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High-Field, Multifrequency EPR Spectroscopy Using Whispering Gallery Dielectric Resonators

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High-field/high frequency EPR spectroscopy measurements are shown. Experiments were carried out at 240- and 316-GHz frequencies. The employed apparatus uses a novel combination of far infrared molecular lasers and of probehead exploiting dielectric resonators working in the whispering gallery modes. This approach constitutes a relatively simple method of multifrequency EPR spectroscopy and opens appealing perspectives in high-sensitivity EPR spectroscopy up to the THz regime. © 2000 Academic Press

Key Words: **EPR spectroscopy; high magnetic field; multifrequency; dielectric resonator; whispering gallery modes.**

I. INTRODUCTION

High-field–high-frequency electron paramagnetic resonance (HF^2EPR) spectroscopy is a recent field of investigation undergoing rapid growth and offering new significant research opportunities (*1–5*). A number of spectrometers for HF^2EPR operating at 95 GHz are present in laboratories working in different research fields ranging from material science to biophysics and have also become commercially available (*6*).

Although many applications and in particular the requirement of a multifrequency approach suggest the extension of HF^2EPR to higher field/frequency, this development is hindered by some technical difficulties connected, in particular, with the performances of the radiation sources, the sample resonators, and the handling of the submillimeter radiation. Only a few laboratories are consequently involved in the development and use of EPR apparatuses working at frequencies higher than 200 GHz (*7–13*).

Although it is possible to profitably perform HF^2EPR in the absence of a resonator, there are several good reasons to search for efficient resonating structures at submillimeter waves. The use of resonating structures is in general desirable in EPR spectroscopy every time one performs experiments dealing with a very small quantity or very diluted samples, that is to say all the times it is necessary to perform experiments which deserve very high sensitivity. Additional advantages of the use of resonators are: (i) the possibility of selecting the appropriate polarization status of the radiation, (ii) the ability to control the lineshape of the signal making use of an automatic control of frequency (AFC) in order to select either absorption or dispersion modes at resonance, (iii) the ability to implement pulse techniques with relatively small peak powers. Several approaches have been adopted in this search by different laboratories, depending on the frequency range and the experimental requirements. Up to 150 GHz the realization of EPR spectrometers is in principle an extension of the well-established X band and Q band technologies. Closed structures including single-mode waveguides and rectangular or cylindrical cavities are used by many groups in W and D bands and commercial spectrometers are currently available in this frequency range (*11, 14–18*). At higher frequencies the intrinsic dimensions and the insertion losses of the different components make the same approach very difficult or impossible. A cylindrical cavity resonating in the TE_{012} mode at 300 GHz would have about 0.2 mm^3 total volume which makes it useless for most applications. On the other side the losses of a single-mode copper rectangular waveguide in this frequency range can be calculated as 7 dB/m (*1*).

At these frequencies other approaches which make use of the quasi-optical techniques (*11, 19, 20*) thus become convenient. Quasi-optics is located at a bordering realm where neither microwaves techniques nor geometrical optics is appropriate, a range of frequency in which the wavelength of the processed signal is not negligible compared to the size of the beam. Some spectrometers have been built using these techniques. They generally make use of Fabry–Perot multimodal resonators and several other devices which ideally constitute the high-frequency analogues of the components of a standard low-frequency EPR spectrometer: phase shifters, circulators, magic Tees, etc. (*11, 19*). Special care is also devoted to the search for the appropriate propagating structures. Via space propagation, refocusing dielectric lenses as well as the use of oversized metallic or corrugated waveguides have been applied in several laboratories, showing the advantages of these alternatives to the single-mode waveguides at these frequencies (*11*).

Assembling high-frequency EPR spectrometers is becoming a very interesting activity in which a successful change in a single component may give rise to the breakthrough that would make this relatively young technique enter a more mature age.

