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A continuous-wave and pulsed electron spin resonance spectrometer operating at 275 GHz

H. Blok,* J.A.J.M. Disselhorst, S.B. Orlinskii, and J. Schmidt

Huygens Laboratory, Department of Molecular Physics, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

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Abstract

An electron paramagnetic resonance (EPR) spectrometer is described which allows for continuous-wave and pulsed EPR experiments at 275 GHz (wavelength 1.1 mm). The related magnetic field of 9.9 T for $g \sim 2$ is supplied by a superconducting solenoid. The microwave bridge employs quasi-optical as well as conventional waveguide components. A cylindrical, single-mode cavity provides a high filling factor and a high sensitivity for EPR detection. Even with the available microwave power of 1 mW incident at the cavity a high microwave magnetic field B_1 is obtained of about 0.1 mT which permits $\pi/2$-pulses as short as 100 ns. The performance of the spectrometer is illustrated with the help of spectra taken with several samples.

Keywords: EPR; ESE; High field; High-frequency; mm-Wave

1. Introduction

In the last decade the interest in electron paramagnetic resonance (EPR) spectroscopy at frequencies higher than 9–35 GHz has grown considerably [1]. In particular EPR at 95 and 140 GHz is now widely applied [2] and several groups are presently developing the EPR technology to frequencies around 300 GHz and higher [3,4]. The advantages of working at such high frequencies are manifold. First one benefits from the increased spectral resolution in the EPR as well as in the electron nuclear double resonance (ENDOR) spectra. In EPR spectroscopy of single crystals one can separate signals of sites with slightly different g-tensors. In random samples the anisotropy of the g-tensor allows to perform orientationally selective EPR and ENDOR experiments. Second, the absolute sensitivity increases dramatically as a result of the large Boltzmann factor and the fact that very tiny samples can be used. Third, spin systems with $S > 1/2$ with large zero-field splitting become accessible. Applications of high-frequency EPR range from semiconductor materials, spin cluster systems and metallo proteins to organic radicals in proteins [5]. The many possible applications have even led to ultrawide band multifrequency EPR spectrometers [6].

The EPR experiments performed at 95 and 140 GHz demonstrate that it is attractive to dispose of cw as well as pulsed techniques [7]. Continuous-wave methods are usually applied to systems with relatively short spin–spin relaxation times and are excellently suited to measure lineshapes and hyperfine structures. Pulsed EPR methods allow to study T_1- and T_2-type relaxation processes and moreover appear to be very well suited to perform ENDOR experiments. With these aspects in mind we have decided to push the spectral resolution and the absolute sensitivity of cw and pulsed EPR to the limit that can be achieved with conventional superconducting magnet technology by constructing a 275.7 GHz EPR spectrometer that employs a superconducting magnet with a maximum field of 14 T and that allows for cw as well as pulsed operation.

In this contribution we present the design and performance of this spectrometer. Inspired by the examples set by other groups [8–10] we have used quasi-optical transmission techniques to eliminate the unacceptably

* Corresponding author. Fax: +31715275936.
E-mail address: huib@molphys.leidenuniv.nl (H. Blok).

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high-transmission losses of conventional waveguide technology at this high frequency. The problem of separating the reflected cw EPR signal or the electron-spin-echo (ESE) signal from the excitation beam and the problem of combining the signal beam with the beam of the local oscillator for the superheterodyne detection process has been solved by taking advantage of specific properties of the quasi-optical microwave components. A combination of a Gunn diode at 91.9 GHz and a tripler produces a cw output of about 5 mW at 275.7 GHz. By using a PIN switch that modulates the output of the Gunn diode at 91.9 GHz, pulses are obtained at 275.7 GHz with an on–off ratio of more than 80 dB. An important aspect of the spectrometer is that a tunable single-mode cavity is used. The advantage is that even with this moderate microwave power pulsed EPR experiments can be performed with pulse durations of about 100 ns. The use of the single-mode cavity also leads to an excellent absolute sensitivity of $\approx 10^8$ spins per mT at a bandwidth of 1 Hz. The spectrometer is flexible and can easily be switched from cw to pulsed operation as is demonstrated by several experimental results obtained on various samples.

2. Experimental

2.1. Outline of the spectrometer

In Fig. 1 the block diagram of the EPR spectrometer is presented in which four major parts can be distinguished. First the W-band microwave sources for the excitation of the sample and for the provision of local oscillator energy for the bridge. Second the mm-wave pseudo-optic bridge and the heterodyne detection system. Third the transmission line connecting the bridge with the probehead and the tunable single-mode cavity which is inserted in a variable-temperature cryostat. Fourth the superconducting magnet.

