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Optical detection of transition metal ion electron paramagnetic resonance by coherent Raman spectroscopy

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Abstract

Coherent Raman scattering in combination with optical heterodyne detection provides an attractive new technique for the measurement of electron paramagnetic resonance (EPR). The technique is applicable to both electronic ground and excited states. In contrast to conventional ODMR techniques, it monitors the *precessing* magnetisation and produces phase-sensitive spectra. We have demonstrated the feasibility of the experiment using the $^4A_2$ to $^4E(^4T_2)$ transition of Cr^{3+} in Al_2O_3 (ruby).

1. Introduction

The combination of magnetic resonance spectroscopy with optical irradiation can increase the sensitivity and information content in many cases and extend the range of applications to systems that would otherwise be difficult or impossible to investigate. The most widely used scheme of optically detected magnetic resonance [1], which has, in specific systems, made possible the detection of magnetic resonance in individual molecules [2,3], detects changes in the luminescence when the magnetic resonance condition is fulfilled. This scheme has been applied primarily to the detection of magnetic resonance in electronically excited states. However, it is also possible to monitor the change in the magnetic circular dichroism (MCD) or Faraday rotation when a ground state electron paramagnetic resonance (EPR) transition is partially saturated [l]. The signal detected in these experiments monitors the magnetisation component aligned with the magnetic field.

An alternative approach to the optical detection of magnetic resonance is shown schematically in Fig. 1. Transition $|1\rangle \leftrightarrow |2\rangle$ represents a magnetic resonance transition, which is excited by a radiofrequency (rf) or microwave (mw) field. If a laser couples to the adjacent optical transition $|1\rangle \leftrightarrow |3\rangle$ it transfers coherence from the rf transition into transition $|2\rangle \leftrightarrow |3\rangle$ which is not directly excited by the laser. If transition $|2\rangle \leftrightarrow |3\rangle$ is also an allowed optical transition, the coherence is the source of an optical field, whose frequency is the algebraic sum (in Fig. 1 the difference) of the frequencies of the two incident

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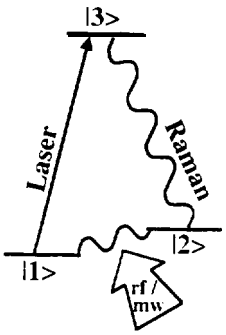

Fig. 1. Principle of coherent Raman scattering: a laser field couples to the optical transition $|1> \leftrightarrow |3>$ while a radiofrequency (rf) or microwave (mw) field excites the magnetic resonance transition $|1> \leftrightarrow |2>$ The combined action of the two fields excites coherence in all three transitions, in particular also in transition $|2> \leftrightarrow |3>$

fields. Phase matching conditions cause this Raman field to propagate collinearly with the incident laser field.

The Raman field must be detected in the presence of the incident laser field, which is often many orders of magnitude more intense. One possible approach is to separate the two fields by a combination of polarisation selection and a Fabry-Perot interferometer that is resonant with the Raman field but blocks the unshifted laser field [4,5].

An alternative approach is optical heterodyne detection, where the two fields are allowed to interfere on a detector. The frequency difference between the two fields, i.e. the microwave frequency, leads to a beat signal, which can easily be separated from the constant background. This approach to the detection of coherent Raman scattering has been employed in the kHz to MHz frequency range, e.g. for the detection of nuclear magnetic resonance (NMR) transitions [6-8]. In this Letter we report the extension of this technique to the microwave frequency range for the detection of EPR signals at a frequency of 13.8 GHz.

2. Experimental apparatus

The requirements for this experiment are closely related to those of a conventional EPR [9] experiment, with the addition of a transverse (to the field direction) laser beam that detects the precessing magnetisation. Fig. 2 shows schematically our realisation of this scheme.