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Application of dielectric resonators is a well-established practice in several different fields including magnetic resonance. Limitations to the use of the usual dielectric resonators operating in TE and TM modes in HF^{2}EPR have already been thoroughly discussed in the literature (*21*). Their application at frequencies higher than 95 GHz suffers limitations even more severe than those of the standard metallic resonators, particularly in terms of radiation confinement and size of the components. Dielectric resonators working in the whispering gallery modes (WGMDR) offer, on the contrary, a valuable alternative in this frame for some main reasons: (i) they can be oversized with respect to wavelength; (ii) they show an intrinsic multifrequency response; (iii) they show a very good confinement of the electromagnetic radiation; (iv) they are relatively easily operated; (v) they are very cheap and easy to construct and assemble; (vi) they can be loaded with a large quantity of sample (with low dielectric losses) without a relevant degradation of the Q merit factor.

A series of works (*22–24*) showed the capabilities of this type of resonators in EPR experiments carried out at different frequencies up to 75 GHz.

The present paper reports the first results of HF^{2}EPR completely performed in the laboratory at IFAM–CNR in Pisa. The apparatus presents a number of innovations that, in perspective, make the approach appealing for the developments of EPR spectroscopy. The main features of the apparatus can be so summarized:

- the unique combination of a radiation source formed by a far infrared (FIR) laser optically pumped by a CO_2 laser with a probehead based on a WGMDR;
- the source is intrinsically operating as a multifrequency device. It is optimized to give high power at the frequencies of interest ($<$400 GHz according to the magnet available). It therefore meets the requirements of a source useful for EPR measurements and will be named in the following millimeter laser (MML);
- the operation of the apparatus containing the MML and the WGMDR at different frequencies (240 and 316 GHz) was the basis of the measurements here shown. This could be considered a starting point for the extension of operation at a higher frequency/field.

The results here presented then encourage the use of the apparatus for the extension of multifrequency EPR measurements at higher and higher frequencies where lasers become more performant than other submillimeter wave sources. Moreover as predicted and preliminarily shown in previous works, we could confirm that the probehead based on WGMDR works very well at these frequencies (*25, 26*).

Section II gives a general description of the new HF^{2}EPR apparatus and shows the main instrumental performances. Section III presents EPR experiments performed with different samples at 240 and 316 GHz. Finally, Section IV discusses the results of the experimental observations and indicates the main perspectives and expectations in the frame of EPR studies at further increased frequencies.

II. EXPERIMENTAL

The spectrometer scheme is shown in Fig. 1. The homebuilt source is a metallic waveguide FIR laser, optically pumped by a single- line, single-mode, oversized waveguide CO_2 laser in continuous wave. The overall laser system is provided by an active control apparatus in order to reduce both amplitude and frequency noise due to thermal fluctuations.

The CO_2 laser is made up by a 1.50-m-long cavity supported by a invar bar frame. The optical cavity is terminated on one side by a 80% ZnSe mirror with a focal length of 10 m and with a planar 150 lines/mm grating Littrow mounted on the other side. To tune the frequency of the emitted radiation the mirror is mounted on a piezoelectric ceramic. The zero-order reflection of the grating can be used either to monitor the laser power or in an optoacoustic cell for laser frequency stabilization. The oversized waveguide is a 1.43-m-long Pyrex tube with a 9-mm inner diameter provided with a fine alignment assembly. The CO_2 laser emits 75 W at 9R(20) and 95 W at 10P(20) single lines. The FIR laser also has a waveguide structure. The waveguide is a 3.5-m-long brass pipe having 36-mm inner diameter and is supported by a diamagnetic stainless steel frame which is thermalized within 0.01°C in order to minimize thermal expansion of the cavity. The length of the FIR cavity is tuned by means of a piezoelectric actuator and a micrometer. In the experiments here discussed the FIR laser operated at 240 and 316 GHz using as lasing active medium methyl iodide and trioxane, respectively. The power emitted at these frequencies, measured with a technique described in Ref. (*27*), is about 20 and 4 mW, respectively. The characteristics of the realized source have been optimized to obtain the best performances just at the long wave radiation, therefore this unique source is called millimeter laser.