The microwave bridge operates in reflection mode and can be used for continuous-wave as well as for pulsed EPR experiments. Two microwave sources at 91.9 and 89.7 GHz energize two diode triplers. The first is used to generate the excitation power at 275.7 GHz and the second to generate a microwave field at 269.1 GHz to drive the local oscillator of the superheterodyne receiving system. The intermediate frequency (IF) of this receiver is 6.6 GHz. An important aspect of

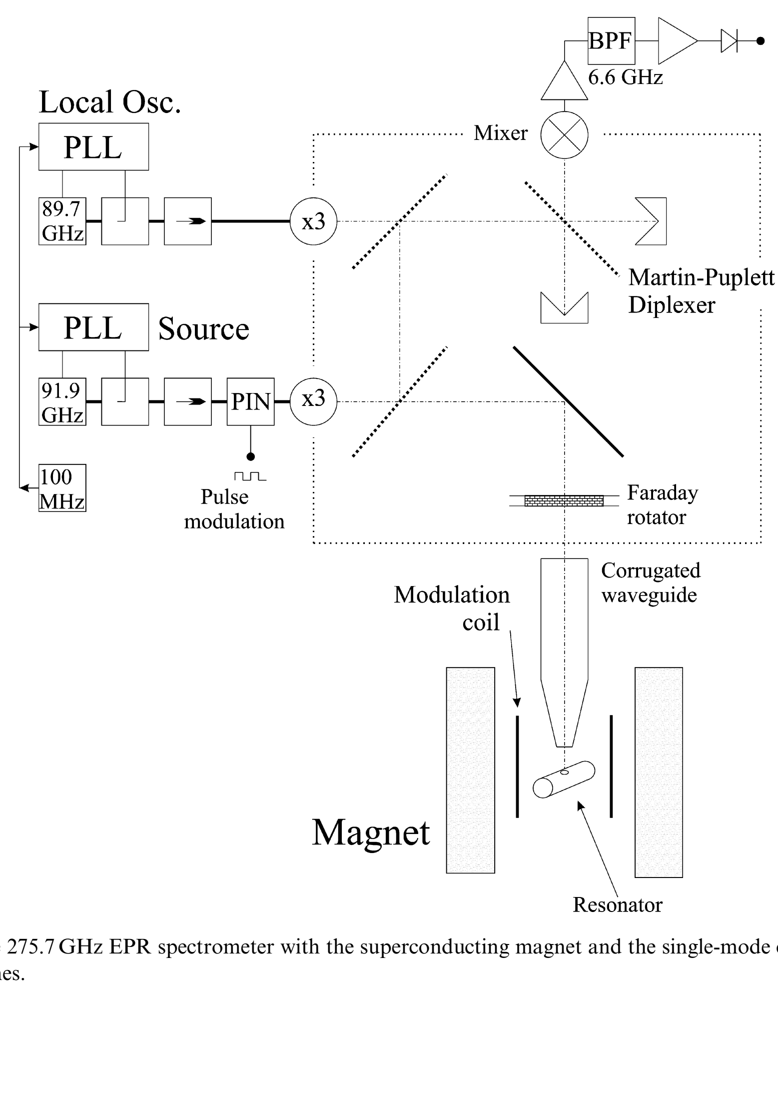

Fig. 1. A block diagram of the 275.7 GHz EPR spectrometer with the superconducting magnet and the single-mode cavity. The pseudo-optic part is indicated within the dotted lines.

the bridge is that for the transport of the high-frequency microwave energy pseudo-optical, confined beams of electromagnetic waves in free space are used. The advantage of applying this technique is that the microwave transmission losses, which would be unacceptably high when using traditional waveguides, are almost negligible. The transmission line connecting the bridge with the probehead at the bottom of the variable-temperature cryostat is a special oversized, HE_{11} corrugated waveguide. The attraction of this structure is that the high-frequency microwaves are confined to a lateral dimension of 18 mm and that the transmission losses over the length of 1.2 m are very low. The probehead contains a tunable single-mode TE_{011}, resonant cavity in which the sample is positioned. The magnet is a solenoid-type superconducting coil with a maximum field of 14 T. These items will be discussed in more detail after some general remarks about the use of the pseudo-optical beams.

2.2. Pseudo-optical beams

In pseudo-optical systems beams of transverse electromagnetic waves are used to transport microwave energy from one place to another and Gaussian beams are a good representation for the propagation of the electromagnetic waves in free space when the system dimensions are less than a few hundred wavelengths [11]. The beams can be focused by lenses and mirrors but, in contrast to ray optics, diffraction and the curved nature of the wavefront has to be taken into account in the description of their propagation. Gaussian beams convert and divert hyperbolically with a wavefront with varying curvature towards a non-zero minimum dimension, the waist (w_0). At this position the wavefront is a plane wave. A fundamental Gaussian beam has a flat wavefront at the aperture at $z = 0$ with a field amplitude E_r that varies in the x–y plane according to a Gaussian function: $E_r = E_0 \exp(-r^2/w^2)$, with $r^2 = x^2 + y^2$ and produces a traveling wave (beam) in the z-direction. This beam remains Gaussian in the x–y plane, decreases in amplitude and expands in width. The width w varies with z as $w^2 = w_0^2[1 + (z/z_0)^2]$. The wavefront varies like a spherical wave with a radius $R = z[1 + (z_0/z)^2]$. In both formulas $z_0 = (\pi w_0^2/\lambda)$ is also called the Rayleigh range or confocal distance, indicating the boundary between decreasing and increasing wavefront radius. Nearly all of the energy of a Gaussian beam (98.9%) is confined within a cross-sectional area with a diameter three times the width w of the beam and since the beam is a free propagating electromagnetic wave the losses in the propagation path are negligible, especially when the beam handling is done with metallic mirrors. Mirrors have perfect reflecting properties, do not need anti-reflection coatings and can be machined very accurately. The dimensions of the mirrors should be chosen such that the aperture is sufficient to suppress higher-order modes possibly introduced by diffraction effects at the mirror boundaries.

