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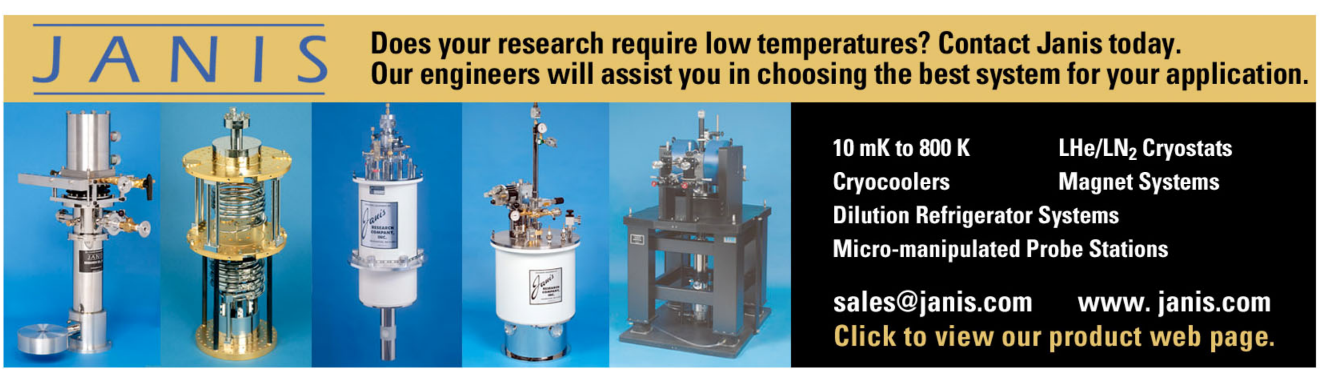

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A high-field/high-frequency heterodyne induction-mode electron paramagnetic resonance spectrometer operating at 360 GHz

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We present design details of and first measurements with a novel continuous wave (cw) high-field/high-frequency electron paramagnetic resonance spectrometer operating at a microwave frequency of 360 GHz and a magnetic field of up to 14 T. The spectrometer design incorporates a heterodyne mixer detection scheme with a quasi-optical transmission line and a bimodal induction mode Fabry–Perot cavity. First cw experiments on polycrystalline 1,1-diphenyl-2-picryl-hydrazyl and bisdiphenylene-β-phenylallyl benzolate in polystyrene at room temperature and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl in frozen solution at 190 K demonstrate the high Zeeman resolution achievable and allow an estimate of the present detection sensitivity of 4×10^9 spins/G at a detection bandwidth of 1 Hz. © *1999 American Institute of Physics.* [S0034-6748(99)03709-0]

I. INTRODUCTION

Electron paramagnetic resonance (EPR) at high magnetic fields (B_0) and microwave (mw) frequencies has become increasingly important lately.[1–10] However, only very few spectrometers operating at frequencies above 200 GHz have been described so far.[6–10] While for many applications, such as quinone and nitroxide radicals, the g anisotropy is large enough to meet the high-field condition $B_0\Delta g/g_{\rm iso} > \Delta B_{1/2}^{\rm hfi}$ already with *W*-band EPR, this is not the case for other systems, such as chlorophyll radicals ($\Delta B_{1/2}^{\rm hfi}$ is the inhomogeneous linewidth due to unresolved hyperfine interactions). Especially in the case of samples that cannot yet be obtained in their deuterated forms, a further increase in the B_0 field and the mw frequency becomes unavoidable to achieve sufficient spectral resolution.

II. EXPERIMENT

The sub-mm wavelength spectrometer developed in the Berlin laboratory operates at a mw frequency of 360 GHz with B_0 fields up to 14 T. In the following the essential features of the experimental setup will be introduced and first test spectra will be presented to illustrate the enhanced resolution and detection sensitivity obtained so far.