The propagation of the exciting radiation from the output of the MML laser to the head of the probe is made through oversized copper pipes measuring 12 mm in internal diameter. The necessary changes in the direction of the beam are realized using 90° curved sections of the same hollow pipes with the typical attenuation of 1.5 dB per curve.

A small fraction of the radiation was tapped out just after the output window of the MML using a dielectric waveguide and sent to a pyroelectric detector; this signal is monitored during the magnetic field sweep in order to check the source stability and correct for the amplitude fluctuations of the MML. The radiation flows in the main arm of the apparatus, goes through the probe, and is recovered at a cryogenic bolometer detector.

The detector is a magnetically enhanced liquid helium cooled InSb hot electrons bolometer (QMC Instruments Ltd.). It has a noise equivalent power of 0.9 pW/Hz at 1 kHz and relaxation time scale of the order of 1 μs. The superconducting magnet Teslatron (Oxford Instruments) is continuously sweep-

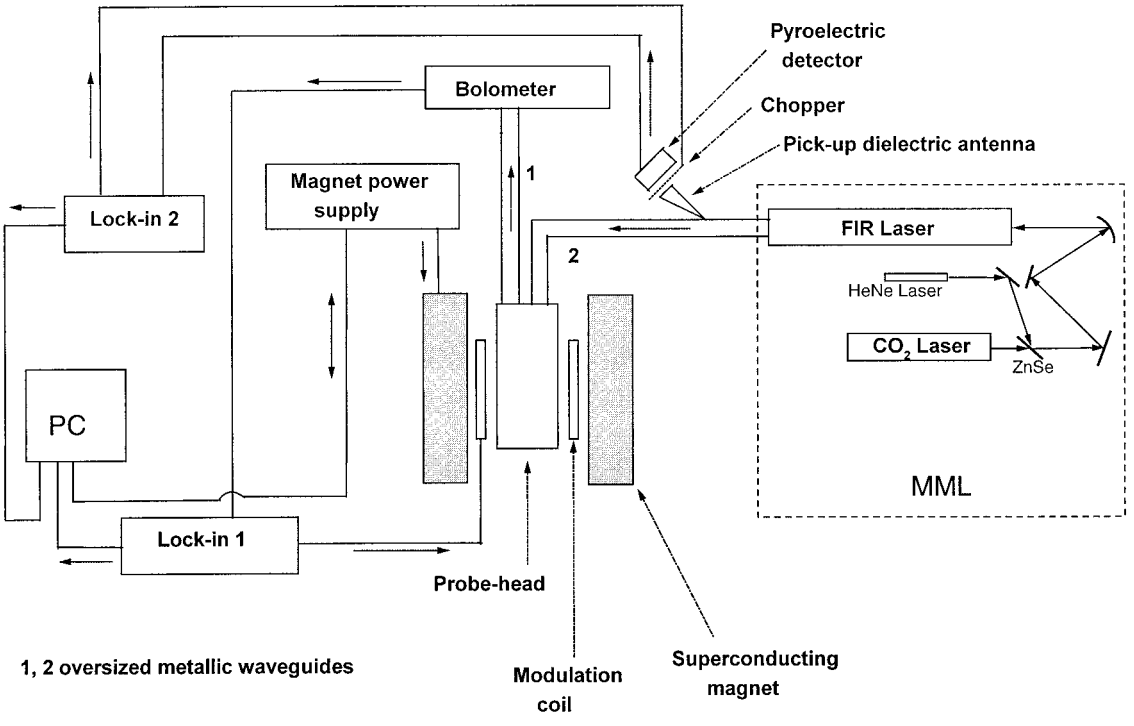

FIG. 1. Scheme of the spectrometer.

able from zero to 12 T with homogeneity of 10 ppm in 1-cm-diameter spherical volume at the center of the main coil and a stability of 10 ppm/h. It has an 88-mm-wide warm bore in which the probe can be fitted. The field modulation is supplied by a coil wound around the probehead giving a maximum of 0.8 mT up to a frequency of 10 KHz.