A mirror that proves to be very useful in the design of the microwave bridge is the so-called rooftop mirror. This type of mirror is a combination of two flat mirrors touching each other along the rooftop line at a 90° angle. An incoming wave is reflected back in the same direction but owing to the fact that the resulting E-field at both reflection points has to be normal to the mirror planes the polarization of this reflected wave will be different. The rotation of the polarization is two times the angle between the incoming polarization and the rooftop line. More specifically when the incoming polarization is +45° then the reflected polarization is −45° with respect to the rooftop line, i.e., the incoming and reflected beams are orthogonally polarized.

Other important tools to manipulate the polarized beams in the microwave bridge are grids made of many thin, parallel wires. These wire grids act as virtually perfect mirrors for a wave with the E-field vector parallel to the wires whereas they are transparent to the orthogonally polarized waves. For our operating frequency a polarizer with wires of 20 μm at a pitch of 60 μm has a typical insertion loss of less than 0.1 dB for the properly polarized waves and a cross-polarization attenuation better than 30 dB.

The third quasi-optical component that plays an important part in the microwave bridge is the Martin–Puplett diplexer. It is used to combine the beam carrying the EPR signal and the beam of the local oscillator and to give them the same polarization. It consists of two rooftop mirrors combined with a wire-grid polarizer, which is rotated over 45°. An incoming wave, polarized in the direction of the rooftop line will then be split into two orthogonally polarized components. One will be reflected towards the first mirror, rotated over 90° and then pass through the polarizer. The other component will pass through the polarizer and after reflection from the second rooftop mirror will be reflected at the polarizer to recombine with the first component. There will be a phase difference between the two components if the path lengths between the polarizer and the two rooftop mirrors differ. One of the mirrors is movable and can be adjusted for the second component to be either in-phase or out of phase with the first one. The resulting output wave is then either horizontally or vertically polarized. When another wave with a perpendicular polarization and a different wavelength is projected onto the polarizer the same process will result in an output with the same polarization as the first one, provided that the path-length difference $\Delta = n_1\lambda$ for the first and $\Delta = (n + 1/2)\lambda_2$ for the second wave. The resulting combined wave has a well-defined polarization and is directed towards the microwave mixer which is polarization sensitive.

2.3. Microwave bridge

The layout of the microwave bridge, which is built by Radiometer Physics GmbH in Meckenheim in Germany, is given in Fig. 2. The microwave source is a Gunn diode oscillator at 91.9 GHz that is phase-locked to a 100 MHz crystal oscillator and whose output of 60 mW is fed into a frequency tripler. After the tripler about 5 mW is available at 275.7 GHz. In pulsed operation the output of the Gunn oscillator at 91.9 GHz is converted into pulses by a PIN switch with an on–off ratio of 20 dB, an insertion loss of 1.2 dB and a switching time of 5 ns. As a result of the non-linear behavior of the tripler the on–off ratio at 275.7 GHz is more than 80 dB. This high on–off ratio enables the detection of the faint echo signals against the noise in the IF band originating in the mixer. The 275.7 GHz output of the tripler is converted into a free propagating Gaussian beam with a waist of 1.8 mm by a scalar feed horn and transformed to a convergent beam by an off-axis focusing elliptical mirror. This beam is transmitted through a grid polarizer and then projected by a flat mirror to a waist at the entrance of a corrugated, circular waveguide. The waist w_0 at the entrance of the corrugated waveguide is 5.45 mm which is about three times smaller than the inside diameter of 18 mm of this waveguide. As already mentioned, in this way virtually all microwave energy is coupled into the waveguide. A Faraday rotator (QMC Instruments Ltd, England) is positioned in this beam which rotates the polarization of the wave over 45° in a clockwise direction.

The second microwave source is also phase-locked to the same 100 MHz crystal oscillator and provides an output of 50 mW at 89.7 GHz. This 89.7 GHz signal is also tripled and the resulting signal at 269.1 GHz with a