The mw source is a phase locked tripled 120 GHz Gunn oscillator providing an output power of $\approx$0.9 mW at 360 GHz (Fig. 1). For detection a heterodyne mixer scheme is employed. It consists of a subharmonic mixer detector with a bandwidth of 100 MHz operating at the second harmonic of the local (LO) frequency. The LO is provided by a phase locked doubled 90.3 GHz Gunn oscillator to yield a LO frequency of 180.6 GHz. The resulting intermediate frequency (IF) is 1.2 GHz. The noise figure of the detection mixer, 12 dB double side band noise, is comparable to the most sensitive bolometer detectors while providing a much higher time resolution of 10 ns (compared to 1 μs for commercially available InSb hot electron bolometers). This is a prerequisite for the planned extension to time-resolved EPR with light excitation.

In the current setup down conversion detection of the IF is performed as a magnitude detection only. Since this approach does not yet allow for phase sensitive detection, in a second stage of development the transmitter and receiver Gunn sources will be phase locked to a common reference frequency. The use of a quadrature IF mixer in the final down conversion stage will then allow for simultaneous detection of absorption and dispersion signal components. This upgrade is currently in progress.

At wavelengths in the sub-mm range fundamental mode mw waveguides become exceedingly lossy. Therefore, we employ (see Fig. 1) a quasi-optical transmission line setup in which a Gaussian beam is launched via a corrugated horn antenna into free space. All focusing elements are low-loss off-axis elliptical mirrors.

Inside the magnet bore an oversized waveguide with horizontal corrugation and a tapered section (overall length 1080 mm) for coupling to the Fabry–Perot sample resonator is used. The Gaussian beam couples to the hybrid HE_{11} mode of the corrugated waveguide which has minimal electric mw field at the walls, thereby minimizing losses and cross polarization.

The linear polarization of the Gaussian beam is utilized in an induction mode detection scheme.[11] The linearly polarized mw is passed through a free-standing wire grid polarizer

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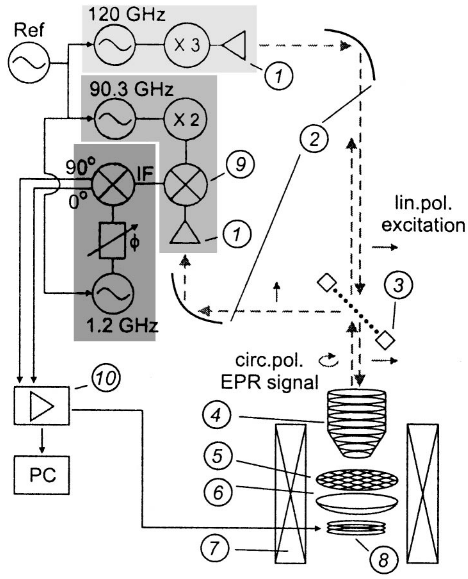

FIG. 1. Experimental setup with corrugated horn antennas (1), off-axis elliptical mirrors (2), wire grid polarizer (3), tapered corrugated waveguide (4), coupling mesh (5), half-symmetric Fabry–Perot resonator (6), superconducting 14 T magnet (7), field modulation coils (8), subharmonic mixer detector (9), and lock-in amplifier (10).

(12 wires/mm, 25 μm diameter) before being coupled into the corrugated waveguide. In the cylindrically symmetric resonator the excitation mw represents a composition of two circularly polarized modes with opposite polarization, only one of which can interact with the spin system and become attenuated upon magnetic resonance. Recombined with the unattenuated component this yields elliptically polarized mw that is reflected toward the wire grid polarizer. Here only the component perpendicular to the excitation mw is reflected onto the receiver antenna. This induction mode setup provides an attenuation of the excitation with respect to the EPR signal of 20–30 dB. Being realized with a minimum number of components, it is robust and easy to align.

The wire grid polarizer in combination with a slightly tilted second one is also used in a polarizer/analyzer setup as a variable attenuator with a dynamic range of 20 dB. The overall insertion loss from transmitter to receiver horn can be estimated to 5 dB.