A close up of the resonating structure including the WG-MDR is shown in Fig. 2. The probe includes an adapter containing a wire polarizer requested to recover the correct linear polarization, a transition from metallic to dielectric waveguide, and finally the resonating assembly. The latter includes a section of tapered quartz waveguide and the 15-mm-diameter disc-shaped single or stacked WGMDR (*26, 28*); the dielectric waveguide must be properly tapered in order to get a suitable value of the external evanescent field and of the phase velocity of the wave propagating in the dielectric waveguide (*25*). Finally a 45° mirror harvests the radiation delivered by the sharpened tip of the dielectric waveguide and feeds the output metallic waveguide. The geometrical profile of the tapered region is a critical parameter for the minimization of the irradiation power losses; the practical implementation of this tapered section could be further optimized in the whole frequency band of interest. The WGMDR operates, in a resonant mode with the magnetic field orthogonal to the static magnetic field. The probe is set in the reaction (also known as absorption) configuration (see Fig. 2b).

The 15-mm-diameter resonator is realized in high-density polyethylene. The sample can be loaded between two polyethylene discs. The part of this resonator active for the interaction of the radiation with the sample is the volume between the two discs, bounded by the external rim and the fictitious surface of the modal caustic (*25, 28*) whose radius is 6.6 mm at 240 GHz and 6.8 mm at 316 GHz. Small quantities of the samples were carefully placed within the active volume. The measured Q factor of the resonator loaded with the sample assumes values up to 5000 at 240 GHz, depending on the coupling conditions.

The system provides different adjustments which concern the matching of the energy from the transmission line to the resonator and the tuning of its resonance frequency. The former operation is carried out by changing the distance between the exciting dielectric waveguide and the resonator placed in the same plane (movements along the x and y axis in Fig. 2b); this allows one to obtain any condition between the undercoupling and the overcoupling, depending on the Q factor and on the coupling efficiency between resonator and waveguide. The latter operation includes the use of a movable metallic ring, with the overall diameter equal to that of the resonator, moved along the axis of the polyethylene disc (z axis in Fig. 2a). This variable interaction with the evanescent field of the resonator forces a readjustment of the field distribution and consequently of the resonant frequency (*25, 26, 29*). This device also offers the possibility of implementing an AFC for systems with nontunable sources. It must be pointed out that while the frequency tuning operation does not significantly affect the Q of the resonator, the operation described above for the matching of energy to the resonator simultaneously changes the Q factor and the resonance frequency (*30, 31*).