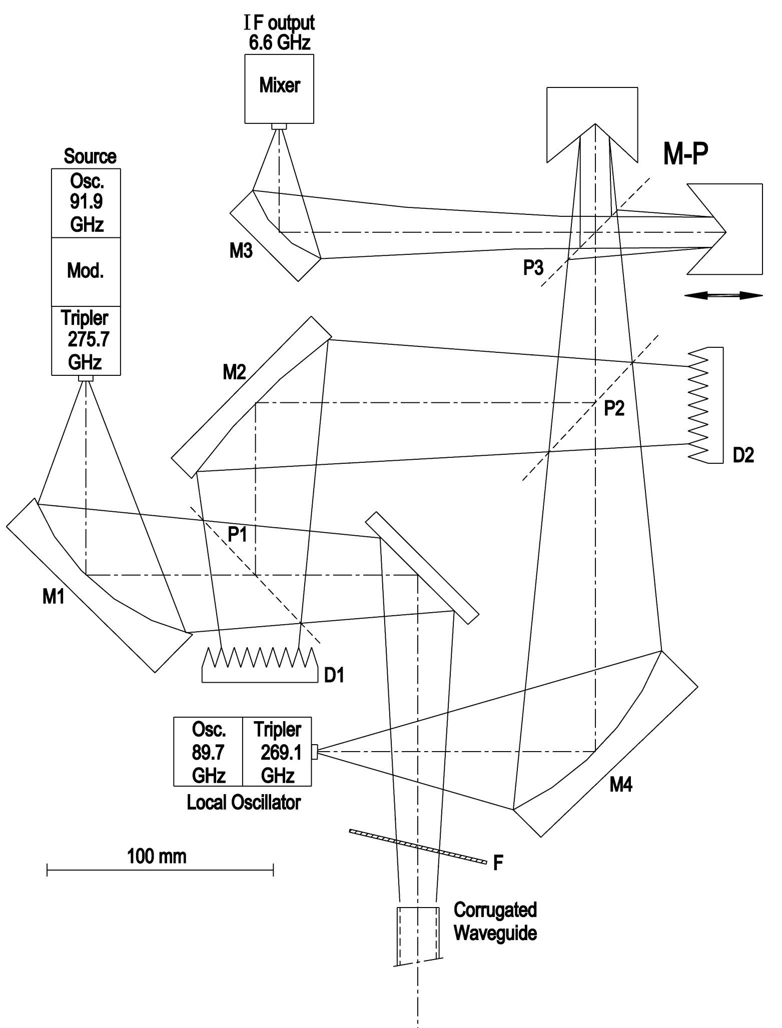

Fig. 2. The layout of the pseudo-optical bridge. Centerlines and contours of Gaussian beams are indicated. P1 and P2 are vertically oriented wire-grid polarizers. P3 is a tilted wire-grid polarizer. M_1, M_2, M_3, and M_4 are elliptical focusing mirrors. D1 and D2 are dumps for cross-polarization leakage. *F* is the 45° Faraday rotator. M–P is the Martin–Puplett diplexer.

power of 2 mW serves as the local oscillator for the superheterodyne receiver.

The reflected cw EPR signal or the ESE signal produced by the sample in the resonator is also linearly polarized and travels back through the corrugated waveguide. Its polarization is now rotated over 45° counterclockwise with respect to the propagation direction by passing through the Faraday rotator and consequently is orthogonally polarized with respect to the incoming wave. The beam is reflected from the grid polarizer and refocused towards the Martin–Puplett diplexer via a grid polarizer, acting as a mirror. The output of the local oscillator at 269.1 GHz is orthogonally polarized and projected through the same polarizer. The Martin–Puplett diplexer is adjusted such that the incoming beams are not only combined but that they also have the same polarization at the output side. The output of the diplexer is then focused towards a waist at the entrance of a scalar horn and coupled to the mixer diode where the 6.6 GHz IF signal is produced. This signal is amplified by an IF amplifier with a bandwidth of 280 MHz and a gain of 50–80 dB, rectified and fed to a lock-in detector for cw operation or to a boxcar integrator and data acquisition electronics when the system is used in pulsed mode. The outputs are presented on a Bruker EleXsys system, which also controls the magnet sweeps.

2.4. Corrugated waveguide and probehead

A corrugated circular waveguide (Thomas Keating Ltd in Billingshurst, England) with an inside diameter of 18 mm is used to transport the microwave energy to the resonator at the bottom of a variable-temperature cryostat which in turn is positioned in the room-temperature bore of the superconducting magnet. The circumferentially corrugated structure of the wall presents a high longitudinal surface reactance to the microwave field. To this end the corrugations have a depth of $\lambda/4$ and a spacing of $\lambda/2$. The Gaussian beam emanating from the bridge is focused at the entrance of this waveguide and couples very effectively to a HE_{11} mode, which has zero-field amplitude at the wall and propagates with very low loss and with conservation of its polarization in this waveguide. At the end of the 1 m long waveguide a corrugated tapered transition (Thomas Keating Ltd) modifies the propagation path from the large circular waveguide into a fundamental-mode rectangular one with inside dimensions of 0.44×0.88 mm. The microwave losses in the corrugated waveguide and the taper are less than 0.1 dB. From the 5 mW of microwave power available at the source tripler a little more than 1 mW reaches the cavity. The losses are mainly attributable to the Faraday rotator and the small section of fundamental-mode rectangular waveguide at the end of the taper.