The sample, which is cooled by helium gas, is placed in a split-coil magnet, which provides a homogeneous (better than 1 part in 10^4 over the sample volume) variable magnetic field (zero to 1 tesla). Perpendicular to the variable field, a weak ($< 2 \times 10^{-4}$ tesla) microwave field of frequency 13.8 GHz is applied. The laser beam, which is derived from a single-mode ring dye laser, passes through the sample parallel to the microwave field. The optical wavelength of 597 nm is in resonance with the zero phonon line of the $^4A_2$ to ^4E transition of ruby [10]. The transmitted laser beam and the Raman field are detected with a high speed InGaAs photodiode (New Focus Mode1 1437 with 200 Ω termination, $\cong$ 15 GHz electrical bandwidth). The beat signal is amplified and mixed with the microwaves used for the excitation. To reduce drift and low-frequency noise, the polarisation of the incident laser beam is modulated between opposite circular polarisations by a photoelastic modulator (PEM), and the demodulated microwave signal is passed through a lock-in amplifier referenced to the PEM-driver. The signal resulting from this detection scheme is directly proportional to the conventional EPR signal. As in conventional EPR, it is possible to measure the absorption and dispersion signals separately by adjusting the phase of the microwave reference.

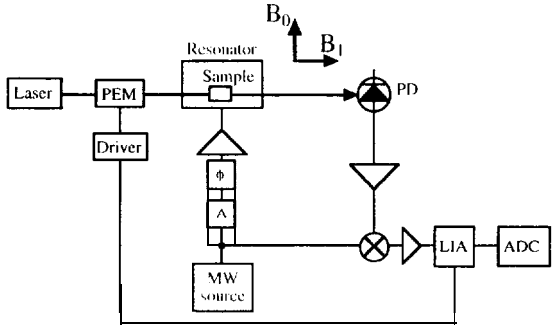

Fig. 2. Schematic representation of the expenmental apparatus. PEM = photoelastic modulator. PD = photodiode, A = attenuator, ϕ = phase shifter, B = magnetic field, LIA = lock-in amplifier, ADC = A/D converter.

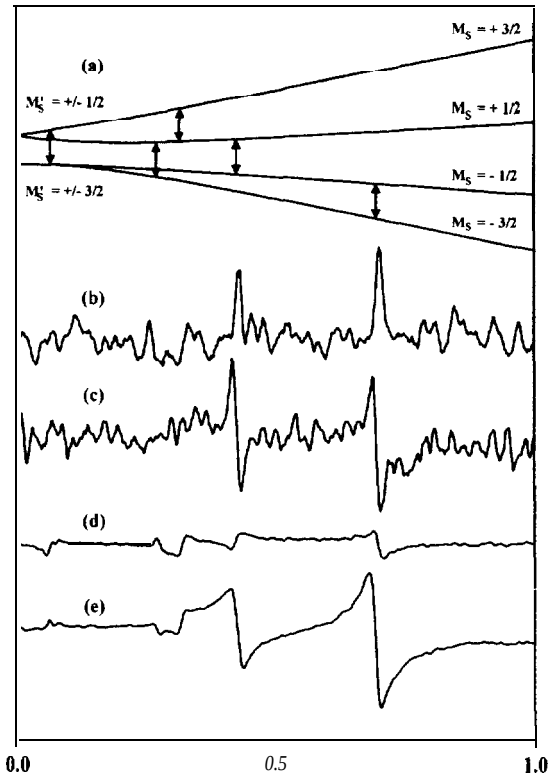

Fig. 3. (a) Energy level scheme of the ground state of Cr^{3+} in ruby; arrows denote the expected transitions at a microwave frequency of 13.8 GHz. (b,c) Absorption and dispersion spectra measured with a peak microwave field of 14 μT at a temperature of 78 K. (d,e) Same with peak microwave field of 140 μT and a temperature of 11 K.

3. Experimental results

The sample used in our initial experiments was a single crystal of ruby (Cr^{3+} in Al_2O_3) with a nominal concentration of 0.5% (Cr:Al by atoms). The laser beam passed along the crystalline c-axis with a path length of 2 mm. Fig. 3a shows the energy level scheme of the Cr^{3+} electronic ground state with the magnetic field perpendicular to the crystalline c-axis as a function of the magnetic field strength. The spin-Hamiltonian parameters (ground-state splitting $2D = -11.45$ GHz and $g_\perp = 1.98$) used for this calculation are taken from previous EPR studies [9,11]. The magnetic fields at which EPR transitions are expected are indicated.