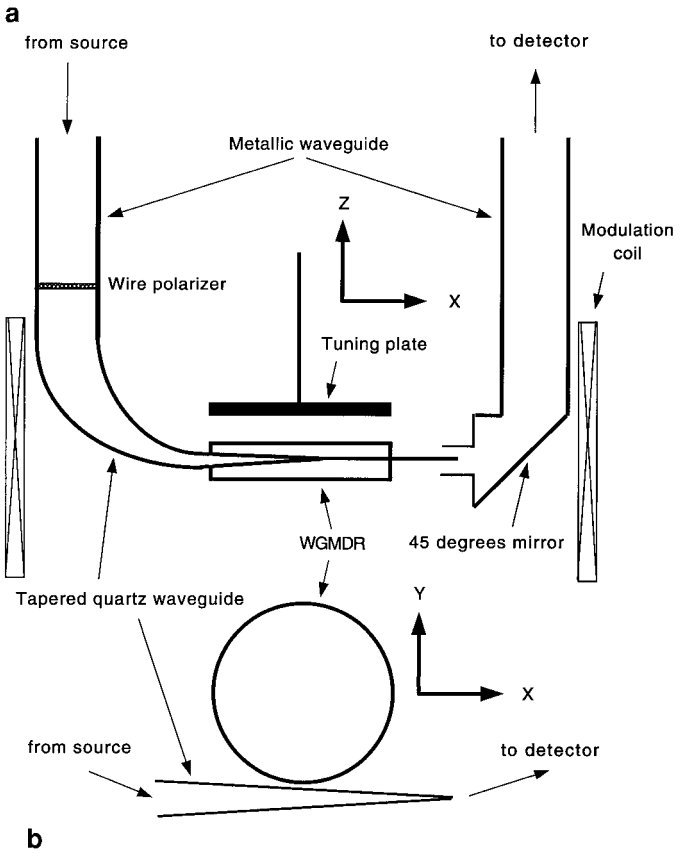

FIG. 2. Close up of the resonating structure. (a) Side view; (b) top view.

III. EPR MEASUREMENTS

EPR experiments were carried out on polycrystalline samples of DPPH (2,2-diphenyl- 1- picrylhydrazyl; Sigma) on a powdered sample of divalent manganese diluted in MgO and on a polypyrrole sample. All of the spectra were recorded at room temperature using the probe described above with a phase-sensitive detection with time constant of 3 s. The samples of DPPH were taken from the same batch used by one of authors (L.A.P.) in previous HFEPR experiments (*9*). Samples of DPPH of different size were prepared to test the sensitivity of our spectrometer. When a small quantity of DPPH is used (less than 10 μg) the expected lineshape was obtained. In order to obtain the intrinsic linewidth of the paramagnetic sample the amplitude of modulation was reduced, as usual, until the width of the EPR line became constant. The spectra at 240 and 316 GHz are reported in Fig. 3. In the spectrum at 240 GHz the WGMDR was loaded with a small sample of less than 10 μg while in the 316-GHz experiment, due to the lower power of the laser, we had to use a larger sample which was evenly distributed in the active zone of the resonator. The powder spectrum of DPPH at 240 GHz compares well with the spectra of the same sample obtained in different laboratories and with different techniques (*9*). The spectrum shows a single dipolar broadened, exchange narrowed line. At 240 GHz the observed linewidth is 0.45 mT, with a signal-to-noise ratio of 300; the minimum number of detectable spins can be estimated of the order of 10^{12} spin/0.1 mT. This figure is mainly limited by the irradiation losses due to the tapering of the dielectric waveguide. It must be pointed out that sensitivity in HF^2EPR is generally given as the minimum number of detectable spin with no mention of the power at the sample. In most cases, however, power is the main factor limiting sensitivity. At 316 GHz the observed linewidth is 0.72 mT, which is greater than the value reported in Ref. (*9*). As already mentioned, the 316-GHz experiment was run with a different sample than the one we used at 240 GHz. This sample was distributed in a larger volume in the active zone of the resonator. This is most probably the origin of the additional broadening observed at this frequency.

When the automatic frequency control is not operated the EPR line is more and more distorted as the mass of the paramagnetic sample increases, since both the magnetic absorption and the dispersion greatly affect the response of the resonator. Moreover the lineshape depends on the position of the fixed MML frequency along the resonance curve of the resonator, since the magnetic dispersion gives a signal related to the derivative of the resonance curve. This effect has been experimentally verified, for a fixed resonance mode, by changing the position of the tuning plate and/or the distance between the resonator and the exciting waveguide.

As usual for superconducting magnets the main coil shows a sizeable hysteresys depending on the sweep rate. The accurate determination of the observed resonance field is made by slowly sweeping the field across the signal in two different directions and taking the average. The g value measured for DPPH is 2.0037(1), which compares well with the reported values at frequencies higher than 95 GHz (*9*).

