to large relativistic effects, but can be expected to give a reasonable estimate. For example, the Verdet

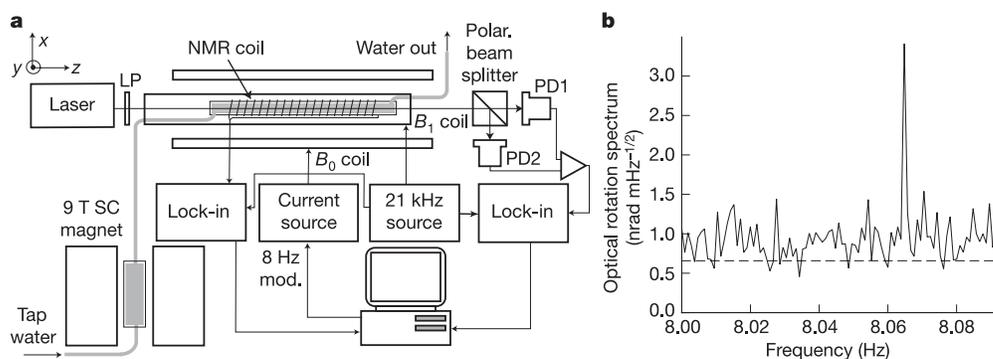


Figure 2 | Detection of nuclear-spin-induced optical rotation in water.

a, Diagram showing the experimental set-up for detection of optical rotation in water. Water is spin-polarized by flowing through a superconducting (SC) magnet and is adiabatically spin-locked to a field B_1 oscillating at 21 kHz in the y direction as it flows into a cylindrical glass tube placed in a uniform field B_0 in the x direction. The polarization rotation of laser light polarized with a linear polarizer (LP) is measured with a balanced polarimeter consisting of a polarizing beam splitter cube and two photodiodes (PD1 and PD2) and a lock-in amplifier referenced to the NMR frequency. The NMR

signal is also independently measured with a pick-up coil wound around the glass tube. A current source modulates the B_0 field on and off resonance at 8 Hz to avoid cross-talk. **b**, Data collected at 770 nm, and displayed as the Fourier spectral density of the optical rotation lock-in amplifier output for water with proton polarization $P = 5.3 \times 10^{-6}$. Taking into account the definite phase of the NMR signal, the signal-to-noise ratio after 1,000 s of averaging is equal to 4.5. The dashed line is the shot noise level for 2.9 mW detected laser power, calculated from the photocurrent in the photodetectors.

constant of Xe, calculated using the same equation with H^{hf} replaced by $H^{\text{B}} = \mu_{\text{B}} \mathbf{L} \cdot \mathbf{B}$, gives a result 40% smaller than the measured Verdet constant²², as could be expected, as contributions of higher excited states and the continuum are not included. However, in ^{129}Xe there is a substantial cancellation of contributions to the vector polarizability proportional to the nuclear spin between transitions to $6s$ and $5d$ excited states because they have similar oscillator strengths but opposite signs of the hyperfine constants, a_k . Using hyperfine constants²³ and oscillator strengths for a few of the lowest excited states²⁴, we estimate from equations (1) and (3) optical rotation of $3.5 \times 10^{-5} \text{ rad cm}^{-1}$ for a 1 M concentration of fully polarized ^{129}Xe spins at 770 nm, significantly larger than the measured value of $(5.8 \pm 0.6) \times 10^{-6} \text{ rad cm}^{-1} \text{ M}^{-1}$. This indicates that other atoms of similar nuclear charge but without cancellation between s and d states can have substantially larger optical rotation than ^{129}Xe .

The NMR frequency shift caused by circularly polarized light has been calculated for ^{129}Xe and other noble gases using several *ab initio* methods¹⁴. The results are converted to NSOR using equations (2) and (3), and plotted in Fig. 3a for two different sets of orbitals used in the multi-configuration self-consistent field (MCSCF) method. The excellent agreement with measured values may be somewhat fortuitous, as relativistic corrections are estimated¹⁴ to be of the order of 100%.

The size of NSOR in water cannot be easily estimated from equation (1) because the excited molecular level structure is very complicated and not all hyperfine constants are known. However, the measured optical rotation is in very good agreement with the size