In Fig. 3 a schematic drawing is presented of the horizontally positioned TE_{011} cylindrical cavity that contains the sample. The cavity is coupled to the short piece of rectangular waveguide at the end of the tapered side of the corrugated waveguide through a small hole with a diameter of 0.34 mm in its shortened end. The diameter of the cavity is 1.40 mm and the length can be varied between 0.80 and 1.40 mm to enable tuning of the cavity to the operating frequency of 275.7 GHz. The actual length depends on the amount and type of material (sample and sample tube) in the cavity. The tuning is performed by moving two plungers at both sides of the cavity symmetrically and synchronously inward or outward with the help of two coupled differential reduction mechanisms. In this way the position of the coupling hole is maintained in the center between the

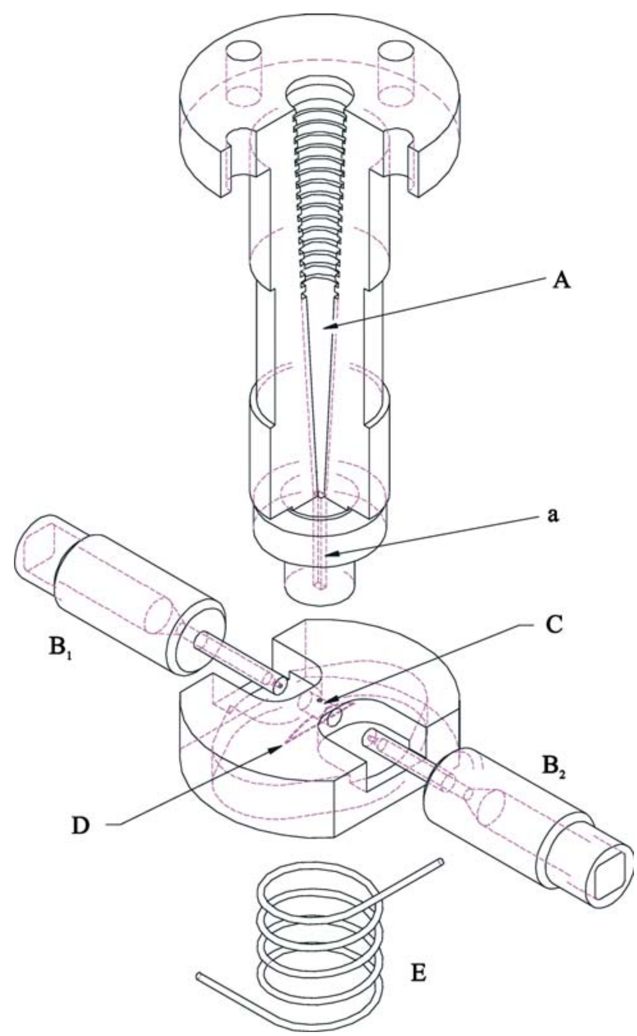

Fig. 3. The 275.7 GHz resonator construction. A is the corrugated transition towards the fundamental mode waveguide (a). B_1 and B_2 are the plungers with a central hole for the sample tube that can be moved synchronously to tune the cavity. C is the cavity with the coupling hole on top. D is the tangential slit for sample illumination. E is the modulation coil.

two plungers. The positioning of the plungers can be achieved with an accuracy of about 1 μm. The loaded quality factor $Q \approx 1500$. The sample is contained in a thin-walled suprasil quartz tube with an outside diameter of 0.25 mm and an inside diameter of 0.15 mm. This tube is inserted in the cavity through two 0.4 mm diameter holes through the center of the plungers. This sample tube can be rotated over 360°. The coupling between the fundamental-mode rectangular waveguide and the cavity is varied by rotating the cavity-plunger combination around a vertical axis that goes through the rectangular waveguide and the coupling hole. A coil is positioned directly underneath the cavity to enable the generation of a low-frequency modulation field in the same direction of the main magnetic field for lock-in detection of the resonance signal in cw operation. The coil is mechanically isolated from the cavity block. Provisions are made to implement RF coils around the resin plungers with Au plated tips for ENDOR experiments. Illumination of the sample with light can be realized through a tangential slit with a width of 0.1 mm in the bottom of the cavity.

2.5. Variable-temperature cryostat

The combination of the corrugated waveguide and the probehead is inserted in a variable-temperature, helium gas-flow cryostat (SpectrostatCF by Oxford Instruments Ltd in England) that in turn is positioned in the room-temperature bore of the superconducting magnet. The whole insert including the probehead and the sample can be cooled from 300 to 4.5 K by the flow of cold helium gas with a precision and stability of about 0.1 K. At the top of the cryostat a 0.2 mm thick kapton window, transparent to the microwaves, separates the helium atmosphere from the ambient.

2.6. Magnet

The magnet, type TeslatronTH14, constructed by Oxford Instruments Ltd in England, is a superconducting solenoid with a warm bore of 88 mm diameter and a maximum obtainable field of 14 T. It has a specified homogeneity of 10^{-5} over a volume with a diameter of 3 mm. In view of the fact that the linear dimensions of the sample size are only 0.1 mm the variation of the magnetic field over the sample is assumed to be of the order of 0.01 mT. The magnet is operated with the power supply leads permanently connected to the magnet. The inductance of the magnet is only 53.6 Henry and sweeps of 1 T can be performed in 20 min, which is very advantageous for paramagnetic systems with a large g anisotropy. The long-term stability over a period of 20 min is 0.02 mT whereas the short-term stability on a timescale of 1 s is 0.01 mT. The disadvantage of this system compared to a persistent magnet equipped with a separate superconducting sweep coil is the relatively high helium consumption. Without energizing the coils the helium boil-off rate is 0.1 liter per hour and at a field of 10 T it is 0.3 liter per hour.