A powder sample of divalent manganese dispersed in MgO was also used as an independent test of our spectrometer. The spectra of Mn^{2+} diluted in MgO at 240 and 316 GHz are reported in Fig. 4, which shows the expected hyperfine sextet

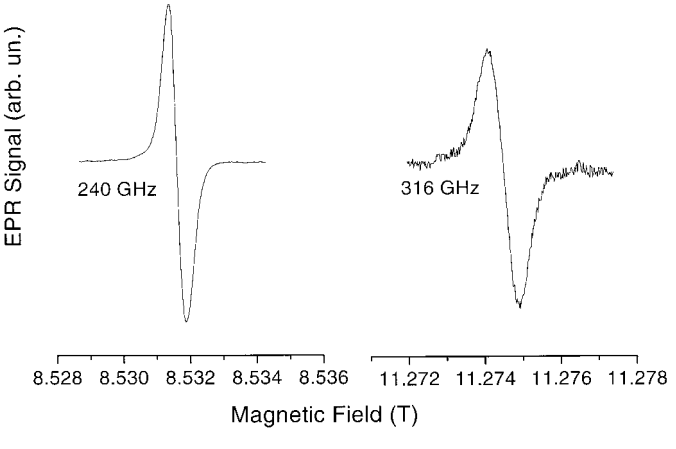

FIG. 3. EPR powder spectra of DPPH at 240 and 316 GHz.

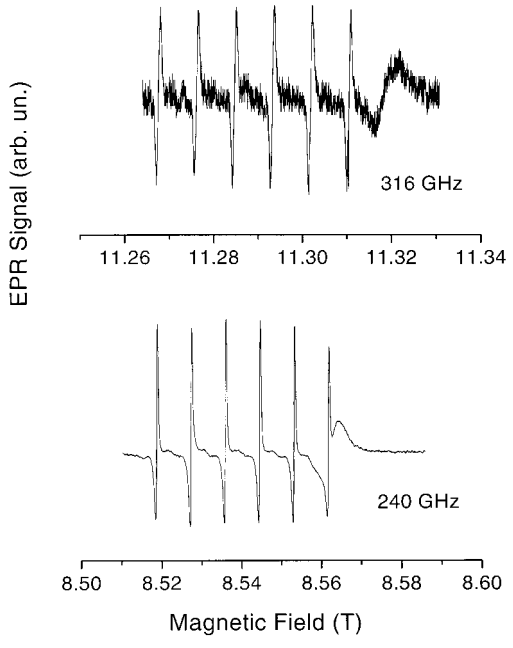

FIG. 4. EPR powder spectra of Mn^{2+} diluted in MgO at 240 and 316 GHz.

with lines separated by ca. 8.6 mT and some other additional features most probably due to paramagnetic impurities in the sample. The same loaded resonator was used at the two frequencies. The observed g factor is 2.0017(1).

The broad signal which is almost superimposed to the high-field component of the Mn^{2+} spectrum at 240 GHz is totally resolved in the 316-GHz spectrum and is attributed to some paramagnetic impurity. The observed linewidth of the single hyperfine component is 0.47 mT at 240 GHz and 0.6 mT at 316 GHz. The ratio between these linewidths is close to 316/240; accordingly the origin of this broadening is very likely due to field inhomogeneities.

Preliminary results were also obtained in a polypyrrole sample, which is a conducting material characterized by an EPR linewidth strongly dependent on the concentration of oxygen in the gas in which it is embedded (*32*); this feature makes this sample particularly attractive for studies of relaxation processes via nonlinear EPR techniques (*33*). Measurements on few micrograms of polypyrrole, made under standard conditions, give an EPR line 0.29 mT wide, as shown in Fig. 5.