Fig. 3b–e shows some spectra obtained by measuring the microwave signal as a function of the static magnetic field. The incident power was 39 mW for spectra (b) and (c) and 44 mW for (d) and (e). The approximate beam diameter was 1.4 mm for spectra (b) and (c) and 3.6 mm for (d) and (e). The microwave frequency was 13.85 GHz for spectra (b) and (c) and 13.87 GHz for (d) and (e). The peak microwave amplitude was 14 μT for spectra (b) and (c) and 140 μT for (d) and (e). The sample was cooled to 78 K for spectra (b) and (c) and to 11 K for (d) and (e). The phase of the microwave field at the sample was advanced by 90 degrees for spectra (c) and (e) relative to spectra (b) and (d) respectively.

The experimental conditions for the spectra shown in Fig, 3 were chosen to illustrate the characteristics of coherent Raman detected EPR, which resemble in many respects more closely conventional EPR than MCD-detected EPR. Spectra (b) and (c) were recorded at relatively high temperature, where spin–lattice relaxation [9] was sufficiently fast to prevent the EPR transitions from becoming saturated by moderate microwave power. In these circumstances, both absorption and dispersion phase signals are observed with their characteristic lineshapes. At lower temperature and higher microwave power the EPR spectrum becomes distorted due to saturation, as shown by spectra (d) and (e): the most strongly allowed EPR transitions become broadened and their absorption phase signal reduces in size relative to their dispersion phase signal. The low field transitions ($B < 0.3$ T) are only weakly allowed in our experimental geometry. Accordingly, they are not observed in spectra b) and c), while they become observable in spectra (d) and (e) without undergoing the power broadening observed for the stronger transitions.

4. Discussion

Optical heterodyne detection yields a signal that is proportional to the *amplitude* of the Raman field times the amplitude of the local oscillator, i.e. the unshifted laser field. This is in contrast to the polarisation selection and Fabry-Perot scheme for separat-

ing the Raman field from the unshifted laser light, which yields a signal proportional to the square of the Raman field. Comparison of the practical sensitivity can be made with an earlier experiment, in which a Fabry-Perot scheme was used to detect EPR(24 GHz) of donor spins in a semiconductor (n-CdS) [4]. In that experiment, a Raman field that was up to 10^7 times less intense than the unshifted light could be detected. Our instrument, which is not (yet) optimised for sensitivity, can detect approximately 10^{-14} mW of frequency shifted light in the presence of 1 mW of unshifted laser light, with a 1 second integration time. It is highly unlikely that even a modem multipass Fabry-Perot interferometer design could match this performance.

The main advantages of optically detected magnetic resonance (ODMR) over conventional detection include high temporal [12] and spatial [12–14] resolution, In favourable systems, it can also offer improved sensitivity [2,3]. These advantages, which have been exploited in experiments with luminescence detection, are equally present in coherent Raman experiments. Furthermore, the experiment provides important information about the relationship between the optical and magnetic properties of a sample that cannot be obtained with magnetic resonance spectroscopy. In particular, the amplitude and phase of the Raman-detected signal reflect the orientational dependencies of both the magnetic susceptibility and the optical polarisability. In the presence of magnetic anisotropy, centres with different orientations are resonant with the microwave field at different static magnetic fields [9,15]. This allows the relative orientation of the optical polarisability and magnetic susceptibility to be studied even in samples containing randomly orientated magnetic centres.

Compared to more conventional optically detected EPR techniques like MCD-detected EPR [1], which detect magnetic resonance by its effect on the *populations* of magnetic states, our experiment does not require partial saturation of the magnetic resonance transitions. This not only reduces the requirement on the available microwave power and the relaxation times, but also eliminates the need to know the relaxation rates for simulation of the spectra, which is usually impossible to obtain in sufficient detail. While the relative orientation of optical polarisability and magnetic susceptibility tensors should also influence these experiments, it has been found in practice that distinguishing this orientational dependence from anisotropic relaxation processes is exceedingly difficult. Magneto-optical magnetisation studies, which rely on distinguishing centres of different orientations through their different thermal population differences, cannot provide such information with the accuracy of magnetic resonance experiments [16].

Bloembergen and co-workers were the first to propose that excitation of EPR in transition metal ion containing materials might be used to generate microwave frequency modulation of light [17]. We have realised this proposal experimentally and applied it to the observation of transition metal ion EPR. We expect the technique to have a large potential, in particular, for studying transition metal ions in biological systems like metalloproteins. As a first step in this direction, we have obtained preliminary data on a low spin ferric haem protein in a frozen aqueous solution.

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