3. System performance

Four samples were used to test the performance of the spectrometer in cw and pulsed EPR experiments at room temperature and at 5 K. The first sample is a powder of MgO doped with Mn^{2+} ions at a concentration of about 10^{-4} mol/mol. It was used to perform cw EPR experiments at room temperature and to test the homogeneity of the magnetic field over the sample. In Fig. 4 the complete cw EPR spectrum of this sample is presented while the insert shows a detailed recording of a hyperfine component. The linewidth observed for the six hyperfine components is 7×10^{-2} mT. This value is identical to that observed at 95 GHz and shows that the inhomogeneity of the magnetic field is of the order of 10^{-2} mT or less at a resonance field of 9.8 T over the sample volume of $150 \times 150 \times 150$ (μm)^3. The detailed recording of one of the hf components illustrates that there is a small instability of the magnetic field of the order of 10^{-2} mT during the sweep.

The second sample is a solution of a stable Proxyl radical in toluene at a concentration of 10^{-4} mol/mol. The sample volume in the cavity is 17 nanoliter. In Fig. 5 the cw EPR spectrum of this sample with its characteristic splitting in three components caused by the hyperfine interaction with the ^{14}N nuclear spin ($I = 1$) is

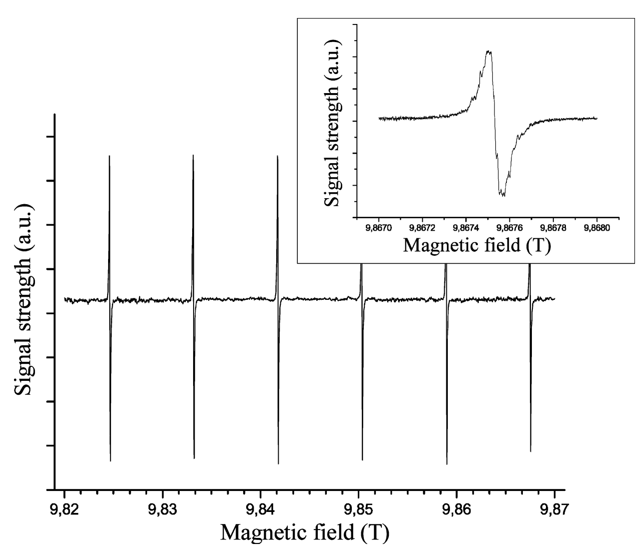

Fig. 4. The cw spectrum of the $m_S = +1/2 \leftrightarrow m_S = -1/2$ transition of Mn^{2+} ($S = 5/2, I = 5/2$) in MgO. In the insert a recording is shown of one of the hyperfine components of the Mn^{2+} spectrum. This spectrum indicates that the inhomogeneity over the sample is $\leqslant 10^{-2}$ mT and that the instability of the magnetic field during the sweep $\approx 10^{-2}$ mT. The field modulation is at 1000 Hz with an amplitude of 10^{-2} mT.

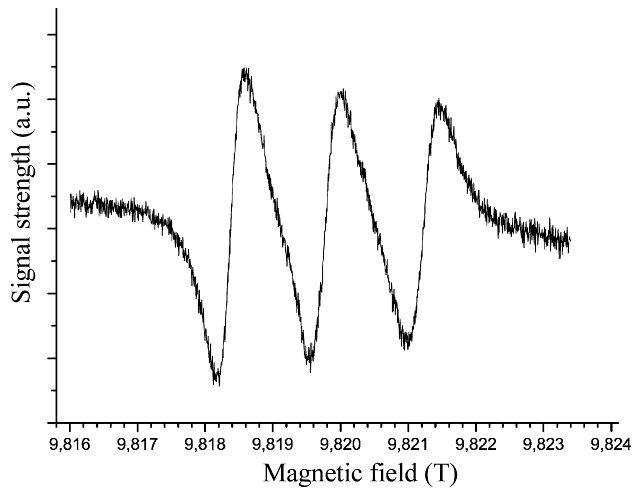

Fig. 5. The cw EPR spectrum of 17 nanoliter of a 10^{-4} mol/mol solution of a proxyl radical in toluene.