As far as the signal-to-noise ratio is concerned, particular attention was paid to the analysis of the coupling conditions between the resonator and the waveguide; this coupling can be varied in a simple way by changing their reciprocal distance. When this distance increases the coupling coefficient decreases; however, an increase of the Q-factor of the resonator is in general observed (*31*). In addition, the radiation scattered by the resonator itself decreases, as experimentally observed working with the resonator out of resonance. The latter effect, which can become relevant, was also studied by numerical

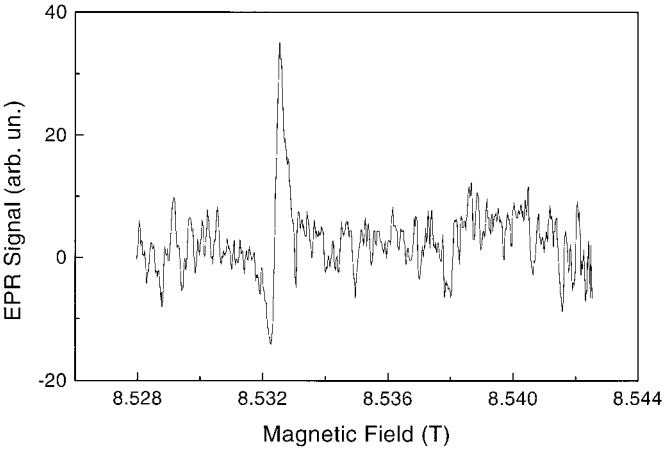

FIG. 5. EPR spectrum of a polypyrrole sample at 240 GHz.

calculation (*34*). It mainly depends on the fraction of the evanescent field outside the dielectric waveguide, which is in turn determined by its diameter. The combination of these effects gives the dependence of the signal-to-noise ratio for a DPPH sample at 316 GHz vs the fraction of the power transmitted to the detector, as reported in Fig. 6. In this figure the transmitted power, obtained by changing the distance between the resonator and the waveguide, is normalized to the power revealed when the resonator is far from the waveguide. All spectra obtained in this way show the same lineshape, confirming that the employed sample weakly perturbs the resonator.

IV. CONCLUSIONS

In conclusion, the above results show that the unique combination of molecular laser sources and probehead based on

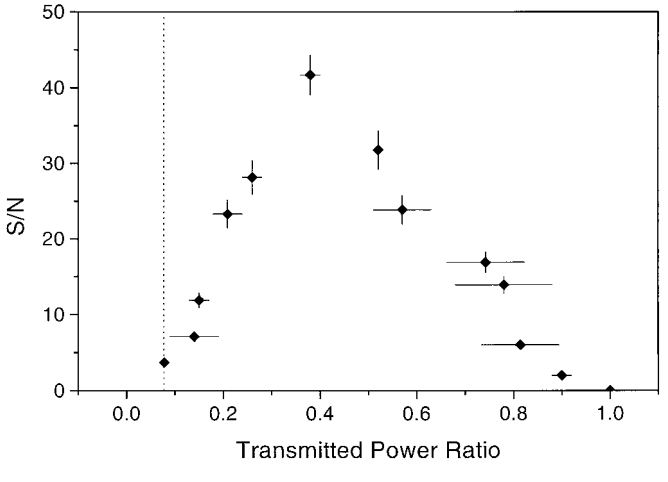

FIG. 6. Signal-to-noise ratio vs transmitted power ratio for EPR spectra of DPPH at 316 GHz. The dotted vertical line represents the maximum coupling condition.

whispering gallery dielectric resonators is one of the appealing aspects of this line of research and a viable path for HF^{2}EPR spectroscopy applications. This is particularly important in view of the use of higher frequencies and fields. In fact, in the range of frequencies approaching the THz region, FIR molecular lasers have no competitors in terms of emitted power and spectral quality. In addition, the operation of laser sources with suitable pulse techniques could make possible a true Fourier transform EPR spectroscopy (*35*). On the other hand the probeheads exploiting WGMDR are inexpensive, easy to realize, and relatively easily operated and have already proved very performant in terms of Q factor ($>$5000 at 400 GHz with polyethylene discs) (*21*) and of usable active quantity of samples (tens of cubic millimeters for low-loss samples).

Work is in progress to realize sample holders adapted to the measurements of liquid samples and probes which allow variable temperature measurements.

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