The sample-containing half-symmetric Fabry–Perot resonator typically operates in a TEM_{006} mode. Coupling to the tapered waveguide is achieved through the flat mirror which actually is a highly reflective inductive mesh (typically 30 wires/mm). It can be exchanged for a mesh with different reflectivity thus allowing for variable coupling for different samples. The sample is placed onto the spherical mirror. Tuning is achieved by translating this mirror from the top of the magnet via a micrometer screw and three brass rods with a length of 1150 mm. A typical value for the loaded Q factor with nonlossy samples is $Q=800$. Directly underneath the curved mirror we have mounted the field modulation coils for lock-in detection. To minimize microphonics both mesh holder and modulation coil holder have been fabricated from Macor ceramics. In the current setup we can measure the EPR signals with modulation field strengths up to 1.5 mT. A new Fabry–Perot resonator design with integrated radio frequency coil for high-power electron-nuclear double resonance (ENDOR) is currently being developed. Both the original mw and transmission line/resonator setup were built by Farran Technology, Ltd.

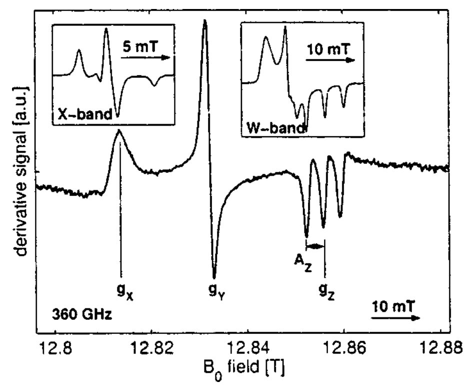

FIG. 2. 4-hydroxy-TEMPO in water/glycerol ($T=200$ K) at 360, 95.6, and 9.7 GHz.

The superconducting magnet is an Oxford Instruments Teslatron H system with a field strength up to 14 T (12.8 T for $g=2$ systems), a homogeneity of 3 ppm in a 10 mm sphere and a warm bore diameter of 88 mm. An integrated superconducting sweep coil allows to sweep a range of ± 100 mT in up to 70 mT/min with the main coil in persistent mode. The static flow cryostat (Oxford Instruments CF1200) provides a temperature range of 3.8 to 300 K. Probehead space diameter inside the cryostat is 62 mm.

III. MEASUREMENTS

As a typical example for a room temperature experiment we have measured polycrystalline samples of 1,1-diphenyl-2-picryl-hydrazyl free radical (DPPH). The 360 GHz EPR signal is a single exchange-narrowed structureless line that shows no significant broadening when compared to the linewidth in X band.

The Mn^{2+} ion in MnO/MgO powder is used to calibrate the B_0 axis.[3] Its spectrum consists of six hyperfine lines with a line width of 0.1 mT that are spread over a field range of 43.5 mT around $g=2.001\,01$.

The absolute sensitivity of the spectrometer has been estimated by measuring samples consisting of bisdiphenylene-β-phenylallyl benzolate free radical (BDPA) in polystyrene film containing a known number of spins. It is as high as 4×10^9 spins/G (1 G=0.1 mT) at a detection bandwidth of 1 Hz.

The spectrum of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO) in water/glycerol frozen solution at 190 K demonstrates the enhanced resolution achievable by 360 GHz EPR (Fig. 2). The isotropic orientation distribution of the solute molecules leads to the typical powder EPR pattern of a rhombic g-tensor system, but with resolved z component of the nitrogen ^{14}N hyperfine (hf) splittings A_z and spread over ≈ 50 mT. For comparison, the inserts show spectra of the same sample at X band (9.7 GHz) and W band (95.6 GHz). While at X band the hf split-

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ting dominates the Zeeman interaction and at *W* band both interactions are still of comparable magnitude, in the sub-mm band the Zeeman interaction clearly dominates the spectrum.

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