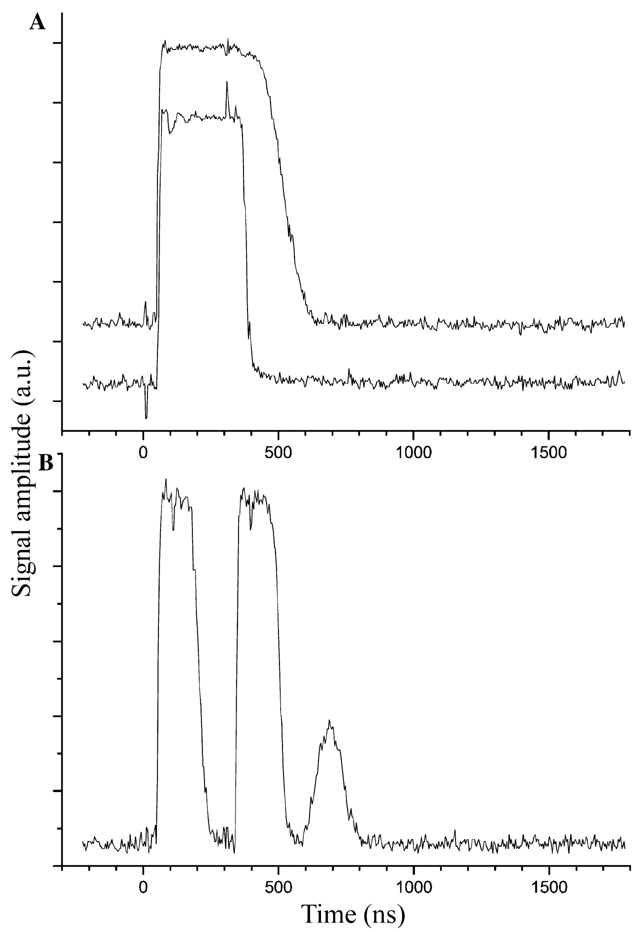

Fig. 6. (A) The resonant and non-resonant pulse responses of the coal sample at room temperature. (B) The electron spin echo response upon two 140 ns pulses.

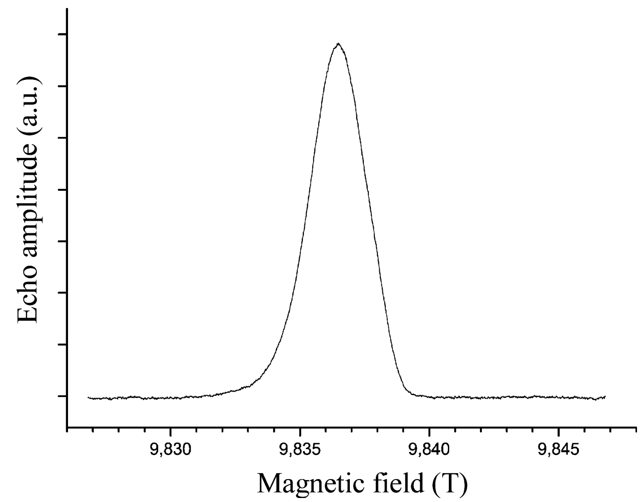

Fig. 7. The electron-spin-echo detected EPR spectrum of a small ($150 \times 150 \times 150\,\mu m^3$) coal sample at room temperature. Pulse duration 100 ns, separation 200 ns.

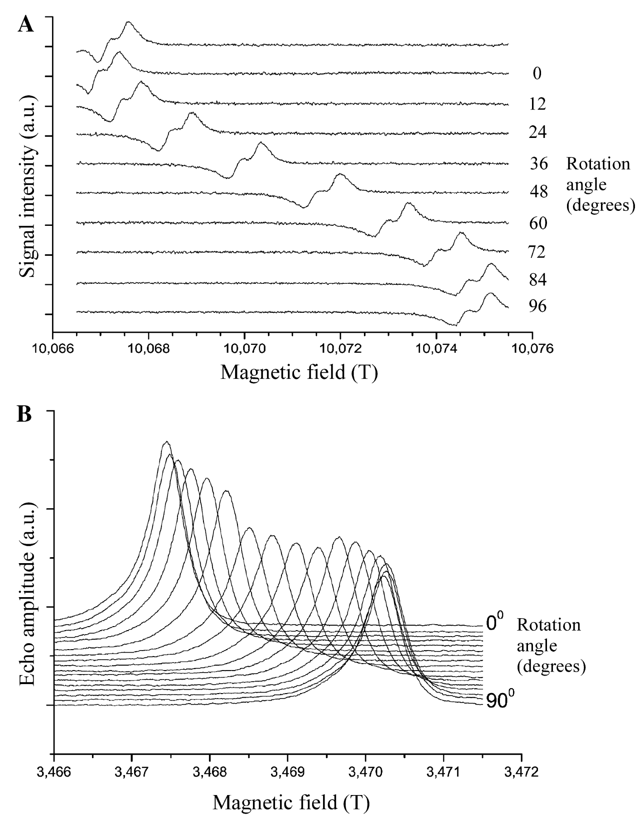

Fig. 8. (A) The orientation dependence of the EPR signal of two shallow donors in a single crystal of the wide-band-gap semiconductor ZnO at 20 K. The magnetic field is rotated from parallel with the crystal *c*-axis to perpendicular in steps of 12°. (B) A similar orientation dependence, taken with a pulsed EPR spectrometer operating at 95 GHz and 1.2 K.

presented. From the observed signal-to-noise ratio of about 20 we conclude that the threshold sensitivity at room temperature of the spectrometer is 1.4×10^8 spins/ 0.1 mT/Hz^2.