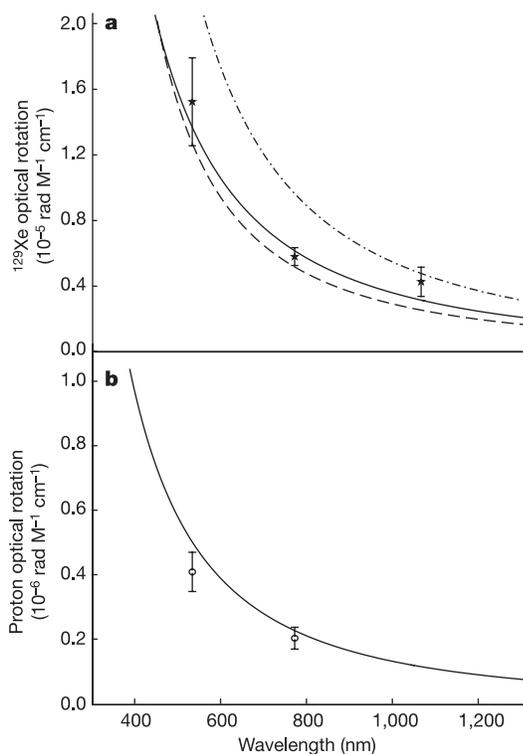


Figure 3 | Dependence of optical rotation on laser wavelength. Shown are the optical rotation angle per unit length for 1 M concentration of fully polarized ^{129}Xe spins in liquid Xe (a) and protons in water (b) as a function of laser wavelength. The error bars include combined statistical (± 1 s.d.) and systematic uncertainties. In a, the solid line is a fit to the wavelength dependence given by equation (1) with $\hbar\omega_k = 10$ eV. The results of a MCSCF *ab initio* calculation¹⁴ using complete active space 'CAS' and restricted active space 'RAS-III' of atomic orbitals are shown with dashed and dash-dotted lines, respectively. In b, the solid line is the optical rotation expected from nuclear magnetization due to the Faraday effect, assuming $B = 4\pi M$ in a long cylindrical cell, that is, $\kappa_{\text{H}} = 1$.

expected from the Faraday effect assuming $B = 4\pi M$, as shown with the solid line in Fig. 3b. This indicates that the excited-state electron wavefunction is not strongly enhanced at the location of the protons. In contrast, for ^{129}Xe the measured NSOR is more than 100 times larger than the rotation expected from the Faraday effect. The observed NSOR can be interpreted as an enhancement by a factor κ_{Xe} of the contact magnetic field $B_{\text{c}} = 8\pi\kappa_{\text{Xe}}M/3$, in analogy with the Fermi-contact interaction between alkali-metal atoms and noble gas nuclei²⁵. Our measurements give $\kappa_{\text{Xe}} = 135 \pm 13$, which is of the same order of magnitude as the enhancement for the alkali-metal electron wavefunctions during collision with ^{129}Xe atoms²⁵. Our measurements can also be compared with an *ab initio* calculation of laser-induced NMR frequency shifts in CS_2 (ref. 12). The calculated frequency shifts, converted to NSOR using equations (2) and (3) and compared with the expected Faraday rotation in CS_2 , give contact enhancement factors for ^{13}C and ^{33}S of $\kappa_{\text{C}} = 4.2$ and $\kappa_{\text{S}} = 14.7$, respectively, confirming the general trend of increase in κ with the nuclear charge.

Although in this first demonstration of NSOR the signal-to-noise ratio (SNR) is significantly lower than for traditional magnetic detection, it could be improved in several ways. Decreasing the laser wavelength (λ) increases the signal as $1/\lambda^2$ far from optical resonances, and even faster closer to resonances. At typical NMR frequencies, it should also be easy to realize photon shot-noise sensitivity for higher laser powers. The sensitivity of rotation measurements could be further improved by using a multi-pass or an optical cavity arrangement. For example, an effective optical path of 9 m has been demonstrated for simple organic liquids using a 1-cm-long cell placed in an optical cavity²⁶. The sample volume could be reduced by focusing the light into a thin capillary with a volume $V \approx 2\lambda^2 l$ determined by diffraction losses, where l is the path length. For a 1-cm-long capillary sample with a volume of 100 nl in an optical cavity with an effective length of 10 m, placed in a 10 T magnetic field and probed with 1 W of light at 400 nm wavelength, we estimate (based on scaling of our current results) an SNR of 1,000 for proton spins in water after 1 s of averaging; the SNR would be further enhanced for heavier nuclei. Another promising technique is to use a liquid-filled hollow optical fibre. Light guiding and detection of optical rotation in a liquid-filled photonic bandgap fibre has recently been demonstrated^{27,28}. The required sample volume for a single-mode hollow fibre is of the order of $V \approx 4\lambda^2 l$. For example, the same SNR of 1,000 could be achieved with a 10 nl sample volume using a 10-m-long fibre that can be coiled inside a magnet. For solutions containing molecules with a large molar mass, the maximum interaction length will be reduced owing to Rayleigh scattering, but the SNR per unit sample volume in a hollow fibre remains the same. Ultimate sensitivity with picolitre samples can be obtained by using a hollow fibre with mirrors at both ends²⁹. Thus, NSOR could be detected from small samples with a sensitivity higher than, or comparable to, that obtained in micro-coil NMR³⁰.

The optical rotation technique demonstrated here also has several unique advantages for the detection of NMR signals in transparent samples compared with magnetic detection. Using a two-dimensional photodiode array or CCD camera, one could obtain a real-time two-dimensional image of the nuclear magnetization without application of magnetic field gradients. The spatial resolution of such an image is in principle limited only by light diffraction. With a constant field gradient in the direction of the laser beam, one could also obtain a three-dimensional image of the precessing magnetization with high spatial resolution. For heavy atoms, the NSOR signal is significantly enhanced compared with the rotation due to the Faraday effect, allowing NMR signals to be detected in the presence of large magnetic field noise or radio-frequency fields at the NMR frequency. Another class of possible applications involves studies of correlation between optical and NMR spectroscopy. If the laser frequency is tuned near an optical resonance, the NSOR signal will be preferentially enhanced for nuclear spins that have a large overlap with the

excited-state electron wavefunction created by the optical excitation. Such two-dimensional optical-NMR spectroscopy could be useful for interpretation of circular dichroism data in complex molecules.

Received 15 April; accepted 11 July 2006.

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Acknowledgements This work was supported by the US DOE and the US NSF. We thank W. Happer's group for use of the 9 T superconducting magnet and S. Smullin for comments on the manuscript.

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