The third sample, coal containing free radicals, is used to test the spectrometer in pulsed operation from room temperature down to 5 K. In Fig. 6A the Free

Induction Decay (FID) signal is shown following a $\pi/2$ pulse with a duration of 300 ns and an incident microwave power of about 0.1 mW at room temperature. It is seen that the FID signal can already be observed 30 ns after the termination of the microwave pulse. This very short dead time is explained by the low power of 1 mW needed to create the $\pi/2$ pulse that prevents the overloading of the receiving system and by the bandwidth of about 200 MHz of the cavity ($Q \approx 1500$), which corresponds to a response time of about 1.6 ns. In Fig. 6B it is shown that a series of two $2\pi/3$ pulses with a duration of 140 ns and separated by 300 ns produces an ESE signal at 600 ns. In Fig. 7 the ESE detected EPR signal of the coal sample is displayed.

In Fig. 8A we present an example of an orientational study of two shallow donors with slightly different g-tensors in a single crystal of ZnO. In Fig. 8B a similar set of recordings taken with the help of an ESE spectrometer at 95 GHz is shown. The figure illustrates the increased spectral resolution at 275 GHz. First it is seen that the signals of the two donors are separated by 0.6 mT whereas at 95 GHz the splitting is almost unobservable. Second the variation of the resonance positions with the orientation is tripled compared to the experiment at 95 GHz. Further it is seen that the rotation device in the probehead allows rotation of the sample in one plane with a precision of 1–2°.

4. Conclusion

The experimental results presented in the previous section show that cw and pulsed EPR spectroscopy can be performed routinely at a frequency as high as 275 GHz. Quasi-optical techniques are applied to transport the microwave power with very low losses and by using the polarization properties of quasi-optical components the microwave beams can be manipulated such that a microwave bridge is formed with properties analogous to those at lower frequencies based on waveguide technologies. One of the remarkable aspects is that it proves possible to use a cylindrical single-mode cavity with a loaded quality factor of about 1500 that can be tuned mechanically with a high precision and reproducibility to the operating frequency of the microwave bridge. The advantage is that with the modest incident microwave power of about 1 mW a B_1 microwave magnetic field of about 0.1 mT is generated corresponding to a $\pi/2$ pulse as short as 100 ns. A second advantage is that a very high absolute sensitivity is achieved and that very small samples can be accommodated with dimensions of the order of $100 \times 100\,\mu m$ containing paramagnetic impurities at concentrations of $10^{16}\,cm^{-3}$. The spectrometer also allows for optical excitation of the sample by a slit in the bottom of the cylindrical cavity. Provisions for performing ENDOR experiments have been prepared. We hope to report about these ENDOR experiments in a forthcoming publication.

Acknowledgments

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References

[1] D.E. Budil, K.A. Earle, W.B. Lynch, J.H. Freed, Electron paramagnetic resonance at 1 mm wavelengths, in: A.J. Hoff (Ed.), Advanced EPR Applications in Biology and Biochemistry, Elsevier, Amsterdam, 1989.

[2] T.F. Prisner, S. Un, R.G. Griffin, Pulsed ESR at 140 GHz, Isr. J. Chem. 32 (1992) 357–363.

[3] M.R. Fuchs, T.F. Prisner, K. Möbius, A high-field/high-frequency heterodyne induction-mode EPR spectrometer operating at 360 GHz, Rev. Sci. Instrum. 70 (1999) 3681–3683. M.R. Fuchs, Ph.D. Thesis FU Berlin (2000). Available from http://darwin.inf.fu-berlin.de/2000/7.

[4] V.F. Tarasov, G.S. Shakurov, Submillimetre EPR spectrometer, Appl. Magn. Reson. 2 (1991) 571–576.

[5] J.H. Freed, New technologies in electron spin resonance, Annu. Rev. Phys. Chem. 51 (2000) 655–689.

[6] A.K. Hassan, L.A. Pardi, J. Krzystek, A. Sienkiewicz, P. Goy, M. Rohrer, L.-C. Brunel, Ultrawide band multifrequency high-field emr technique: a methodology for increasing spectroscopic information, J. Magn. Reson. 142 (2000) 300–312.

[7] M. Rohrer, O. Brügmann, B. Kinzer, T.F. Prisner, A pulsed 180 GHz EPR spectrometer, Appl. Magn. Res. 21 (2001) 257–274.

[8] K.A. Earle, D.E. Budil, J.H. Freed, Electron spin resonance at 250 GHz using quasioptical techniques, in: W. Warren (Ed.), Advances in Magnetic and Optical Resonance, 19, Academic Press, New York, 1996.

[9] K.A. Earle, D.S. Tipikin, J.H. Freed, Far-infrared electron-paramagnetic-resonance spectrometer utilizing a quasioptical reflection bridge, Rev. Sci. Instrum. 67 (1996) 2502–2513.

[10] G.M. Smith, J.C.G. Lesurf, R.H. Mitchel, P.C. Riedi, Quasi-optical cw mm-wave electron spin resonance spectrometer, Rev. Sci. Instrum. 69 (1998) 3924–3937.

[11] J.C.G. Lesurf, Millimetre-Wave Optics, Devices and Systems, Adam Hilger, Bristol, 1990.